



EUROPEAN COMMISSION

**Integrated Pollution Prevention and Control (IPPC)**

**Reference Document on  
Best Available Techniques in the Ferrous Metals Processing  
Industry**

**December 2001**



## EXECUTIVE SUMMARY

This Reference Document on best available techniques in ferrous metals processing reflects an information exchange carried out according to Article 16(2) of Council Directive 96/61/EC. The document has to be seen in the light of the preface which describes the objectives of the document and its use.

This BREF document consists of 4 Parts (A – D). Parts A to C cover the different industrial sub-sectors of the Ferrous Metals Processing sector: A, Hot and Cold Forming; B, Continuous Coating; C, Batch Galvanizing. This structure was chosen because of the differences in nature and scale of the activities covered by the term FMP.

Part D does not cover an industrial sub-sector. It comprises the technical descriptions of a number of environmental measures which are techniques to be considered in the determination of BAT in more than one sub-sector. This was done to avoid repetition of technical descriptions in the three Chapters 4. These descriptions have to be viewed always in connection with the more specific information, referring to the application in individual sub-sectors, which is given in the relevant Chapter 4.

### Part A: Hot and Cold Forming

The hot and cold forming part of the ferrous metal processing sector comprises different manufacturing methods, such as hot rolling, cold rolling and drawing of steel. A great variety of semi-finished and finished products with different lines of production is manufactured. Products are: hot and cold rolled flats, hot rolled long products, drawn long products, tubes and wire.

#### Hot Rolling

In hot rolling the size, shape and metallurgical properties of steel are changed by repeatedly compressing the hot metal (temperature ranging from 1050 to 1300 C°) between electrically powered rollers. The steel input for hot rolling varies in form and shape - cast ingots, slabs, blooms, billets, beam blanks - depending on the product to be manufactured. Products obtained from hot rolling are usually classified in two basic types according to their shape: flat and long products.

Total EU production in 1996 of hot rolled (HR) products was 127.8 million tonnes of which flats accounted for 79.2 million tonnes (ca. 62%) [Stat97]. Germany is the largest manufacturer of the flats, with 22.6 million tonnes followed by France with 10.7 million tonnes, Belgium 9.9 million tonnes, Italy 9.7 million tonnes and UK 8.6 million tonnes. The vast majority of HR flat products is wide strip.

The remaining 38 % of HR products are long products with about 48.5 million tonnes in 1996. The two major manufacturing countries are Italy with about 11.5 million tonnes and Germany with 10.3 million tonnes; followed by UK (7 million tonnes) and Spain (6.8 million tonnes). The largest part of the long products sector in tonnage terms is the production of wire rod which stands for roughly a third of the total production followed by reinforcing bars and merchant bars with an approximate share of one quarter of the production each.

In steel tube manufacture, the EU, which produced 11.8 million tonnes in 1996, (20.9 % of total world production) is the largest producer followed by Japan and the U.S. The European steel tube industry has a highly concentrated structure. Five countries – Germany (3.2 million tonnes), Italy (3.2 million tonnes), France (1.4 million tonnes), United Kingdom (1.3 million tonnes) and Spain (0.9 million tonnes) - account for roughly 90 % of total EU production. In

some countries, a single company can account for 50 % or more of the national output. In addition to the major integrated steel tube manufacturers (mainly producing welded tubes), there are a relatively large number of small and medium-sized firms that are independent. Some manufacturers, often small in tonnage terms, operating in high value-added markets, concentrate on the manufacture of special dimensions and grades of tubes according to particular customer specifications.

Hot rolling mills usually comprise the following process steps: conditioning of the input (scarfing, grinding); heating to rolling temperature; descaling; rolling (roughing including width reduction, rolling to final dimension and properties) and finishing (trimming, slitting, cutting). They are classified by the type of product that they produce and by their design features: blooming and slabbing mills, hot strip mills, plate mills, bar and rod mills, structural and section mills and tube mills.

The main environmental issues of hot rolling are emissions to air, especially NO<sub>x</sub> and SO<sub>x</sub>; the energy consumption of furnaces; (fugitive) dust emissions from product handling, rolling or mechanical surface treatment; oil- and solid-containing effluents and oil-containing wastes.

For NO<sub>x</sub> emissions of reheating and heat treatment furnaces, industry reported concentrations of 200 – 700 mg/Nm<sup>3</sup> and specific emissions of 80 – 360 g/t; while other sources reported up to 900 mg/Nm<sup>3</sup> and – with combustion air preheating of up to 1000 °C – of up to more than 5000 mg/Nm<sup>3</sup>. SO<sub>2</sub> emissions from furnaces depend on the fuel used; ranges were reported from 0.6 – 1700 mg/Nm<sup>3</sup> and 0.3 – 600 g/t. The scattering of energy consumption for these furnaces was 0.7 to 6.5 GJ/t; with a typical range being 1 – 3 GJ/t.

As for dust emissions from product handling, rolling or mechanical surface treatment, very few data were submitted referring to the individual processes. The concentration ranges reported were:

- Scarfing: 5 – 115 mg/Nm<sup>3</sup>
- Grinding: < 30 – 100 mg/Nm<sup>3</sup>
- Mill stands: 2 – 50 mg/Nm<sup>3</sup> and
- Coil handling: approximately 50 mg/Nm<sup>3</sup> .

Emissions to water from hot rolling basically comprise oil- and solid-containing effluents in the range of 5 to 200 mg/l total suspended solids and 0.2 – 10 mg/l hydrocarbons. Oil-containing wastes from waste water treatment were reported ranging from 0.4 – 36 kg/t depending on the mill type.

For more details and for emission and consumption data for other process steps of hot rolling, refer to Chapter A.3 where the available data are presented with qualifying information.

The key findings regarding BAT for individual process steps and different environmental issues of hot rolling are summarized in Table 1. All emission figures are expressed as daily mean values. Emissions to air are based on standard conditions of 273 K, 101.3 kPa and dry gas. Discharges to water are indicated as daily mean value of a flow-rate-related 24-hour composite sample or a flow-rate-related composite sample over the actual operating time (for plants not operated in three shifts).

There was consensus in the TWG on the best available techniques and associated emission/consumption levels presented in the table, except where a ‘split view’ is explicitly recorded.

<b>Best Available Techniques / Split views on BAT</b>	<b>BAT-associated emission and consumption levels / Split views on associated levels</b>
<b>Storing and handling of raw materials and auxiliaries</b>	
<ul style="list-style-type: none"> <li>Collection of spillages and leakages by suitable measures, e.g. safety pits and drainage.</li> </ul>	
<ul style="list-style-type: none"> <li>Separation of oil from the contaminated drainage water and reuse of recovered oil.</li> </ul>	
<ul style="list-style-type: none"> <li>Treatment of separated water in the water treatment plant.</li> </ul>	
<b>Machine scarfing</b>	
<ul style="list-style-type: none"> <li>Enclosures for machine scarfing and dust abatement with fabric filters.</li> </ul>	split view on dust level: < 5 mg/Nm <sup>3</sup> < 20 mg/Nm <sup>3</sup>
<ul style="list-style-type: none"> <li>Electrostatic precipitator, where fabric filters cannot be operated because of very wet fume.</li> </ul>	split view on dust level: < 10 mg/Nm <sup>3</sup> 20 - 50 mg/Nm <sup>3</sup>
<ul style="list-style-type: none"> <li>Separate collection of scale/swarf from scarfing.</li> </ul>	
<b>Grinding</b>	
<ul style="list-style-type: none"> <li>Enclosures for machine grinding and dedicated booths, equipped with collection hoods for manual grinding and dust abatement by fabric filters.</li> </ul>	split view on dust level: < 5 mg/Nm <sup>3</sup> < 20 mg/Nm <sup>3</sup>
<b>All surface rectification processes</b>	
<ul style="list-style-type: none"> <li>Treatment and reuse of water from all surface rectification processes (separation of solids).</li> </ul>	
<ul style="list-style-type: none"> <li>Internal recycling or sale for recycling of scale, swarf and dust.</li> </ul>	

**Table 1: Key findings regarding BAT and associated emission/consumption levels for hot rolling**

Best Available Techniques / Split views on BAT	BAT-associated emission and consumption levels / Split views on associated levels
<b>Re-heating and heat treatment furnaces</b>	
<ul style="list-style-type: none"> <li>General measures, e.g. regarding furnace design or operation &amp; maintenance, as described in chapter A.4.1.3.1.</li> </ul>	
<ul style="list-style-type: none"> <li>Avoiding excess air and heat loss during charging by operational measures (minimum door opening necessary for charging) or structural means (installation of multi-segmented doors for tighter closure).</li> </ul>	
<ul style="list-style-type: none"> <li>Careful choice of fuel and implementation of furnace automation/control to optimise the firing conditions.                             <ul style="list-style-type: none"> <li>- for natural gas</li> <li>- for all other gases and gas mixtures</li> <li>- for fuel oil (&lt; 1 % S)</li> </ul> </li> </ul>	SO <sub>2</sub> levels: < 100 mg/Nm <sup>3</sup> < 400 mg/Nm <sup>3</sup> up to 1700 mg/Nm <sup>3</sup>
Split view: <ul style="list-style-type: none"> <li>limitation of sulphur content in fuel to &lt; 1 % is BAT</li> <li>lower S limit or additional SO<sub>2</sub> reduction measures is BAT</li> </ul>	
<ul style="list-style-type: none"> <li>Recovery of heat in the waste gas by feedstock pre-heating</li> <li>Recovery of heat in the waste gas by regenerative or recuperative burner systems</li> <li>Recovery of heat in the waste gas by waste heat boiler or evaporative skid cooling (where there is a need for steam)</li> </ul>	Energy savings 25 - 50 % and NO <sub>x</sub> reductions potentials of up to 50 % (depending on system).
<ul style="list-style-type: none"> <li>Second generation low-NO<sub>x</sub> burners</li> </ul>	NO <sub>x</sub> 250 - 400 mg/Nm <sup>3</sup> (3% O <sub>2</sub> ) without air pre-heating reported NO <sub>x</sub> reduction potential of about 65 % compared to conventional.
<ul style="list-style-type: none"> <li>Limiting the air pre-heating temperature. Trade-off energy saving vs. NO<sub>x</sub> emission: Advantages of reduced energy consumption and reductions in SO<sub>2</sub>, CO<sub>2</sub> and CO have to be weighed against the disadvantage of potentially increased emissions of NO<sub>x</sub></li> </ul>	
Split view: <ul style="list-style-type: none"> <li>SCR and SNCR are BAT</li> <li>Not enough information to decide whether or not SCR/SNCR are BAT</li> </ul>	achieved levels <sup>1</sup> : SCR: NO <sub>x</sub> < 320 mg/Nm <sup>3</sup> SNCR: NO <sub>x</sub> < 205 mg/Nm <sup>3</sup> , ammonia slip 5 mg/Nm <sup>3</sup>
<ul style="list-style-type: none"> <li>Reduction of heat loss in intermediate products; by minimizing the storage time and by insulating the slabs/blooms (heat conservation box or thermal covers) depending on production layout.</li> <li>Change of logistic and intermediate storage to allow for a maximum rate of hot charging, direct charging or direct rolling (the maximum rate depends on production schemes and product quality).</li> </ul>	
<ul style="list-style-type: none"> <li>For new plants, near-net-shape casting and thin slab casting, as far as the product to be rolled can be produced by this technique.</li> </ul>	
<sup>1</sup> These are emission levels reported for the one existing SCR plant (walking beam furnace) and the one existing SNCR plant (walking beam furnace).	

**Table 1 continued: Key findings regarding BAT and associated emission/consumption levels for hot rolling**

<b>Best Available Techniques / Split views on BAT</b>	<b>BAT-associated emission and consumption levels / Split views on associated levels</b>
<b>Descaling</b>	
<ul style="list-style-type: none"> <li>Material tracking to reduce water and energy consumption.</li> </ul>	
<b>Transport of rolled stock</b>	
<ul style="list-style-type: none"> <li>Reduce unwanted energy loss by coil boxes or coil recovery furnaces and heat shields for transfer bars</li> </ul>	
<b>Finishing train</b>	
<ul style="list-style-type: none"> <li>Water sprays followed by waste water treatment in which the solids (iron oxides) are separated and collected for reuse of iron content.</li> </ul>	
<ul style="list-style-type: none"> <li>Exhaust systems with treatment of extracted air by fabric filters and recycling of collected dust.</li> </ul>	split view on dust level: < 5 mg/Nm <sup>3</sup> < 20 mg/Nm <sup>3</sup>
<b>Levelling and welding</b>	
<ul style="list-style-type: none"> <li>Suction hoods and subsequent abatement by fabric filters</li> </ul>	split view on dust level: < 5 mg/Nm <sup>3</sup> < 20 mg/Nm <sup>3</sup>
<b>Cooling (machines etc.)</b>	
<ul style="list-style-type: none"> <li>Separate cooling water systems operating in closed loops</li> </ul>	
<b>Waste water treatment/ scale- and oil-containing process water</b>	
<ul style="list-style-type: none"> <li>Operating closed loops with recirculating rates of &gt; 95 %</li> </ul>	
<ul style="list-style-type: none"> <li>Reduction of emissions by using a suitable combination of treatment techniques (described in detail in Chapters A.4.1.12.2 and D.10.1).</li> </ul>	SS: < 20 mg/l Oil: < 5 mg/l <sup>(1)</sup> Fe: < 10 mg/l Cr <sub>tot</sub> : < 0.2 mg/l <sup>(2)</sup> Ni: < 0.2 mg/l <sup>(2)</sup> Zn: < 2 mg/l
<ul style="list-style-type: none"> <li>Recirculation of mill scale collected in water treatment to the metallurgical process</li> <li>Oily waste/sludge collected should be de-watered to allow for thermal utilisation or safe disposal.</li> </ul>	
<b>Prevention of hydrocarbon contamination</b>	
<ul style="list-style-type: none"> <li>Preventive periodic checks and preventive maintenance of seals, gaskets, pumps and pipelines.</li> <li>Use of bearings and bearing seals of modern design for work- and back-up rolls, installation of leakage indicators in the lubricant lines (e.g. at hydrostatic bearings).</li> <li>Collection and treatment of contaminated drainage water at the various consumers (hydraulic aggregates), separation and use of oil fraction, e.g. thermal utilisation by blast furnace injection. Further processing of the separated water either in the water treatment plant or in dressing plants with ultra filtration or vacuum evaporator.</li> </ul>	Reduction in oil consumption by 50-70 %.
<sup>1</sup> oil based on random measurements <sup>2</sup> 0.5 mg/l for plants using stainless steel	

**Table 1 continued: Key findings regarding BAT and associated emission/consumption levels for hot rolling**

Best Available Techniques / Split views on BAT	BAT-associated emission and consumption levels / Split views on associated levels
<b>Roll shops</b>	
<ul style="list-style-type: none"> <li>• Use of water-based degreasing as far as technically acceptable for the degree of cleanliness required.</li> <li>• If organic solvents have to be used, preference is to be given to non-chlorinated solvents.</li> <li>• Collection of grease removed from roll trunnions and proper disposal, such as by incineration.</li> <li>• Treatment of grinding sludge by magnetic separation for recovery of metal particles and recirculation into the steelmaking process.</li> <li>• Disposal of oil- and grease-containing residues from grinding wheels, e.g. by incineration.</li> <li>• Deposition of mineral residues from grinding wheels and of worn grinding wheels in landfills.</li> <li>• Treatment of cooling liquids and cutting emulsions for oil/water separation. Proper disposal of oily residues, e.g. by incineration.</li> <li>• Treatment of waste water effluents from cooling and degreasing as well as from emulsion separation in the hot rolling mill water treatment plant.</li> <li>• Recycling of steel and iron turnings into the steelmaking process.</li> </ul>	

**Table 1 continued: Key findings regarding BAT and associated emission/consumption levels for hot rolling**

### Cold Rolling

In cold rolling, the properties of hot rolled strip products, e.g. thickness, mechanical and technological characteristics, are changed by compression between rollers without previous heating of the input. The input is obtained in the form of coils from hot rolling mills. The processing steps and the sequence of processing in a cold rolling mill depend on the quality of the steel treated. The following process steps are used for **low alloy and alloy steel (carbon steel)**: pickling; rolling for reduction in thickness; annealing or heat treatment to regenerate the crystalline structure; temper rolling or skin pass rolling of annealed strip to give desired mechanical properties, shape and surface roughness, and finishing.

The process route for **high alloy steel (stainless steel)** involves additional steps to that for carbon steels. The main stages are: hot band annealing and pickling; cold rolling; final annealing and pickling (or bright annealing); skin pass rolling and finishing.

Cold rolled products are mainly strips and sheets (thickness typically 0.16 - 3 mm) with high quality surface finish and precise metallurgical properties for use in high specification products.

Cold rolled wide strip production (sheets and plates) was about 39.6 million tonnes in 1996. [EUROFER CR]. The main producing countries were Germany with about 10.6 million tonnes, France with 6.3 million tonnes, Italy with 4.3, UK with 4.0 million tonnes and Belgium with 3.8 million tonnes.



Cold rolled narrow strip, obtained from cold rolling narrow hot strip or from slitting and cold rolling hot rolled sheet, amounted to about 8.3 millions tonnes in 1994 (2.7 million tonnes of cold rolled and 5.5 million tonnes of slit strip)

The cold rolled strip industry in the EU is both concentrated and fragmented. The largest 10 companies account for 50 % of the production while another 140 companies account for the remaining 50 %. The structure of the sector is marked by national differences in company size and industry concentration. Most of the largest companies are situated in Germany, which dominate the market with about 57 % of EU production (1.57 million tonnes in 1994). The majority of companies, however, can be classified as small or medium-sized enterprises. [Bed95]

In 1994, Germany produced about 35 % of the slit strip, with 1.9 million tonnes, followed by Italy and France each with a production of 0.9 million tonnes.

The main environmental issues of cold rolling are: acidic wastes and waste water; degreaser fume, acidic and oil mist emissions to air; oil-containing wastes and waste water; dust, e.g. from descaling and decoiling; NO<sub>x</sub> from mixed acid pickling and combustion gases from furnace firing.

As for acid emissions to air from cold rolling, these may arise from pickling and acid regeneration processes. Emissions differ, depending on the pickling process used – basically the acid used. For hydrochloric acid pickling, HCl emissions of 1 – 145 mg/Nm<sup>3</sup> maximum (up to 16 g/t) were reported; with the range reported by industry being 10 – < 30 mg/Nm<sup>3</sup> (~ 0.26 g/t). For sulphuric acid pickling, H<sub>2</sub>SO<sub>4</sub> emissions of 1 – 2 mg/Nm<sup>3</sup> and 0.05 – 0.1 g/t were reported.

For mixed acid pickling of stainless steel, HF emissions were reported in the range of 0.2 – 17 mg/m<sup>3</sup> (0.2 – 3.4 g/t). Additionally to acidic air emissions, NO<sub>x</sub> is generated. The scattering rang was reported to be 3 - ~ 1000 mg/Nm<sup>3</sup> (3 – 4000 g/t specific emission) with doubts being raised on the lower end levels.

Only little data was available for dust emissions from steel handling and descaling operations. Reported ranges for mechanical descaling are 10 – 20 g/t for specific emissions and concentration ranging from < 1 – 25 mg/m<sup>3</sup>.

For more details and for emission and consumption data for other process steps of cold rolling, refer to Chapter A.3 where the available data are presented with qualifying information.

The key findings regarding BAT for individual process steps and different environmental issues of cold rolling are summarized in Table 2. All emission figures are expressed as daily mean values. Emissions to air are based on standard conditions of 273 K, 101.3 kPa and dry gas. Discharges to water are indicated as daily mean value of a flow-rate-related 24-hour composite sample or a flow-rate-related composite sample over the actual operating time (for plants not operated in three shifts).

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Best Available Techniques / Split views on BAT	BAT-associated emission and consumption levels / Split views on associated levels																		
<b>Decoiling</b>																			
<ul style="list-style-type: none"> <li>Water curtains followed by waste water treatment in which the solids are separated and collected for reuse of iron content.</li> <li>Exhaust systems with treatment of extracted air by fabric filters and recycling of collected dust.</li> </ul>	split view on dust level: < 5 mg/Nm <sup>3</sup> < 20 mg/Nm <sup>3</sup>																		
<b>Pickling</b>																			
<p>General measures to reduce acid consumption and waste acid generation as described in Chapter A.4.2.2.1. should be applied as far as possible, especially the following techniques:</p> <ul style="list-style-type: none"> <li>Prevention of steel corrosion by appropriate storage and handling, cooling etc.</li> <li>Reduction of load on pickling step by mechanical pre-descaling in a closed unit, with an extraction system and fabric filters.</li> <li>Use of electrolytic pre-pickling.</li> <li>Use of modern, optimised pickling facilities (spray or turbulence pickling instead of dip pickling).</li> <li>Mechanical filtration and recirculation for lifetime extension of pickling baths.</li> <li>Side-stream ion-exchange or electro-dialysis (for mixed acid) or other method for free acid reclamation (described in Chapter D.6.9) for bath regeneration.</li> </ul>																			
<b>HCl pickling</b>																			
<ul style="list-style-type: none"> <li>Reuse of spent HCl.</li> <li>or Regeneration of the acid by spray roasting or fluidised bed (or equivalent process) with recirculation of the regenerate; air scrubbing system as described in Chapter 4 for the regeneration plant; reuse of Fe<sub>2</sub>O<sub>3</sub> by-product.</li> </ul>	<table border="0"> <tr><td>Dust</td><td>20 -50</td><td>mg/Nm<sup>3</sup></td></tr> <tr><td>HCl</td><td>2 – 30</td><td>mg/Nm<sup>3</sup></td></tr> <tr><td>SO<sub>2</sub></td><td>50 - 100</td><td>mg/Nm<sup>3</sup></td></tr> <tr><td>CO</td><td>150</td><td>mg/Nm<sup>3</sup></td></tr> <tr><td>CO<sub>2</sub></td><td>180000</td><td>mg/Nm<sup>3</sup></td></tr> <tr><td>NO<sub>2</sub></td><td>300 – 370</td><td>mg/Nm<sup>3</sup></td></tr> </table>	Dust	20 -50	mg/Nm <sup>3</sup>	HCl	2 – 30	mg/Nm <sup>3</sup>	SO <sub>2</sub>	50 - 100	mg/Nm <sup>3</sup>	CO	150	mg/Nm <sup>3</sup>	CO <sub>2</sub>	180000	mg/Nm <sup>3</sup>	NO <sub>2</sub>	300 – 370	mg/Nm <sup>3</sup>
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<ul style="list-style-type: none"> <li>Totally enclosed equipment or equipment fitted with hoods and scrubbing of extracted air.</li> </ul>	<table border="0"> <tr><td>Dust</td><td>10 - 20</td><td>mg/Nm<sup>3</sup></td></tr> <tr><td>HCl</td><td>2 – 30</td><td>mg/Nm<sup>3</sup></td></tr> </table>	Dust	10 - 20	mg/Nm <sup>3</sup>	HCl	2 – 30	mg/Nm <sup>3</sup>												
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<b>H<sub>2</sub>SO<sub>4</sub> Pickling</b>																			
<ul style="list-style-type: none"> <li>Recovery of the free acid by crystallisation; air scrubbing devices for recovery plant.</li> </ul>	<table border="0"> <tr><td>H<sub>2</sub>SO<sub>4</sub></td><td>5 - 10</td><td>mg/Nm<sup>3</sup></td></tr> <tr><td>SO<sub>2</sub></td><td>8 – 20</td><td>mg/Nm<sup>3</sup></td></tr> </table>	H <sub>2</sub> SO <sub>4</sub>	5 - 10	mg/Nm <sup>3</sup>	SO <sub>2</sub>	8 – 20	mg/Nm <sup>3</sup>												
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**Table 2: Key findings regarding BAT and associated emission/consumption levels for cold rolling**

Best Available Techniques / Split views on BAT	BAT-associated emission and consumption levels / Split views on associated levels
<b>Mixed acid pickling</b>	
<ul style="list-style-type: none"> <li>• Free acid reclamation (by side-stream ion exchange or dialysis)</li> <li>• or acid regeneration - by spray roasting:</li> <li style="text-align: right;">- or by evaporation process:</li> </ul>	Dust < 10 mg/Nm <sup>3</sup> HF < 2 mg/Nm <sup>3</sup> NO <sub>2</sub> < 200 mg/Nm <sup>3</sup>  HF < 2 mg/Nm <sup>3</sup> NO <sub>2</sub> < 100 mg/Nm <sup>3</sup>
<ul style="list-style-type: none"> <li>• Enclosed equipment/hoods and scrubbing, and additionally:</li> <li>• Scrubbing with H<sub>2</sub>O<sub>2</sub>, urea etc.</li> <li>• or NO<sub>x</sub> suppression by adding H<sub>2</sub>O<sub>2</sub> or urea to the pickling bath</li> <li>• or SCR.</li> </ul>	for all: NO <sub>x</sub> 200 - 650 mg/Nm <sup>3</sup> HF 2 – 7 mg/Nm <sup>3</sup>
<ul style="list-style-type: none"> <li>• Alternative: use of nitric acid-free pickling plus enclosed equipment or equipment fitted with hoods and scrubbing.</li> </ul>	
<b>Heating of acids</b>	
<ul style="list-style-type: none"> <li>• Indirect heating by heat exchangers or, if steam for heat exchangers has to be produced first, by submerged combustion.</li> <li>• Not using direct injection of steam.</li> </ul>	
<b>Minimization of waste water</b>	
<ul style="list-style-type: none"> <li>• Cascade rinsing systems with internal re-use of overflow (e.g. in pickling baths or scrubbing).</li> <li>• Careful tuning and managing of the ‘pickling-acid regeneration-rinsing’ system.</li> </ul>	
<b>Waste water treatment</b>	
<ul style="list-style-type: none"> <li>• Treatment by neutralisation, flocculation, etc., where acidic water blow-down from the system cannot be avoided.</li> </ul>	SS: < 20 mg/l Oil: < 5 mg/l <sup>1</sup> Fe: < 10 mg/l Cr <sub>tot</sub> : < 0.2 mg/l <sup>2</sup> Ni: < 0.2 mg/l <sup>2</sup> Zn: < 2 mg/l
<b>Emulsion systems</b>	
<ul style="list-style-type: none"> <li>• Prevention of contamination by regular checking of seals, pipework etc. and leakage control.</li> <li>• Continuous monitoring of emulsion quality.</li> <li>• Operation of emulsion circuits with cleaning and reuse of emulsion to extend lifetime.</li> <li>• Treatment of spent emulsion to reduce oil content, e.g. by ultrafiltration or electrolytic splitting.</li> </ul>	
<b>Rolling and tempering</b>	
<ul style="list-style-type: none"> <li>• Exhaust system with treatment of extracted air by mist eliminators (droplet separator).</li> </ul>	Hydrocarbons: 5 – 15 mg/Nm <sup>3</sup> .
<sup>1</sup> oil based on random measurements <sup>2</sup> for stainless steel < 0.5 mg/l	

**Table 2 continued: Key findings regarding BAT and associated emission/consumption levels for cold rolling**

Best Available Techniques / Split views on BAT	BAT-associated emission and consumption levels / Split views on associated levels
<b>Degreasing</b>	
<ul style="list-style-type: none"> <li>• Degreasing circuit with cleaning and reuse of the degreaser solution. Appropriate measures for cleaning are mechanical methods and membrane filtration as described in chapter A.4.</li> <li>• Treatment of spent degreasing solution by electrolytic emulsion splitting or ultrafiltration to reduce the oil content; reuse of separated oil fraction; treatment (neutralisation etc.) of separated water fraction prior to discharge.</li> <li>• Extraction system for degreasing fume and scrubbing.</li> </ul>	
<b>Annealing furnaces</b>	
<ul style="list-style-type: none"> <li>• For continuous furnaces, low NO<sub>x</sub> burners.</li> </ul>	NO <sub>x</sub> 250–400 mg/Nm <sup>3</sup> without air pre-heating, 3 % O <sub>2</sub> . Reduction rates of 60 % for NO <sub>x</sub> (and 87 % for CO)
<ul style="list-style-type: none"> <li>• Combustion air pre-heating by regenerative or recuperative burners or</li> <li>• Pre-heating of stock by waste gas.</li> </ul>	
<b>Finishing/Oiling</b>	
<ul style="list-style-type: none"> <li>• Extraction hoods followed by mist eliminators and/or electrostatic precipitators or</li> <li>• Electrostatic oiling.</li> </ul>	
<b>Levelling and welding</b>	
<ul style="list-style-type: none"> <li>• Extraction hoods with dust abatement by fabric filters.</li> </ul>	split view on dust level: < 5 mg/Nm <sup>3</sup> < 20 mg/Nm <sup>3</sup>
<b>Cooling (machines etc.),</b>	
<ul style="list-style-type: none"> <li>• Separate cooling water systems operating in closed loops.</li> </ul>	
<b>Roll shops</b>	
Refer to BATs listed for roll shops in hot rolling.	
<b>Metallic by-products</b>	
<ul style="list-style-type: none"> <li>• Collection of scrap from cutting, heads and tails and recirculation into the metallurgical process.</li> </ul>	

Table 2 continued: Key findings regarding BAT and associated emission/consumption levels for cold rolling

## Wire Drawing

Wire drawing is a process in which wire rods/wires are reduced in size by drawing them through cone-shaped openings of a smaller cross section, called dies. The input is usually wire rod of diameters ranging from 5.5 to 16 mm obtained from hot rolling mills in the form of coils. A typical wire drawing plant comprises the following process lines:

- Pre-treatment of the wire rod (mechanical descaling, pickling)
- Dry or wet drawing (usually several drafts with decreasing die sizes)
- Heat treatment (continuous-/discontinuous annealing, patenting, oil hardening)
- Finishing

The European Union has the world largest wire drawing industry, followed by Japan and North America. It produces about 6 million tonnes of wire per year. Including the various wire products, such as barbed wire, grill, fencing, netting, nails etc, the production of the sector reaches more than 7 million tonnes per year. The European wire drawing industry is characterised by a large number of medium sized, specialised companies. The industry's output, however, is dominated by a few large producers. It is estimated that about 5 % of the companies account for 70 % of the industry's output (25 % of the companies for 90 %).

Over the past 10 years, independent wire drawing companies have become increasingly vertically integrated. Approximately 6 % of the wire drawers in Europe are integrated producers representing about 75 % of the total production of steel wire [C.E.T].

The largest producer of steel wire is Germany with 32 % (about 1.09 million tonnes) of EU wire production, followed by Italy (approx. 22 %, 1.2 million tonnes), UK, Benelux (mainly Belgium), France and Spain.

The main environmental aspects of wire drawing are: air emissions from pickling, acidic wastes and waste water; fugitive soap dust (dry drawing), spent lubricant and effluents (wet drawing), combustion gas from furnaces and emissions and lead-containing wastes from lead baths.

For air emissions from pickling, HCl concentrations of 0 - 30 mg/Nm<sup>3</sup> were reported. In continuous annealing and patenting lead baths are used. Generating lead containing wastes, 1 - 15 kg/t for continuous annealing and 1 -10 kg/t for patenting. Reported Pb air emissions for patenting are < 0.02 - 1 mg/Nm<sup>3</sup> and Pb concentrations in quench water overflow 2 - 20 mg/l.

For more details and for emission and consumption data for other process steps of wire drawing, refer to Chapter A.3 where the available data are presented with qualifying information.

The key findings regarding BAT for individual process steps and different environmental issues of wire drawing are summarized in Table 3. All emission figures are expressed as daily mean values. Emissions to air are based on standard conditions of 273 K, 101.3 kPa and dry gas. Discharges to water are indicated as daily mean value of a flow-rate-related 24-hour composite sample or a flow-rate-related composite sample over the actual operating time (for plants not operated in three shifts).

There was consensus in the TWG on the best available techniques and associated emission/consumption levels presented in the table.

Best Available Techniques	BAT-associated emission and consumption levels
<b>Batch pickling</b>	
<ul style="list-style-type: none"> <li>• Close monitoring of bath parameters: temperature and concentration.</li> <li>• Operating within the limits given in Part D/Chapter D.6.1 ‘Open Pickling Bath Operation’.</li> <li>• For of pickling baths with high vapour emission, e.g. heated or concentrated HCl-bath: installation of lateral extraction and possibly treating of the extraction air for both new and existing installations.</li> </ul>	HCl 2 – 30 mg/Nm <sup>3</sup> .
<b>Pickling</b>	
<ul style="list-style-type: none"> <li>• Cascade Pickling (capacity &gt;15 000 tonne wire rod per year) or</li> <li>• Reclamation of free acid fraction and reuse in pickling plant.</li> <li>• External regeneration of spent acid.</li> <li>• Recycling of spent acid as secondary raw material.</li> <li>• Non-acid descaling, e.g shot blasting, if quality requirements allow it.</li> <li>• Counter current cascade rinsing.</li> </ul>	
<b>Dry drawing</b>	
<ul style="list-style-type: none"> <li>• Enclosing the drawing machine (and connecting to a filter or similar device when necessary), for all new machines with drawing speed <math>\geq 4</math> m/s.</li> </ul>	
<b>Wet drawing</b>	
<ul style="list-style-type: none"> <li>• Cleaning and reuse of drawing lubricant.</li> <li>• Treatment of spent lubricant to reduce oil content in the discharge and/or to reduce waste volume, e.g. by chemical breaking, electrolytic emulsion splitting or ultrafiltration.</li> <li>• Treatment of discharge water fraction.</li> </ul>	
<b>Dry and wet drawing</b>	
<ul style="list-style-type: none"> <li>• Closed cooling-water loops.</li> <li>• Not using once-through cooling water systems.</li> </ul>	
<b>Batch annealing furnaces, continuous annealing furnaces for stainless steel and furnaces used in oil hardening and tempering</b>	
<ul style="list-style-type: none"> <li>• Burning of the protective gas purge.</li> </ul>	
<b>Continuous annealing of low carbon wire and patenting,</b>	
<ul style="list-style-type: none"> <li>• Good housekeeping measures, as described in chapter A.4.3.7 for the lead bath.</li> <li>• Separate storage of Pb-containing wastes, protected from rain and wind.</li> <li>• Recycling of Pb-containing wastes in non-ferrous metals industry</li> <li>• Closed loop operation of quench bath.</li> </ul>	Pb < 5 mg/Nm <sup>3</sup> , CO < 100 mg/Nm <sup>3</sup> TOC < 50 mg/Nm <sup>3</sup> .
<b>Oil-hardening lines</b>	
<ul style="list-style-type: none"> <li>• Evacuation of the oil mist from quench baths and removal of the oil mists, when appropriate.</li> </ul>	

**Table 3: Key findings regarding BAT and associated emission/consumption levels for wire drawing**

## Part B: Continuous Hot Dip Coating

In the hot dip coating process, steel sheet or wire is continuously passed through molten metal. An alloying reaction between the two metals takes place, leading to a good bond between coating and substrate.

Metals suitable for the use in hot dip coating are those which have a melting point low enough to avoid any thermal changes in the steel product; for example, aluminium, lead, tin and zinc.

The production of continuous hot dip coating lines in the EU was about 15 Mt in 1997. The vast majority of coatings applied in continuous hot dip coating is zinc. Aluminium coatings and, especially, terne coatings played only a minor role.

Galvanized steel	81 %
Galvannealed steel	4 %
Galfan	4 %
Aluminized steel	5%
Aluzinc	5%
Ternex	1 %

In general, **continuous coating lines for sheet** comprise the following steps:

- Surface cleaning by means of chemical and/or thermal treatment
- Heat treatment
- Immersion in a bath of molten metal
- Finishing treatment

**Continuous wire galvanizing plants** involve the following steps:

- Pickling
- Fluxing
- Galvanizing
- Finishing

Main environmental issues concerning this sub-sector are acidic air emissions, wastes and waste water; air emissions and energy consumption of furnaces, Zinc-containing residues, oil- and chrome-containing waste waters.

For detailed emission and consumption data, refer to Chapter B.3 where the available data are presented with qualifying information.

The key findings regarding BAT for individual process steps and different environmental issues of continuous hot dip galvanizing are summarized in Table 4. All emission figures are expressed as daily mean values. Emissions to air are based on standard conditions of 273 K, 101.3 kPa and dry gas. Discharges to water are indicated as daily mean value of a flow-rate-related 24-hour composite sample or a flow-rate-related composite sample over the actual operating time (for plants not operated in three shifts).

There was consensus in the TWG on the best available techniques and associated emission/consumption levels presented in the table.

Best Available Techniques	BAT-associated emission and consumption levels
<b>Pickling</b>	
<ul style="list-style-type: none"> <li>Refer to the BAT chapter of Part A/Cold rolling Mills.</li> </ul>	
<b>Degreasing</b>	
<ul style="list-style-type: none"> <li>Cascade degreasing.</li> <li>Cleaning and recirculation of degreasing solution; appropriate measures for cleaning are mechanical methods and membrane filtration as described in chapter A.4.</li> <li>Treatment of spent degreasing solution by electrolytic emulsion splitting or ultrafiltration to reduce the oil content; reutilisation of separated oil fraction, e.g. thermally; treatment (neutralisation etc.) of the separated water fraction.</li> <li>Covered tanks with extraction and cleaning of extracted air by scrubber or demister.</li> <li>Use of squeeze rolls to minimize drag-out.</li> </ul>	
<b>Heat treatment furnaces</b>	
<ul style="list-style-type: none"> <li>Low-NOx burners.</li> <li>Air pre-heating by regenerative or recuperative burners.</li> <li>Pre-heating of strip.</li> <li>Steam production to recover heat from waste gas.</li> </ul>	NOx 250 - 400 mg/Nm <sup>3</sup> (3% O <sub>2</sub> ) without air pre-heating CO 100 - 200 mg/Nm <sup>3</sup>
<b>Hot dipping</b>	
<ul style="list-style-type: none"> <li>Separate collection and recycling in the non-ferrous metals industry for zinc-containing residues, dross or hard zinc.</li> </ul>	
<b>Galvannealing</b>	
<ul style="list-style-type: none"> <li>Low-NOx burners.</li> <li>Regenerative or recuperative burner systems.</li> </ul>	NOx 250-400 mg/Nm <sup>3</sup> (3% O <sub>2</sub> ) without air pre-heating
<b>Oiling</b>	
<ul style="list-style-type: none"> <li>Covering the strip oiling machine or</li> <li>Electrostatic oiling.</li> </ul>	
<b>Phosphating and passivation/chromating</b>	
<ul style="list-style-type: none"> <li>Covered process baths.</li> <li>Cleaning and reuse of phosphating solution.</li> <li>Cleaning and reuse of passivation solution.</li> <li>Use of squeeze rolls.</li> <li>Collection of skinpass/temper solution and treatment in waste water treatment plant.</li> </ul>	
<b>Cooling (machines etc.)</b>	
<ul style="list-style-type: none"> <li>Separate cooling water systems operating in closed loops.</li> </ul>	
<b>Waste water</b>	
<ul style="list-style-type: none"> <li>Waste water treatment by a combination of sedimentation, filtration and/or flotation/ precipitation/flocculation. Techniques described in Chapter 4 or equally efficient combinations of individual treatment measures (also described in part D).</li> <li>For existing continuous water treatment plants which only achieve Zn &lt; 4 mg/l, switch to batch treatment.</li> </ul>	SS: < 20 mg/l Fe: < 10 mg/l Zn: < 2 mg/l Ni: < 0.2 mg/l Cr <sub>tot</sub> : < 0.2 mg/l Pb: < 0.5 mg/l Sn: < 2 mg/l

Table 4: Key findings regarding BAT and associated emission/consumption levels for continuous hot dip galvanizing



### Aluminizing of Sheet

Most BAT are the same as for hot dip galvanising. However, there is no need for a waste water treatment plant as only cooling water is discharged.

BAT for heating:

Gas firing. Combustion control system

### Lead-Tin Coating of Sheet

Best Available Techniques	BAT-associated emission and consumption levels
<b>Pickling</b>	
Enclosed tanks and venting to a wet scrubber, treatment of waste water from the scrubber and pickling tank.	HCl < 30 mg/Nm <sup>3</sup> <sup>(1)</sup>
<b>Nickel plating</b>	
<ul style="list-style-type: none"> <li>Enclosed process, ventilated to a wet scrubber.</li> </ul>	
<b>Hot dipping</b>	
<ul style="list-style-type: none"> <li>Air knives to control coating thickness.</li> </ul>	
<b>Passivation</b>	
<ul style="list-style-type: none"> <li>A no-rinse system and hence no rinse waters.</li> </ul>	
<b>Oiling</b>	
<ul style="list-style-type: none"> <li>Electrostatic oiling machine.</li> </ul>	
<b>Waste water</b>	
<ul style="list-style-type: none"> <li>Waste water treatment by neutralising with sodium hydroxide solution, flocculation/precipitation.</li> <li>Filter cake de-watering and disposed to landfill.</li> </ul>	
<sup>1</sup> daily mean values, standard conditions of 273 K, 101.3 Pa and dry gas	

**Table 5: Key findings regarding BAT and associated emission/consumption levels for continuous lead-tin coating of sheet**

## Coating of Wire

The key findings regarding BAT for individual process steps and different environmental issues of wire coating are summarized in Table 6. All emission figures are expressed as daily mean values. Emissions to air are based on standard conditions of 273 K, 101.3 kPa and dry gas. Discharges to water are indicated as daily mean value of a flow-rate-related 24-hour composite sample or a flow-rate-related composite sample over the actual operating time (for plants not operated in three shifts).

There was consensus in the TWG on the best available techniques and associated emission/consumption levels presented in the table.

Best Available Techniques	BAT-associated emission and consumption levels
<b>Pickling</b>	
<ul style="list-style-type: none"> <li>Enclosed equipment or equipment fitted with hoods and scrubbing of extracted air.</li> <li>Cascade pickling for new installations above a capacity of 15 000 tonne/year per line.</li> <li>Recovery of free acid fraction.</li> <li>External regeneration of spent acid for all installations.</li> <li>Reuse of spent acid as secondary raw material.</li> </ul>	HCl 2 - 30 mg/Nm <sup>3</sup> .
<b>Water consumption</b>	
Cascaded rinsing, possibly in combination with other methods to minimize water consumption, for all new and all large installations (> 15 000 tonne/year).	
<b>Waste water</b>	
<ul style="list-style-type: none"> <li>Waste water treatment by physico-chemical treatment (neutralisation, flocculation, etc.).</li> </ul>	SS: < 20 mg/l Fe: < 10 mg/l Zn: < 2 mg/l Ni: < 0.2 mg/l Cr <sub>tot</sub> : < 0.2 mg/l Pb: < 0.5 mg/l Sn: < 2 mg/l
<b>Fluxing</b>	
<ul style="list-style-type: none"> <li>Good housekeeping with special focus on reducing iron carry-over and bath maintenance.</li> <li>Regeneration of flux baths on site (side-stream iron removal).</li> <li>External reutilisation of spent flux solution.</li> </ul>	
<b>Hot dipping</b>	
<ul style="list-style-type: none"> <li>Good housekeeping measures as described in Chapter B.4</li> </ul>	Dust < 10 mg/Nm <sup>3</sup> Zinc < 5 mg/Nm <sup>3</sup>
<b>Zn-containing wastes</b>	
<ul style="list-style-type: none"> <li>Separate storage and protection from rain and wind, and reuse in the non-ferrous metals industry.</li> </ul>	
<b>Cooling water (after the zinc bath)</b>	
<ul style="list-style-type: none"> <li>Closed loop or reuse of this relatively pure water as make-up water for other applications.</li> </ul>	

**Table 6: Key findings regarding BAT and associated emission/consumption levels for wire coating**

## Part C: Batch Galvanizing

Hot dip galvanizing is a corrosion protection process in which iron and steel fabrications are protected from corrosion by coating them with zinc. Prevalent in batch hot dip galvanizing is job galvanizing - also referred to as general galvanizing - in which a great variety of input materials are treated for different customers. The size, amount and nature of the inputs can differ significantly. Galvanizing of pipes or tubes which is carried out in semi- or fully-automatic special galvanizing plants is usually not covered by the term job galvanizing.

The items to be coated in batch galvanizing plants are steel fabrications, such as nails, screws and other very small items; lattice grates, construction parts, structural components, light poles and many more. In some cases tubes are also galvanized in conventional batch coating plants. Galvanized steel is used in construction, transport, agriculture, power transmission and everywhere that good corrosion protection and long life are essential.

The sector operates with short lead times and short order books to give enhanced service to customers. Distribution issues are important, and so plants are located close to market concentrations. Consequently, the industry consists of a relatively large number of plants (about 600 all over Europe), servicing regional markets in order to minimize distribution costs and increase economic efficiency. Only a few 'niche' operators are prepared to transport certain classes of fabrication for longer distances in order to exploit their special expertise or plant capability. Opportunities for these specialist operators are limited.

In 1997 the tonnage of galvanized steel was about 5 million. The largest share was produced by Germany with 1.4 million tonnes and 185 galvanizing plants (in 1997). Second largest producer was Italy with 0.8 million tonnes (74 plants), followed by UK and Ireland with 0.7 million tonnes (88 plants) and France 0.7 million tonnes (69 plants).

Batch galvanizing usually comprises the following process steps:

- Degreasing
- Pickling
- Fluxing
- Galvanizing (melt metal coating)
- Finishing

A galvanizing plant, essentially, consists of a series of treatment or process baths. The steel is moved between tanks and dipped into the baths by overhead cranes.

The main environmental issues for batch galvanizing are emissions to air (HCl from pickling, and dust and gaseous compounds from the kettle); spent process solutions (degreasing solutions, pickling baths and flux baths), oily wastes (e.g. from cleaning of degreasing baths) and zinc-containing residues (filter dust, zinc ash, hard zinc).

For detailed emission and consumption data, refer to Chapter .3 where the available data are presented with qualifying information.

The key findings regarding BAT for individual process steps and different environmental issues of batch galvanizing are summarized in Table 7. All emission figures are expressed as daily mean values. Emissions to air are based on standard conditions of 273 K, 101.3 kPa and dry gas. Discharges to water are indicated as daily mean value of a flow-rate-related 24-hour composite sample or a flow-rate-related composite sample over the actual operating time (for plants not operated in three shifts).

There was consensus in the TWG on the best available techniques and associated emission/consumption levels presented in the table.

Best Available Techniques	BAT-associated emission and consumption
<b>Degreasing</b>	
<ul style="list-style-type: none"> <li>• Installation of a degreasing step, unless items are totally grease free.</li> <li>• Optimum bath operation to enhance efficiency, e.g. by agitation.</li> <li>• Cleaning degreasing solutions to extend lifespan (by skimming, centrifuge, etc.) and recirculation, reutilization of oily sludge or</li> <li>• 'Biological degreasing' with in situ cleaning (grease and oil removal from degreaser solution) by bacteria.</li> </ul>	
<b>Pickling + stripping:</b>	
<ul style="list-style-type: none"> <li>• Separate pickling and stripping unless a downstream process for the recovery of values from “mixed” liquors is installed on site or is available through a specialist external contractor.</li> <li>• Reuse of spent stripping liquor (external or internal e.g. to recover fluxing agent).</li> </ul> <p>In case of combined pickling and stripping:</p> <ul style="list-style-type: none"> <li>• Recovery of values from “mixed” liquors, e.g. use for flux production, recovery of acid for re-use in the galvanizing industry or for other inorganic chemicals</li> </ul>	
<b>HCl pickling</b>	
<ul style="list-style-type: none"> <li>• Close monitoring of baths parameters: temperature and concentration.</li> <li>• Operating within the limits given in Part D/Chapter D.6.1 ‘Open Pickling Bath Operation’.</li> <li>• If heated or higher concentrated HCl-baths are used: installation of extraction unit and treatment of extracted air (e.g. by scrubbing).</li> <li>• Special attention to actual pickling effect of bath and use of pickling inhibitors to avoid over-pickling.</li> <li>• Recovery of free acid fraction from spent pickle liquor or external regeneration of pickling liquor.</li> <li>• Zn removal from acid.</li> <li>• Use of spent pickle liquor for flux production.</li> <li>• Not using spent pickle liquor for neutralisation</li> <li>• Not using spent pickling liquor for emulsion splitting</li> </ul>	HCl 2 – 30 mg/Nm <sup>3</sup>
<b>Rinsing</b>	
<ul style="list-style-type: none"> <li>• Good drainage between pre-treatment tanks.</li> <li>• Implementation of rinsing after degreasing and after pickling.</li> <li>• Static rinsing or rinsing cascades.</li> <li>• Reuse of rinse water to replenish preceding process baths. Waste water-free operation (in exceptional cases where waste water is generated, waste water treatment is required).</li> </ul>	

**Table 7: Key findings regarding BAT and associated emission/consumption levels for batch galvanizing**

Best Available Techniques	BAT-associated emission and consumption
<b>Fluxing</b>	
<ul style="list-style-type: none"> <li>• Control of bath parameters and the optimised amount of flux used are also important to reduce emission further down the process line.</li> <li>• For flux baths: internal and external flux bath regeneration.</li> </ul>	
<b>Hot dipping</b>	
<ul style="list-style-type: none"> <li>• Capture of emissions from dipping by enclosure of the pot or by lip extraction and dust abatement by fabric filters or wet scrubbers.</li> <li>• Internal or external reuse of dust, e.g. for flux production. The recovery system should ensure that dioxins, which may occasionally be present at low concentration due to upset conditions in the plant, do not build up as the dusts are recycled.</li> </ul>	Dust < 5 mg/Nm <sup>3</sup>
<b>Zn-containing wastes</b>	
<ul style="list-style-type: none"> <li>• Separate storage and protection from rain and wind, and reuse of contained values in the non-ferrous or other sectors.</li> </ul>	

**Table 7 continued: Key findings regarding BAT and associated emission/consumption levels for batch galvanizing**



## PREFACE

### 1. Status of this document

Unless otherwise stated, references to “the Directive” in this document means the Council Directive 96/61/EC on integrated pollution prevention and control.

This document forms part of a series presenting the results of an exchange of information between EU Member States and industries concerned on best available techniques (BAT), associated monitoring, and developments in them. It is published by the European Commission pursuant to Article 16(2) of the Directive, and must therefore be taken into account in accordance with Annex IV of the Directive when determining “best available techniques”.

### 2. Relevant legal obligations of the IPPC Directive and the definition of BAT

In order to help the reader understand the legal context in which this document has been drafted, some of the most relevant provisions of the IPPC Directive, including the definition of the term “best available techniques”, are described in this preface. This description is inevitably incomplete and is given for information only. It has no legal value and does not in any way alter or prejudice the actual provisions of the Directive.

The purpose of the Directive is to achieve integrated prevention and control of pollution arising from the activities listed in its Annex I, leading to a high level of protection of the environment as a whole. The legal basis of the Directive relates to environmental protection. Its implementation should also take account of other Community objectives such as the competitiveness of the Community’s industry thereby contributing to sustainable development.

More specifically, it provides for a permitting system for certain categories of industrial installations requiring both operators and regulators to take an integrated, overall look at the polluting and consuming potential of the installation. The overall aim of such an integrated approach must be to improve the management and control of industrial processes so as to ensure a high level of protection for the environment as a whole. Central to this approach is the general principle given in Article 3 that operators should take all appropriate preventative measures against pollution, in particular through the application of best available techniques enabling them to improve their environmental performance.

The term “best available techniques” is defined in Article 2(11) of the Directive as “the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole.” Article 2(11) goes on to clarify further this definition as follows:

“techniques” includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;

“available” techniques are those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator;

“best” means most effective in achieving a high general level of protection of the environment as a whole.

Furthermore, Annex IV of the Directive contains a list of “considerations to be taken into account generally or in specific cases when determining best available techniques ... bearing in mind the likely costs and benefits of a measure and the principles of precaution and prevention”. These considerations include the information published by the Commission pursuant to Article 16(2).

Competent authorities responsible for issuing permits are required to take account of the general principles set out in Article 3 when determining the conditions of the permit. These conditions must include emission limit values, supplemented or replaced where appropriate by equivalent parameters or technical measures. According to Article 9(4) of the Directive, these emission limit values, equivalent parameters and technical measures must, without prejudice to compliance with environmental quality standards, be based on the best available techniques, without prescribing the use of any technique or specific technology, but taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In all circumstances, the conditions of the permit must include provisions on the minimization of long-distance or transboundary pollution and must ensure a high level of protection for the environment as a whole.

Member States have the obligation, according to Article 11 of the Directive, to ensure that competent authorities follow or are informed of developments in best available techniques.

### **3. Objective of this Document**

Article 16(2) of the Directive requires the Commission to organise “an exchange of information between Member States and the industries concerned on best available techniques, associated monitoring and developments in them”, and to publish the results of the exchange.

The purpose of the information exchange is given in recital 25 of the Directive, which states that “the development and exchange of information at Community level about best available techniques will help to redress the technological imbalances in the Community, will promote the world-wide dissemination of limit values and techniques used in the Community and will help the Member States in the efficient implementation of this Directive.”

The Commission (Environment DG) established an information exchange forum (IEF) to assist the work under Article 16(2) and a number of technical working groups have been established under the umbrella of the IEF. Both IEF and the technical working groups include representation from Member States and industry as required in Article 16(2).

The aim of this series of documents is to reflect accurately the exchange of information which has taken place as required by Article 16(2) and to provide reference information for the permitting authority to take into account when determining permit conditions. By providing relevant information concerning best available techniques, these documents should act as valuable tools to drive environmental performance.

### **4. Information Sources**

This document represents a summary of information collected from a number of sources, including in particular the expertise of the groups established to assist the Commission in its work, and verified by the Commission services. All contributions are gratefully acknowledged.

### **5. How to understand and use this document**

The information provided in this document is intended to be used as an input to the determination of BAT in specific cases. When determining BAT and setting BAT-based permit conditions, account should always be taken of the overall goal to achieve a high level of protection for the environment as a whole.



The rest of this section describes the type of information that is provided in each section of the document.

In each of the sections A, B and C, Sub-chapters 1 and 2 provide general information on the industrial sector concerned and on the industrial processes used within the sector.

Sub-chapters 3 provides data and information concerning current emission and consumption levels reflecting the situation in existing installations at the time of writing.

Sub-chapters 4 describe in more detail the emission reduction and other techniques that are considered to be most relevant for determining BAT and BAT-based permit conditions. This information includes the consumption and emission levels considered achievable by using the technique, some idea of the costs and the cross-media issues associated with the technique, and the extent to which the technique is applicable to the range of installations requiring IPPC permits, for example new, existing, large or small installations. Techniques that are generally seen as obsolete are not included.

Sub-chapters 5 present the techniques and the emission and consumption levels that are considered to be compatible with BAT in a general sense. The purpose is thus to provide general indications regarding the emission and consumption levels that can be considered as an appropriate reference point to assist in the determination of BAT-based permit conditions or for the establishment of general binding rules under Article 9(8). It should be stressed, however, that this document does not propose emission limit values. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economical and technical viability of upgrading them also needs to be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and levels presented in sub-chapters 5 will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimization of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document is fully taken into account by permitting authorities.

Since the best available techniques change over time, this document will be reviewed and updated as appropriate. All comments and suggestions should be made to the European IPPC Bureau at the Institute for Prospective Technological Studies at the following address:

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## Scope

The scope of this work on Ferrous Metal Processing is closely linked to the scope of the earlier work on Primary and Secondary Iron and Steel which covered the iron and steel production to the casting process. Starting with the semi-finished products ingots, slabs, blooms and billets obtained from ingot casting or continuous casting the further manufacturing steps, like hot rolling, cold rolling and drawing, hot dip metal coating and the related pre- and after treatment of the shaped steel products, will be covered.

Section 2.3 a of Annex I to Directive 96/61/EC only explicitly names hot rolling mills (> 20 t/h), but cold rolling mills and associated processes, like pickling and degreasing, will also be covered.

Section 2.3 c of the Annex refers to protective smelt metal coats (>2 t/h). No distinction is made between continuous hot dip coating of steel and the hot dip coating of fabricated steel products. Therefore batch hot dip coating of steel fabricates, known as general galvanizing, is part of the work.

Smitheries and ferrous metal foundries (Section 2.3 b and 2.4 of Annex I) are not included in this work and neither are electroplating nor organic coating of steel.

Main operational steps regarding *continuous processing* that will be covered are:

- Reheating and heat treatment of input materials, like slabs, blooms, billets and ingots.
- Surface rectification and preparation processes:  
scarfing, grinding, descaling, degreasing, pickling
- Shaping of steel: rough milling, hot rolling, cold rolling, drawing.
- Processes yielding in special material or product qualities:  
annealing, temper rolling/skin pass rolling
- Hot dip metal coating and finishing.

Regarding *batch hot dip coating* of fabricated steel products the following operational steps will be addressed:

- Surface preparation of fabricated steel: degreasing, rinsing, pickling, fluxing, drying.
- Coating with molten metal.
- After treatment/finishing: cooling, greasing.

This BREF document consists of 4 Parts (A – D). Parts A to C cover the different industrial sub-sectors of the Ferrous Metals Processing sector: A, Hot and Cold Forming; B, Continuous Coating; C, Batch Galvanizing. This structure was chosen because of the differences in nature and scale of the activities covered by the term FMP.

Part D does not cover an industrial sub-sector. It comprises the technical descriptions of a number of environmental measures which are techniques to be considered in the determination of BAT in more than one sub-sector. This was done to avoid repetition of technical descriptions in the three Chapters 4. These descriptions have to be viewed always in connection with the more specific information, referring to the application in individual sub-sectors, which is given in the relevant Chapter 4.



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**PART A**  
**Hot and Cold Forming**  
**(Rolling and Drawing of Steel)**





## A.1 GENERAL INFORMATION ON HOT AND COLD FORMING

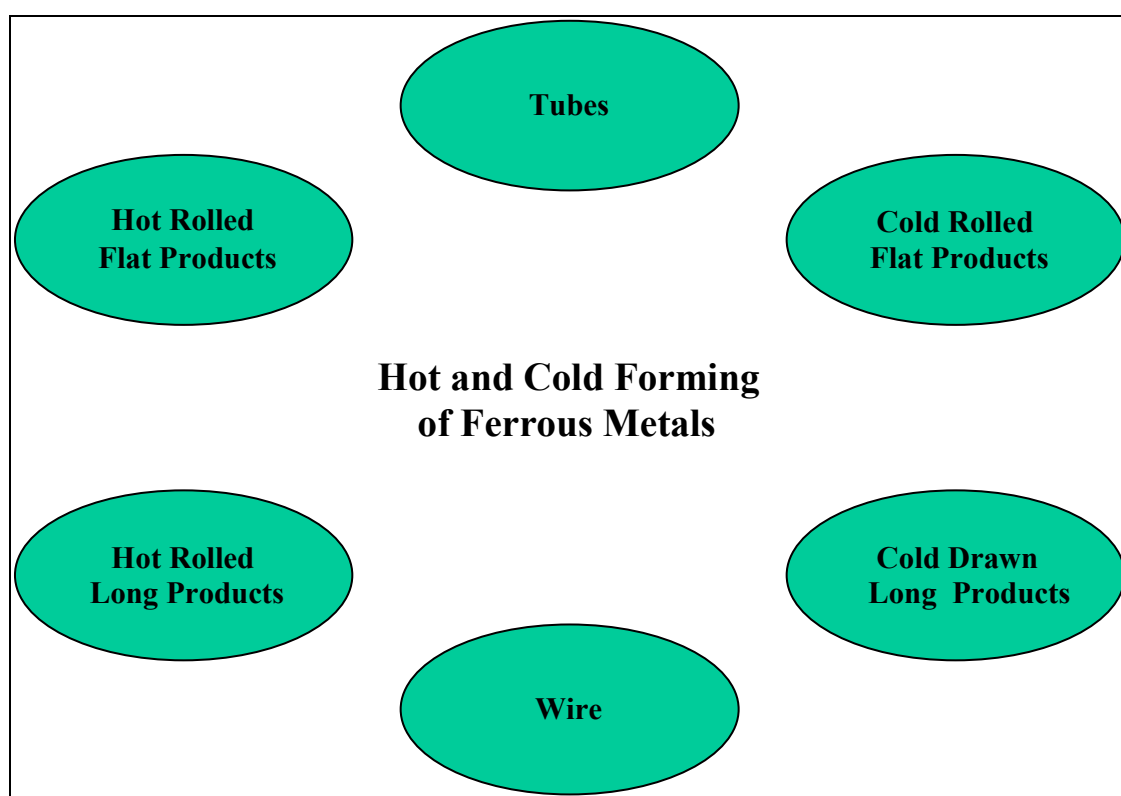
The hot and cold forming part of the ferrous metal processing sector comprises different manufacturing methods, like hot rolling, cold rolling and drawing of steel. A great variety of semi-finished and finished products with different lines of production is manufactured.

Literature dealing with the ferrous metals sector uses different ways of splitting and structuring the sector and for delivering data. Some reports distinguish with regard to the forming process: hot - cold; or with regard to the shape of the final product: flat - long.

Others (e.g. NACE <sup>1</sup>) separate in groups: iron and steel production (including most of the hot and cold rolled products as well as continuous coated strip), manufacture of steel tubes and 'other first processing of steel' (cold drawing, cold rolling of narrow strip, wire drawing etc.).

To put together general information on the sector, statistical data (productivity, number/ size of plants, distribution etc.) and economic information is difficult as most of the available sources for data use different basis and different splitting of the sector, thus making it impossible to compare the given data.

To present the general information on the hot and cold forming sector in this BREF, an outline in accordance with the manufactured products; as is shown in Figure A.1-1, was chosen.



**Figure A.1-1: Hot and Cold Formed Products covered by this BREF**

<sup>1</sup> General industrial classification of economic activities within the European Community

## A.1.1 Hot Rolled Flat Products

The total production of hot rolled (HR) products in the EU decreased from 131.7 million tonnes in 1994 [EGKS95] to 127.8 million tonnes in 1996 [Stat97]. Roughly, 62 % of these HR products fall into the category: flats with an annual production of 79.2 million tonnes. Table A.1-1 presents production data for individual flat products for each Member State in 1996.

	HR Wide Flats [1000 t]	HR Narrow Strip [1000 t]	HR Wide Strip [1000 t]	HR Plate [1000 t]	Total HR Flat Products [1000 t]
<b>Austria</b>	0	0	2621	340	<b>2961</b>
<b>Belgium</b>	0	0	9350	566	<b>9916</b>
<b>Denmark</b>	0	0	0	388	<b>388</b>
<b>Finland</b>	0	0	1670	576	<b>2246</b>
<b>France</b>	1	0	9871	845	<b>10717</b>
<b>Germany</b>	103	623	19138	2748	<b>22612</b>
<b>Greece</b>	0	9	346	4	<b>359</b>
<b>Ireland</b>	0	0	0	0	<b>0</b>
<b>Italy</b>	185	48	8061	1385	<b>9679</b>
<b>Luxembourg</b>	0	0	0	0	<b>0</b>
<b>Netherlands</b>	0	0	4136	15	<b>4151</b>
<b>Portugal</b>	0	0	0	0	<b>0</b>
<b>Sweden</b>	46	32	2832	569	<b>3479</b>
<b>Spain</b>	0	190	3385	575	<b>4150</b>
<b>UK</b>	88	145	7396	958	<b>8587</b>
<b>Total</b>	<b>423</b>	<b>1047</b>	<b>68806</b>	<b>8969</b>	<b>79245</b>

Reference year 1996

**Table A.1-1: Production of Flat Products in EU 15 in 1996 [Stat97]**

Regarding the total production of HR flats, Germany is the largest manufacturer with more than double the production of the follow-up producers (France, Belgium, Italy and UK). The vast majority of HR flat products is wide strip.

Beginning of 1993 74 production units for flats were in operation in EU 12. Number and size of these plants are given in Table A.1-2.

	Total number of plants	Total average hourly technical capacity [t/h]	Number of plants with an average hourly technical capacity over 20t/h
Narrow Strip Mills	17	45	15
Wide Strip Mills	25	474	25
Heavy and Medium Plate Mills	32	109	23
Sheet Mills	7	12	
Universal Flat Mill	2	31	
Re-rolling Mills for Hot Wide Strip	8	677	

**Table A.1-2: Size distribution of Flat Product manufacturing facilities [EUROSTAT]**

## A.1.2 Hot Rolled Long Products

The remaining 38 % of HR products are categorized as long products. Production figures for all Members States are given in Table A.1-3.

	Track Material [1000 t]	Heavy sections/ profiles [1000 t]	Reinforcing Steel Bars [1000 t]	Merchant Bars [1000 t]	Wire rod [1000 t]	HR Long Products [1000 t]
<b>Austria</b>	238	0	159	90	389	<b>876</b>
<b>Belgium</b>	0	61	8	174	805	<b>1048</b>
<b>Denmark</b>	0	0	58	158	0	<b>216</b>
<b>Finland</b>	1	0	91	210	294	<b>596</b>
<b>France</b>	255	303	923	1215	1766	<b>4462</b>
<b>Germany</b>	243	1914	1566	1287	5268	<b>10278</b>
<b>Greece</b>	0	0	635	56	197	<b>888</b>
<b>Ireland</b>	0	311	0	0	0	<b>311</b>
<b>Italy</b>	106	927	3725	3538	3270	<b>11566</b>
<b>Luxembourg</b>	55	1255	282	260	463	<b>2315</b>
<b>Netherlands</b>	0	0	453	0	152	<b>605</b>
<b>Portugal</b>	0	0	523	0	138	<b>661</b>
<b>Sweden</b>	48	17	128	587	107	<b>887</b>
<b>Spain</b>	64	1180	2315	1381	1883	<b>6823</b>
<b>UK</b>	211	1951	650	2071	2147	<b>7030</b>
<b>Total</b>	<b>1221</b>	<b>7919</b>	<b>11516</b>	<b>11027</b>	<b>16879</b>	<b>48562</b>

**Table A.1-3: Production of Long Products in EU 15 in 1996**  
[Stat97]

The two major manufacturing countries are Italy and Germany followed by UK and Spain. The largest part of the long products sector in tonnage terms is the production of wire rod which stands for roughly a third of the total production followed by reinforcing bars and merchant bars with an approximate share of one quarter of the production each.

Table A.1-4 compiles the size distribution for the long product manufacturing facilities. In 1993 a total of 306 units were in operation.

Hourly technical capacity (HTC) [t/h]	< 20	20 - 39	40 - 59	60 - 79	80 - 99	100 - 119	120 - 139	>=140	Total
Long Products*	89	56	53	44	28	14	10	12	306
Heavy Sections only	3	2	5	4	3	6	1	3	27
Wire Rod only	4	7	7	8	5	3	2	3	39
Wire rod + reinforcing bars in coils	0	3	3	2	4	0	4	3	19
HTC [t/h]	< 30	30 - 49	50 - 69	70 - 89	>=90				Total
Heavy Sections + Merchant Bars	3	2	4	3	1				13
HTC [t/h]	< 20	20 - 39	40 - 59	60 - 79	80 - 89	>=90			Total
Merchant Bars only	55	12	12	7	2	1			89
HTC [t/h]	< 20	20-39	40 - 59	60 - 79	80 - 99	100 - 149			Total
Merchant Bars + Reinforcing Bars in length	3	5	4	2	7	2			23

\*except extrusion presses, forging machinery and sheet piling profiling lines.

**Table A.1-4: Size distribution of Long Product manufacturing facilities**  
[EUROSTAT]

### A.1.3 Tubes

With a production accounting for 20.9 % of the world's total production, the EU is the largest manufacturer of steel tubes followed by Japan and the U.S. The European steel tube industry has a highly concentrated structure. Five countries - Germany, Italy, France, United Kingdom and Spain - account for roughly 90 % of the total EU production. In some countries, a single company can account for 50 % or more of the national output. In addition to the major integrated steel tube manufacturers (mainly producing welded tubes), there are a relatively large number of small and medium-sized firms that are independent. Some manufacturers, often small in tonnage terms, operating in high value added markets, concentrate on the manufacture of special dimensions and grades of tubes according to particular customer specifications. At the end of 1994, there were 280 production units in the EU belonging to an estimated 245 enterprises. Of these, 67 were specialised in cold drawing of seamless or welded tubes. [Pan97]

Statistical information from the European Steel Tube Association -for 1994 and the EU 12 - refer to 252 production sites belonging to estimated 193 companies. [CEAM]

Steel tubes cover three product categories, which differ considerably in manufacturing process, raw materials, and investment requirements. These categories are classified as:

- Seamless tubes.
- Welded steel tubes of circular cross-section over 406.4 mm in outside diameter.
- Welded steel tubes of circular cross -section up to and including 406.4 mm in outside diameter together with welded steel tubes of non-circular cross-section of any perimeter.

It should be noted that sometimes tubes of different categories (e.g. seamless and welded tubes) and of different grade (e.g. commercial grade, high quality) are manufactured in the same mill.

About 26.4 % of the tubes produced are seamless tubes, of the remaining 73.6 % welded tubes about 18.9 % are of large diameter. The major part of the total steel tube sector is small diameter tubes with a share of 54.7 %. [CEAM]

Table A.1-5 shows the steel tube production and number of sites and number of employees for individual Member States.

	Seamless Steel Tubes [1000 t] <sup>1</sup>	Welded Steel Tubes [1000 t] <sup>1</sup>	Total Steel Tubes [1000 t] <sup>1</sup>	Number of Production sites <sup>2</sup>	Number of Employees <sup>2</sup>
<b>Austria</b>	234	255	489	N/A	N/A
<b>Belgium</b>	---	118	118	3	554
<b>Denmark</b>	---	60	60	4	1100
<b>Finland</b>	---	330	330	N/A	N/A
<b>France</b>	566	834	1400	32	8785
<b>Germany</b>	1295	1991	3286	65	22774
<b>Greece</b>	N/A	N/A	N/A	26	840
<b>Ireland</b>	N/A	N/A	N/A	1	45
<b>Italy</b>	711	2508	3219	49	9050
<b>Luxembourg</b>	---	95	95	N/A	N/A
<b>Netherlands</b>	---	393	393	5	775
<b>Portugal</b>	---	---	---	2	380
<b>Sweden</b>	131	90	221	N/A	N/A
<b>Spain</b>	242	662	904	29	4200
<b>UK</b>	73	1215	1288	36	6325
<b>Total</b>	<b>3252</b>	<b>8551</b>	<b>11803</b>	<b>252</b>	<b>54828</b>

<sup>1</sup> reference year 1996

<sup>2</sup> reference year 1994

**Table A.1-5: Steel Tube production, number of plants and employees [CEAM]**

As can be seen in Table A.1-6, welded steel tube producing plants are predominantly small and medium sized plants with only 22 out of 161 plants having more than 500 employees. With seamless tube producing plants this effect is not as obvious, as 13 out of 32 plants can be characterized as large plants.

	Number of Companies				Total
	Small Plants ( $< 100^*$ )	Medium (100 - 499 $^*$ )	Large		
			(500 - 999 $^*$ )	(>1000 $^*$ )	
<b>Seamless tubes</b>	5	14	6	7	32
<b>Welded Steel Tubes:</b>	78	61	14	8	161
<b>Welded Tubes OD &gt; 406.6mm</b>	6	17	2	2	27
<b>Welded Tubes OD <math>\leq</math> 406.4mm</b>	72	44	12	6	134
<b>Total</b>	83	75	20	15	193

\*Number of Employees

**Table A.1-6: Number and size of tube plants in 1994**  
[CEAM]

## A.1.4 Cold Rolled Flat Products

The total production of cold rolled products in 1994 was 39.7 million tonnes in EU 15. Production of stainless and electrical sheet stood at 2.3 and 1.14 million tonnes respectively, representing 6.4 % and 3.2 % of the total. [EGKS95]

### Cold rolled wide strip

Cold rolled sheets and plates production was 39.6 millions tonnes in 1996. [EUROFER CR] Table A.1-7 gives the production of cold rolled sheet and strip for individual Member States. The number and production capacity for different cold rolling mills in the EU is shown in Table A.1-8.

	Production of Cold Rolled Sheet and Strip [1000 t]
<b>Austria</b>	1289
<b>Belgium</b>	3852
<b>Denmark</b>	0
<b>Finland</b>	890
<b>France</b>	6296
<b>Germany</b>	10615
<b>Greece</b>	380
<b>Ireland</b>	0
<b>Italy</b>	4271
<b>Luxembourg</b>	336
<b>Netherlands</b>	2088
<b>Portugal</b>	202
<b>Sweden</b>	1174
<b>Spain</b>	3093
<b>UK</b>	4026
<b>Total</b>	<b>38512</b>

**Table A.1-7: CR Sheet and Strip production in 1996**  
[Stat97]

	<b>Number of Mills</b>	<b>Average Hourly Technical capacity [t/h]</b>	<b>Scheduled for Close-down after 1993</b>
<b>Wide Strip Tandem Mills</b>	44	138	2
<b>Wide Strip Reversing Quatro High Mills</b>	36	31	--
<b>Wide Strip Multiple-Cylinder Cold Mills</b>	43	16	--
<b>Skin Pass Mills</b>	91	63	4

**Table A.1-8: Number and nominal capacity of CR Mills [EUROSTAT]**

### **Cold rolled (narrow) strip**

The number of companies declined from 166 in 1989 to 141 in 1995 with 61 plants in Germany, 22 in Italy, 16 in UK, 15 in Belgium/Luxembourg, 13 in France, 10 in Spain, 2 in Greece, 1 in Portugal and 1 in Netherlands. Production in the EU was 2.98 million t in 1994. [Pan97]

Cold rolled strip production can be divided into different production sectors: cold rolling narrow hot strip with a width of less than 500 mm (further referred to as CR strip) and cold rolling wide hot rolled sheet and subsequent slitting (further referred to as slit strip). Around two thirds of the total narrow strip requirement in the EU is produced by slitting wide sheet. [Bed95]

The cold rolled strip industry in the EU (15) is both concentrated and fragmented. The largest 10 companies account for 50 % of the production while another 140 companies account for the remaining 50 %. The structure of the sector is marked by national differences in company size and industry concentration. For example in France, small companies are producing specialist high value strip products whilst in Spain a significant number of larger companies is producing lower value strip. Most of the largest companies are situated in Germany, which is dominating the market with about 57 % of the EU (15) production (1.57 million tonnes in 1994). The majority of companies, however, can be classified as small or medium-sized enterprises. [Bed95]

The distribution and average size of companies in the EU is given in Table A.1-9.

	<b>Number of CR Strip Producers</b>	<b>Average Production per Company [1000 t]</b>	<b>Average Number of Employees</b>
<b>Germany</b>	60	26	167
<b>Italy</b>	22	18	58
<b>UK</b>	16	13	73
<b>Spain</b>	10	18	80
<b>France</b>	13	7	80
<b>Rest of the EU</b>	30	11	70
<b>Total EU (15)</b>	<b>151</b>	<b>18</b>	<b>109</b>

Reference year 1994

**Table A.1-9: Distribution and average company size of Cold Rolling Strip plants [Bed95]**

The production of cold rolled strip in EU (15) for 1994 was estimated to be 2.77 million tonnes with

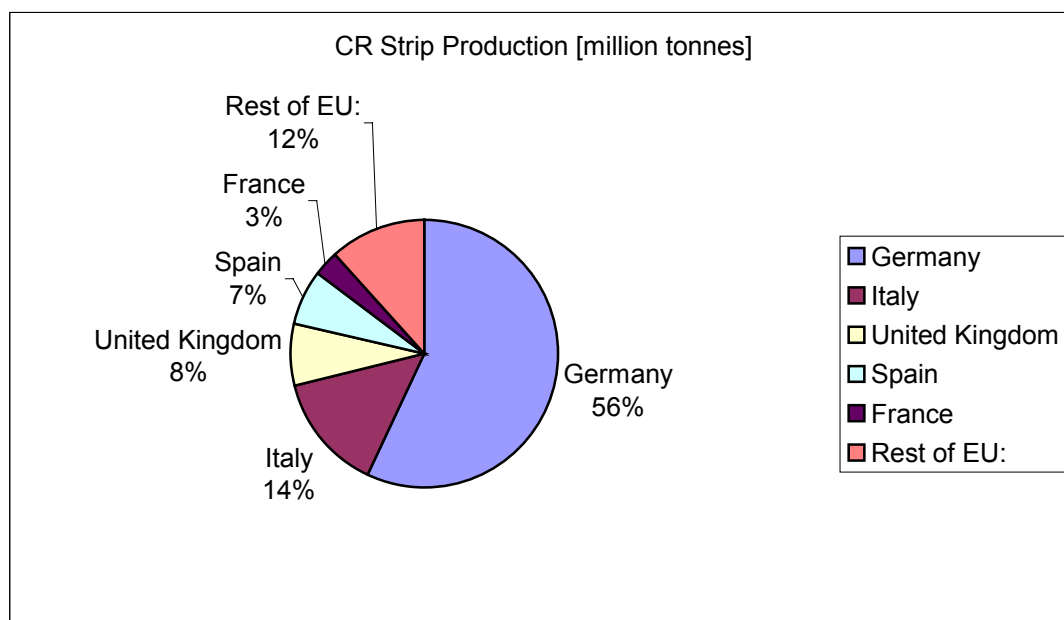
- 2.09 million tonne of non-alloy steel strips (C-content < 0.25 %)
- 0.46 million tonne of non-alloy steel strips (C-content > 0.25 %)
- 0.12 million tonnes of coated steel strip.
- 0.10 million tonnes of HSS and other alloy strips.

A breakdown of the total strip production (CR rolled strip and slit strip) by countries is given in Table A.1-10, Figure A.1-2 and Figure A.1-3.

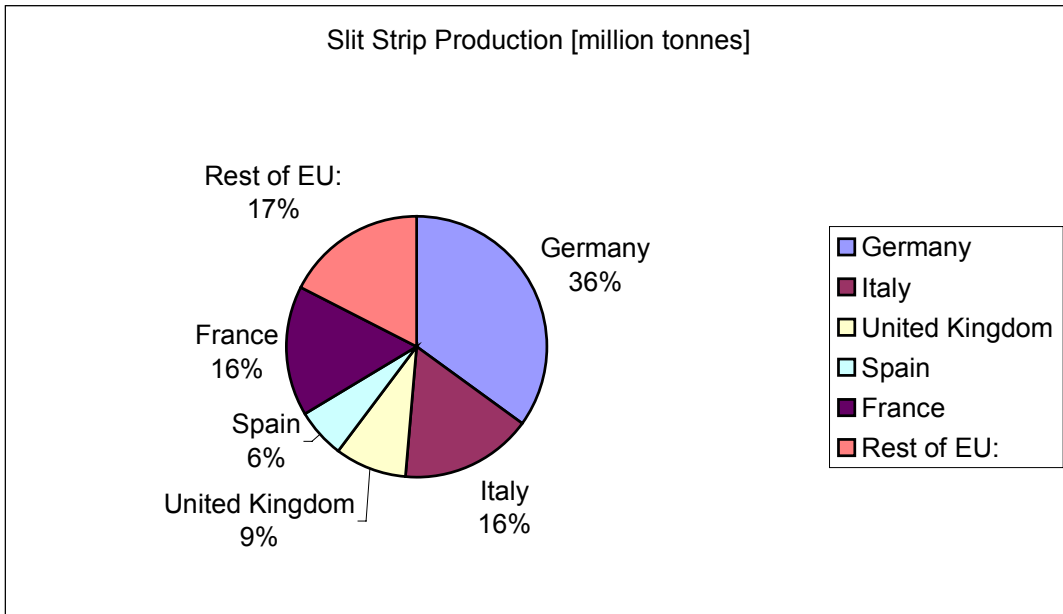
	CR Strip Production [1000 t]	Slit Strip Production [1000 t]	Total Strip production [1000 t]
<b>Germany</b>	1570	1950	3520
<b>Italy</b>	390	900	1290
<b>UK</b>	210	500	710
<b>Spain</b>	180	330	510
<b>France</b>	90	900	990
<b>Rest of EU:</b>	320	970	1290
<b>Sweden</b>	140		
<b>Benelux</b>	100		
<b>Greece</b>	30		
<b>Portugal</b>	30		
<b>Finland</b>	10		
<b>Austria</b>	10		
<b>Total</b>	<b>2760</b>	<b>5550</b>	<b>8310</b>

Reference year 1994

**Table A.1-10: Production of CR strip and slit strip**  
[Bed95]



**Figure A.1-2: CR Strip production in 1994**  
[Bed95]



**Figure A.1-3: Slit strip production**  
[Bed95]

### A.1.5 Cold Drawn Long Products/ Bright Steel Bars

The production of bright steel bars in the EU was about 2.4 million tonnes in 1994. The number of companies declined from 154 in 1988 to 130 in 1995 with a number of 46 companies in Germany, 26 in Spain, 25 in Italy, 15 in United Kingdom, 14 in France, 2 in Portugal, 1 in Denmark and 1 in Belgium. Bright steel bars are used by industries such as the manufacture of motor vehicles, machinery, electrical goods and other industries, where high quality basic material is compulsory. [Pan97]

### A.1.6 Wire

The European Union has the world largest wire drawing industry, followed by Japan and North America. It produces about 6 million tonnes of wire per year. Including the various wire products, like barbed wire, grill, fencing, netting, nails etc, the production of the sector reaches more than 7 million tonnes per year. The European wire drawing industry is characterised by a large number of medium sized, specialised companies with an average of 121 employees and an annual turnover of ECU 13.7 million per company. The industry's output, however, is dominated by a few large producers. It is estimated that about 5 % of the companies account for 70 % of the industry's output (25 % of the companies for 90 %).

Over the past 10 years, independent wire drawing companies have become increasingly vertically integrated. Downstream wire drawing and producing finished wire products have shown a high degree of integration, but also upstream there has been some integration between steel making and wire rod producing industries and wire drawing. Approximately 6 % of the wire drawers in Europe are integrated producers representing about 75 % of the total production of steel wire [C.E.T].

The largest producer of steel wire is Germany with 32 % of the wire production followed by Italy (approx. 22 %), UK, Benelux (mainly Belgium), France and Spain. Other Member States which have a small wire drawing industry are Sweden, Austria, Greece and Portugal. The



distribution of wire drawing installations in EU, size and number of plants for individual Member States is given in Table A.1-11.

	Wire Production [1000 t] <sup>1</sup>	Wire Products [1000 t] <sup>1</sup>	Number of plants <sup>2</sup>	Average number of employees per plant <sup>2</sup>
<b>Austria</b>	120	115	2	N/A.
<b>Benelux</b>	619	246	20	325
<b>Denmark</b>	N/A.	N/A.	N/A.	N/A.
<b>Finland</b>	N/A.	N/A.	N/A.	N/A.
<b>France</b>	406	102	36	136
<b>Germany</b>	1908	89	85	125
<b>Greece</b>	140	60	2	N/A.
<b>Ireland</b>	N/A.	N/A.	N/A.	N/A.
<b>Italy</b>	1250	300	74	58
<b>Portugal</b>	82	30	2	N/A.
<b>Sweden</b>	135	63	11	85
<b>Spain</b>	463	138	26	N/A.
<b>UK</b>	735	105	25	110
<b>Total</b>	5858	1248	283	121

<sup>1</sup> reference year 1996

<sup>2</sup> reference year 1994

**Table A.1-11: Wire drawing industry in the EU  
[C.E.T.] [Euro-Strategy]**



## A.2 APPLIED PROCESSES AND TECHNIQUES IN HOT AND COLD FORMING

Hot and cold forming activities covered in this BREF are hot rolling, cold rolling and drawing of steel.

### A.2.1 Hot Rolling Mills

#### A.2.1.1 Process Overview

In hot rolling the size, shape and metallurgical properties of the steel slabs, blooms, billets or ingots are changed by repeatedly compressing the hot metal (temperature ranging from 1050 to 1300 C°) between electrically powered rollers. The steel **input** for hot rolling differs in form and shape, depending on the process route and on the product to be manufactured:

**Cast ingots**, predominantly with square cross section, are used for the manufacture of slabs and blooms on slabbing-/ blooming mills. Slabs and blooms are further processed to plates or strips on other rolling mills. Nowadays, the use of cast ingots and slabbing/blooming is decreasing as continuous casting has made this step obsolete. Approximately 93.7 percent (1995) of the crude steel produced in Europe is cast continuously into semi-finished products such as slabs, blooms or billets. Only a minor part is cast into discrete moulds to produce ingots for some special products (e.g. heavy plates).

**Slabs** (400 up to 2500 mm wide and 40 to 500 mm thick) are semi-finished, continuous cast products for the rolling of flat products.

**Billets** (of square or rectangular shape with cross sections of 2500 mm<sup>2</sup> to 14400 mm<sup>2</sup> (50 x 50 mm to 120 x 120 mm)) and **blooms** (of square or rectangular shape with cross sections of 14000 mm<sup>2</sup> up to approx. 100000 mm<sup>2</sup> (120 x 120 mm up to 250 x 400 mm)) are semi-finished continuous cast products used for the rolling of long products.

**Beam blanks** (with dimensions of 170 x 240 mm up to 500 x 1120 mm) are continuously cast to near net shape. Beam blanks are used for rolling of long products. [EUROFER HR]

Hot rolling mills usually comprise the following process steps:

- Conditioning of the input (scarfing, grinding).
- Heating to rolling temperature.
- Descaling.
- Rolling (roughing including width reduction, rolling to final dimension and properties).
- Finishing (trimming, slitting, cutting).

Products obtained from hot rolling are usually classified in two basic types according to their shape: flat and long products. Tubes, are also covered by the term 'long product' in this document.

Figure A.2-1 shows an overview of products manufactured for various purposes and applications.

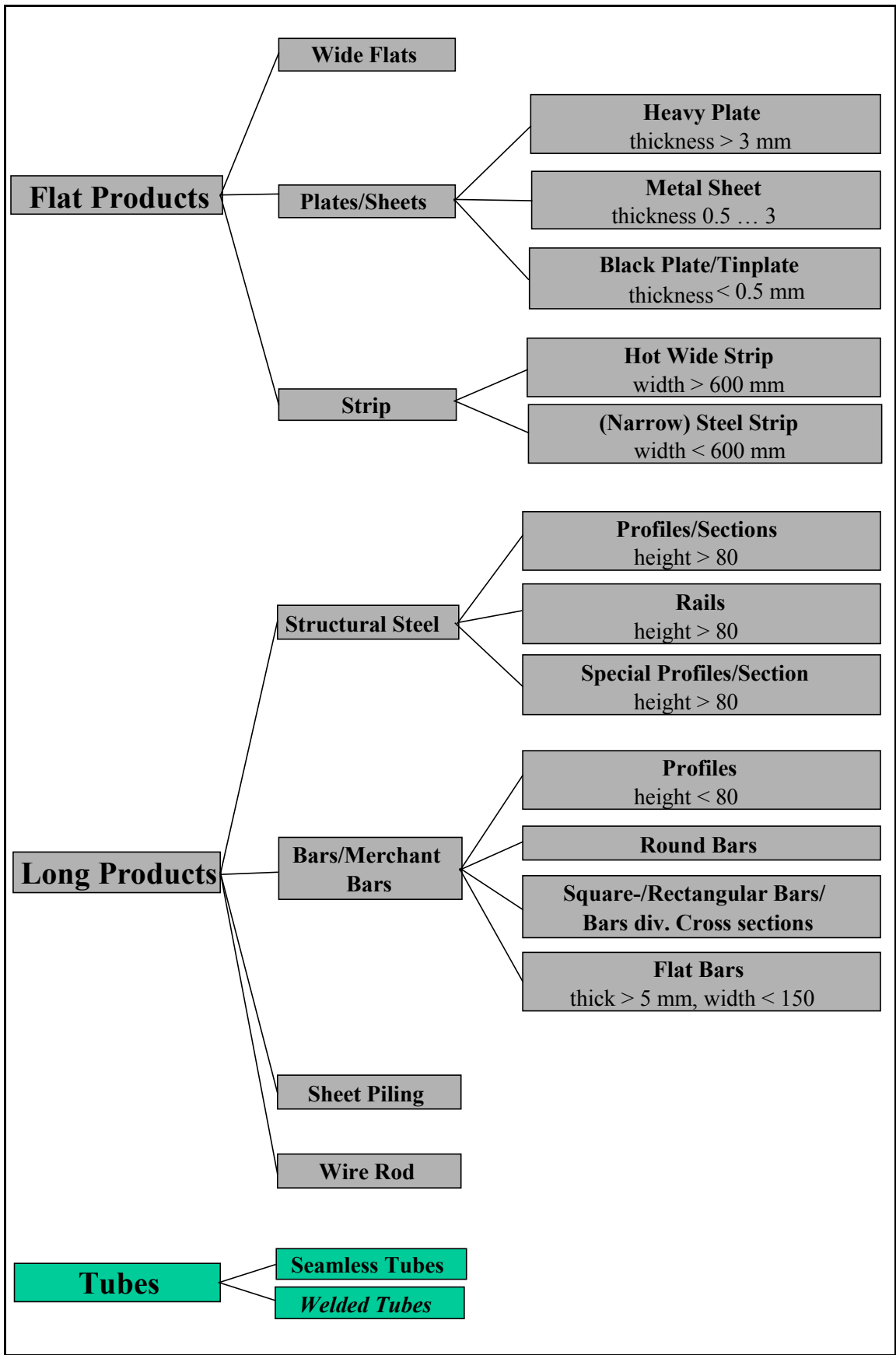


Figure A.2-1: Overview of Hot Rolled Products

Hot rolling mills are classified by the type of product that they produce and by their design features. The following chapters give an inside on the different mill layouts and manufacturing sequences. More detailed information on the individual processing steps, which are often similar in different mills, is given thereafter.

### A.2.1.1.1 Blooming/Slabbing Mills

Blooming and slabbing mills are used to roll cast ingots into semi-finished products, like blooms and slabs, for further processing on other mills. The raw material is heated in soaking pits to ca. 1300 °C and subsequently formed on heavy two-high reversing stands in 15 - 30 rolling passes.

The material to be rolled is moved along roller tables, positioned with the aid of manipulators, and fed into the roll gap. The material is rotated repeatedly by 90 ° about its long axis during the series of passes.

The main difference between blooming and slabbing stands is the greater height of the stands used for rolling slabs. This is associated with the product characteristics, as slabbing mills are mainly used to roll flat semi-finished products they require a bigger lift height of the upper rolls.

Another rolling system is the universal slabbing stand. Working pairs of rolls are arranged horizontally and vertically in succession. The vertical rolls form the narrow sides.

The rolled semi-finished products are cropped with shears at both ends, and divided into ordered lengths. Surface defects of the product maybe removed by flame descaling (scarfing). [Ullmann's]

With the growth of continuously cast products, the number and importance of slabbing and blooming mills has decreased. From 1988 the number dropped by 18 to a total of 67 in 1993 (see Table A.2-1)

	Number of Plants	Average capacity [t/h]
<b>Blooming Mills</b>	13	85
<b>Blooming and billeting</b>	8	84
<b>Blooming and slabbing</b>	13	187
<b>Blooming, slabbing, billeting</b>	6	109
<b>Slabbing (only) mills</b>	5	284
<b>Billeting (only) mills</b>	20	83
<b>Billeting and slabbing mills</b>	2	122
<b>Total</b>	67	122

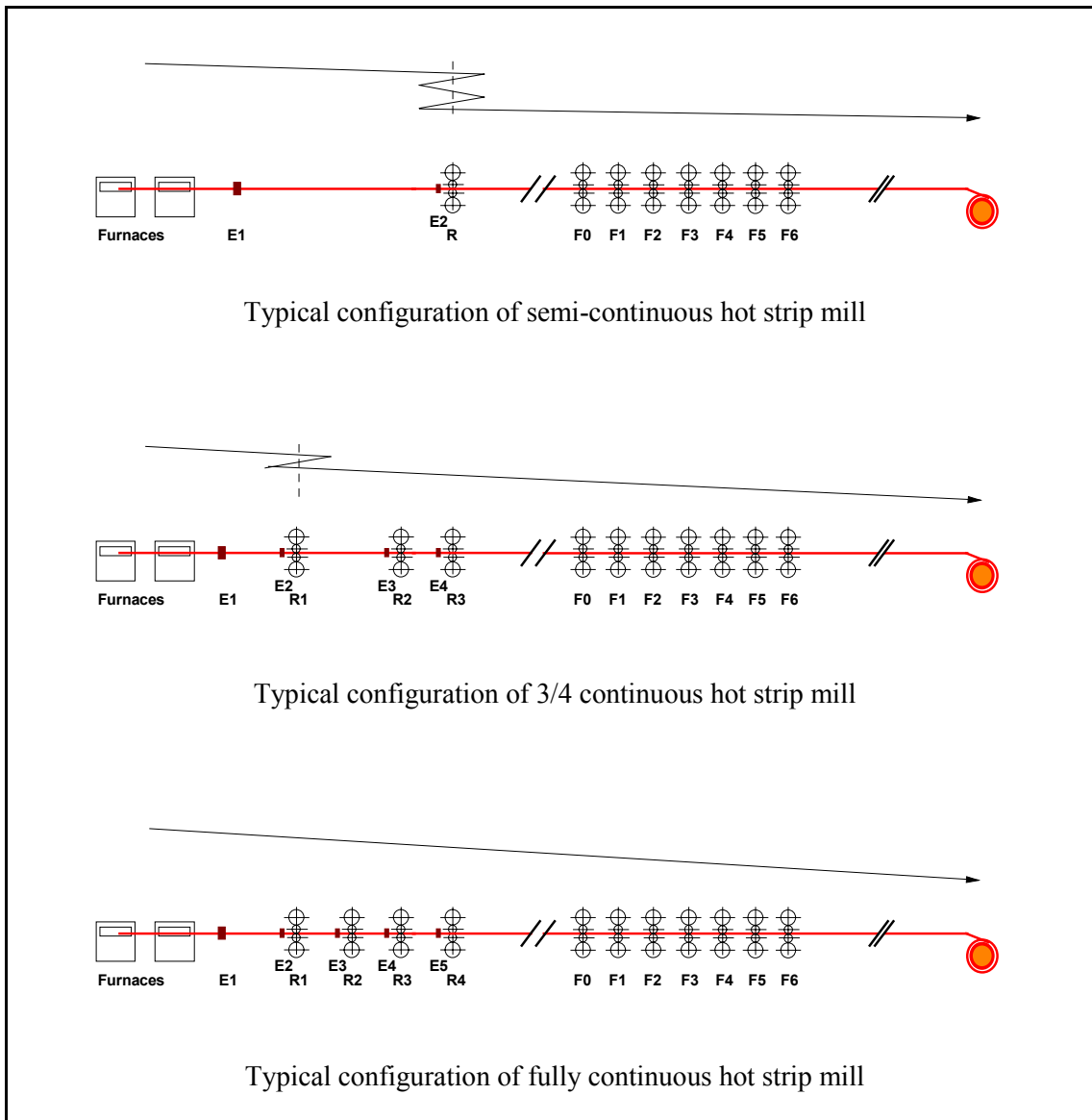
Table A.2-1: Semi-finished product mills [EUROSTAT]

### A.2.1.1.2 Hot Strip Mills

For the production of hot strip, the heated slab - after descaling - passes the roughing mill, where it is reduced from a thickness of approx. 120 - 300 (500) mm to approx. 20 - 50 mm (transfer bar). Roughing can also include a reduction in width.

This roughing is done either in several passages through an individual rolling stand by repeated reversing, or in a continuous passage through several roughing stands. The designations of strip

mills (semi-continuous hot strip mill, 3/4 continuous hot strip mill and continuous hot strip mill, see Figure A.2-2) originate from this plant configuration.



E= Edger R= Roughing stand F= Finishing stand

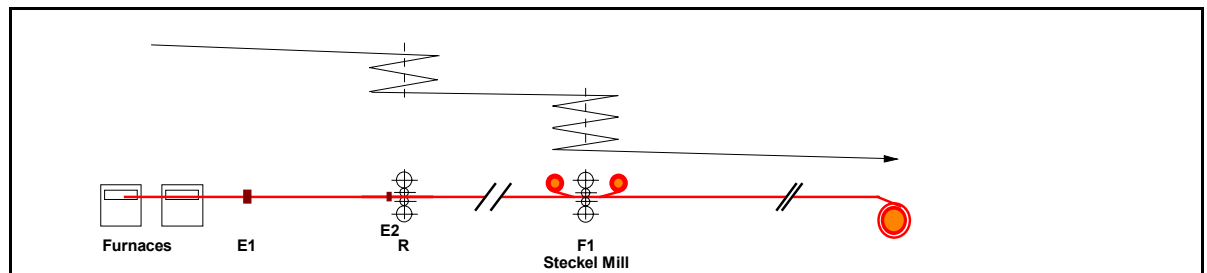
**Figure A.2-2: Typical designs for Hot Strip Mills [EUROFER HR]**

The material reduced to a transfer bar is directed to the finishing train via an intermediate roller table, which in some cases is combined with a so-called coil box. Before entering a train of rolling stands for thickness reduction to the final size (between 1.2 and approx. 20 mm) the transfer bar is cropped. Temperature controlled rolling in the finishing train, involving controlled strip cooling installed at the delivery roller table, provides the requested technological parameters (strength, toughness, etc.) of the hot strip. At the end of the rolling mill the finished product is wound up in a coil.

Hot strip, which is not foreseen for further processing in the cold mills is partly sold with rolled strip edges, but depending on the planned external use the strip has to be conditioned. This coil finishing includes side trimming, cutting to small bands on slitting lines and cutting into sheets. [EUROFER HR]

## Steckel Mill

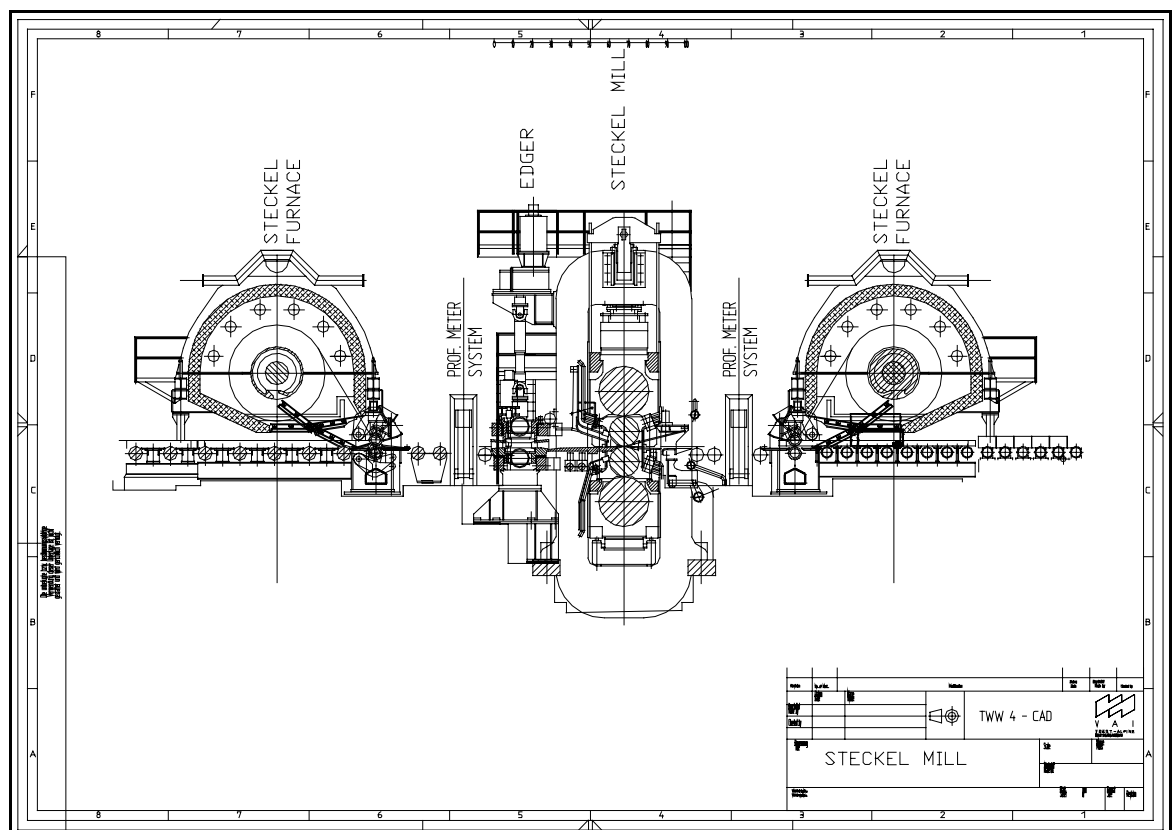
A special method of hot strip production is rolling in so-called STECKEL mills. Here the prematerial is usually processed into strip by reversing through a roughing stand and a finishing stand, in some cases even by reversing through one stand only.



E= Edger    R= Roughing stand    F= Finishing stand

**Figure A.2-3: Typical STECKEL Mill configuration**  
[EUROFER HR]

To keep the heat losses during the rather long forming process within reasonable limits and to handle the relatively long strip more easily, heated coiling devices referred to as STECKEL coilers are attached on both sides of the rolling stand (finishing stand), where the rolled stock is temporarily stored.



**Figure A.2-4: STECKEL Mill with coiling furnaces**  
[EUROFER HR]

### Sendzimir Planetary mill

Mills of this type are characterised by the use of rotating backup rolls which drive the work rolls so that the surface of the latter move in a direction opposite to that of the workpiece. The work rolls are held in cages, which rotate around the backup rolls in a synchronised manner. To facilitate the use of thicker ingoing material (slabs) planetary mills may be assisted by attached eccentric presses.

Special kinds of planetary mills are the single planetary mill - only the bottom roll set is designed as planetary type and either a rotating top roll or fixed die is arranged above passline - and the 'Krupp-Platzer' planetary mill where intermediate rolls are arranged between the work rolls and backup roll. [EUROFER HR]

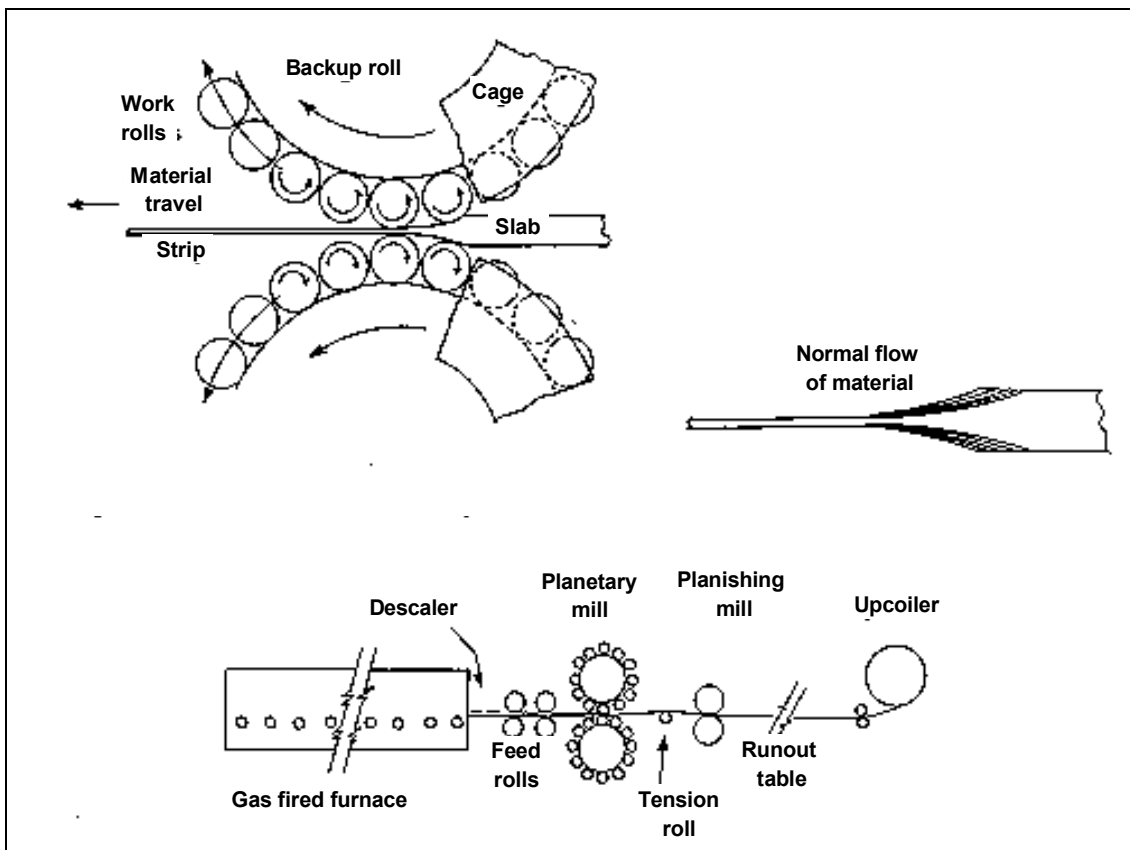


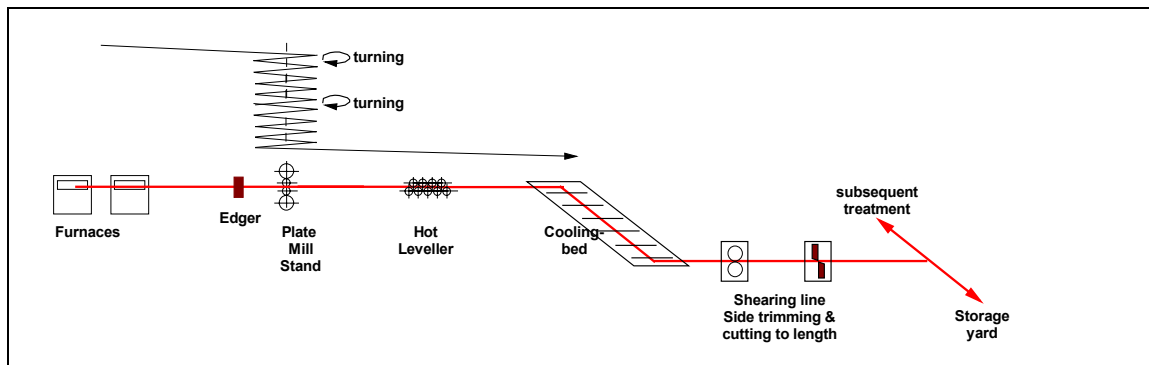
Figure A.2-5: Planetary Mill (SENDZIMIR)  
[EUROFER HR]

#### A.2.1.1.3 Plate Mills

Production of heavy plates (thickness between 5.0 and 380 mm, width up to 5.2 m) is done by reversing operation at one mill stand or in tandem operation.

After rolling, the plates are placed on a cooling bed (cross transfer) and cooled to room temperature and/or temperatures down to max. 500°C for further processing. [EUROFER HR]





**Figure A.2-6: Typical Plate Mill configuration**  
[EUROFER HR]

In special cases the rolled product is heat treated by water cooling systems (e.g. water curtains) immediately after hot rolling. Hot and/or cold levellers are arranged in front or behind the cooling bed to straighten the plates.

After the cooling process on the cooling bed, secondary treatment of the sheets is performed in the finishing shops (shearing, side trimming cutting to length). A part of the production is subjected to a subsequent heat treatment prior to shipment. Such treatments include annealing, spheroidise annealing, stress relieving, normalising, quenching and tempering.

### Clads

Special products such as multi-layer plates (clads) require a separate preparation and rolling technique (mainly a two-heat rolling operation). In such products, a corrosion-resistant surface material is permanently bonded to lower-cost, possibly stronger, carbon steel.

The first step involves the fabrication of ‘sandwiches’ which consist of plates of the cladding and the backing materials with thickness in the exact proportion to produce the required plate size with the percentage of metals ordered. The assembly is then rolled to the desired gauge, width and length, with the two materials becoming permanently bonded because of the high rolling pressure.

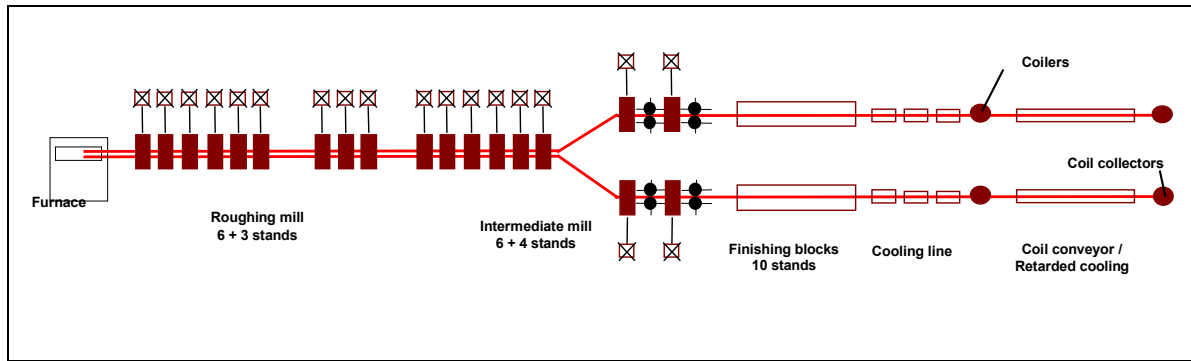
In the rolling operation, drafts are usually limited and the finishing temperatures are carefully controlled. In some cases the sandwiches are rolled in a first stage into slabs, cut to required sizes and in a second heat, final rolled either on hot strip mills or on the plate mill. Sometimes heat treatments are required to produce the desired corrosion resistance and physical properties, the resultant scale being removed by sand- or shot blasting. [EUROFER HR]

#### A.2.1.1.4 Bar and Rod Mills

Bars and rods (wire rods) constitute hot rolled products of relatively small cross sections produced in coiled or straight form. For the rolling operation profiled rolls are in use to give the steel its desired final shape.

#### Wire rods

Wire rods generally have circular cross sections with a diameter of 5 to 14 mm. Larger cross sections and different section shapes such as oval, square, hexagonal, octagonal etc. Can also be rolled on wire rod mills with adequately shaped rollers. Hot rolled wire rod is mainly used for further processing by cold drawing or cold rolling.



Note: Example of a 2 strand, 30 stand wire rod mill with Stelmor controlled cooling

**Figure A.2-7: Typical layout of a Wire Rod Mill**  
[EUROFER HR]

The billets fed into rod mills are heated to hot rolling temperature in pusher or walking beam furnaces. A descaling system is installed between the furnace exit and the first rolling stand.

Rod mills are continuous mills with roughing, intermediate and finishing sections. The rolling stands are 2-high and their number is generally in excess of 25, depending on the cross section of the billets feeding the mill (80 to 155 mm). Roughing and intermediate sections may be multi-strand (up to 4 strands), while finishing sections are always single stranded.

Crop shears are installed between the different sections of the mill and are used to provide a clean cut for improved introduction into the following roll stand. Crop shears are also used to cut the bar engaged into the rolling process in case of an incident downstream in the mill.

In-line heat treatment of the wire rod is performed with water cooling ramps located between the final rolling stands and the coilers, followed by air cooling of the coils laid on conveyor belts. Controlled air-flow gives the wire rod the desired micro-structure for further processing (STELMOR<sup>®</sup> cooling). [EUROFER HR]

## Bars

Hot rolled bars include basically two types of steel products, **merchant steels** or engineering steels with round, square, rectangular, hexagonal, octagonal, L-shaped, [-shaped, I-shaped cross sections smaller than 1600 mm<sup>2</sup> and **concrete reinforcing bars** (re-bars) with round cross sections, 6 to 40 mm diameter, mostly with ribs on their surface.

Bar rolling mills are similar to the first sections of wire rod rolling mills. They have generally single strand 2-high mills with roughing, intermediate and finishing groups followed by shears that cut the hot rolled product to long bars, which are then conveyed to a cooling bed. High capacity mills are all continuous with alternating horizontal and vertical stands, while the front groups of lower capacity mills are of the 'open' type.

After cooling the bars are cut to commercial lengths and may be straightened at a cold straightening machine.

Re-bars are often heat-treated in-line by intensive water-cooling to obtain high tensile strength (TEMPCORE<sup>®</sup> process). A different way for increasing the tensile strength of re-bars is a mechanical treatment after cooling: The bars are deformed by torsion beyond their yield strength until the desired tensile strength is obtained. [EUROFER HR]

## Cold Drawing of Steel Bars

Cold drawing concerns the manufacture of steel bars or sections by cold drawing, grinding or peeling of hot rolled steel bars into so called 'bright steel bars', having form and characteristics required by the users. Cold finishing during cold drawing operations hardens and increases the tensile strength of the steel, while at the same time reducing the ductility, which may require an annealing treatment of the product after drawing. Bright steel bars are mainly of circular, square, rectangular or hexagonal cross-section, but all kinds of cross-sections can be produced according to demand. Products are non-alloy steel bars, alloy steel bars of different grades including high-speed steel and other tool steel and shapes and sections of different steel grades. [Pan97]

Bright steel bars are used by industries such as the manufacture of motor vehicles, machinery, electrical goods and other industries, where high quality basic material is compulsory.

### A.2.1.1.5 Structural/Section Mills

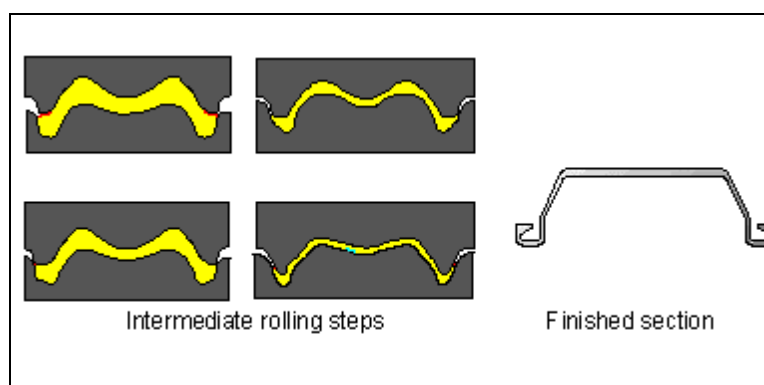
As most other types of mills, section rolling mills are divided into roughing, intermediate and finishing stands, preceded by a descaling machine installed between the reheating furnace and the roughing mill.

Roughing stands are generally reversing, 2-high stands. The rolls have several sets of profiles, which are used in sequence. The upper roll can be moved vertically in order to progressively reduce the gap between the rolls and thus to reduce the passing section.

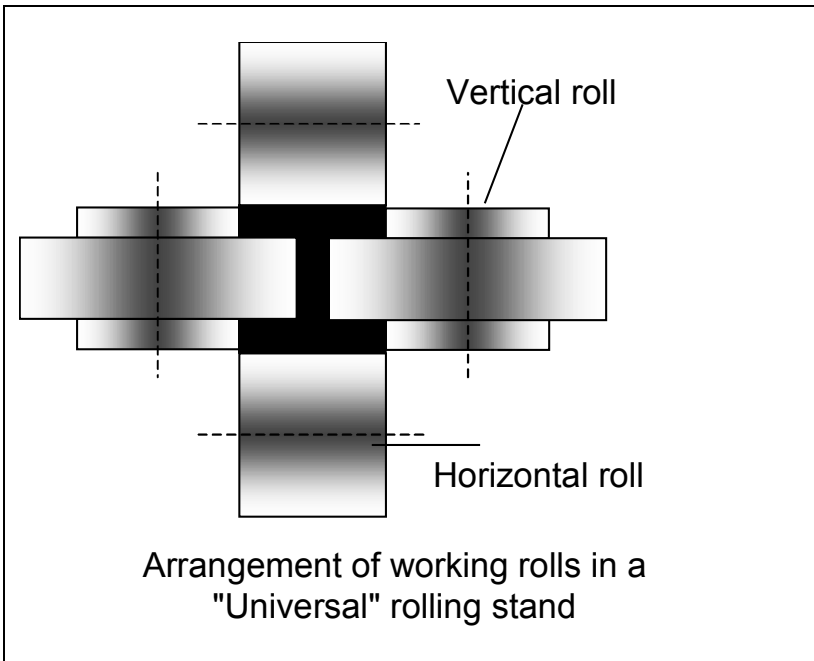
Cropping shears or hot saws are generally installed between the different sections of the mills and are used to provide a clean cut bar end to facilitate the introduction into the following rolling stand.

On leaving the finishing stand or train, the bars are divided to cooling bed length or to commercial length by saws. After cooling on the cooling bed, the bars are straightened on mechanical or hydraulic straightening machines and cut to length by saws as required. [EUROFER HR]

To yield the different profile shapes required for sections/structurals, either duo-stands with 2 grooved rolls or 'universal' stands with 2 horizontal and 2 vertical rolls are used as shown in Figure A.2-8 and Figure A.2-9.



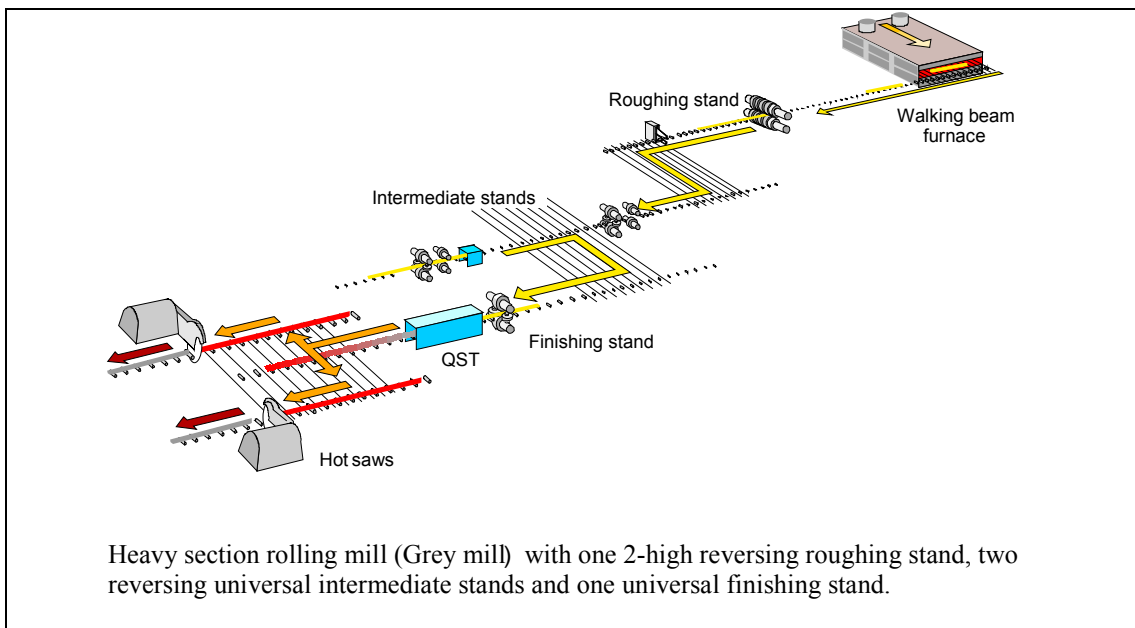
**Figure A.2-8: Profiled rolls for sheet piling sections**  
[EUROFER HR]



**Figure A.2-9: Universal stands for parallel flanged products**  
[EUROFER HR]

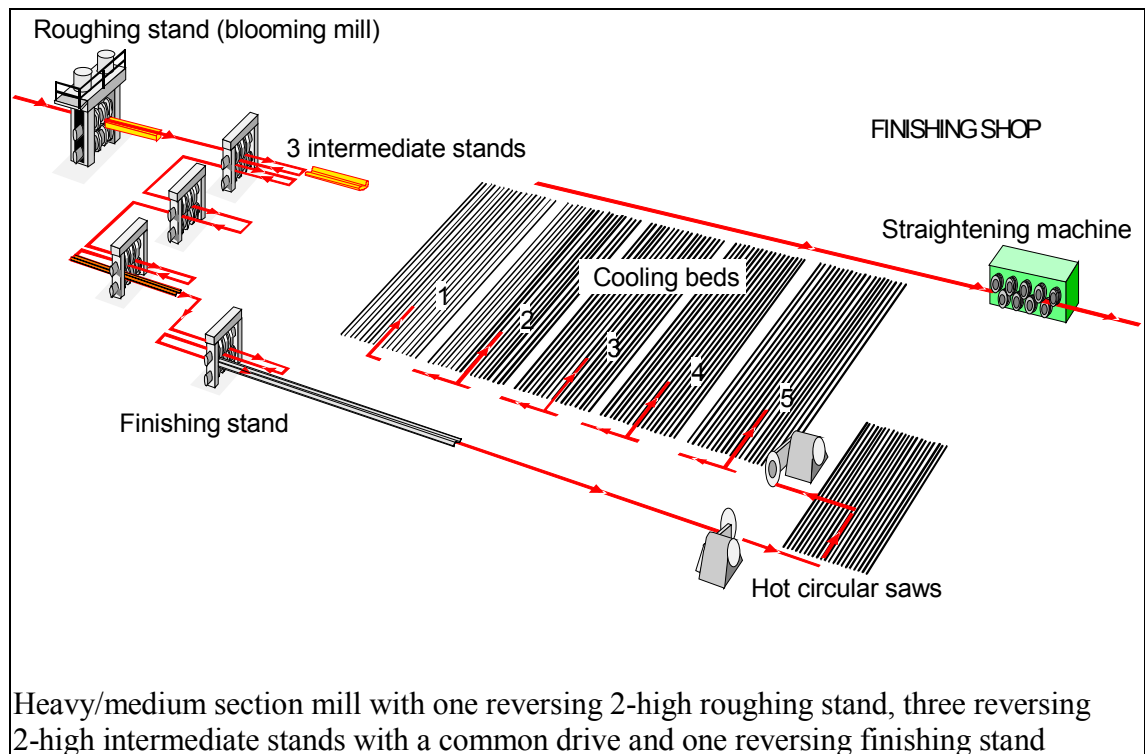
Geometry control is of utmost importance in section rolling since rather tight tolerances are common for hot rolled sections. Measuring devices applying sophisticated techniques including laser beam technology and radioactive sources are of common use.

The designs of section mills vary greatly according to the manufacturing programme. Figure A.2-10 shows the layout of a heavy section mill with universal stands, specialised in parallel flange H and I beams. It includes in-line heat treatment (QST - Quenching and Self-Tempering) to obtain an optimal micro-structure for high strength and high ductility applications.



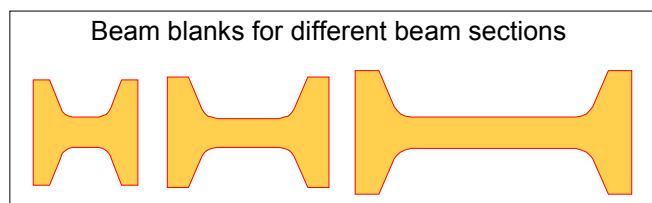
**Figure A.2-10: Plant layout of a Heavy Section Mill**  
[EUROFER HR]

Figure A.2-11 shows the layout of a heavy/medium section mill specialised in the rolling of sheet piling sections. The intermediate stands are of the 'open' type with one common drive. The 2-high finishing stand can be exchanged by a universal stand for the production of parallel flanged products.



**Figure A.2-11: Plant layout of a Heavy/Medium Section Mill for sheet piling [EUROFER HR]**

Section mills increasingly use near-net-shape, continuously cast semis called beam blanks (see Figure A.2-12) to increase productivity and decrease energy input.



**Figure A.2-12: Examples of beam blanks cross sections [EUROFER HR]**

If the production rhythm and the manufacturing programme allow, hot charging of continuously cast semis - from the casting machine run-out area to the reheating furnace of the rolling mill - is more and more applied. Considerable savings in energy consumption may be achieved, but this depends on the proximity of the rolling mill to the continuous casting plant.

### A.2.1.1.6 Tube Mill

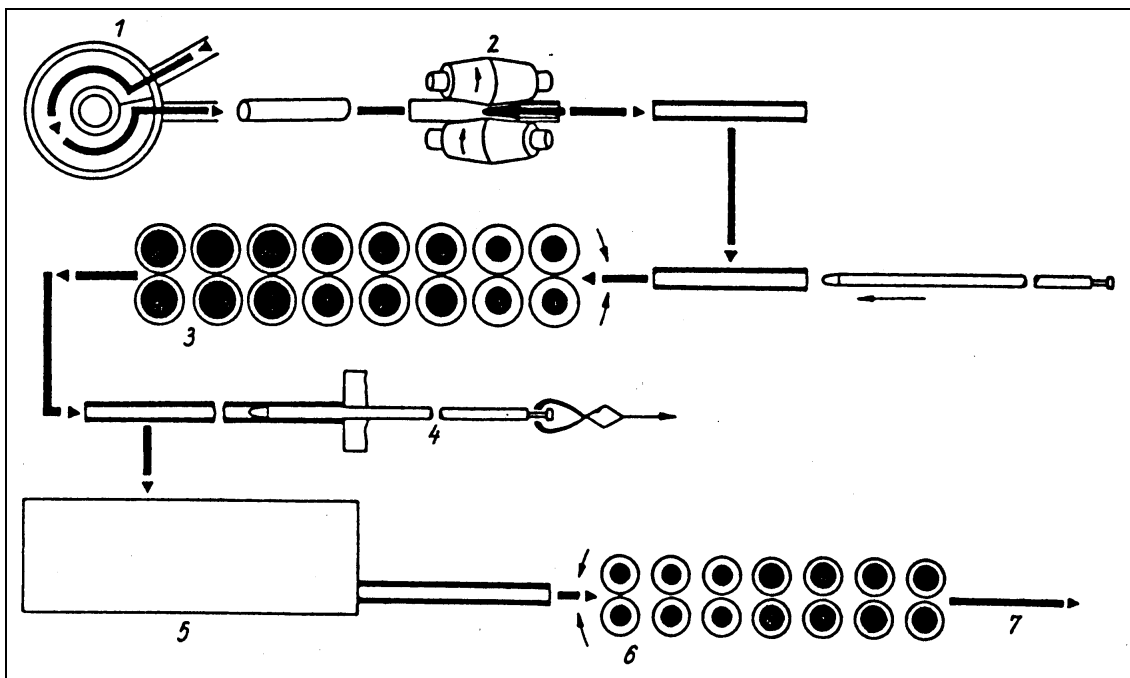
#### Seamless tube

Seamless tube production consists basically of the following manufacturing steps:

- Heating of the input.
- Piercing (press-piercing or oblique rolling).
- Elongation/Stretching.
- Final Rolling.
- Heat Treatment.

The most important types of plants used today are mandrel mills, plug mills, push bench mills and pilger mills. Figure A.2-13 and Figure A.2-14 show some typical tube mill designs.

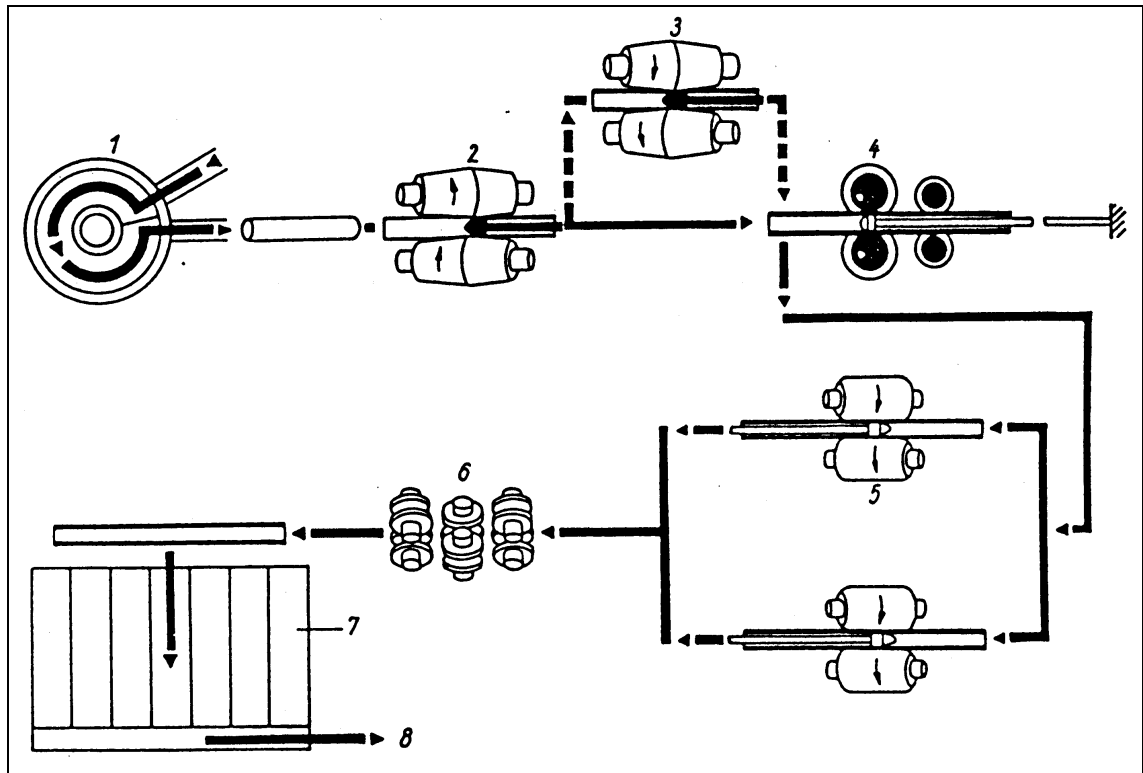
Raw material for the production of unalloyed and medium-alloy steel tubes are continuously cast round billets or blooms, although sometimes billets with square cross sections are used. The raw material for high-chrome steel tubes are mainly round bars, rolled from cast billets. The input is heated to rolling temperature in rotary hearth furnaces fired with natural gas or oil. Then a hollow billet (ingot) is produced by piercing. The most important hole-piercing process uses inclined rollers. The hole is produced by two inclined rolls rotating in the same direction, so that the ingot is rolled with a screw motion over a piercer plug to form a hollow bloom. The piercer plug is fixed to a freely rotating rod supported by a thrust bearing on the exit side.



- 1 Rotary hearth furnace  
2 Cross-rolling piercer  
3 Mandrel mill (offset 45°)  
4 Stripper

- 5 Re-heating furnace  
6 Stretch-reducing mill (off-set 60 °)  
7 To cooling bed and finishing lines

**Figure A.2-13: Mandrel mill**  
[Tech Metal]



1 Rotary hearth furnace  
 2 Cross rolling piercer  
 3 Cross-rolling elongator  
 4 Plug mill

5 Reeler  
 6 Sizing mill  
 7 Cooling bed  
 8 To finishing shop

**Figure A.2-14: Plug mill**  
 [Tech Metal]

Longitudinal rolling, transverse rolling, or presses are used for the elongating stage. The most important one is the continuous tube rolling process, as it is one of the most efficient and productive processes.

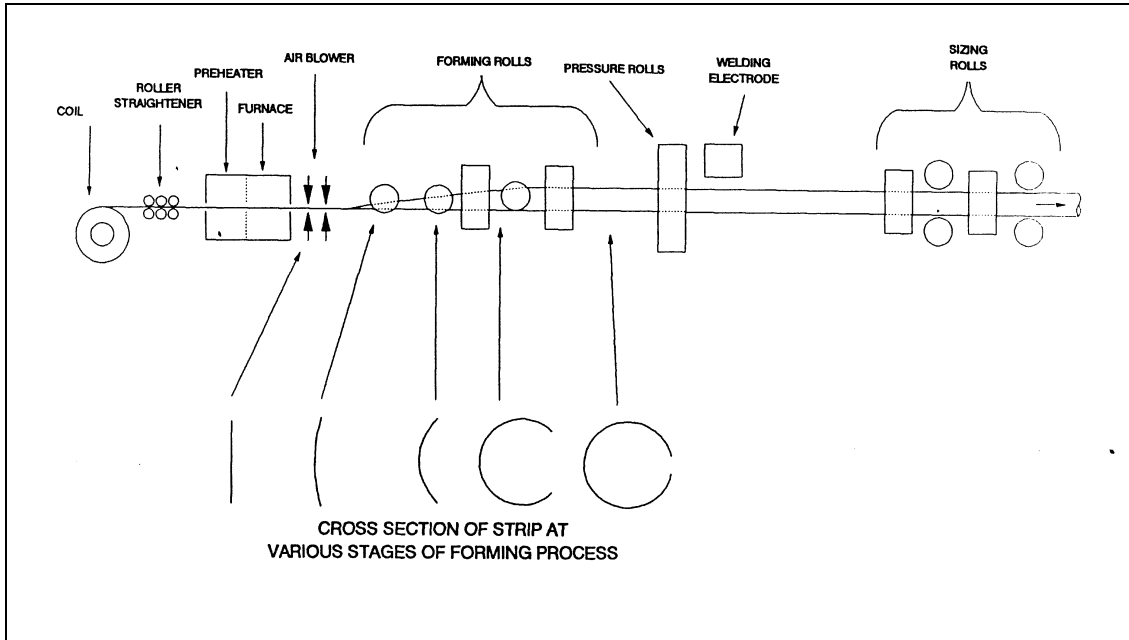
Several rolling stands are used simultaneously, usually 6 -8 two-high stands per group, at an angle of  $90^\circ$  to each other. The reduction of the wall thickness takes place between the rolls and a cylindrical lubricated mandrel.

Rolling to the finished size is carried out without an inner mandrel in sizing mills or stretch-reducing mills. Sizing mills have 2 - 10 stands, and can have two or three rolls per stand. As the circumference is reduced, the wall thickness is increased. In stretch reducing mills, which normally have three rolls per stand, and up to 30 stands, an increase of wall thickness is avoided, as tensile forces are applied between the stands during the process.

Tubes for undemanding applications can be shipped immediately after rolling. For more exacting quality requirements, especially good toughness properties, separate heat treatment is usually carried out after rolling. This can include normalising and tempering.

## Welded tubes

Welded tubes are produced from cold rolled or hot rolled steel strip; hot rolled wide strip; or thick plate. In principal the production sequence comprises bending of the strip or plate to an open tube and closing the gap by welding. Figure A.1-1 shows a schematic of continuous tube production (Fretz-Moon process).



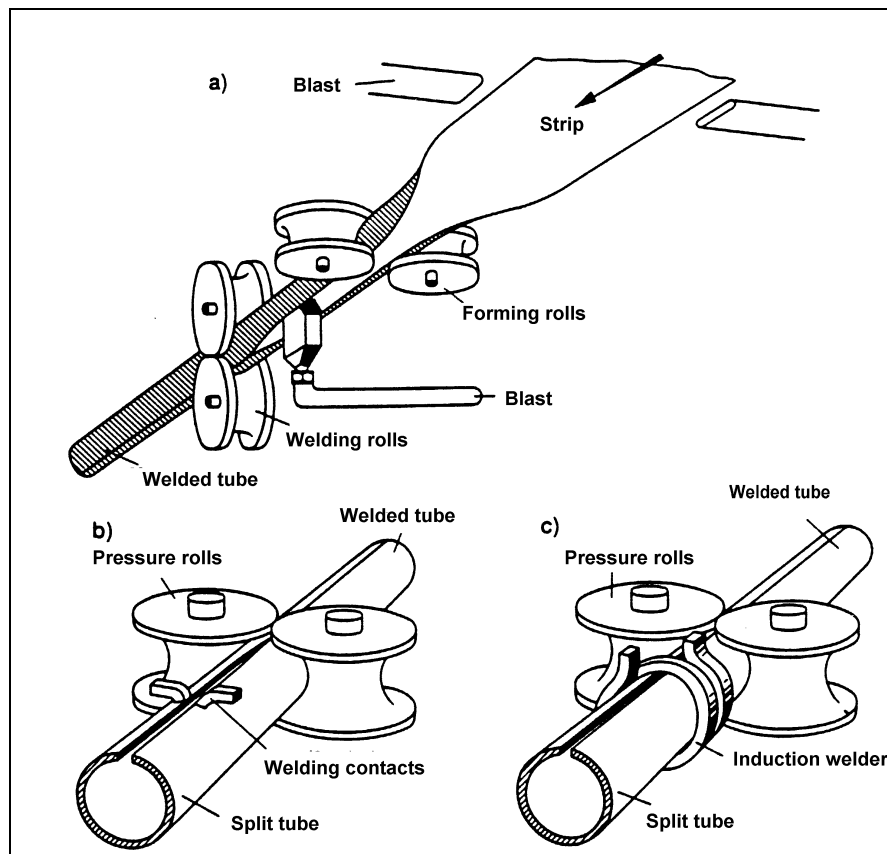
**Figure A.2-15: Flow sheet for continuous tube production [HMIP]**

In the Fretz-Moon process (pressure welding) coils of hot-rolled strip are heated to a high temperature in a tunnel furnace. The edges of the strip are heated to welding temperature by additional burners. The strip is formed into a tube with a longitudinal gap. A two-roll compression device at 90 ° then reduces the gap and presses the edges together so they become welded.

The semi-finished tube passes without further heating through a stretching mill, where the dimensions are reduced as required. A flying saw cuts the continuous tube into lengths, which are then cooled on a cooling bed.

Alternative welding processes are **resistance pressure welding**, in which the required welding heat is generated by high-frequency alternating current, conduction or induction. The properties of the welded seams can be improved, either by continuous heat treatment or by separate heat treatment of the individual tube. **Fusion Welding** is mainly used to produce steel pipes with large diameters (> 457.2 mm). Figure A.2-16 shows the main tube welding processes.





a Fretz-Moon welding process  
 b High-frequency conductive welding  
 c High-frequency inductive welding

**Figure A.2-16: Tube welding processes**  
 [EUROFER HR]

### A.2.1.2 Surface Rectification and Conditioning of Input

Slabs, blooms and billets can have surface defects, like cracks, folds or seams. Surface preparation of rolling stock is necessary to ensure flawless surfaces of the rolled product. Surface defects of semi-finished products, can also be removed by the following processes.

#### Scarfig

Scarfig removes surface defects of carbon steel grades by an oxy-fuel flame. The flame is used to rapidly melt and oxidise the steel surface while a separate supply of high pressure oxygen to the cutter propels the slag product from the surface. Scarfig is either done by hand (for small lot sizes) or by machine.

The scale from machine scarfig is washed from the steel surface by high pressure water and led to a water pit where the scale is removed by crane. The water is treated and recirculated. From manual scarfig operation scrap collection is carried out by means of magnets.

Dust emissions from scarfig operation are collected and, usually, abated by electrostatic precipitators (wet or dry).

#### Grinding

For stainless steels and special steel grades, thermal removal of the surface defects is not possible. Therefore defects have to be eliminated by grinding. The grinding process is either

carried out manually or by machines. Manual grinding is performed by use of hand held power tools, in some cases booths equipped with fume extraction to bag filter units. Grinding machines are equipped with a roller table on which the work piece is supported and on which it can be moved. The grinding wheel is mounted on a carriage that permits it to be moved back and forth over the work piece. The unit is positioned in an enclosure, which collects the dust generated during grinding and ducts it to a bag filter before discharge to atmosphere.

### **Cutting to-size slabs**

In some cases the slabs have to be cut to the appropriate size. Wedge-type slabs, which result from adjustment of the width in the continuous casting plant (mould adjustment) and from change of the lot size, have to be conditioned by torch cutting to obtain the desired geometrical shape.

## **A.2.1.3 Reheating- and Heat Treatment Furnaces**

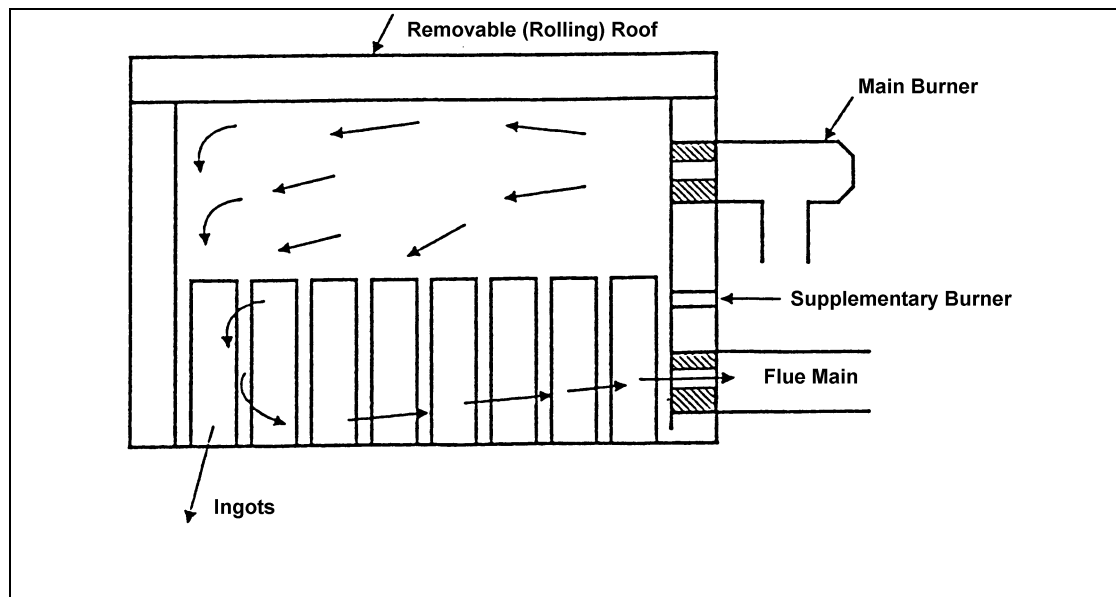
For hot rolling the steel input has to be heated to appropriate rolling temperature between 1050 and 1300 °C and a uniform temperature distribution has to be ensured.

Depending on the charge material and the hot rolling process, reheating is done in different types of furnaces such as pit furnaces, pusher type furnaces, walking beam furnaces, rotary hearth furnaces or others. These furnaces are fired directly, usually by oil, natural gas or plant gases such as COG and BFG. Depending on the heating media, different waste gas emissions will occur (mainly SO<sub>2</sub> and NO<sub>x</sub>).

### **A.2.1.3.1 Batch Furnaces**

Batch type furnaces are often used for speciality steels and forgings. A typical example of the batch type furnace is the **soaking pit**, used to reheat ingots, slabs and other feedstock. It consists of refractory lined chambers in which the input is placed vertically (ingots) or horizontally (slabs). A moveable cover allows the input to be charged and removed for rolling. Cast ingots can be charged immediately after stripping to conserve energy. The typical soaking pit capacity is 50 to 170 tonnes with a thermal input of 9.5 MW (Th) and a heating rate of 10.7 t/h.

Soaking pits are no longer in widespread use as more and more steel is continuously cast, a process, which often bypasses the soaking pits. An example of the soaking pit furnace is shown in Figure A.2-17. [EUROFER HR]



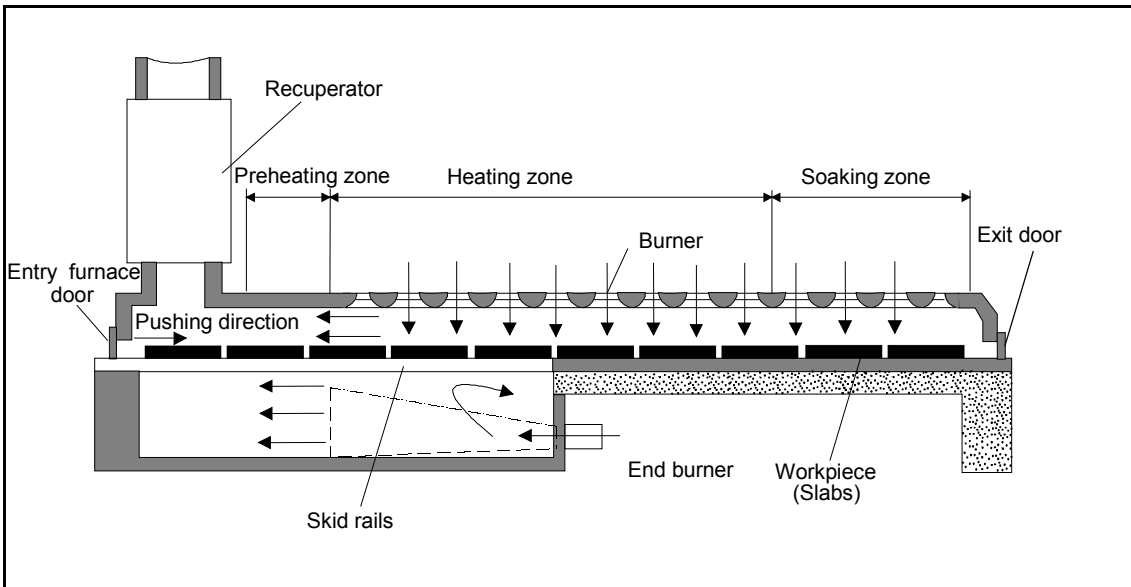
**Figure A.2-17: Pit furnace**  
[ETSU-NP-54]

Another type of the batch furnace is the bogie hearth furnace. The stock is carried into the furnace chamber on a bogie. The furnace chamber is closed by means of a door and the stock is heated. When the targeted temperature is reached, the door is opened, the bogie with the stock is removed and the slab or casting is taken away for further use. [EUROFER HR]

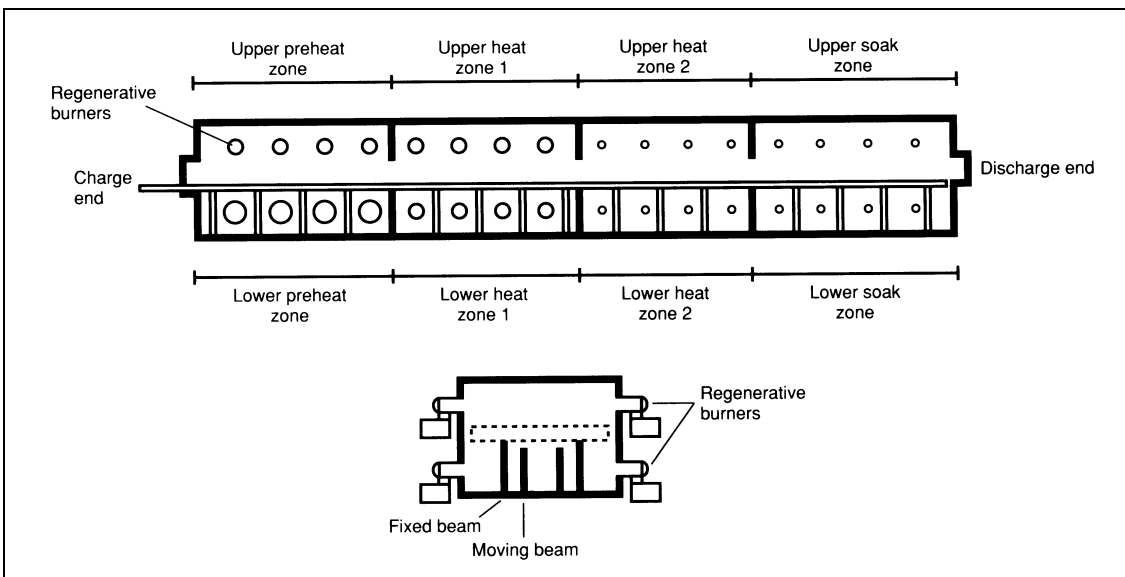
### **A.2.1.3.2 Continuous Furnaces**

Larger furnaces are usually fed continuously. The stock is pushed through the furnace by the following stock (**pusher type furnace**) or is moved through by walking beams (**walking beam furnaces**), a walking hearth or on/between rollers.

Examples of the larger size (> 20 MW<sub>Th</sub>) furnaces - the pusher and walking beam furnaces – are shown in Figure A.2-18 and Figure A.2-19. The largest currently in operation are walking beam furnaces of approx. 125 MW (Th) and pusher furnaces of 200 MW (Th). [EUROFER HR]

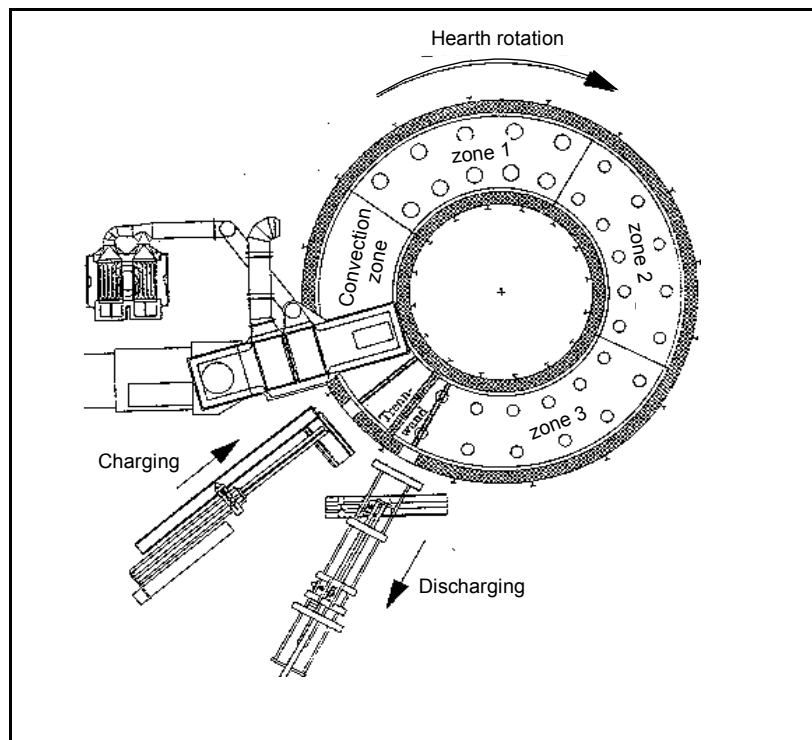


**Figure A.2-18: Pusher type furnace**  
[DFIU98]



**Figure A.2-19: Walking beam furnace**  
[ETSU-G77]

In a **rotary hearth furnace** (see Figure A.2-20) the charge material is placed onto a rotary hearth. During the furnace campaign (hearth is rotating) the material is heated and, after completion of a rotation, discharged.



**Figure A.2-20: Typical design of rotary hearth furnace [EUROFER HR]**

#### **A.2.1.4 Descaling**

Prior to rolling adherent scale, which forms during reheating must be removed, in order to avoid a contamination of the stock surface by scale impressed by the rolls (so-called 'rolled in matter').

Mechanical descaling, where the adherent scale is mechanically broken in a light pass (mostly in two-high stands) and then sprayed off or mechanically removed (brushing), is rarely applied any more. Today, a common method of descaling is breaking and spraying off the scale by means of high-pressure water. Power water with pressures of 120 to 250 bar (exceptionally 600 bar) is applied via flat jet nozzles onto the material surface. For the cleaning effect, the impact pressure (i.e. the pressure determined by the distance of the descaling nozzles to the rolling stock) is more important than the system pressure. The following techniques are applied throughout the whole rolling process:

- Primary descaling in so-called high pressure descalers installed before the entry into the roughing train and equipped with 1 or 2 pairs, some times adjustable, descaling headers.
- Mill stand descaling by means of descaling headers arranged above and below the plate passage on both sides of reversing stand and on the entry side in case of continuous stands.
- Descaler at entry of the finishing train for removing secondary scale, i.e. the scale formed on the rough strip at the conveying roller table of the roughing train and finishing train.
- Pairs of mill stand descaling sprays at the entry of the first stand of the finishing train. [EUROFER HR].

In case of production lines for long products the descaling headers are either designed as spray rings or as combination of vertical and horizontal headers, sometimes adjustable to material cross section, for proper descaling of all material surfaces. [EUROFER HR]

### **A.2.1.5 Edging**

Edging is usually applied in the manufacture of strip and plate. The slabs produced in the continuous casting plant are supplied in certain defined, stepped dimensions of widths. The width has to be reduced to the specified dimension of the rolled strip, with a trimming allowance as narrow as possible (scrap minimization and yield improvement). In most cases, this width reduction is performed on so-called edgers (vertical rolling stands) - recently even in slab presses - which are installed in front of the roughing unit. The accuracy of the width reduction and optimum adherence to the rectangular shape effect the amount of scrap arising from cropping (head and tail end) in the rolling mill and in the finishing shops (trimming).

### **A.2.1.6 Roughing**

Roughing depicts the first bulk reduction done on the incoming hot roll stock for the production of strip, rod and sections. Generally, the roughing train consists of one or more horizontal stands for thickness reduction, including edgers (vertical stands) situated in front of the stand for width adjustment. Reversing roughing mills are sometimes equipped with edgers on both ends of the mill stand [EUROFER HR]

### **A.2.1.7 Strip Rolling/Finishing Train**

In general, the finishing mill consists of a number of rolling stands positioned after one another. The stands have staggered roll gaps so that the thickness reduction to the requested final thickness is done in one pass of the transfer bar. The number of stands depends on the grade and material thickness of the input (slabs) as well as on the thickness range of the finished strip.

Crop shears arranged in front of the finishing stands serve to cut the ends of the rough strip, which may have the form of a tongue or fishtail. This ensures safe entry into the finishing train and avoids damage to the rolls as well as generation of scrap.

In most cases, an additional descaling device (descaling sprays) as described above is installed between crop shears and finishing train. Sometimes there is also an additional vertical stand, which is mainly used for strip guidance, but occasionally for minor width adjustments as well.

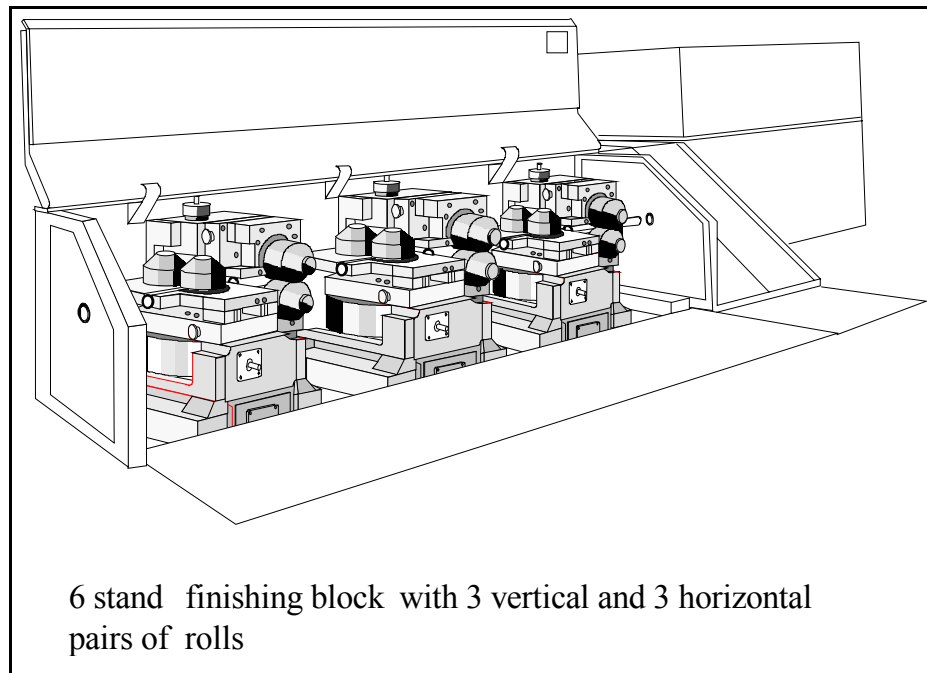
### **Coilers**

Hot strips with length up to 2 km and even more are wound up on so named down (sometimes up-) coilers at the end of the rolling mill by speeds up to 20 m/s and more. The hot band is guided around an expandable mandrel by special arranged wrapper rollers. After approx. 3 - 4 windings the wrapper rollers are lifted and the band is coiled onto the expanded mandrel. After the coiling operation is finished, the mandrel is collapsed and the hot coil is transported to a strapping station by means of a coil car. [EUROFER HR]

### **A.2.1.8 Rod Rolling/Finishing Train**

The finishing train of rod mills usually consists of rolling blocks with up to 10 sets of alternating horizontal and vertical roller pairs as shown in Figure A.2-21.

Rolling speeds of more than 100 m/s are achieved at the final stages. The material used for the roughing and intermediate rolls is generally hardened steel or cast iron while the finishing rolls are made of carbide, a particularly wear resistant material. The typical calibration used for wire rod mills is a sequence of alternating round and oval calibres.



**Figure A.2-21: Roller arrangement of wire rod finishing section [EUROFER HR]**

### **A.2.1.9 Plate Rolling**

Plate rolling by reversing operation is similar to roughing in strip production. The slabs are formed into plates in the so-called multi-stage rolling operations, where the slabs are stretched, turned by 90° by means of conical rollers on a special roller table, spread, turned again and rolled to the requested thickness.

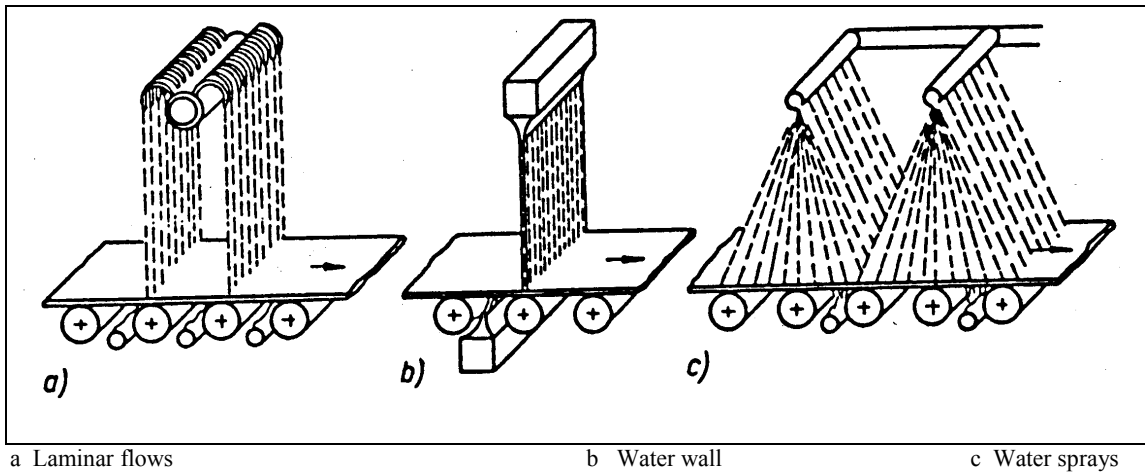
### **A.2.1.10 Transport of Roll Stock between Rolling Stands**

Usually, roller tables arranged along the entire strip rolling train are used as a means of transport for the rolling stock. These roller tables consist of individual metallic hollow and/or solid rollers with single drive or group drive by means of an electromotor and gear, if necessary.

In special cases, for example later modernisation of a rolling mill including increase of the weight of single products or installation of additional equipment, the distance between roughing stand and finishing stand is no longer sufficient to de-couple the two processes. So-called coil boxes - developed by STELCO, Steel Company of Canada Ltd. - are then inserted as intermediate storing devices. [EUROFER HR]

### **A.2.1.11 Cooling Lines**

In connection with an appropriate temperature control within the finishing trains, the cooling line provides the desired mechano-technological parameters to the material. The steel is rapidly cooled using either water sprays, water walls or laminar flows (see Figure A.2-22).



**Figure A.2-22: Different types of water cooling**  
[Tech Metal]

Widest spread nowadays is the use of laminar flow cooling on run out tables. Usually, the spray headers (arranged on top and bottom of the passline) are grouped into sections, sometimes of different water flow volume. Each section and/or each header is individually controllable so that desired cooling temperature may be realised. Cooling lines and the individual sprays are computer controlled, whereas the spray headers are switched on and off in accordance to complex mathematical-empirical models, supported by peripheral temperature measurements. [EUROFER HR]

### A.2.1.12 Sheet and Plate Production

For sheet production the hot produced coils are decoiled by means of uncoiling reels and supplied to a shearing line which is equipped with levellers to straighten the strip. The rolled sheets with desired length are piled and stored in the storage yard. [EUROFER HR]

Plate production is carried out on shearing lines following the rolling process. The plates are trimmed on both sides, cropped and cut to desired length. Cutting to size for special blanks is done by CNC-cutting equipment (torch-, plasma- or laser beam-cutting units). The internal quality of plates may be determined by ultrasonic techniques. Automatically working devices may be installed on the shearing line run out table.

Finishing operations are computer controlled in the most installations. Consideration is also being given to the in-line quenching and heat-treatment of plates following the last rolling pass as a means of conserving energy. [EUROFER HR]

### A.2.1.13 Plate Heat Treatment

Finished plates are partly subject to heat treatment. In **annealing** steel is heated to a subcritical temperature to relieve stresses. For **normalising** steel is heated above its critical temperature and air-cooled. The purpose is to refine grain sizes and to obtain a carbide distribution, which will dissolve more readily, austenite. **Quenching**, **tempering** and other methods may also be applied.

Several different types of furnaces are used for these purposes, such as walking beam type, roller hearth or car bottom furnaces. The heating and combustion system of such furnaces are



comparable with the systems related to stock re-heating. All usually available heating media may be used for firing the treatment furnaces. [EUROFER HR]

#### A.2.1.14 Roll Shop

The workrolls as well as the back-up rolls for both finishing and roughing mills are conditioned according to well-defined specifications, depending on the product to be rolled. Conditioning of the rolls is performed at the roll shop where typical machine shop techniques are applied, such as machining and grinding. [EUROFER HR]

A roll shop generally includes the following:

- Cooling area where work rolls are cooled either in open air or by water sprinkling.
- Preparation area where the shocks are dismantled and set-up (In some cases the roll shop machines allow reconditioning of rolls without prior dismantling).
- Cleaning area where the rolls to be reconditioned are cleaned from deposits and lubricants, (The cleaning techniques include steam cleaning, application of alkali degreasing solutions, application of organic solvents).
- Typical machine shop equipment including lathes and grinding machines which have individual cooling system where the cooling liquid is continuously processed in order to separate turnings and grinding sludge [EUROFER HR].

#### A.2.1.15 Water Circuits / Water Management in Hot Rolling Mills

Throughout the hot rolling process and linked process steps water is used for cooling and for technological reasons. Electric motors, re-heating furnaces, control rooms and power systems, instruments and process control are usually cooled indirectly. The steel, rolls, saws, cropped ends, coilers and hot run out tables are cooled directly. Water is also used for scale breaking, flushing scale and for scale transport. Wherever the water is in contact with the rolled material (process water) and rolling equipment it will be contaminated with scale and oil.

The simplest water feeding system applied is an **open system** (once-through system) as shown in Figure A.2-23. The water is taken from natural resources (river, lake or ground water), flows through the various consumers of the hot mill and is released again to the watercourse.

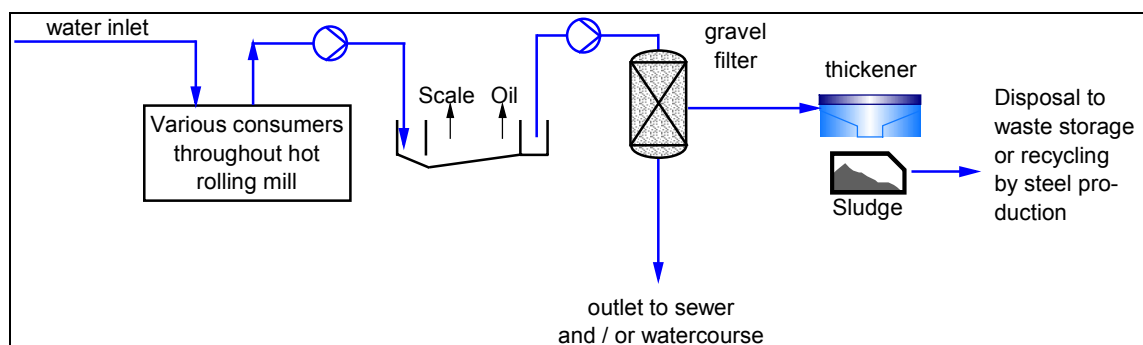


Figure A.2-23: Example of a once through water system [EUROFER HR]

The polluted cooling and process waters are collected and treated prior to discharge. First treatment stage is a sedimentation basin in which solids, mainly iron oxides, are allowed to settle at the bottom of the basin.

The sedimented solids are discharged via appropriate devices (scraper, screw, etc.) and, in the case of integrated steel plants, returned to the production process via the hot metal route. The oil pollutants floating on the surface are removed by means of suitable skimming devices and are discharged to the respective collecting basins.

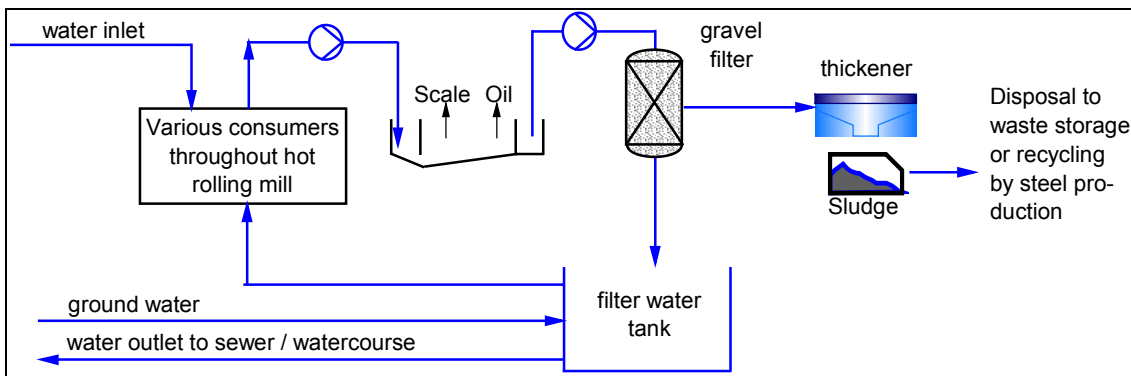
The pre-cleaned overflow is supplied via pipes to the filter batteries whose number, size and capacity are designed in conformity with the water volume. In most cases these filters are gravel filters, i.e. the overflowing water is cleaned by passing through gravel beds.

The pollutants in the gravel filters must be removed by back-washing in order to maintain the function and separation efficiency of the filters. The purified waste water from the filters is discharged into the sewage system and/or lakes and rivers.

The sludge-bearing waters (mostly containing iron oxide) from the filter batteries are separated in a thickener. The overflow is recirculated to the cleaning circuit system. The high-quality feed material contained in the sludge is further dewatered and disposed off or returned to the steel production process, provided the appropriate technical equipment is available.

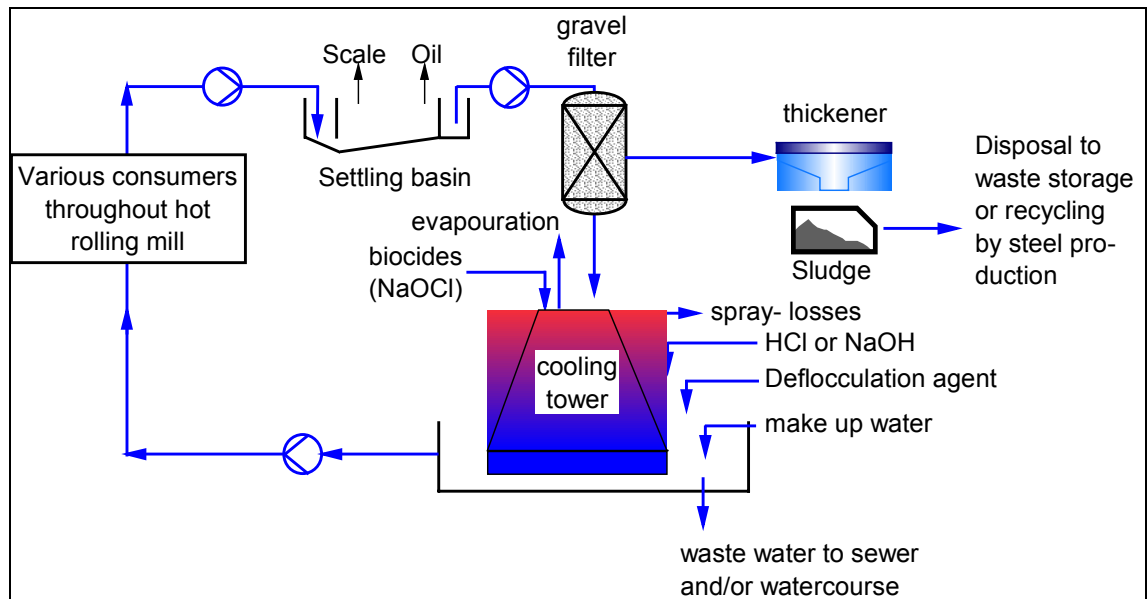
In order to reduce or avoid waste water discharge from hot rolling operations semi-closed - and closed circuits are implemented.

In **semi-closed circuits**, as shown in Figure A.2-24, the water is treated and partly reused depending on the temperature. The water treatment devices are the same as for open systems, but the filtered waste water is not directly disposed off. Instead it is conveyed into a filter water basin and mixed with cold fresh water, if necessary. Depending on the temperature of the mixed water, the filtered water is returned to the different consumers in the hot rolling mill and only the overflow is discharged. Accordingly, the volume of the circulating water depends on the seasons and the geographical situation.



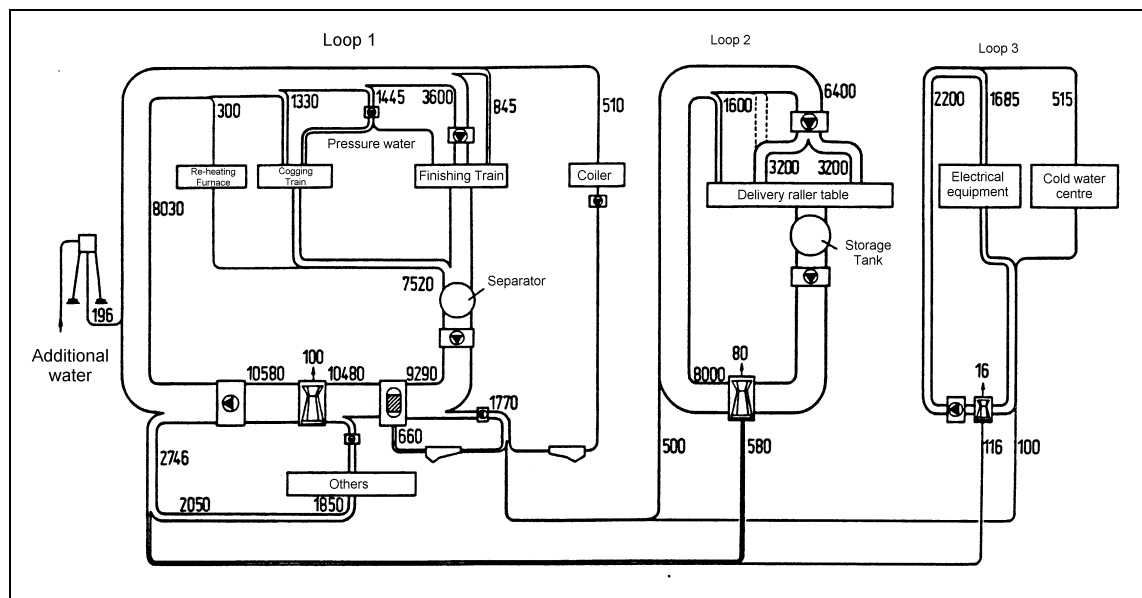
**Figure A.2-24: Example of semi-closed water circuit**  
[EUROFER HR]

With application of **closed water circuits** (see Figure A.2-25) the purified water is not discharged, but re-cooled in cooling towers or heat exchangers to required temperature and is reused in the rolling process. For plants using cooling towers, water consumption is restricted to additional water (approx. 3 - 5 %) needed to make up for evaporation and for blow down losses. When heat exchangers are used, large re-circulating volumes of re-cooling water are required.



**Figure A.2-25: Example of closed circuit water system [EUROFER HR]**

Water feeding- and treatment systems in hot rolling mills are usually very complex, with several, partly interconnected water loops and multiple-stage use of water. In some cases the hot rolling mill water circuit is coupled with water feeding systems of other iron and steel production units, as for example continuous casting. Reasons for this connection are the similarity of the waste water contents and the proximity of the installations.

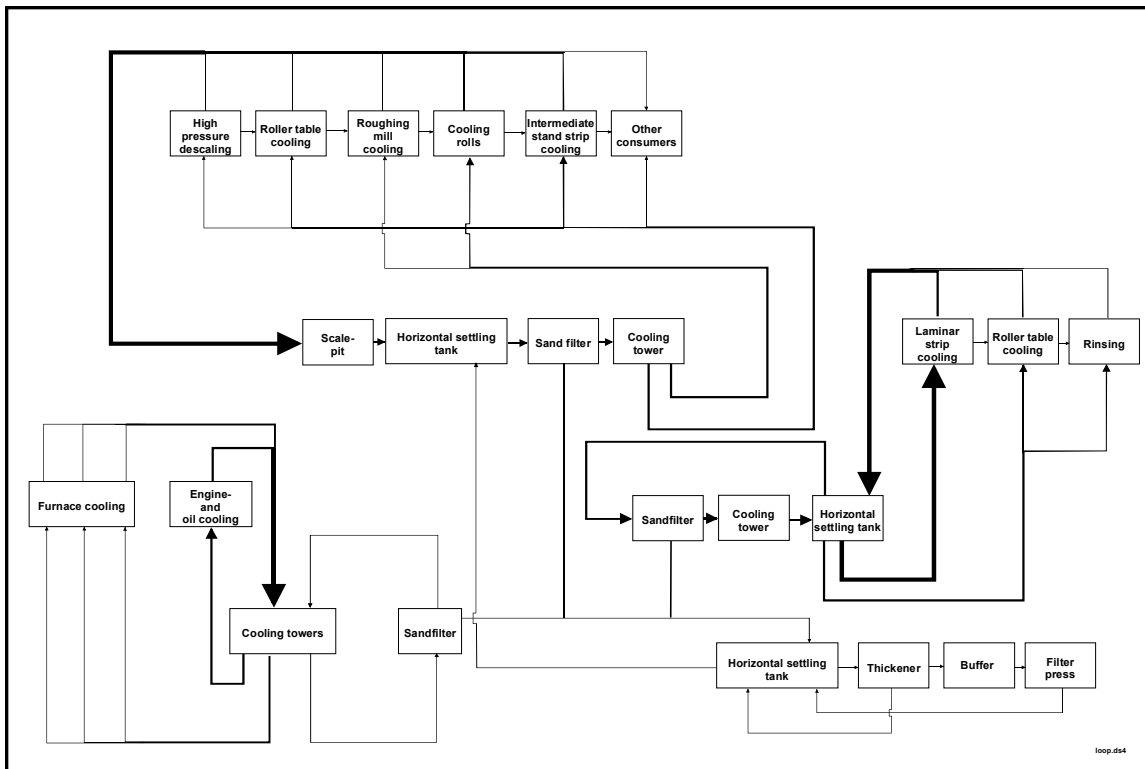


Notes: 1) Figures given represent water flow in  $\text{m}^3/\text{h}$   
 2) Mill capacity: 270000 t per month

**Figure A.2-26: Water loops for hot strip rolling mill [StuE-96-7]**

Figure A.2-26 shows the water circuit of a hot wide strip mill where 3 water loops are established. Loop 1, with 8030 m<sup>3</sup>/h, comprises the cogging stand, finishing train and re-heating furnace; loop 2 (8000 m<sup>3</sup>/h) delivery roller table and loop 3 (2200 m<sup>3</sup>/h) mainly the electrical equipment. The Loops are connected in a way that water input for loop 2 and 3 is supplied by the clean waterside of loop 1. Process water of loop 2 and 3 is sent to the treatment facilities of loop 1 and also blow-down water can be discharged to loop 1.

Figure A.2-27 shows another example of a water management system for hot wide strip mill. The loops established in this case are for furnace- and engine cooling, for roller stands and for laminar strip- and roller table cooling.



**Figure A.2-27: Use of water loops in a hot rolling mill [DFIU98]**

The prevention of effluents by using water in loops or in multiple stages is a well-known and wide spread practice within the steel industry. Hot rolling mills offer a high potential for reduction in water consumption and waste water discharge, because of the large quantities of water needed.

### A.2.1.16 Waste and By-product Management in Hot Rolling Mills

Apart from waste water, hot rolling operations generate different kinds of solid and liquid by-products and waste.

- Metallic waste and by-products.
- Scarfing scale/swarf.
- Dusts from scarfing and rolling.
- Mill scale (oil free and oily).
- Water treatment and mill scale sludge.
- Grinding sludge (roll shop).
- Oil and greases.

**Metallic by-products/waste**, like scrap, downgrades, crop ends, etc. arising from hot rolling, is usually rather clean and is easily recycled into metallurgical processes (e.g. BOF).

Oilfree **scale** and low oil-content (< 1 %) scale, is fed back directly to the metallurgical process, usually via the sinter plant. Oily, ferrous sludges with up to 80 % FeO<sub>n</sub> content, like **oily mill scale** and **grinding sludges**, obtained from water treatment plants have to be conditioned before internal recycling.

Scale is also sold for external use (e.g. to cement manufacturers) or it is supplied to an external company for treatment (usually thermal treatment to burn the oil content). Thermal treatment plants can yield a product with an iron-content of about 60 - 70 %. If the thermal treatment plant is fed with oily mill-scale of about 4.5 % no additional energy supply is required.

**Oxide dusts** from air cleaning devices, for example from bag filters for oxide removal at the mill stands, are recyclable to the steel production (e.g. sinter plant) without risks.

**Oil and grease**, separated and collected at various stages, are energy sources and can be utilized as secondary fuels, for example by injection into the blast furnace or in the coke making process. Dewatering might be a precondition. Alternatively, these materials can be used at the coke ovens to increase coal bulk density prior to carbonisation. [EUROFER HR], [Com2 HR]

**Spent emulsion** from the roll shop or other consumers can be split into components: oil and water. The separated oil can be thermally utilized or recycled externally. [Com2 HR]

## A.2.2 Cold Rolling Mills

### A.2.2.1 Process Overview

In cold rolling the properties of hot rolled strip products, e.g. thickness, mechanical and technological characteristics, are changed by compression between rollers without previous heating of the input. The input is obtained in form of coils from hot rolling mills.

The processing steps and the sequence of processing in a cold rolling mill depends on the quality of the steel treated. **Low alloy and alloy steel (carbon steels)** processing usually follows the order: pickling, rolling, annealing, temper rolling/skin pass rolling and finishing.

The process route for **high alloy steel (stainless steel)** requires an initial annealing step prior to pickling due to the hardness of the steel quality and, further more, several additional annealing and/or pickling steps during rolling may be necessary.

Cold rolled products are mainly strips and sheets (thickness typically 0.16 - 3 mm) with high quality surface finish and precise metallurgical properties for use in high specification products.

### Cold Rolling Mills (CR Strip Mills)

Typical layouts for cold rolling mills are shown in (Figure A.2-28), the plants usually comprise:

- **Continuous pickling line**, where the oxide layer formed during the hot rolling is removed by pickling with sulphuric, hydrochloric or a mixture of nitric and hydrofluoric acid. A stretcher leveller or an in-line skin-pass may be used to improve the shape of the strip and provide mechanical breaking of the oxide layer.
- **Cold rolling mill** generally consisting of a 4-stand or a 5-stand four-high tandem mill or of a four-high reversing mill. Cold rolling reduces the initial thickness of the hot rolled strip by typically 50 to 80 %.
- **Annealing facilities** to restore the ductility of the steel strip that is lost as the result of work hardening during the cold rolling.
- **Temper mills** to give the annealed material the required mechanical properties (prevents the formation of Lüders lines during drawing). The material is subject to a slight skin pass rolling typically on a four-high skin pass mill. The roughness of the work rolls of the mill is transferred to the strip by the roll pressure.
- **Inspection and finishing lines**, here coils with different length may be welded together to meet the required weight or may be slit to required width. Also coils are cut into sheets with required length and width. At the same time defective sections of strip can be discarded.
- **Packaging lines for coils or sheets** according to the destination and/or the means of transport.
- **Roll shop**, where the work rolls and the backup rolls for the cold rolling mill and the temper mill are prepared.

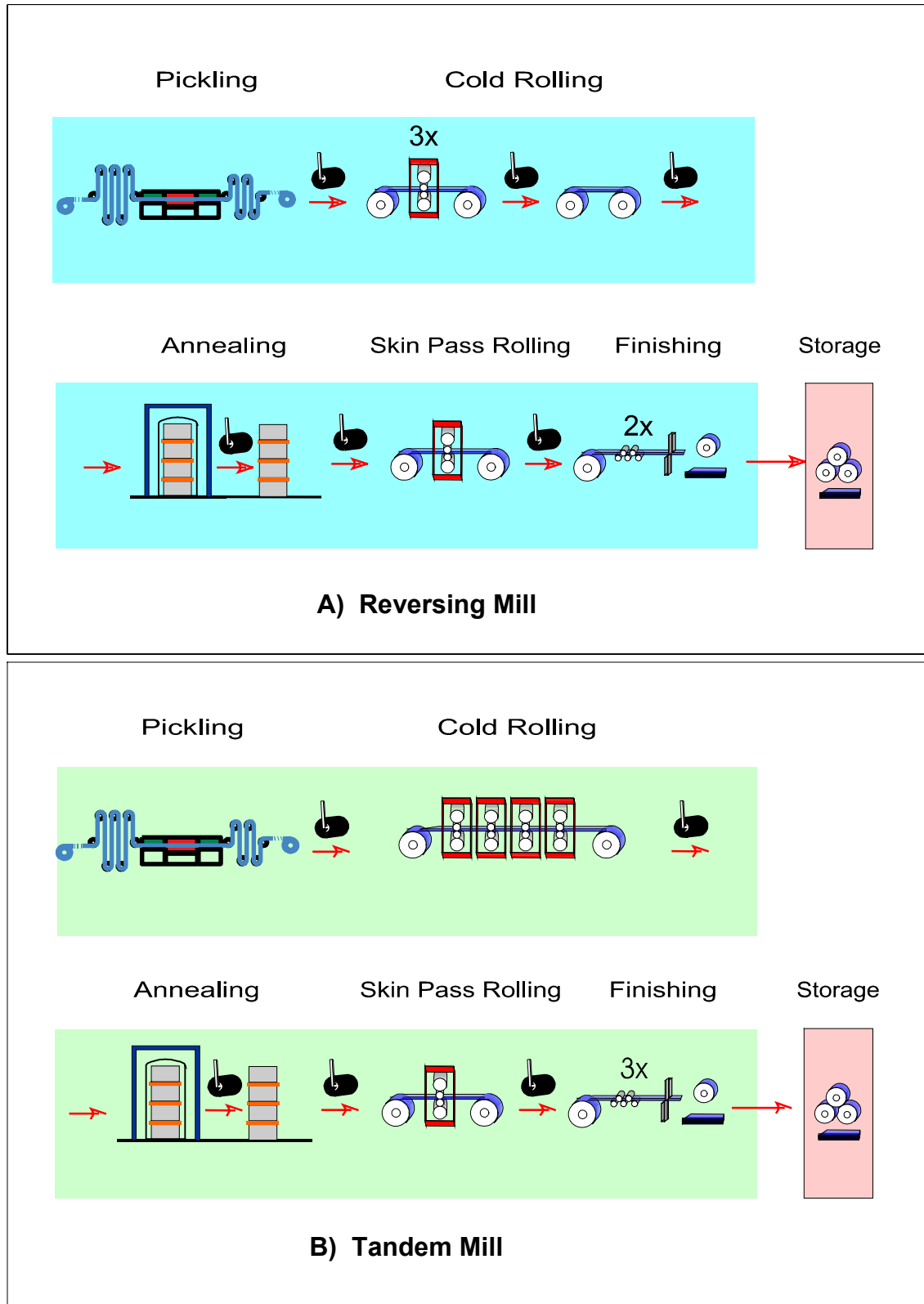


Figure A.2-28: Typical configurations of cold rolled strip mills  
[EUROFER CR]

For electrical steel sheet production the mill design is quite similar to those described above. The rolling mill usually comprises a four-high reversing mill stand, which is enlarged to rolling and alternative skin pass rolling operation (rough pass up to 7 % deformation). For higher Si-contents, flash butt welding of head and tail of the coils to an endless strip has to be replaced by ‘agraphing’ the ends of the coils.

Technical trends and developments in cold rolled strip production, driven by increasing market demands and competition from alternative materials, aim at increasing the efficiency and the output of plants by minimizing the processing time and the consumption of materials and energy. Simultaneously the environmental impacts of the facilities are reduced. Figure A.2-29 shows as an example a modified plant concept which shortens the process time for annealing and the following operations from 3- 7 days (2 –3 days when hydrogen is used) to approximately 10 minutes. [EUROFER CR], [Com VDMA]

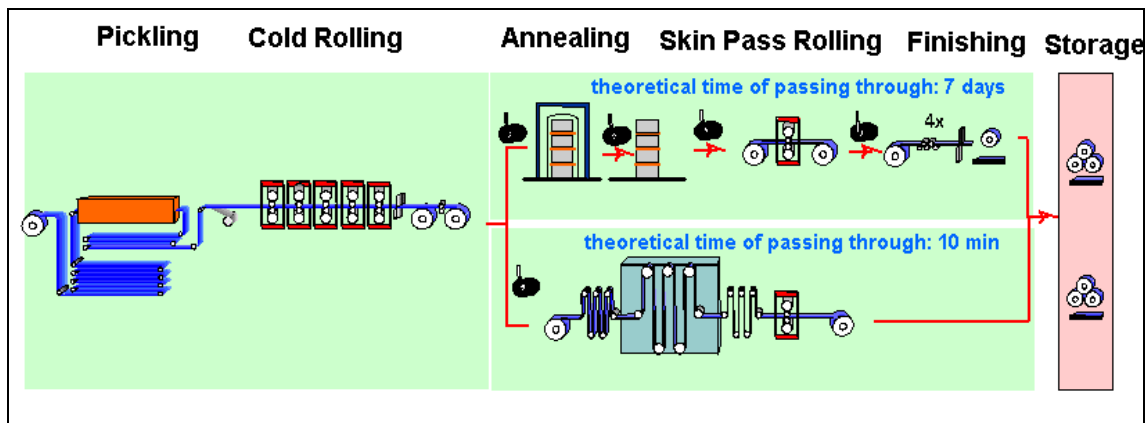


Figure A.2-29: Cold rolling process line with continuous annealing [EUROFER CR]

### A.2.2.2 Pickling of Low Alloy and Alloy HR Steel

The entire surface of the hot rolled coil is covered with a thin layer of scale containing oxides, which must be removed prior to cold rolling. This is done by pickling with hydrochloric acid or sulphuric acid, at temperatures typically ranging from 75 °C to 95 °C.

Once the strip or sheet is pickled, it must be thoroughly rinsed with de-mineralised (or equal quality) water and subsequently dried. Oiling is done either with rolling oil or anticorrosive oil. [EUROFER CR]

#### Pickling lines

Pickling can be done as a batch (usually for bars, rods or tubes), semi-batch or as a continuous process and can also involve a number of stages using several acid baths. The following process description refers to continuous pickling lines on which steel is pickled in coiled shape. Each of the pickling steps described below can also be performed as an individual batch process.

A typical pickling plant may incorporate:

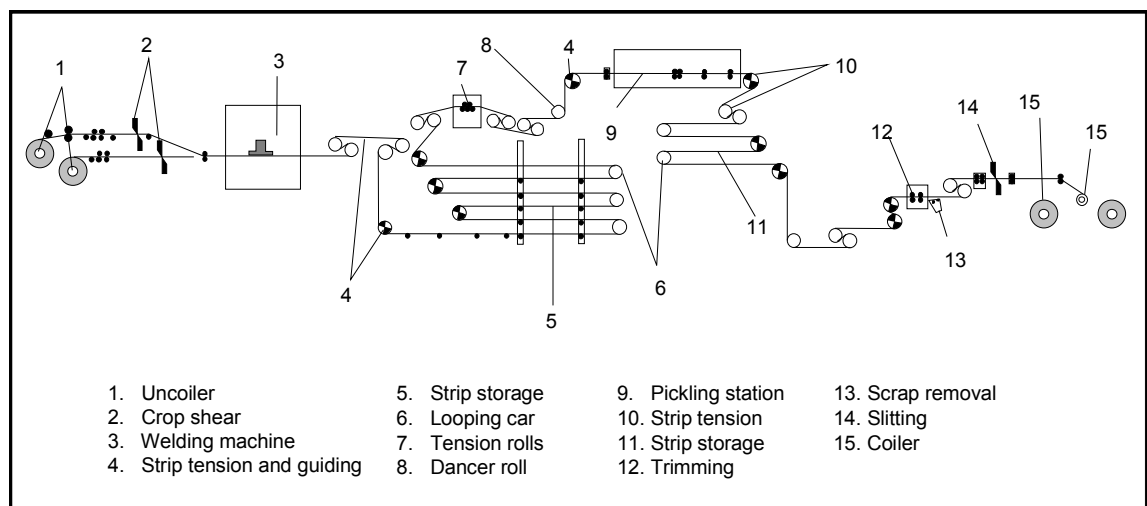


- Anticoil break equipment on the decoiler to avoid the occurrence of flow lines (Lüders' lines) on the entering hot rolled coil.
- Welding of the hot rolled coils to continuous strip to ensure defined constant pickling times.
- Straightening equipment prior to the entry of the hot rolled strip into the pickling tanks. The flatness of the hot rolled strip is increased by straightening, and the capacity for pickling is improved by the scale breaking effect of straightening.
- Chemical pickling zone; deep tank or shallow tank (turbulent) pickling equipment.
- Rinsing zones to remove remaining acid on the strip surface.
- Trimming of the strip to obtain cut edges and exact widths.
- Inspection of the strip for dimensional tolerances, surface defects and residues.
- Oiling of the strip (Note this may not be required in a combined pickling and rolling line).

The pickling is carried out in totally enclosed equipment or tanks fitted with hoods. In both cases the units are under continuous extraction to remove any fumes generated.

Modern pickling plant design comprises pickling tanks equipped with external pumps. Instead of simply passing the steel strip continuously through an acid bath, the acid is pumped via a circulation system through nozzles mounted in the bath itself. The turbulence resulting from this promotes the pickling reactions. [EUROFER CR]

Large continuous pickling lines can have capacities of up to 2.4 million t/a. Figure A.2-30 shows the operational steps in continuous pickling lines. [DFIU98]



**Figure A.2-30: Schematic of a continuous pickling line**  
[DFIU98]

### A.2.2.3 Annealing (I) and Pickling (I) of High Alloy HR Steel

The coils of stainless steel strip produced by hot rolling are known as 'hot band' coils. Due to the presence of an oxide scale and chromium depleted layer formed during the hot rolling the steel must also be descaled / pickled prior to cold rolling. In addition, the greater hardness of the steel compared with carbon steels necessitates an initial annealing (I). The annealing process has three components, heating to annealing temperature, temperature equalisation and cooling. Both continuous and batch annealing processes may be used. [EUROFER CR]

## Annealing

**Ferritic grades** are generally annealed as tightly wound coils in a **batch heat treatment** facility. Such installations may be used for the full heating, temperature equalisation and cooling cycles. One or more coils are placed on the furnace base and covered to form a closed furnace chamber. Heating may be achieved via gas firing or electrical heating. An inert protective atmosphere (nitrogen/hydrogen) is required for metallurgical reasons. Ferritic steels are generally annealed at steel temperatures of up to 800°C. [EUROFER CR]

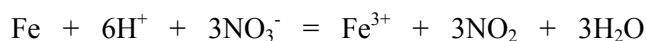
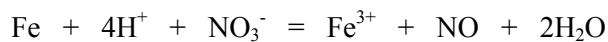
For **continuous annealing of austenitic steels** the steel coil is unwound and passed through one or more heat treatment furnaces. These furnaces typically consist of a refractory (or other form of insulation) lined steel structure and are usually directly fired by gaseous fuels. An oxidizing atmosphere is needed to form a scale, which is rich in oxygen to allow a better pickling. The waste gases are exhausted via flues under natural or forced draft. Strip temperatures typically up to 1100°C are necessary for annealing austenitic steels. The steel strip then passes through the cooling section and may be cooled using gas jets, air, water sprays or water quenching. Continuous annealing is generally combined with a descaling/pickling plant as described above to form a continuous annealing and pickling line. [EUROFER CR]

## Descaling and Pickling

After annealing the steel is descaled to produce a steel surface suitable for cold rolling. Mechanical descaling such as shot blasting or scale breaking may be used prior to chemical pickling to remove the heavy scale burden. However, careful control of such mechanical processes is necessary to minimize damage to the strip surface, which could affect the final product quality.

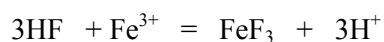
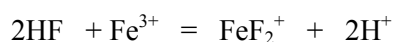
Final scale removal including the removal of the chromium depleted layer beneath the scale is generally done by pickling in a mixture of nitric and hydrofluoric acids at temperatures of up to 70°C. The acid concentrations employed depend on the material being processed but are normally in the range 10 - 18 % nitric acid and 1 - 5 % hydrofluoric acid.

The chemical reactions that take place during the pickling of stainless steels are complex and involve the removal of the adherent scale layer by the combined action of the acids used. The dominating chemical reaction during pickling is the dissolution of metals by the nitric acid. As a by-product of these reactions both nitrogen monoxide and nitrogen dioxide are formed. The reactions shown below are for the dominant metal iron but similar reactions also occur for the alloy elements present in the stainless steel such as nickel and chromium.



The NO<sub>x</sub> generated is partially soluble in the acid but once the limit of solubility is reached the NO<sub>x</sub> fumes transfer to the gaseous phase and are released from the pickling tanks. The rate of formation of NO<sub>x</sub> increases with increasing temperature.

The metal ions formed in the dissolution reactions then react with the hydrofluoric acid leading to the formation of metal complexes.



The combination of these two sets of reactions results in the consumption of both nitric and hydrofluoric acids. To maintain the optimum conditions for descaling regular additions of fresh

acid are made as required. The iron fluoride complexes produced in the dissolution reactions have a limited solubility and if the concentration of iron is allowed to reach 5 % (40 g/l) then precipitation of iron fluoride will commence. This precipitation causes the formation of large quantities of a hard crystalline sludge.

Pickling line design is usually the same as for pickling of low alloy steels. Except, that on exit from the last pickling tank the steel strip is rinsed with water to remove traces of acid, dried, but no application of oil is necessary because of the corrosion resistance of the steel. [EUROFER CR]

## **A.2.2.4 Cold Rolling of the Pickled Hot Rolled Strip**

### **A.2.2.4.1 Low Alloy and Alloy Steel**

In cold rolling the pickled hot rolled bars, sheets or strips are passed through sets of rolls on reversing mills or on continuous in-line mills. Low carbon steels which are less hard, are generally rolled in multi-stand tandem mills due to a higher capacity of these mills. They consist of a series of four or six-high stands. The strip enters the first stand and undergoes an initial thickness reduction, further reductions are achieved in each subsequent stand until the final gauge is attained.

For low carbon strip generally an emulsion of 0.5 to 4 % (10 – 20 % for direct application) of oil in water is necessary for

- Lubrication.
- Cooling of the strip, work and back-up rolls.
- Removal of Fe-particles.

In the rolling process the wide strip is mainly deformed in a longitudinal direction, with transverse deformation being practically negligible. The thickness reduction of the material is obtained by the influence of the rolling forces and the strip tensions (forward and back) applied. The cold forming process leads to a corresponding hardening of the material. Exact mass flow control (control of rolling force and/or position), assisted by laser control of the strip speed and tension, may be used. Additional automatic control loops for flatness (roll bending, zone cooling, etc.) are used to obtain the required flatness of the strip. The roughness texture of the strip surface is applied in the last stand of the tandem mill.

For optimum strip surface cleanliness it is important to avoid contamination of the tandem emulsion by the hydraulic oil, by the Morgoil oil, by grease or by the cooling water (used to cool the emulsion). Precautions taken to avoid any contamination may include:

- Continuous monitoring of oil levels.
- Monitoring of the oil concentration.
- Regular control of hydraulic equipment and bearings.
- Monitoring of emulsion parameters such as temperature, pH value, saponification index, acid value, conductivity.
- Filtering of the tandem emulsion (using techniques such as magnetic filters, paper filters, precoat filters).

To clean the strip and remove any remaining soap or oil, it may be subjected to chemical and/or electrochemical degreasing. For this purpose, cleaning zones are installed on the entry side of the downstream processing plants such as hot dip galvanising plants or continuous annealing plants. [EUROFER CR]

### **Conventional discontinuous rolling**

The pickled hot rolled strip is fed into the cold rolling mill coil by coil. This results in a variation in the strip thickness corresponding to the geometrical conditions of the line at the strip ends during threading and at the exit of the coil end.

To produce 'mill clean sheet', often a thin emulsion with a maximum concentration of 1 % can be used on the last stands of the tandem mill. The emulsion is usually applied via spray nozzles onto the rolls and the strip. Sometimes higher concentrations are used in direct application systems.

Discontinuous rolling offers a high degree of process flexibility to account for variations in product mix. The technique is preferable for certain steel qualities. [EUROFER CR]

### **Continuous Rolling**

To achieve the narrowest possible thickness tolerances, maximum output and optimum productivity figures, a shallow tank turbulence pickling plant can be coupled with a tandem mill, which is enlarged by one stand. Usually an accumulator and a welding machine before a tandem has the same good results and a bigger increased capacity. The use of a welding machine and the accumulator allows coils to be joint and the strip to be fed to the mill continuously.

On a tandem line, the entering pickled hot rolled strip is reduced to the desired final thickness on a single pass through the line. Owing to the installation of several separate emulsion systems, a special emulsion can be applied in the last stand to increase the cleaning effect. For this purpose, either a detergent or a thin emulsion (1 % oil content) can be used.

Continuous rolling can allow good control of the strip thickness for coil ends and of surface quality. This can have a beneficial effect on material yield. In addition it allows oil consumption to be optimised. [EUROFER CR]

#### **A.2.2.4.2 High Alloy Steel**

After the initial annealing and pickling the steel is generally rolled to the required thickness on reversing cluster mills for a number of passes until the desired dimensions are achieved or until work hardening necessitates further annealing.

The process of cold reduction generates heat, part of which is transferred to the rolling oil which is sprayed onto the steel and rolls for cooling as well as lubrication. This heat is subsequently dissipated through heat exchangers to cooling water systems.

Mineral oils are generally used as rolling oil and close control of the oil cleanliness is necessary for optimum performance. This may be achieved using oil filtration circuits, which incorporate media element filters or powder pre-coat filter systems. Although the use of mineral oils predominates, emulsion cooling systems similar to those used for carbon steels may be employed. In such cases additional precautions must be taken to control oil cleanliness in order to avoid strip marking.

Collection hoods are fitted to the mill and operate under continuous extraction to remove oil mist that is generated. [EUROFER CR]

### A.2.2.5 Annealing of Low Alloy and Alloy Steel

The basic stages of the annealing process comprise:

- Heating to annealing temperature (above 650 °C).
- Holding at annealing temperature.
- Cooling.

This annealing process may be carried out in batch furnaces or continuous furnaces. The annealing cycle has a significant influence on the mechanical properties and, consequently, on the formability of the steel strip. The main parameter controlling the annealing cycle is the temperature profile. It varies, depending on whether the annealing is carried out in a continuous or batch furnace, and depending on the required strength or hardness of the product. The annealing cycle depends on a number of parameters including the actual material analysis, the reduction realised during cold rolling, the required mechanical properties and the required surface cleanliness, the type of protective gas, etc.

Continuous annealing and batch annealing are considered to be complementary processes and not fully interchangeable. Production related issues are integral to the selection of the annealing technique.

#### A.2.2.5.1 Batch Annealing

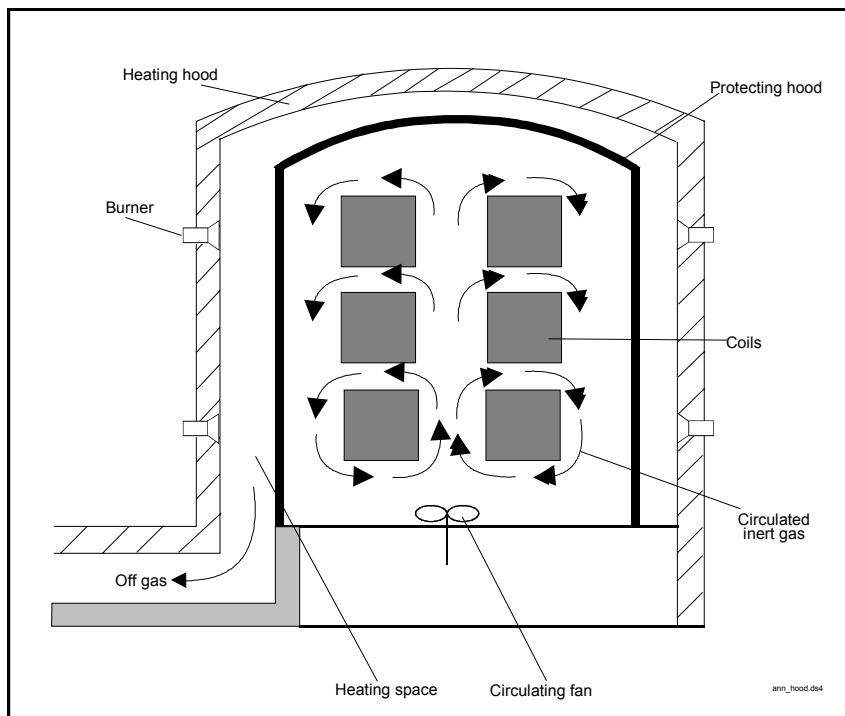
##### Degreasing /Cleaning by means of alkali

Prior to the annealing process the strip may be cleaned (degreased) to produce a cleaner surface. The cleaning serves to remove oil residues from the steel surface. The process is similar to that used for acid pickling except for the chemicals that are used. The most frequently used cleaning agents are phosphates, alkaline silicates, caustic soda and soda ash. Electrolytic cleaning and brushes are also used in some cases to remove iron fines from the strip surface.

The steel sheet is unwound from the coil and passed through cleaning tanks, which may be stirred to improve the cleaning effect. Subsequently, the steel is rinsed with water and recoiled. The degreasing solution can be regenerated and recycled.

##### Annealing

The cold rolled coiled strip is stacked in a hood furnace for annealing (see Figure A.2-31). The combustion chamber (space between heating and protecting hood) is heated by oil or gas burners. Heat passes through the protective hood into where the steel coils are stacked. A circulating fan provides as uniform temperature distribution as possible. The atmosphere in conventional plants is usually HNX gas (a nitrogen-hydrogen mixture with a hydrogen content close to the flammability limit). The atmosphere can also be 100 % H<sub>2</sub> as in parts of the working cycle of high convection furnaces.



**Figure A.2-31: Schematic of a hood-type annealing furnace [DFIU98]**

The heat passes into the coils through their outer edges, so that these areas are always hotter than the inner windings, especially during heating up. The heat treatment causes the organic residues of the emulsion to partly burn off; partly a distillation process takes place. Products of the reactions taking place are CO/CO<sub>2</sub>, H<sub>2</sub>, FeOx and CH<sub>4</sub>. The strip is heated to recrystallisation temperature, and annealed at about 700 °C resulting in complete recrystallisation of the cold rolled steel. For cooling the coils, the heating hood is removed. The cooling effect can be enhanced by spraying water on the protecting hood; by covering it with a cooling bell and blowing air on it or by using a cooling by-pass system which cools the protective atmosphere under the protective hood. The time necessary for annealing depends on the annealing temperature and the weight of the charge and can take 2 to 7 days.

Annealing in this type of furnace is very slow and also the cooling rate is not suitable for certain steel grades. Therefore an annealing process in a 100 % hydrogen atmosphere was developed yielding in shorter annealing times and more rapid cooling.

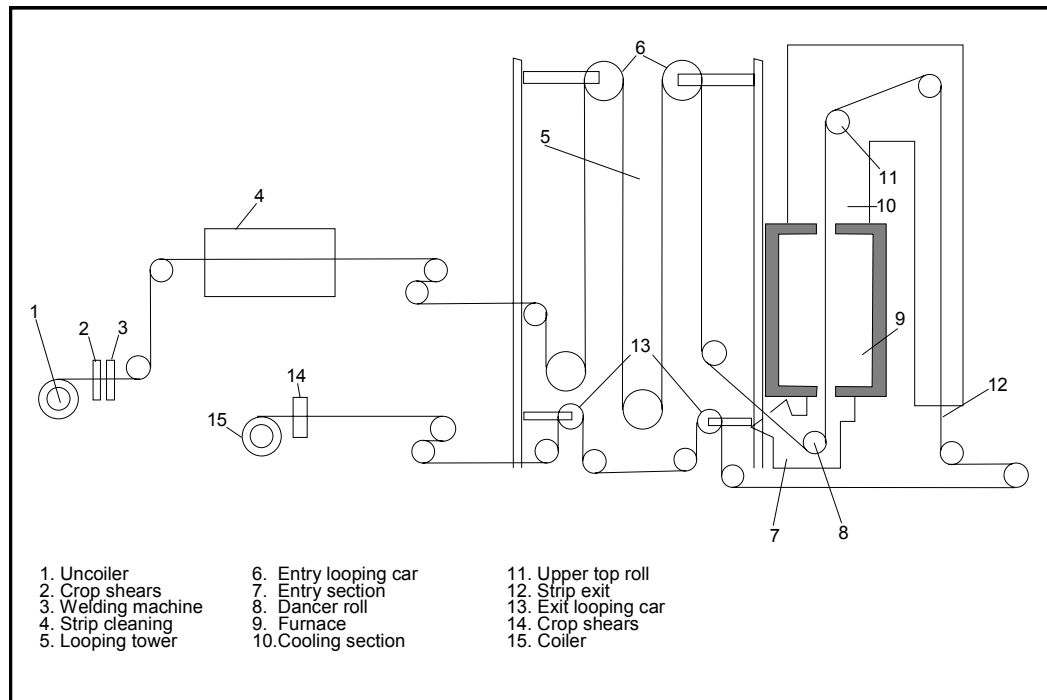
#### A.2.2.5.2 Continuous Annealing

For continuous annealing the coils are welded together on the entry side of the plant and subjected to the following process steps:

- Alkaline/electrolytic cleaning of the strips.
- Heating and holding at the required annealing temperature.
- Cooling (slow jet cooling, high gas jet cooling (using cooling rates up to 150 °C/s, hot water quench (HOWAQ), overaging, roll cooling, final cooling, misting jet cooling).

The continuous annealing is carried out by passing the steel strip through a multi-zone heating furnace with heating chamber, annealing chamber, cooling zone, tempering zone and a second cooling zone. The steel is heated to a range between 650 °C and 830 °C and then cooled by gas jets, gas-water sprays, contact rolls or water quenching, depending on the desired metallurgical

properties. These furnaces are usually fired by gas (direct or indirect) or electrically heated. The steel can be protected by an inert gas atmosphere or a reducing gas atmosphere in parts of the furnace. The principle operational steps for continuous annealing are shown in Figure A.2-32.



**Figure A.2-32: Example of a continuous annealing furnace [DFIU98]**

Continuous annealing gives a shorter processing time (about 10 minutes), less intermediate storage, uniform mechanical properties and a superior surface cleanliness. Continuous annealing is more appropriate for the production of higher strength steels. The layout of the furnace facilitates energy recovery from the exhaust gas.

### A.2.2.6 Annealing (II) and Pickling (II) of High Alloy Steel

#### Degreasing

Prior to the final annealing process, degreasing of the strip may be required to remove any contaminants from the steel surface. This can be achieved using an alkali based cleaning systems, which may be incorporated in the entry section of continuous annealing lines.

The steel coil is unwound and passed through a series of tanks containing the cleaning solutions. Agitation of the solution is usually incorporated to enhance the cleaning. Afterwards the strip is rinsed with water. De-mineralised water can be used for the final rinsing step. [EUROFER CR]

#### Annealing

The process route for final annealing and pickling is dictated by the surface finish required. Examples of this are EN standard finish '2R' which requires a bright annealing treatment and surface finish '2B' which requires annealing and pickling.

Bright annealing is generally conducted in an electrically heated or gas fired furnace with a protective inert atmosphere of nitrogen and/or hydrogen. Both batch annealing and continuous

annealing may be used. Degreasing of the steel surface is required to prevent surface discolouration.

Material with a '2B' surface finish is generally processed on continuous annealing and pickling lines. The furnace design and operation is generally similar to that for the annealing of hot band material described above. The steel is unwound and passed through one or more furnaces, which are usually gas fired. Annealing takes place in an oxygen rich atmosphere. This is necessary to ensure that the scale generated in the furnace is of a composition that is readily removable by the downstream chemical pickling processes.

### **Pickling**

Unlike the descaling of hot band material described above, mechanical descaling techniques cannot be employed to assist in the removal of this scale due to the surface damage which would result for the final cold rolled strip. Therefore only chemical pickling is applied. This is done in the same manner as described above for hot band pickling.

Scale of high alloy steel, due to the presence of oxides of alloying elements, cannot always be removed in just a single acid descaling step. Additional treatment or pre-treatment processes may be necessary. These may include scale removal by an initial electrolytic descaling process (using e.g. sodium sulfate) installed prior to the mixed acid section. Generally these facilities operate with neutral salts or acids as the electrolyte. It is appropriate to consider the electrolytic process as a pre-pickling system as satisfactory descaling cannot be achieved with this section alone. However the length of mixed acid section required (and hence the acid consumption and environmental impacts) is considerably reduced. Furthermore the combination of electrolytic and mixed acid can provide an improved surface finish. [EUROFER CR], [Com2 CR]

## **A.2.2.7 Tempering of Cold Rolled Strip**

### **A.2.2.7.1 Low Alloy and Alloy Steel**

After annealing the surface finish and mechanical properties of the steel are modified in line with the customer requirements. This is done by temper rolling which consists of subjecting the strip to a light rolling pass with a thickness reduction between 0.3 and 2 %. Before tempering the strip temperature must be less than 50 °C.

Temper rolling is carried out in the temper mill which comprises typically one or two four-high stands, although two-high or six-high stands are also possible. For tin plate production two four high stands is common. The rolls for these stands have an extremely precise surface finish in order to control the final roughness of the strip in line with the end use of the finished product. Tempering also improves strip flatness.

To avoid residues from the rolling process remaining on the strip cleaning agents, (a wet temper rolling agent), can be used during tempering. The rolls may also be brushed with mechanical polishing equipment and an associated extraction system. [EUROFER CR]

### **A.2.2.7.2 High Alloy Steel**

Similar to the process route for carbon steels temper rolling or skin pass rolling is completed in order to attain the desired surface finish on the steel. This cold rolling treatment, comprising a minimal reduction in gauge (up to 2 %) is generally performed dry without application of oil for cooling. The temper mill usually comprises a single two or four high stand with precision ground rolls.



### A.2.2.8 Finishing

Finishing comprises slitting into coils of different width strip and transversal shearing to obtain sheet. Additional steps such as straightening, sampling, oiling and marking are also completed. In general the techniques used are similar for both low alloy and high alloy steels, however oiling is not required for stainless steels.

The finishing process comprises the following operations:

- Dimensional control (width, thickness and length).
- Inspection for surface defects and their removal.
- Sampling to determine the mechanical and technological properties, the strip roughness structure and the content of residue of particles from roll wear and carbon on the strip surface (statistical sampling).
- Trimming the coils to exact width.
- Straightening the strips to optimum flatness.
- Oiling the strips with electrostatic oiling machines or with oiling machines equipped with sprays or rolls oiling machines (anticorrosive oils or prelubes).
- Marking the finished products with coil number, production date, etc.
- Welding of different smaller coils to bigger coils.

In the finishing shops the coil weights used for maximising productivity are cut into the coil weights ordered by the customers. Defective coil parts are eliminated or if necessary, the material is subjected to additional treatment for removal of the defects. This can include additional annealing, temper rolling or straightening. [EUROFER CR]

#### Strip grinding

Grinding of the steel surface may be used to generate a uniform surface quality as well as rectifying defects. The strip is usually decoiled on dedicated process lines, sprayed with oil and ground with belts of varying surface roughness. Mineral oil is generally used for this process and filtration circuits employed to separate the swarf generated during grinding. [EUROFER CR]

#### Packing

The material, now in its final form, is usually packed ready for despatch to the customer. The packaging is designed to ensure that no damage occurs either during storage or transport to the end user. Control measures also have to be taken to prevent damage from mechanical and climatic sources. In addition the lifting and transport equipment in the production plant should also be designed and operated to minimize damage to the steel. After finishing, packing of the individual items ordered by the customers is done. The packing materials used includes: steel bands, paper, plastic, wood, seaworthy packing, special packing. [EUROFER CR]

### A.2.2.9 Roll Shop

The activities generally consist of the dismantling of the chocks, the grinding of the rolls, the texturing of the work rolls and the reassembling of the rolls.

To satisfy the required strip tolerances and surface standards the rolls must be regularly reground. During this grinding operation the rolls are usually cooled and lubricated with a grinding emulsion. The spent emulsion can be recirculated and filtered, but partial replacement is required periodically. In addition, used oil and grinding sludge are produced which require disposal.

The principal roll texturing systems used include:

- SBT (Shot Blast Texturing): This is a mechanical application of the texture onto the roll using grit blasting.
- EDT (Electron Discharge Texturing): The work rolls are textured by spark generation in an oil bath.
- EBT (Electron Beam Texturing): In this system the roll is placed in a vacuum chamber and the texture is applied by means of an electron beam gun.
- Laser Tex (Laser Texturing): The roll is textured to predetermined roughness by Laser gun.
- Pretex (Premium Texturing): The roll is textured by a rough electrolytical chromium plating. The chromium plating process is fully enclosed and fitted with an exhaust gas system using a wet scrubber. The whole process operates without an effluent discharge, because of the evaporative losses [EUROFER CR].

### A.2.2.10 Water and Process Baths Management in Cold Rolling Mills

Water is used in cold rolling mills to clean the surface of rolling stock, for preparation of pickling and degreasing baths, for rinsing and for cooling. Pickling and related processes (rinsing, gas cleaning operations, acid regeneration) cause acidic waste water streams. In case that degreasing is part of the processing also alkaline waste water arises.

For cooling and lubrication water/oil emulsions are used in the rolling sections, which gives rise to oil and suspended solid loaded waste water streams. Generally, emulsion and degreasing solutions are recycled to the process in closed loops. Water used for indirect cooling is also operated in closed loop circuits. (Classifications and definitions for water circuits are in analogy to those used in hot rolling, refer to Chapter A.2.1.15)

#### A.2.2.10.1 Emulsion System

In cold rolling mills normally emulsion cycles, as shown in Figure A.2-33 are installed. To maintain these loops the circulated liquids have to be treated and conditioned by emulsion settling and cooling. Measures to maintain the quality of the emulsion and to extend the lifetime are described in Chapter 4.

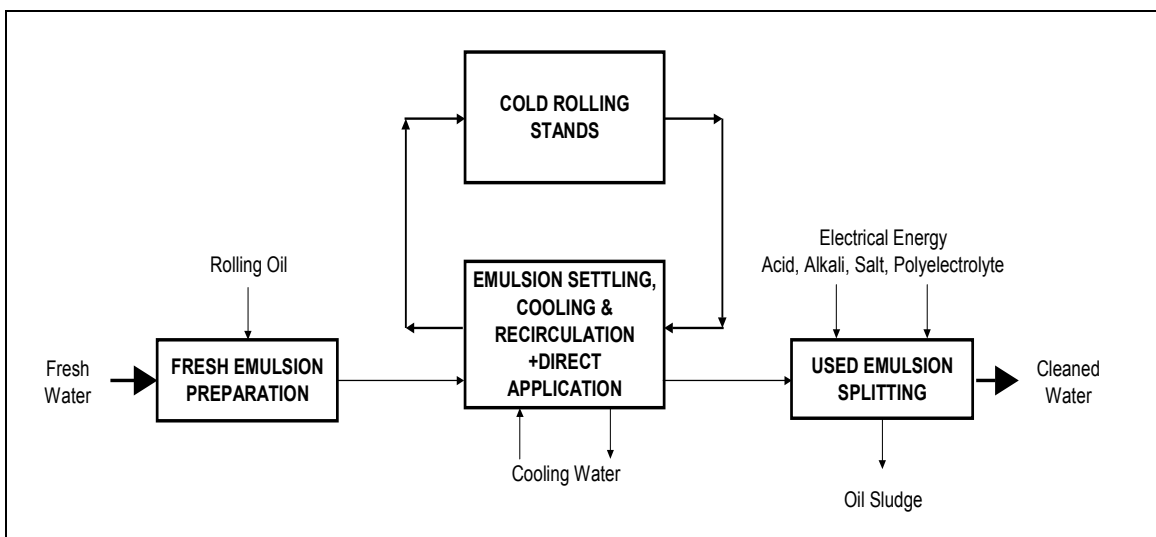
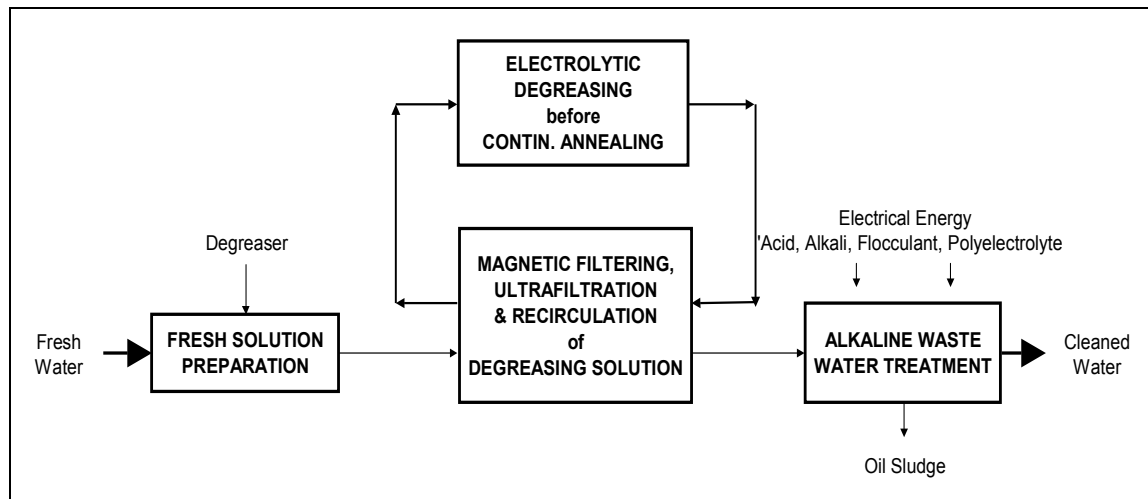


Figure A.2-33: General emulsion flow [EUROFER CR]

### A.2.2.10.2 Degreasing Solution System

In degreasing solutions systems (see Figure A.2-34) the re-circulation of the solution is enabled by removing oil and other contamination, e.g. by magnetic filtering or ultrafiltration. Cleaning measures are described in Chapter 4.



**Figure A.2-34: Degreasing solution flow (continuous annealing line) [EUROFER CR]**

### A.2.2.10.3 Cooling Water Systems

In cold rolling mills, cooling water is required to dissipate excessive heat from the rolling process (rolling energy) and from the annealing furnaces (heating energy). The rolling energy is mainly transferred via the emulsion and/or the emulsion cooler and partly via the lubricant and hydraulic cooler to the cooling water. The main cooling water consumers are:

- Emulsion cooling for tandem line.
- Skin pass mill stand installed downstream to batch annealing plant.
- Continuous annealing plant with skin pass mill stand.
- Cooling of transformers and motors.
- Oil lubrication facilities.

The thermally loaded cooling water is recooled with industrial water in plate heat exchangers, if adequate water supplies are available, or by evaporation in cooling towers. Recooling in heat exchangers offers the advantage that considerable amounts of chemicals for cooling water (such as corrosion inhibitors, hardness stabilisers, dispersants and biocides) can be saved and are not discharged into the sewage system. The cooling water circuits are treated with corrosion inhibitors, but discharge of a partial flow with a high salt content is not necessary with these closed circuits. For cooling tower circuits, in contrast, regular discharge of partial flows to a sewage system is required to counteract salt concentration resulting from evaporation. Moreover, the formation of water vapour (industrial snow), associated with cooling towers and sometimes a problem in some areas in Europe, is avoided.

In principle both the use of recooling and evaporative cooling towers are viable system for use and the choice of system will depend on location and other site specific issues. In some countries taxes are levied on abstraction and discharging water which can affect the choice of system used. [Com2 CR]

Figure A.2-35, Figure A.2-36 and Figure A.2-37 show examples of cooling water cycles.

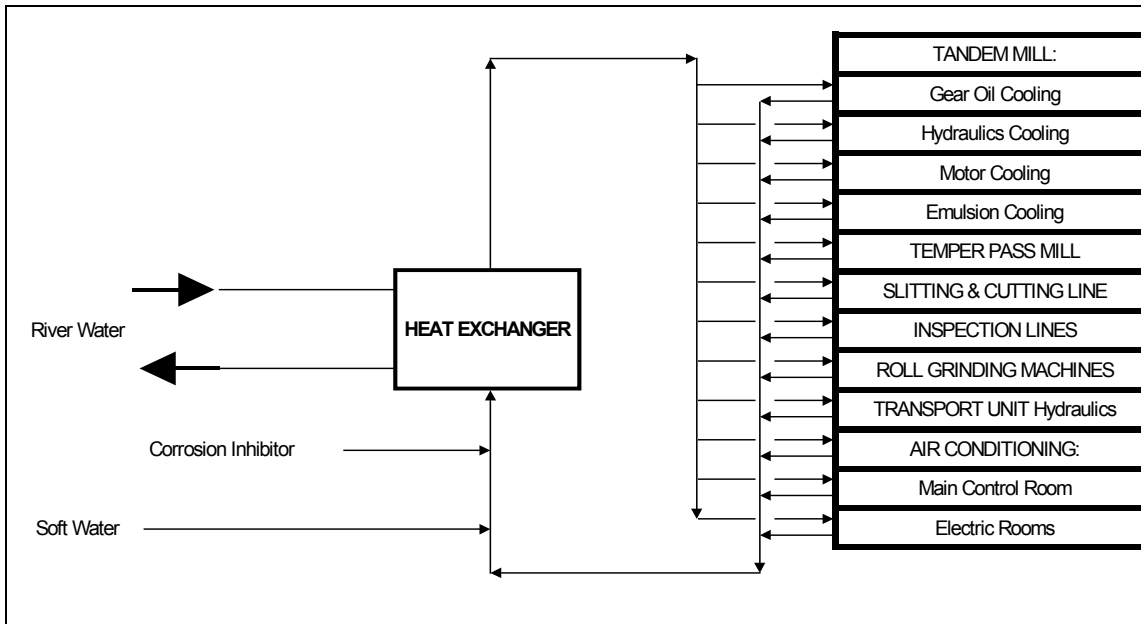


Figure A.2-35: Cooling water system for a cold mill [EUROFER CR]

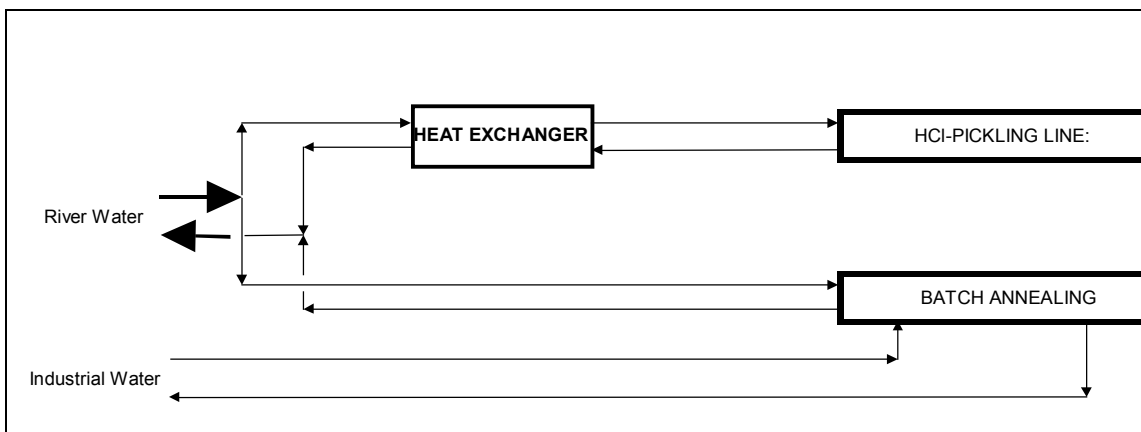


Figure A.2-36: Cooling water system for HCl-pickling and batch annealing [EUROFER CR]

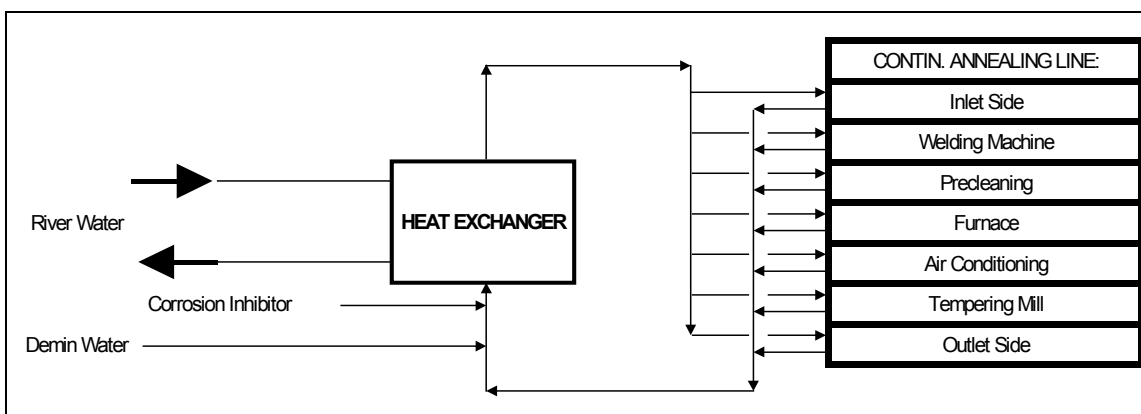


Figure A.2-37: Cooling water system for a continuous annealing line [EUROFER CR]

#### A.2.2.10.4 Waste Water Treatment

Waste water from cold rolling operations, which cannot be regenerated or used elsewhere in the production line, has to be treated prior to discharge.

Acidic waste water from rinsing or acid regeneration is usually treated by neutralisation with agents, such as calcium hydroxide or sodium hydroxide. The dissolved metal ions are precipitated as hydroxides and then separated by sedimentation techniques including clarification or filtration. Flocculants are sometimes used to assist the process. The sludge is de-watered, e.g. by filter presses, to reduce the final volume of sludge.

Where electrolytic chemical pre-pickling processes are used additional effluent treatment steps may be required. Typically these can incorporate chromium (VI) reduction processes using sodium bisulphite or iron (II) compounds.

Alkaline waste water streams may be neutralised using HCl, filtered and then discharged.

Spent coolants/lubricants (emulsions) are treated by emulsion breaking, either done thermal, chemical, mechanical or physical, followed by a separation of water and oily phase

#### A.2.2.11 Waste and By-product Management in Cold Rolling Mills

Cold rolling gives rise to solid residues, such as scrap (cleaning rags, cleaning paper), sludges from the waste water treatment plants, remainder of packing material and dust.

**Scrap** is recycled in the works for steel production. The **oil-containing sludges** from the waste water treatment plants may be used in blast furnaces.

**Acid regeneration sludges** can be recycled in steel plants (EAF and blast furnace) or given to external recycling firms for the production of iron oxides.

The **iron sulphate-heptahydrate** from the sulphuric acid regeneration plant can be used:

- For the production of complex iron-cyan salts.
- As flocculation agents in waste water treatment plants.
- For the production of gas adsorption mass.
- As chemical amelioration agent.
- For the production of iron oxide pigments, and
- For the production of sulphuric acid [Com D].

The **iron oxide** from the hydrochloride acid regeneration can be used in several industries as high quality input, e.g.:

- As input for the production of ferromagnetic materials.
- As input for the production of iron powder, or
- As input for the production of construction material, pigments, glass and ceramics [Com D].

**Sludges from oil recovery** are externally used, either by incineration or for oil recuperation in specially dedicated plants.

Only a small part of the **sludges from waste water treatment** is internally recycled, the vast majority of is landfilled.

**Oily wastes** (oil, emulsion, greases) arising are internally or externally used by incineration.

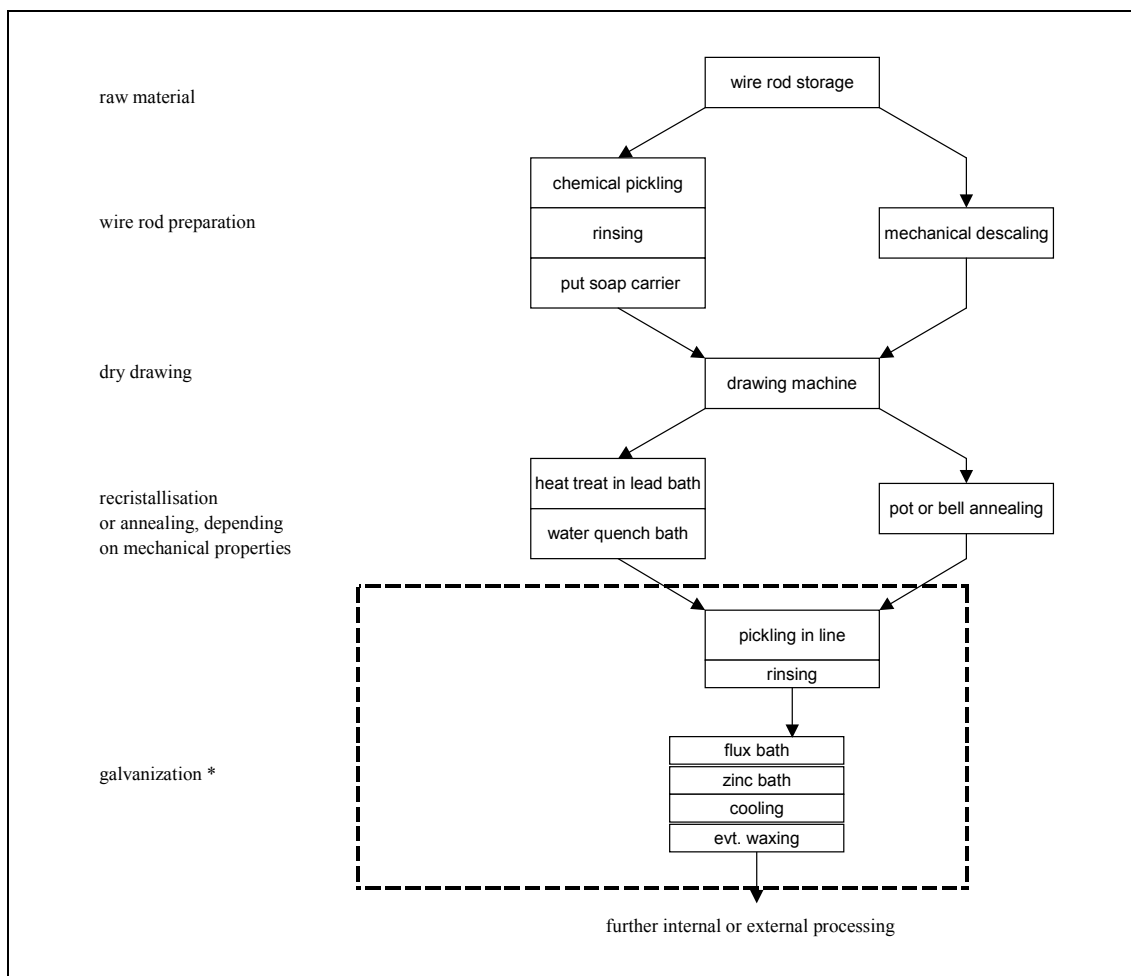
## A.2.3 WIRE PLANTS

### A.2.3.1 Wire Drawing Process Overview

Wire drawing is a process in which wire rods/wires are reduced in size by drawing them through cone-shaped openings of a smaller cross section, so called dies. The input usually is wire rod of diameters ranging from 5.5 to 16 mm obtained from hot rolling mills in form of coils. A typical wire drawing process line comprises the following steps:

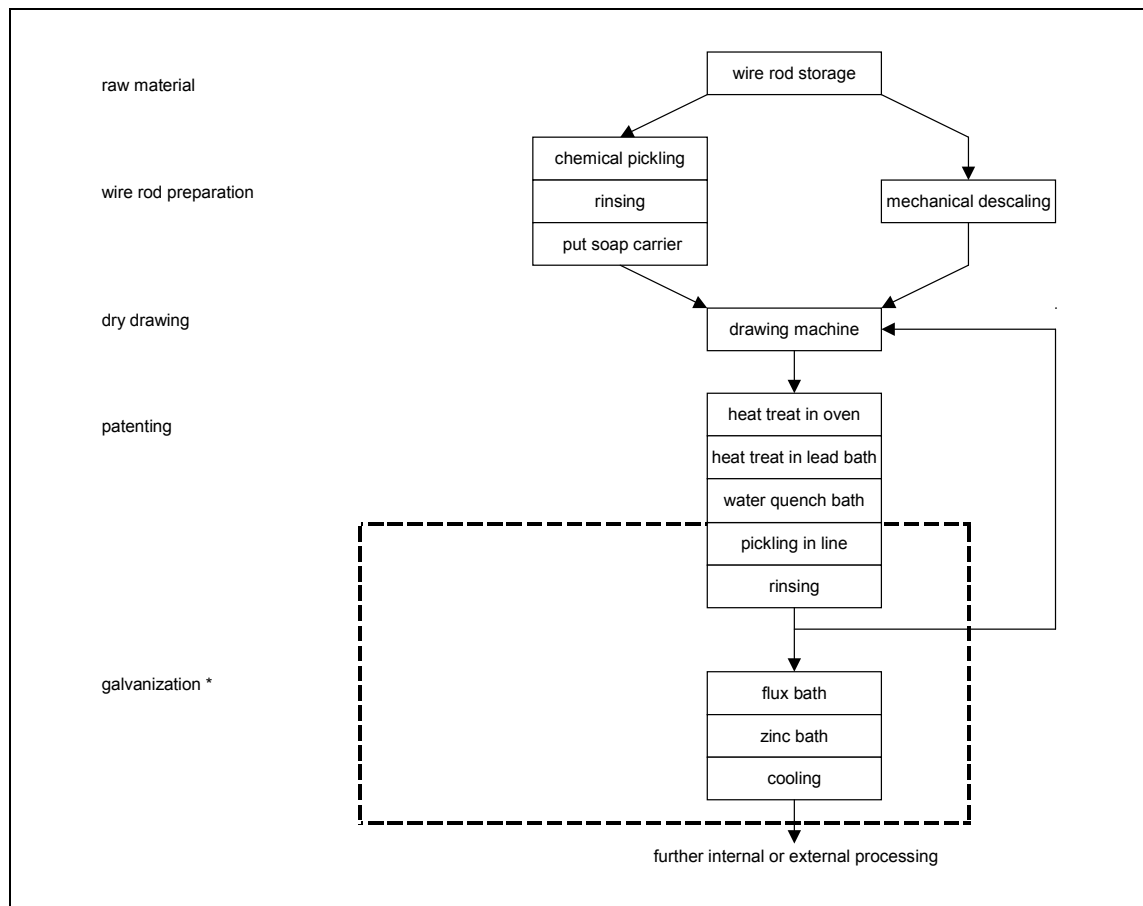
- Pre-treatment of the wire rod (mechanical descaling, pickling).
- Dry or wet drawing (usually several drafts with decreasing die sizes).
- Heat treatment (continuous-/discontinuous annealing, patenting, oil hardening).
- Finishing.

Wire is manufactured in different grades of steel: low carbon steel with carbon content of up to 0.25 %, high carbon steel with a carbon content of over 0.25 %, stainless and other alloy steel. Non-alloy steel wire can be uncoated or coated with zinc, copper, brass, tin, nickel, chrome, plastic or varnish. Wire is sent in coil form to further processing, like coating and manufacturing of finished products (e.g. cable, mesh, barbed wire, wire fencing, grill, springs, nails). [Bekaert94], [Pan97]



\* galvanization is dealt with in Part B of this BREF

Figure A.2-38: Production of low carbon galvanized wire [Bekaert98]



\* galvanization is dealt with in Part B of this BREF

**Figure A.2-39: Production of high carbon galvanized wire [Bekaert98]**

Because of the huge variety of wire products, many different processing schemes exist, dictated by wire diameter and required mechanical and other quality specifications. The process schemes shown in Figure A.2-38 and Figure A.2-39 cover the majority of galvanized wire that is produced in Europe (and worldwide). A fraction is sold as such; a fraction is processed further by wet drawing or by processes that fall out of the scope of the BREF, such as welding, electroplating, weaving, cabling, bunching, painting, plastic coating, cutting to length, etc.

### A.2.3.2 Wire Rod Preparation

Air-cooling after rolling produces an iron oxide-layer (scale) on the wire rod surface. This layer is very hard, brittle and not deformable and must therefore be removed before any further processing can take place. In most cases, this is done by the wire industry. For stainless steel however, this is typically done by the steel mill.

Two techniques for descaling wire rods are applied: mechanical descaling and chemical pickling. Some categories of end products can only be produced from mechanically descaled wire at a reduced drawing speed (needing more drawing machine capacity, meaning higher investment costs). The decision on the descaling technique is therefore done by each individual plant, based on product qualities and economical considerations.

### A.2.3.2.1 Mechanical Descaling of Wire Rod

In the most common mechanical descaling method applied: wire bending, the wire is bent to cause the brittle scale to peel off. Other descaling techniques, like sanding, brushing or shot blasting, are used as a finishing step after wire bending to remove loose scale or are used as stand-alone techniques.

Batch shot blasting is a common technique for mechanical descaling of heavy diameter wire rod (e.g. used for cold heading applications). However mechanical descaling is generally done in a continuous way.

Depending on the finish of the wire rod and the quality requirements of the product, descaling by reverse bending is completed or possibly replaced by an abrasive method such as sanding, brushing, shot blasting or stream descaling. By combining reverse bending with one of these auxiliary methods, complete removal of the oxide layer can be achieved, reaching a similar surface cleanliness as with chemical pickling. [Com2 BG]

Compared to chemical pickling of wire rod, mechanical descaling has the advantage that one production step is eliminated as the descaling unit is normally coupled directly to the drawing machine. On the other hand, it is difficult to obtain the same level of drawability with mechanical descaling. [CET-BAT]

### A.2.3.2.2 Chemical Descaling (Pickling) of Wire Rod

In chemical descaling the mill scale is removed by dissolving in acid. Acids used are:

- Sulphuric or hydrochloric acid for low carbon wire.
- Hydrochloric acid for high carbon wire.

Pickling is mostly done in a batch process. Each roll of wire rod is immersed in the acid bath. The acid slowly dissolves the oxide layer by transforming it into iron chlorides or sulphates. When pickling in HCl an H<sub>2</sub>-inhibitor is used to suppress the reaction:  $2 \text{HCl} + \text{Fe} \rightarrow \text{FeCl}_2 + \text{H}_2$  and reduce the unwanted loss of iron.

After pickling the wire rod coils are rinsed in water. This is usually done in cascade rinsing (e.g. rinsing 3 times) to yield maximum rinsing efficiency and minimum water consumption. [Bekaert94], [Bekaert98]

### A.2.3.2.3 Application of Soap (Lubricant) Carrier

In some cases, soap carrier is applied to enhance the adhesion of the lubricant to the wire. A wide range of soap carriers is available. Selection is made on economical basis and on required properties in downstream processes. Traditional soap carriers include lime, borax and Zn-phosphate. Modern soap carriers are typically mixtures of soluble salts, e.g. sodium and potassium sulphate, chloride, borax, phosphate or silicate. They are adapted to a particular soap and a particular drawing situation.

Soap carrier is applied before drawing by dipping the wire in a watery soap carrier solution. This can be done in a batch process, usually associated with chemical descaling, or continuous in association with mechanical descaling.



### **A.2.3.3 Drawing**

#### **A.2.3.3.1 Dry Drawing of Wire**

Dry drawing is typically used to draw wire rod ( $> 5.5$  mm) to a product diameter of 1 - 2 mm and some times even lower. The diameter of wire is reduced by passing it through a series of dies with diminishing diameter. Before entering the dies, the wire is passed through a dry lubricant. In most cases, soap-based lubricants are used with the soap formulation depending on choice of fats from which the soap is produced, choice of fillers or choice of additives. In exceptional cases (e.g. special steels, wire with special metal coatings) other lubricants like pastes or oils can be used.

The drawing operation heats both (wire and drawing die) through friction of the wire. Cooling is done indirectly, by cooling the capstans in contact with the wire with water.

#### **Wet Drawing of Wire**

Wet drawing is typically used to draw wire with an intermediate product diameter of 1 - 2 mm to final diameter. The wire is also passed through a series of dies with diminishing diameter, but wire, dies and capstans are immersed in a lubricant liquid that provides lubrication and cooling. Typically, soap or oil emulsions (for some applications plain oil) are used. The heat resulting from drawing operation is taken up by the lubricant, which is cooled indirectly with water.

### **A.2.3.4 Heat Treatment of Wire**

Heat treatment of wire has different goals. Therefore different types of heat treatment are available depending on the type of steel (low carbon / high carbon / stainless) and the final use (desired ductility and strength). Heat treatment also thermally removes soap and lubricant residues.

A considerable percentage of the output of the wire industry does not need any heat-treatment. The heavy deformation of the metal crystal structure caused by drawing is mostly a positive property, as it increases the hardness and the strength of the wire in the axial direction.

#### **A.2.3.4.1 Batch Annealing of Low Carbon Steel Wire**

Drawing profoundly deforms the shape of the metal crystals of the wire. Annealing is one of the different methods to re-obtain a suited crystal shape. Batch annealing, typically used for low carbon steel wire to obtain a very soft and ductile end product, is done in bell or pot furnaces.

Batch annealing is done by putting coils of drawn wire in chambers (called "pots" or "bells"), filled with a protective gas. The protective gas is either neutral or reducing. The most common protective gasses are nitrogen, hydrogen, nitrogen/hydrogen mixtures and partly oxidized natural gas (or similar fuel). The chambers are heated from outside, typically by gas or fuel. The warming up from room to peak temperature (roughly 700 °C) takes several hours; also cooling down again takes several hours. In order to keep an over-pressure in the "pots" or "bells", a fraction of the protective gas is continuously purged.

In some cases, the wire is oiled immediately after annealing.

#### **A.2.3.4.2 Continuous (In-Line) Annealing of Low Carbon Steel Wire**

Continuous annealing or strand-annealing has a similar goal as batch annealing: restore a suited crystal texture to the steel in the wire after drawing. But the desired crystal shape and metal properties are different from those that are desired when batch-annealing is applied. Continuous annealing is a typical heat treatment method for low carbon products.

Strand-annealing is a fast continuous process. The wire is heated up to the recrystallisation temperature (500 - 700 °C), is kept at this temperature for a few seconds, and is cooled down again by quenching in a water bath.

A typical line is equipped for 15 - 50 wires and is characterised by a particular  $v \times d$  (wire speed  $\times$  wire diameter). This means that wires of different diameters can be processed together at the same line, but the higher the diameter of a wire, the lower its speed. Modern lines have a  $v \times d$  of 100 - 200 m/min  $\times$  mm (in other words, a 1 mm wire is processed at speeds of 100 - 200 m/min). For specialities, lines with a few or only one wire and/or operating at a lower  $v \times d$ , are used. Strand-annealing is often combined in one production line with other unit processes e.g. with hot-dip coating.

Commonly the wire is heated by passing through a molten lead bath. A fast heat-up is essential for strand-annealing. Due to a very high heat transfer coefficient of lead (3000 W/m<sup>2</sup>.K) equilibrium between wire and lead-bath temperature is reached after a few seconds. Other methods such as an oven or inductive heating are alternatives, only in some niches e.g. one-wire lines, lines operating at low speed or lines designed to run with only one diameter at a time.

After the heat-treatment, the wire is generally quenched in water. This can be followed by in-line pickling with warm or cold HCl to remove oxides which also partly dissolves the potentially dragged lead. Other acids or electrolytically assisted pickling can be used as well. Pickling is followed by a rinsing cascade. At some plants, pickling is done as the first operation of the next process step. Often pickling is omitted after heat treatment under protective atmosphere.

#### **A.2.3.4.3 Continuous (In-Line) Annealing of Stainless Steel Wire**

Stainless and high alloyed steel wire is continuously annealed to obtain suited metal crystal properties for (further) drawing operations. For stainless steel, the heat-treatment is done under a protective gas atmosphere. If no protective atmosphere would be used, the stainless steel wire would be oxidized; removal of these oxides would require pickling with special acids such as HNO<sub>3</sub>, HNO<sub>3</sub>/HF,... (cfr. production of stainless steel strip). The temperature profile used, varies with the type -content of Ni, Cr or other alloying elements- of stainless steel that is processed (700 – 1100 °C).

The wire is passed through tubes or a muffle, under a protective gas. The purge of protective gas is similar to what is described for batch-annealing. The first part of the tubes or muffle is placed in an oven (indirect heating of the wire); the second part is cooled indirectly, e.g. by cooling with water. The heating can be done by electricity (resistance heating, inductive heating) or by combustion. [CET-BAT]

#### **A.2.3.4.4 Patenting**

Patenting is a heat-treatment method typically used for high-carbon and alloyed steel products to create a special crystal structure, which allows easy further deformation. In contrast to

annealing where iron and iron/carbon compounds tend to be separated, patenting yields a structure where the carbon is homogeneously distributed in the iron.

Patenting is done by heating the wire to 850 - 1000 °C, then cooling fast to 450 - 600 °C and keeping the wire for a while at this temperature, and finally quenching in water. Patenting is usually done continuously and often combined with other unit processes, e.g. hot dip coating.

Heating to 850 - 1000 °C is done in an oven where the wire is in contact with the combustion gasses. Intermediate cooling and keeping at 450 - 600 °C is done in a lead bath. For small lines designed for specialities (e.g. fine diameters or mono-wire lines) other heating methods such as heating under protective gas atmosphere and electric ovens can be used. For the patenting of thick diameters, sometimes a molten salt bath is used.

In the fuel fired oven, a slight substoichiometric mixture is used in the burners. In this way, all O<sub>2</sub> is excluded from the oven atmosphere, in order to minimize the formation of iron oxides at the wire surface. Excessive formation of iron oxide leads to high losses of wire material and to excessive consumption of pickling acid, and leads to excessive dragout of lead.

Final cooling is done by quenching in a water bath followed by the same procedure as in continuous annealing.

#### **A.2.3.4.5 Oil Hardening and Tempering (Oil Tempering)**

Oil hardening and tempering creates a special crystal structure in the steel with a high percentage of martensite, resulting in increased hardness and wear resistance combined with good toughness. First, the wire is heated to 850 – 1000 °C, followed by rapid cooling.

Heating is typically done under protective atmosphere using electricity (radiation, inductive heating) or combustion. The purge of protective gas is similar to what is described for batch-annealing. Quenching is traditionally done in oil, but also other quenching media can be used such as water or water with additions. (Note: although it is not unusual to quench in other media than oil, the normal way of referring to this process step is still oil-hardening).

Oil-hardening is always followed by a tempering or stress-relieving step, in order to remove the stresses caused by the extremely fast cooling. This is done by heating the wire again to 300 - 500 °C. Typically a normal oven is used, with electrical heating or direct heating with a typical combustion gas, but also inductive heating can be used.

#### **A.2.3.4.6 Stress-relieving**

The goal of stress-relieving is to remove internal stresses in the wire caused by a previous processing steps, without changing the shape and structure of the steel crystal. The internal stresses can be caused by deformation (mechanical stresses) or by fast cooling (thermal stresses). Stress-relieving as a stand-alone heat-treatment step is a typical process step for the production of PC-strand (wire for prestressed concrete).

Stress-relieving can be done at various temperatures (200 - 500 °C), dependent on the desired characteristics of the final product. Typically a normal oven is used, with electrical heating or direct heating with a typical combustion gas, but also inductive heating can be used. After stress-relieving, the wire is cooled relatively slowly in air or water. [CET-BAT]

### **A.2.3.5 In-line Pickling**

In-line pickling is a typical operation after heat-treatment and/or before hot-dip coating of wire. It is used to clean the wire and to remove metal oxides. The wire is passed continuously through one or more acid baths. The most common acid is HCl, but other acids can be used. The pickling takes place in a very short time (a few seconds), therefore the acid is often heated and/or used in concentrated form. After pickling the wire is rinsed in water.

Finishing of wire includes the application of metallic or non-metallic coatings. Galvanizing of wire is covered in Part B of this BREF. In-line pickling will also be dealt with in detail in Part B of the BREF.

## A.3 PRESENT CONSUMPTION AND EMISSION LEVELS FOR HOT AND COLD FORMING

### A.3.1 Hot Rolling Mills

#### A.3.1.1 Mass Stream Overview

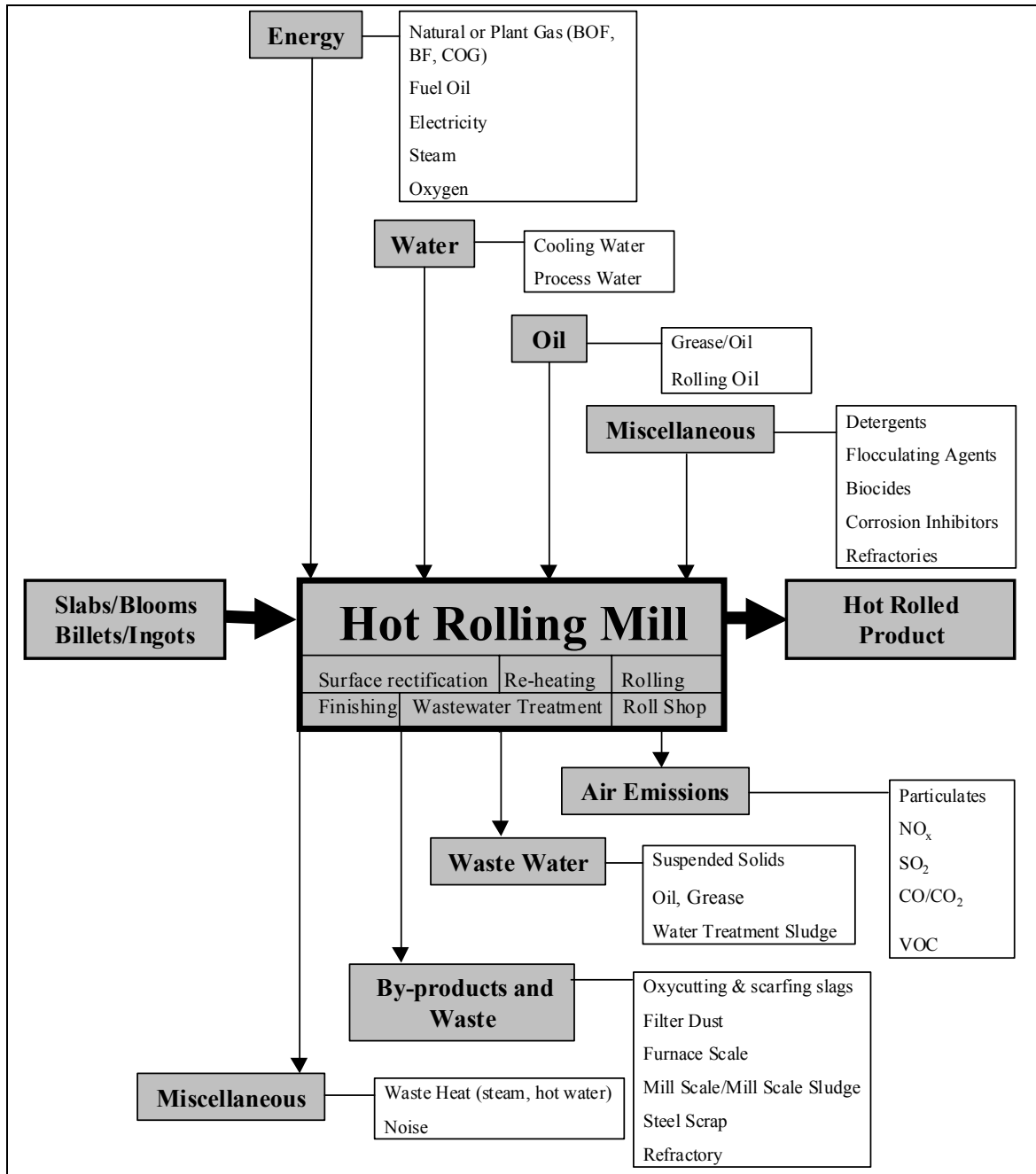


Figure A.3-1: Input/output overview for hot rolling mills

The subsequent chapters present specific input and consumption data, as well as specific output and emission data for individual operational steps associated with the manufacture of hot rolled products.

### A.3.1.2 Surface Rectification and Conditioning of Input

The consumption of fuel (natural gas, liquefied petroleum or plant gases) and oxygen for scarfing depends on the dimensions of the rolling stock. Variations of 20 % in consumption and emissions are possible when the e.g. thickness of a slab is increased from 200 mm to 250 mm. Typical consumption for automatic scarfing of billets was reported as 5 m<sup>3</sup> oxygen/t and 25 MJ (propane)/t steel processed. No data available on water consumption for scarfing or on the amount of waste water, which is generally discharged to the rolling mill or continuous casting water treatment plant and is reused in the mill water system. [EUROFER HR]

During scarfing wet, corrosive fumes with high proportions of sub-micron particles (size range from 0.5 to 250 microns) are generated. Samples of this fume, taken at the electrostatic precipitator inlet, showed concentrations of 60 mg /m<sup>3</sup> for CO, 35 mg /m<sup>3</sup> for NOx and a range of 230 - 3000 mg /m<sup>3</sup> for dust. [HMIP]

<b>Scarfig:</b>		
<b>Input / Consumption Level</b>		
<b>Energy</b>		n.a.
<b>Oxygen</b>		n.a.
<b>Water</b>		n.a.
<b>Output / Emission Level</b>		
	<b>Specific Emission</b>	<b>Concentration</b>
<b>Dust</b> <sup>1</sup>	1 - 80 <sup>2</sup> g/t	5 - 115 <sup>3</sup> mg/m <sup>3</sup>
<b>Filter dust</b>	1.5 - 3.25 <sup>2</sup> kg/t	
	<b>NOx</b> <sup>7</sup>	n.a.
	<b>CO</b> <sup>7</sup>	n.a.
<b>Scale</b>	n.a.	approx. 35 mg/m <sup>3</sup> approx. 60 mg/m <sup>3</sup>
<b>Waste water</b>	no discharge, reused in mill water system	
<b>Grinding:</b>		
<b>Input / Consumption Level</b>		
<b>Energy</b>	no representative data available	
<b>Water</b>	no representative data available	
<b>Output / Emission Level</b>		
	<b>Specific Emission</b>	<b>Concentration</b>
<b>Dust:</b> <sup>4</sup>		
mild steel		< 30 - 100 <sup>5,6</sup> mg/m <sup>3</sup>
stainless steel	n.a.	< 50 <sup>5</sup> mg/m <sup>3</sup>
<b>Swarf</b>	n.a.	
<b>Noise</b>	n.a.	
<b>Scarfig, grinding and shot blasting:</b>		
Scale (dry material)	< 0.2 - 35 <sup>2</sup> kg/t	
<sup>1</sup> Dust emitted in cleaned waste gas <sup>2</sup> Source of data: [EC Study] <sup>3</sup> Resulting range from the sources [SIDMAR], [CITEPA] and [EUROFER HR] <sup>4</sup> [CITEPA] reports 1 - 10 mg/m <sup>3</sup> without distinction of mild and stainless steel <sup>5</sup> Source of data [EUROFER HR] <sup>6</sup> Examples, abatement: fabric filter, V= 2.5 and 7 Nm <sup>3</sup> /s <sup>7</sup> [Com HR]		

Table A.3-1: Consumption and emission levels for surface preparation

The dust generated by scarfing contains mainly iron oxides with some trace alloying elements present in steel. Dust emission factors vary significantly, depending on whether scarfing is done automatic (30 - 60 g/t) or manual (3 g/t). [CITEPA]

Samples of the composition of emitted dust from scarfing show the following metal contents: Cr 0.5 - 10 g/kg, Ni 1 - 5 g/kg, Mn 5 - 20 g/kg, Pb 1.7 - 2.3 g/kg, Cu 7.5 - 8.6 g/kg. [EC Study]

For dust collected from grinding and shot blasting of stainless steel following contents were found: Cr 3 - 100 g/kg, Ni 6 - 20 g/kg, Mn 4 - 10 g/kg. [EC Study]

### A.3.1.3 Reheating and Heat Treatment Furnaces

#### Energy consumption

Integrated steel plants try to valorise as much as possible the gases arising within the works for internal use. Hence blast furnace gas, coke oven gas, BOF gas, natural gas and a lot of different combinations of these gases (so-called mixed gases) are used in continuous furnaces. The energy consumption of the furnaces depends on several parameters such as:

- The furnace design (pusher-type, walking beam, etc.).
- Throughput and shift patterns (operating time) [Com UK].
- The designed length of the recuperation zone in the furnace.
- The burner design.
- The use of recuperators or of a regenerating system.
- The production capacity of the furnace.
- The heating zone arrangement.
- The charging temperature of the stock.
- The heating and discharging temperature.
- The accuracy of the thermal regulation, and.
- The degree of insulation of the furnace [EUROFER HR].

Figure A.3-2 shows the energy balance of a typical reheating furnace in form of a sankey diagram, only half of the energy input is heat to reheat the steel.

#### Dust (particulates)

Because of the nature of the fuel used (BFG previously dedusted, NG no dust) dust emissions are low. Some data reported show an average of 13 g dust/ tonne rolled steel and a median of 8 g/t. The highest emission values correspond to the use of fuel oil. [EUROFER HR], [EC Study]

#### NO<sub>x</sub>

The NO<sub>x</sub> emission level depends mostly on the type of the fuel and on the burner type and design, e.g. ceiling burners emit less NO<sub>x</sub> than front or lateral burners. The use of recuperators or of a regenerative system increases the thermal efficiency of the furnace, but can lead also to a higher NO<sub>x</sub> concentration (up to 3500 mg/Nm<sup>3</sup>). In some countries a higher NO<sub>x</sub> level is allowed for higher air preheat temperatures. In **conventional burners**, high flame temperatures result in high NO<sub>x</sub> emission levels. Typical value for the NO<sub>x</sub> level is 500 mg/Nm<sup>3</sup> (natural gas, 3 % O<sub>2</sub>, combustion air at ambient temperature). The preheating of the combustion air (with recuperative or regenerative systems) can increase the NO<sub>x</sub> level exponentially. [EUROFER HR]

#### SO<sub>2</sub>

The SO<sub>2</sub> emission level depends on the S-content in the available fuel. Reported SO<sub>2</sub> emissions in dependence on fuel type show a difference in the SO<sub>2</sub> emission levels between natural gas, works arising gas and fuel oil. Average values are 9.7 g SO<sub>2</sub>/t for natural gas, 452 g SO<sub>2</sub>/t for

plant gas (mixed coke oven and blast furnace gas) and 803 g SO<sub>2</sub>/t for fuel oil. [EUROFER HR], [EC Study]

**Scale**

The amount of scale generated in the reheating furnaces depends on discharge temperature, material, combustion air regulation, type of fuel, furnace type and throughput time. A clear differentiation between furnace- and mill scale is difficult as the reheated material is descaled in the mill area and both types of scale are collected together. The typical range for furnace scale is 0.07 to 15 kg/t. [EUROFER HR], [Com I], [Com2 HR]

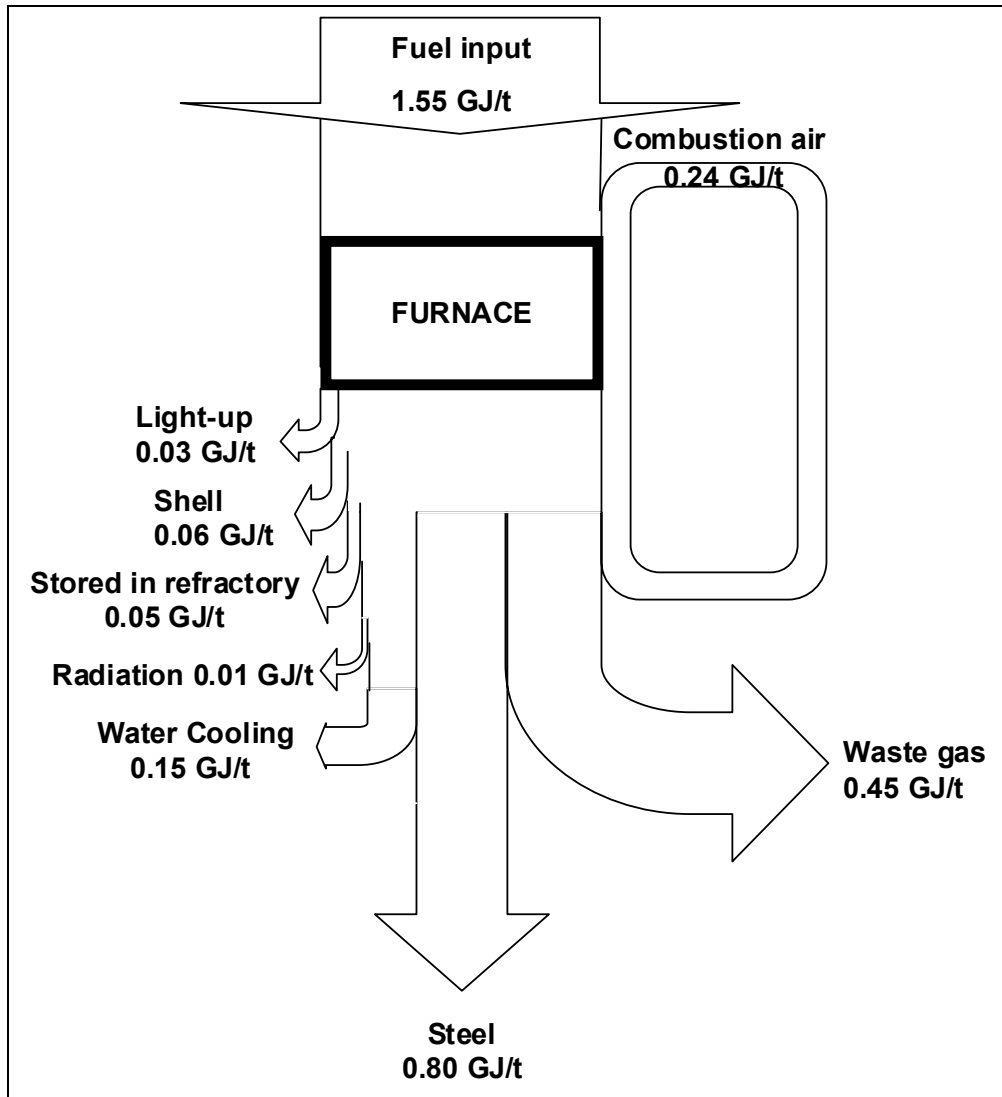


Figure A.3-2: Sankey diagram for a typical reheat furnace as reported in [StTimes 6/93]



Input / Consumption Level		
<b>Energy:</b>	1.1 - 2.2 <sup>6,10</sup> GJ/t	
<b>Cooling water</b> (for components of the re-heating furnace)	closed loop recycled completely	
Output / Emission Level		
	Specific Emission	Concentration
<b>Dust</b> <sup>1</sup>	1 - 10 <sup>6,8</sup> g/t	4 - 20 <sup>6</sup> mg/Nm <sup>3</sup>
<b>NOx</b> <sup>2,3</sup>	80 - 360 <sup>6</sup> g/t	200 - 700 <sup>6</sup> mg/Nm <sup>3</sup>
Conventional burners	2 - 600 <sup>4</sup> g/t	250 <sup>11</sup> - 900 <sup>5</sup> mg/Nm <sup>3</sup>
Low-NOx burner	150 - 500 <sup>4</sup> g/t	
Regenerative burner	1000 - 4000 <sup>4</sup> g/t	
<b>SO<sub>2</sub></b> <sup>3</sup>	0.3 - 600 <sup>6,9</sup> g/t	0.6 - 1300 <sup>6</sup> mg/Nm <sup>3</sup> 400 - 800 <sup>5</sup> mg/Nm <sup>3</sup>
<b>CO</b>	5 - 850 <sup>5,7</sup> g/t	100 - 170 <sup>5</sup> mg/Nm <sup>3</sup>
<b>Hydrocarbon</b> ( for BFG + NG firing)	0 - 5 <sup>5,7</sup> g/t	
<b>Furnace scale</b>		
Reversing, 4-high-Mills	0.5 - 18 <sup>4</sup> kg/t	
Hot Strip Mills	0.1 - 11 <sup>4</sup> kg/t	
Bloom/Billet/ Heavy Section Mills	0.5 - 47 <sup>4</sup> kg/t	
Light/Medium Bar and Section Mills	1 - 30 <sup>4</sup> kg/t	
Wire Rod Mills	0.3 - 20 <sup>4</sup> kg/t	
<b>Waste refractory</b>		
<sup>1</sup> [CITEPA] reports 200 - 1400 g of dust/t for continuous and 100 g/t for soaking pits with fuel oil firing, cautionary note: may not be representative. <sup>2</sup> [EC Study] reports an average of 383 g/t for low-NOx burners, 1690 g/t for regenerative burners and 228 g/t for conventional burners. <sup>3</sup> [CITEPA] reports 5 - 10 g/t for a mixture of blast furnace gas and natural gas, cautionary note: may not be representative. <sup>4</sup> Source of data [EC Study] <sup>5</sup> Reference [CITEPA] <sup>6</sup> Source of data [EUROFER HR] <sup>7</sup> Cautionary note: may not be representative <sup>8</sup> [DFIU98] reports 0.2 - 30 g/t <sup>9</sup> [DFIU98] reports 0.02 - 900 g/t <sup>10</sup> [ETSU-G76] reports typical energy consumption 2.0 – 3.0 GJ/t, scattering from 0.7 – 6.5 GJ/t <sup>11</sup> [Input-HR-1] <sup>12</sup> [Vercaemst 30.3] reported 2.2 – 63 mg/Nm <sup>3</sup>		

Table A.3-2: Consumption and emission levels for reheating/heat treatment furnaces

### A.3.1.4 Descaling

#### Waste

Mill scale from descaling operations, after the reheating furnace and in-between rolling passes, consists mainly of iron oxides, like FeO and Fe<sub>3</sub>O<sub>4</sub>. The exact composition varies, depending on the steel grade rolled and the rolling process, but the iron content is usually about 70 % (on an

oil and moisture free basis). Chemical analysis of mill scales show an average hydrocarbon content of 4.6 % with a scattering range of 0.5 - 8.7 %. High hydrocarbon content may limit recycling. [EC Study] Reported compositions of mill scale sludge show ranges of 25 – 65 % for solids, 30 – 60 % water and 2 – 15 % for oil. [STuE-114-1]

Due to the use of lubrication oil and grease during rolling, mill scale is contaminated. Oil contents depend on process operation, technical equipment and, especially, on the quality of maintenance. Another factor influencing the oil content of mill scale is particle size. The very fine particle portion of mill scale (referred to as mill scale sludge) consists of particles smaller than 63 µm, which tend to adsorb oil. [DFIU98]

The typical range of scale generated is reported as 12.7 - 16 kg/t for oil-free scale and 1.9 - 3.5 kg/t for oily scale. [EUROFER HR]

### Waste water

The process water used for descaling directly after the furnace is usually oil-free. The process water used for descaling within the hot rolling section mostly contains oil due to losses and due to the contact with the rolling equipment. The two waste water streams are usually mixed, resulting in one oil containing, scale loaded waste water stream. The coarse share of the scale load can be removed in settling tanks and, due to relatively low oil contents, be recycled to the metallurgical process.

Input / Consumption Level		
<b>Water:</b>		
Cogging train	n.a. m <sup>3</sup> /t	0.1 - 0.12 <sup>1</sup> m <sup>3</sup> /s
before finishing train	n.a. m <sup>3</sup> /t	0.05 - 0.06 <sup>1</sup> m <sup>3</sup> /s
after finishing train	n.a. m <sup>3</sup> /t	0.03 - 0.04 <sup>1</sup> m <sup>3</sup> /s
<b>Energy</b>	n.a.	
Output / Emission Level		
	Specific Emission	Concentration
<b>Waste water</b>	n.a. m <sup>3</sup> /t	
Containing scale and oil	n.a.	
<b>Oil free scale<sup>3</sup>:</b>		
Reversing, 4-high-Mills	1.6 - 23 <sup>2</sup> kg/t	
Hot Strip Mills	10 - 20 <sup>2</sup> kg/t	
Blooming/Billet/Heavy Profile Mills	9 - 38 <sup>2</sup> kg/t	
Light/Medium Bar and Section Mills	3 - 60 <sup>2</sup> kg/t	
Wire Rod Mills	5 - 20 <sup>2</sup> kg/t	
<b>Oily scale<sup>3</sup>:</b>		
Reversing, 4-high-Mills	1 - 36 <sup>2</sup> kg/t	
Hot Strip Mills	2.7 - 30 <sup>2</sup> kg/t	
Blooming/Billet Mills	0.4 - 28 <sup>2</sup> kg/t	
Light/Medium Bar and Section Mills	0.5 - 20 <sup>2</sup> kg/t	
Wire Rod Mills	0 - 20 <sup>2</sup> kg/t	
<sup>1</sup> Source [DFIU98]		
<sup>2</sup> Source [EC Study]		
<sup>3</sup> Austria reported: Coarse scale 20 – 30 kg/t for flat products, 5 – 10 kg/t for long products, scale sludge (fine scale) from finishing group 3 – 15 kg/t [Com A]		

**Table A.3-3: Consumption and emission levels for descaling**

### A.3.1.5 Hot Rolling

The **energy** demand for the motor-driven rolls depends on the degree of deformation, temperature of the work piece and material hardness. Energy is used in form of electricity.

**Water consumption** and water discharge depend on how the water flow is designed (water management). Water discharge close to 0 m<sup>3</sup>/t can be achieved by closed circuits. Semi-closed circuits have discharge rates of typically up to 11 m<sup>3</sup>/t maximum, whereas open systems (once-through) will lead typically to 11 - 22 m<sup>3</sup>/t.

**Emissions to air** are dust, originating from the mill stands and for strip products from coil handling lines. Fugitive oil emissions originate from the mill stands (work roll lubrication). The quantity of dust emissions from hot rolling depends largely on the rolling speed and the product surface area.

Input / Consumption Level		
Rolling and lubrication oil		
Water	1 - 15.5 <sup>2,3</sup>	m <sup>3</sup> /t
Energy: Deformation energy	72 - 140 <sup>2,4</sup>	kWh/t
Output / Emission Level		
	Specific Emission	Concentration
Particulates (oxides, dust) Mill stands: Coil handling lines	2 - 40 <sup>1</sup> g/t	2 - 50 <sup>2</sup> mg/m <sup>3</sup> ≈ 50 <sup>2</sup> mg/m <sup>3</sup>
Filter dust (collected from rolling stands)	100 - 7 600 <sup>1</sup> g/t	
Fugitive oil emissions <sup>5</sup>	negligible	
Waste water: (containing suspended solids, oil...) Sludge from waste water treatment	0.8 - 15.3 <sup>2</sup> m <sup>3</sup> /t	
Metallic by-products: Crops, rolling rejections, cuttings, etc.	70 - 150 <sup>6</sup> kg/t	
<sup>1</sup> Source of data [EC Study] <sup>2</sup> Source of data [EUROFER HR] <sup>3</sup> [EC Study] reports up to 22 m <sup>3</sup> /t <sup>4</sup> Upper end of range reported by [Com I] <sup>5</sup> Generated inside the mill bay, remarkable in near vicinity of emission source only and from that not significant for releases to air [EUROFER HR] <sup>6</sup> Source [Com A]		

Table A.3-4: Consumption and emission levels for hot rolling

### A.3.1.6 Roll Shop

→ No data available.

### A.3.1.7 Oil, Grease and Hydraulic Oil Flow

Oil and greases used for lubrication and hydraulic oil result in oil-bearing waste water and waste. Large parts of the oil/grease input are carried out of the system by the product, by mill scale, by the waste water or by emission to air. An estimated 300 g/t flat products and an estimated 100 - 800 g/t long products is emitted as hydrocarbon to air due to evaporation, e.g.

when in contact with the hot metal surface. Figure A.3-3 shows an example of oil and grease flow in a steel mill. [DFIU 96]

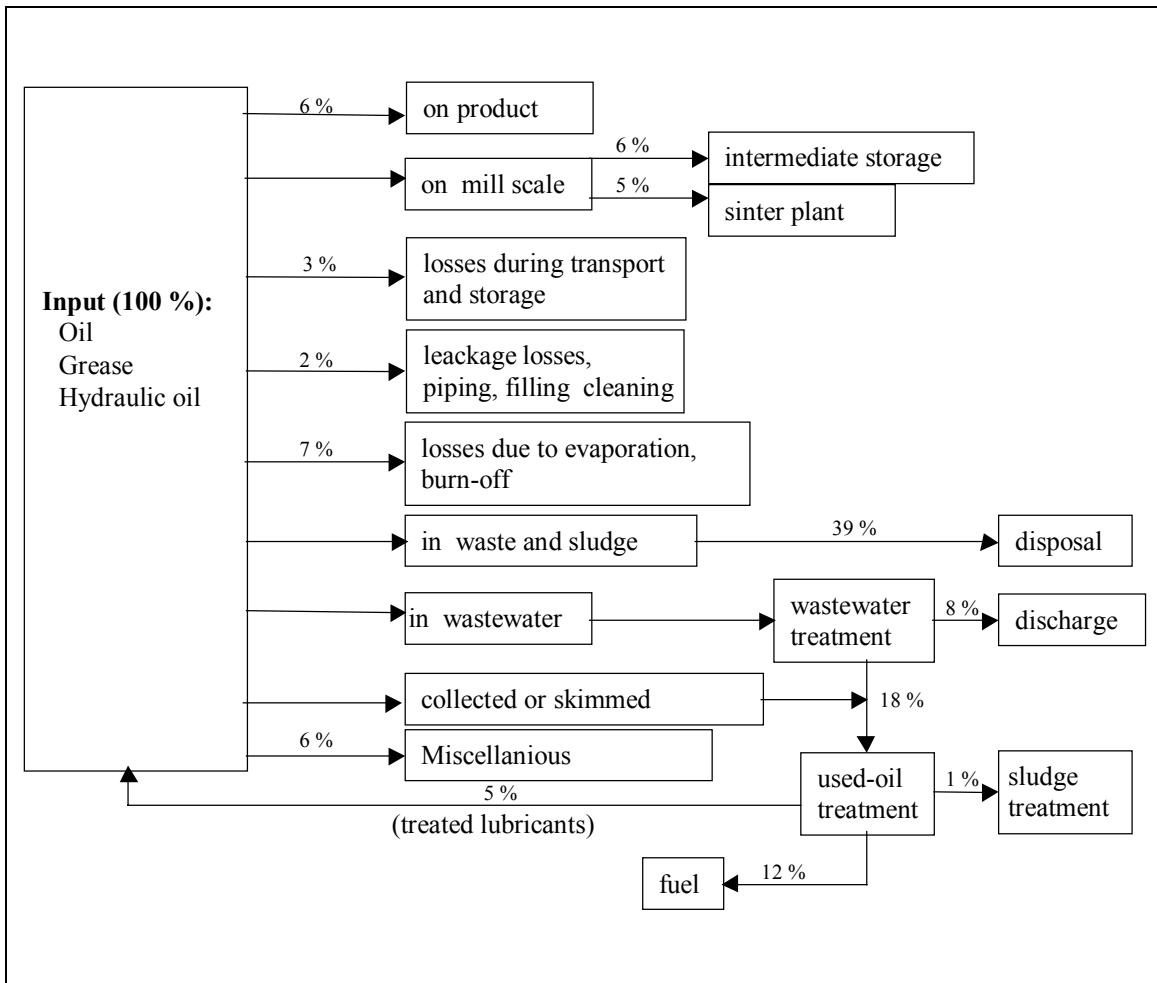


Figure A.3-3: Oily material balance of a typical steel mill as reported in [DFIU 96]

### A.3.1.8 Hot Rolling Mill Waste Water Treatment Plant

Kind and amount of input depends mainly on the design of the water treatment plant and water treatment measures applied, e.g. application of flocculate agents or acids. Quality of water input and the specific water consumption also have an influence.

Waste water from scale removal and flume flushing contains, apart from coarse scale, suspended solids and emulsified oil. Large amounts of water are used for roll and material cooling, which also contain oil and suspended solids. The solid concentrations range from 120 to 2000 mg/l (others report 50 to 1000 mg/l [DFIU98]); oil contents from 10 to 200 mg/l depending on the mill type. [EC Haskoning]

The amount of water discharged from hot rolling mills is reported to range from 0 to 22 m<sup>3</sup>/t including once-through cooling units. When once-through cooling units are excluded, the maximum specific water discharge is up to 11 m<sup>3</sup>/t. Once-through cooling systems do not correspond with 'state of the art'.

Input / Consumption Level		
Processwater		
Flocculating agents		
Others		
Output / Emission Level		
	Specific Emission	Concentration
<b>Discharged water:</b>		
<b>Total suspended solids (TSS)</b>	20 - 1065 <sup>1</sup> g/t	5 - 100 <sup>1,3</sup> mg/l
<b>Chemical oxygen demand (COD)</b>	22 - 65 <sup>1,5</sup> g/t	18 - 43 <sup>1,4</sup> mg/l
<b>Hydrocarbon content</b>	1 - 3 <sup>1</sup> g/t	0.2 - 10 <sup>1</sup> mg/l
<b>Cu</b>		0.009 - 0.26 <sup>2,6</sup> mg/l
<b>Zn</b>		0.004 - 0.35 <sup>2</sup> mg/l
<b>Cd</b>		< 0.05 <sup>6</sup> mg/l
<b>Al</b>		0.04 - 0.14 <sup>2</sup> mg/l
<b>Pb</b>		< 0.1 <sup>2,6</sup> mg/l
<b>Cr</b>		< 0.18 <sup>6</sup> mg/l
<b>Cr<sup>6+</sup></b>		0.01 mg/l
<b>Mn</b>		0.04 - 0.26 <sup>2</sup> mg/l
<b>Fe</b>		0.3 - 2.0 <sup>2</sup> mg/l
<b>Ni</b>		0.01 - 2.0 <sup>2,6</sup> mg/l
<b>Hg</b>		< 0.01 mg/l
<b>Free chlorine</b>		0.1 - 0.5 <sup>2</sup> mg/l
<b>Other parameters:</b>		
pH-value	7 - 8.5 <sup>1</sup>	
Temperature	11 - 30 °C <sup>1</sup>	
<b>Water treatment sludge</b>		
<sup>1</sup> Source of data [EUROFER HR] <sup>2</sup> Source of data [HMIP] <sup>3</sup> [EC Study] reports an extreme of figure of 200 mg/l <sup>4</sup> [EC Study] reports normal range up to 80 mg/l, with two extreme figures: 200 and 450 mg/l <sup>5</sup> [EC Study] reported data are as high as 300, 800 g/t and more <sup>6</sup> Source of data [EC Study]		

**Table A.3-5: Consumption and emission levels of the water treatment plant**

### A.3.1.9 Waste and Recycling

In addition to the information on waste generation for the individual sub-process, Table A.3-6 presents an overview of the waste generated in total by hot rolling operations and of the utilisation potentials. The reference base of the hot rolling mill as a whole was chosen, because a clear distinction of waste sources and attribution of waste amounts to individual processing steps is impossible in a number of cases.

Kind of waste or by-product/Source	Average Specific Mass [kg/t]	Reported Waste <sup>1</sup> [t] (steel production) <sup>2</sup>	Utilization	Percentage <sup>2</sup>
<b>Scale</b> (from scarfing, grinding, shot blasting)	3.5	77900 (22 Mt)	Recycle in-plant Externally used <sup>4</sup> Landfill	95.9 3.4 0.7
<b>Re-heating furnace scale</b>	4	128000 (44.7 Mt)	Recycle in-plant Externally used <sup>4</sup> Externally used <sup>5</sup> Sold <sup>5</sup> Landfill	37.6 13.4 9.7 29.0 10.3
<b>Oil-free millscale</b>	14.1	517000 (36.8 Mt)	Recycle in-plant Externally used <sup>4</sup> Externally used <sup>5</sup> Sold <sup>5</sup> Landfill	74.8 3.6 15.1 2.9 3.6
<b>Oily millscale</b>	11.2	692800 (61.7 Mt)	Recycle in-plant Externally used <sup>4</sup> Externally used <sup>5</sup> Sold <sup>5</sup> Landfill	81.6 1.6 1.5 9.7 5.6
<b>Dust and sludges</b> from air cleaning devices, Flat products	0.23	2363 (10.2 Mt)	Recycle in-plant Externally used <sup>5</sup> Landfill	94.8 0.8 4.4
<b>Dust and sludges</b> from air cleaning devices, Long products	0.71	2492 (3.5 Mt)	Recycle in-plant Externally used <sup>4</sup> Landfill	16.8 24.5 58.7
<b>Waste water treatment sludges</b>	3.4	161000 (11 Mt)	Recycle in-plant Externally used <sup>6</sup> Sold <sup>5</sup> Landfill	7.7 25.3 7.6 59.4
<b>Dismantled refractories</b>	0.5	21900 (46 Mt)	Recycle Externally used <sup>7</sup> Sold <sup>5</sup> Landfill	6.0 7.7 13.8 72.5
Note: data based on [EC Study]; figures given on dry weight-basis <sup>1</sup> Submitted as an answer to a questionnaire activity of the EU. <sup>2</sup> Steel production of the companies that provided information on utilisation. <sup>3</sup> Percentage refers to reported mass/ answered questionnaires. <sup>4</sup> Reported by non-integrated plants, recycling in other steel making plants <sup>5</sup> No indication on further use <sup>6</sup> About a quarter is being recycled in other steel plants <sup>7</sup> Principally in refractory plants				

Table A.3-6: Waste generated in hot rolling mills and utilisation rates

### **A.3.1.10 Noise Issues in Hot Rolling**

Excessive noise from hot rolling is primarily an internal occupational health issue, with precautions normally taken to protect employees where it is not practicable to prevent or reduce the noise at source. In some instances, depending on the location of the process (for example close to a residential area) and the noise characteristics (intermittent, impact and/or high frequency noise is more often a source of complaint than continuous low frequency noise) there can be cause for concern off-site, although this depends on the background noise level and other noise sources nearby.

The most significant sources of noise in the hot rolling process are associated with product handling. Other sources, such as high pressure descaling, reheat furnace induced draft fans and hot/cold sawing can also be significant. The main issues with product handling are associated with impact noise from large diameter pipes and movement of heavy plates, for example. Section mill cooling banks can also be a source of high levels of noise as products are moved during cooling. High pressure descaling (in some cases greater than 250 bar) is another intermittent noise source. Reheat furnace induced draught fans operate continuously but can be variable speed and therefore will cause noise of varying frequency and noise level. Long products, such as sections or rail, are cut to length, on or off line, by either hot or cold saws. High frequency noise is generated by the cutting action/friction. This can be both intermittent and high frequency. The absolute noise levels (in decibel) are equipment/plant specific but can be in excess of 85 dBA.

In terms of product handling, the main method for reducing noise is to devise operating procedures to minimize the amount of contact between products and material handling equipment such as cooling bank skids. Most other sources of noise are normally within buildings and the noise level is moderated to an acceptable level. In the event of specific local problems, additional measures such as local enclosure and/or building insulation may be required, but these can be extremely expensive and are not normally considered to be necessary.

### **A.3.1.11 Commissioning and Decommissioning**

The environmental effects of commissioning or the decommissioning in hot rolling mills are generally not important. Some facilities are available (e.g. N<sub>2</sub> purge in reheat furnaces) to assure safety during commissioning or decommissioning or to permit the installations to be maintained.





## A.3.2 Cold Rolling Mills

### A.3.2.1 Mass Stream Overview

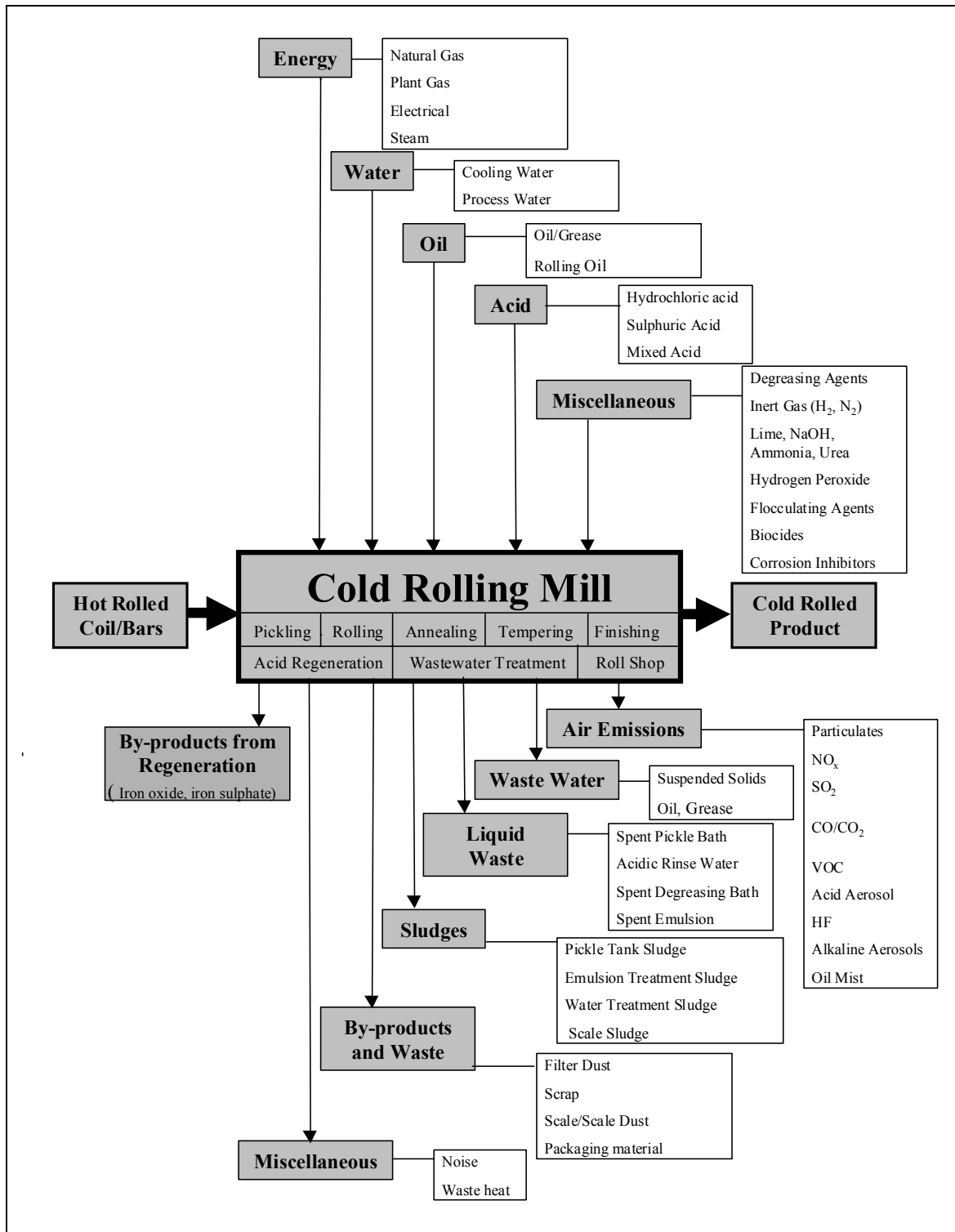


Figure A.3-4: Input/output overview for cold rolling mills

The subsequent chapters present specific input and consumption data, as well as specific output and emission data for individual operational steps associated with cold rolling activities.

### A.3.2.2 Pickling of Low Alloy, Alloy and High Alloy Steel

Hydrochloric, sulphuric and, for stainless steel, a mixture of nitric and hydrofluoric acid are used as pickling agents. Acid consumption varies obviously depending on whether acid is regenerated or not. It also depends on the specific surface area pickled and the thickness of the oxide layer. [EUROFER CR]

Consumption of anticorrosive oil depends on the percentage of oiled products, on the type of oiling machine used (electrostatic oiling or spraying nozzles) and on the oil weight required by the customer. [EUROFER CR]

Energy is required in form of steam for heating the pickling bath, as electrical energy for drives, pumps etc. and as caloric energy (natural gas or LPG) for the regeneration process (HCl). Some plants do not regenerate the acid or subcontract the regeneration, which in both cases can result in lower energy consumption. However for these plants all the fresh acid has to be heated to working temperature. [EUROFER CR]

Additionally, for high alloy steel processing, shot (for the shot blast machine) is needed for hot band mechanical descaling. For NO<sub>x</sub> reduction measures either hydrogen peroxide is needed to be added to the pickling bath to suppress the formation of NO<sub>x</sub> during pickling or ammonia or urea is required for SCR installations. [EUROFER CR]

Water is used for rinsing after pickling and to prepare the pickling baths. Three kinds of process water are created during pickling. These comprise water used for rinsing, spent pickle baths and others (like water from the fume absorbers of the pickling tank exhaust system and flushing water from plant cleaning). The main volume of waste water derives from rinsing, whereas the main load of contamination comes from the continuous or batch exchange of pickle baths. [EUROFER CR]

A primary aim should be to reduce waste water volume and minimize contaminant loading of the waste streams by optimisation of the pickling process. The waste water volume can be reduced by acid regeneration and recycling. Some plants sell spent pickle acid for external use, e.g. in water treatment. Acidic waste water, e.g. from the rinsing section or the fume scrubbers, which cannot be used in other processes of the installation have to be treated/neutralised prior to release. Neutralisation, however, requires the use of additional chemicals, like lime, NaOH or polyelectrolyte.

Scrap, scale dusts and pickle tank sludge arise during pickling operations. From acid regeneration 0.05 to 15 kg sludges (ref. dry material) per tonne of steel arise, with an average of 4.2 kg/t. The sludges have an iron content of 55 - 66 % and, in case of stainless steel processing, 5 - 10 % Cr and 3 - 5 % Ni. [EC Study]

By-products generated by acid regeneration are iron oxides or iron sulphate. The average iron oxide yield from regeneration is 5.5 kg/t. The Fe<sub>2</sub>O<sub>3</sub> content of the by-products is usually > 99 % with low concentrations of other metals, such as Al < 0.1 %; Pb, Cu < 0.03 %; Cr, Ni < 0.02 % and Zn < 0.01 %. Chloride contents range from 0.1 to 0.2 %.

Iron sulphate production ranges from 2.5 to 25 kg/t with an average of 17 kg/t. Less than 0.1 % of the production is reported to be landfilled as the product can be sold to external usage, including water treatment and chemical industries. [EC Study]

Emissions to air generated by pickling depend partly on the acid used for pickling. They are:

- Acid-fumes from the pickling tanks (HCl, H<sub>2</sub>SO<sub>4</sub>), emitted from the outlet chimney of the pickling tank fume exhaust absorber and from the exhaust gas chimney of the acid regeneration plant.
- In case of mixed acid pickling: NO<sub>x</sub>, HF.

- Dust, NO<sub>x</sub>, SO<sub>x</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl from the regeneration plant.
- Gaseous emissions from storage facilities [EUROFER CR].

When pre-descaling is applied for stainless steel grades is carried out by electrolytic pickling with sodium sulfate, chromium containing waste waters and wastes (sludges) may arise.

Many modern pickling lines are operated in association with regeneration plants. Therefore some of the consumption and emission data presented for the individual pickling processes in the following chapters include the regeneration process. A distinction was made where possible. Detailed consumption and emission data for the regeneration plant and the exhaust gas cleaning from pickling tanks are given in the corresponding chapters for techniques to be considered in determination of Best Available Techniques.

### A.3.2.2.1 Hydrochloric Acid Pickling Line and Regeneration Plant

Regeneration of the pickle liquor is done on- or off site. Figure A.3-5 shows the material flow for a HCl pickling line in conjunction with acid regeneration.

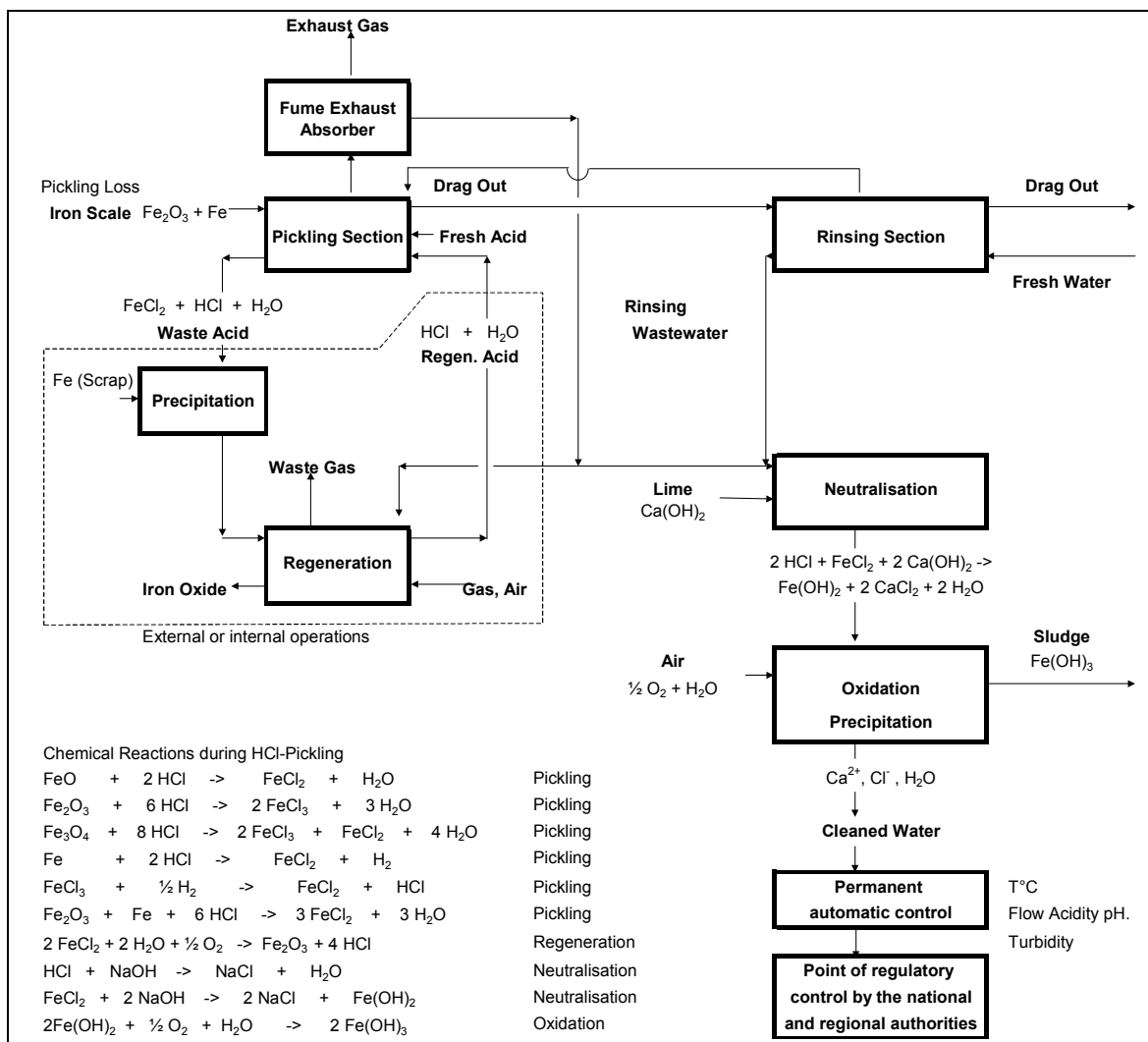


Figure A.3-5: Flow sheet for HCl pickling and acid regeneration [EUROFER CR]

Input / Consumption Level			
<b>Hot rolled strip</b>	1.01 - 1.05	t/t	
<b>Pickling agent:</b>			
HCl (33 %) with regeneration	0.7 - 0.9 <sup>1</sup>	kg/t	
HCl (33 %) without regeneration	12 - 17.5	kg/t	
<b>Anticorrosive oils</b>	0.1 - 0.2	kg/t	
<b>Energy:</b> Steam for bath heating	0.03 - 0.07	GJ/t	
Electrical energy	0.015 - 0.08	GJ/t	
Caloric energy	0.04 - 0.1	GJ/t	
<b>Industrial + demineralised water</b>	0.02 - 0.13	m <sup>3</sup> /t	
<b>Cooling water</b>	0.5 - 0.8	m <sup>3</sup> /t	
Output / Emission Level			
	Specific Emission		Concentration
<b>Waste gas</b>	35 - 100	m <sup>3</sup> /t	
<b>Waste air</b>	50 - 400	m <sup>3</sup> /t	
<b>Exhaust gas from acid regeneration</b> (Dust, SO <sub>2</sub> , NO <sub>x</sub> , CO/CO <sub>2</sub> , HCl, Cl)	24 - 38	m <sup>3</sup> /t	
<b>Exhaust gas from pickling tanks</b>	25 - 400	m <sup>3</sup> /t	
<b>Dust</b> <sup>2</sup>	n.a.		< 5 - 20 mg/m <sup>3</sup>
<b>HCl</b> <sup>3</sup>	0.258	g/t	1 - 30 mg/m <sup>3</sup>
<b>HCl (20 %) recycled</b>	23 - 40	kg/t	
<b>Waste water</b> <sup>4</sup> Spent pickle liquor	0.025 - 0.07	m <sup>3</sup> /t	
<b>Sludge cake</b>	0.043 - 1.2	kg/t	
<b>Pickling tank sludge</b>			
<b>Oil contaminated waste</b>			
<b>Iron oxide (Fe<sub>2</sub>O<sub>3</sub>)</b>	4 - 12 <sup>5</sup>	kg/t	
<b>Scale dust( collected by dedusting system)</b>			
<b>Strip head/tail scrap</b>	30	kg/t	
Notes: Source of data [EUROFER CR]; Production: 300000 - 2500000 t/a			
<sup>1</sup> Germany reported fresh HCl consumption as low as 0.01 kg/t for closed circuit pickling line [Com D]			
<sup>2</sup> [EUROFER CR] reports 10 – 20 mg/Nm <sup>3</sup> , [Corus 31.8] reports < 5 mg/Nm <sup>3</sup> .			
<sup>3</sup> [EUROFER CR] reports emission levels of 10 – 20 mg/m <sup>3</sup> , [EC Study] 1 - 145 mg/m <sup>3</sup> and 2 - 16 g/t and [EPA-453] achieved levels of 2.7 – 3.5 mg/m <sup>3</sup> , [EUROFER 6.9] reports upper level of 30 mg/Nm <sup>3</sup> when including continuous measurements.			
<sup>4</sup> In some cases no acid regeneration, but free acid reduction with scrap, FeCl <sub>2</sub> (used bath): 19.4 kg/t is sold for external use			
<sup>5</sup> Source: [EC Study]			

**Table A.3-7: Consumption and emission levels for HCl pickling plants (incl. regeneration)**

The acid rinsing water from the pickling plant can be used as wash water for gas scrubbers and as process water in the regeneration plant. In case acidic water is not or partially not reused as process water, it is neutralised with lime or NaOH in the neutralisation plant prior to discharge. The sludge is de-watered in filter presses and then disposed of. Input and output of neutralisation, sedimentation and filtration, as well as the concentration of pollutants discharged are given in Table A.3-8.

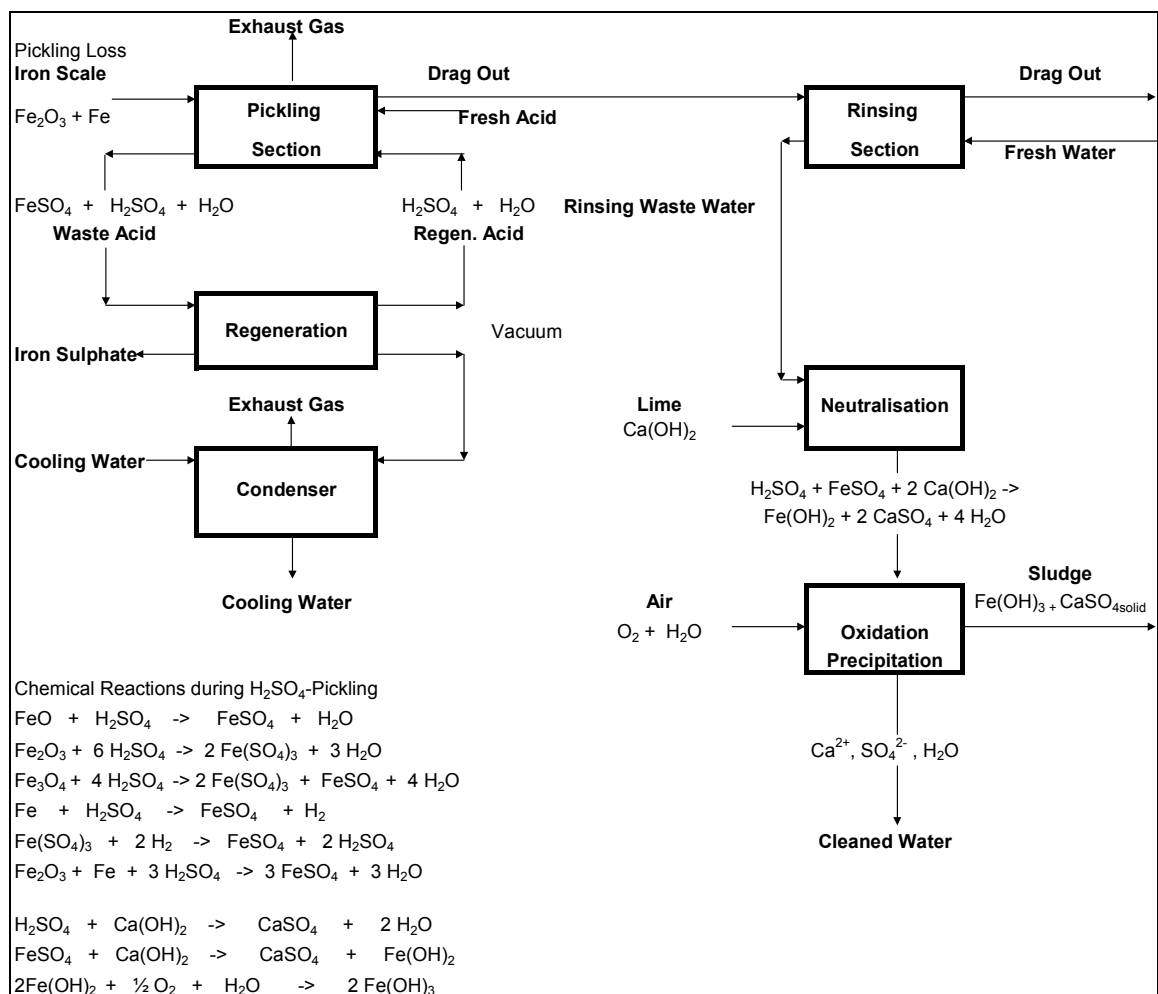
Although acidic waste water from gas scrubbing and other acidic waste water are often neutralised and the sludge is being disposed of, there are processes which allow a recycling of these waste water streams. For hydrochloric acid pickling the possibility of a virtually waste water free operation was reported. [Com D]

Input / Consumption Level		
Raw Waste water	0.025 - 0.07 m <sup>3</sup> /t	
Ca(OH) <sub>2</sub> (95 %)	0.272 - 0.525 kg/t	
Polyelectrolyte	0.22 g/t	
Air	0.259 kg/t	
Energy (electrical)	1 MJ/t	
Output / Emission Level		
Specific Emission		
Sludge Cake	0.043 - 1.2 kg/t	
Waste water	0.025 - 0.07 m <sup>3</sup> /t	
	Suspended solids	2.86 g/t
	Fe total	0.114 g/t

Note: source of data [EUROFER CR]  
<sup>1</sup> Reduction rate based on mass flow of constituent

Table A.3-8: Consumption and emission levels for waste water treatment in HCl-pickling plants

### A.3.2.2 Sulphuric Acid Pickling Line and Regeneration Plant

Figure A.3-6: Flow sheet for H<sub>2</sub>SO<sub>4</sub> pickling and regeneration [EUROFER CR]

Regeneration of the pickle liquor is done on- or off site. Figure A.3-6 shows the material flow for a H<sub>2</sub>SO<sub>4</sub> pickling line with acid regeneration.

Input / Consumption Level		
Hot rolled strip	1.03 - 1.06 t/t	
Pickling agent: 96 % sulphuric acid	7 - 10 kg/t	
Cooling water	3.84 m <sup>3</sup> /t	
Anticorrosive oils <sup>1</sup>	0.15 - 0.3 kg/t	
Energy:		
caloric/steam for bath heating	0.05 - 0.1 GJ/t	
electrical energy for drives	0.02 - 0.05 GJ/t	
Output / Emission Level		
	Specific Emission	Concentration
FeSO <sub>4</sub> -heptahydrate (from regeneration)	26 - 30 kg/t	
Recycled acid (H <sub>2</sub> SO <sub>4</sub> 20 %)	0 - 10 kg/t	
Waste gas	100 - 150 m <sup>3</sup> /t	
Exhaust gas from pickling tanks	50 - 110 m <sup>3</sup> /t	
	H <sub>2</sub> SO <sub>4</sub> 0.05 - 0.1 g/t	1 - 2 mg/m <sup>3</sup>
	SO <sub>2</sub> 0.4 - 1 g/t	8 - 20 mg/m <sup>3</sup>
Exhaust gas from acid regeneration (SO <sub>2</sub> , H <sub>2</sub> SO <sub>4</sub> )	70 - 90 m <sup>3</sup> /t	
Waste water	0.2 - 0.5 m <sup>3</sup> /t	
Oil contaminated waste	4 - 8 E - 5 m <sup>3</sup> /t	
Sludge cake <sup>3</sup>	0.06 - 0.2 kg/t	
Scale dust (collected by dedusting system)		
Scrap (from trimming and head/tail ends of coil)	37 - 45 kg/t	
Note: Source of data [EUROFER CR]; Production: 900000 - 1500000 t/a		
<sup>1</sup> sometimes rolling oil		
<sup>2</sup> waste = dust + sludge		

Table A.3-9: Consumption and emission levels for H<sub>2</sub>SO<sub>4</sub> pickling plants (incl. regeneration)

In case that cooling water from the condenser (acid regeneration) and acidic rinsing water from the pickling plant have to be discharged, they are generally neutralised with lime or NaOH. The sludge is dewatered in filter presses and disposed of. Input and output of neutralisation, sedimentation and filtration, as well as the concentration of pollutants discharged are given in Table A.3-10.

Input / Consumption Level		
Raw Waste water	0.315 m <sup>3</sup> /t	
Ca(OH) <sub>2</sub>	kg/t	
Polyelectrolyte	g/t	
Air	kg/t	
Energy (electrical)	1 MJ/t	
Output / Emission Level		
	Specific Emission	
Sludge cake	kg/t	
Waste water:	0.315 m <sup>3</sup> /t	
Suspended solids	16 - 20 g/t	
Fe total	0.3 - 0.5 g/t	
Note: Source of data [EUROFER CR]		
<sup>1</sup> Reduction rate based on mass flow of constituent		

Table A.3-10: Consumption and emission levels for waste water treatment in H<sub>2</sub>SO<sub>4</sub> pickling plants

### A.3.2.2.3 Mixed ( $\text{HNO}_3$ -HF) Acid Pickling Line and Acid Recovery

Figure A.3-7 shows the material flow for a mixed acid pickling in conjunction with acid recovery.

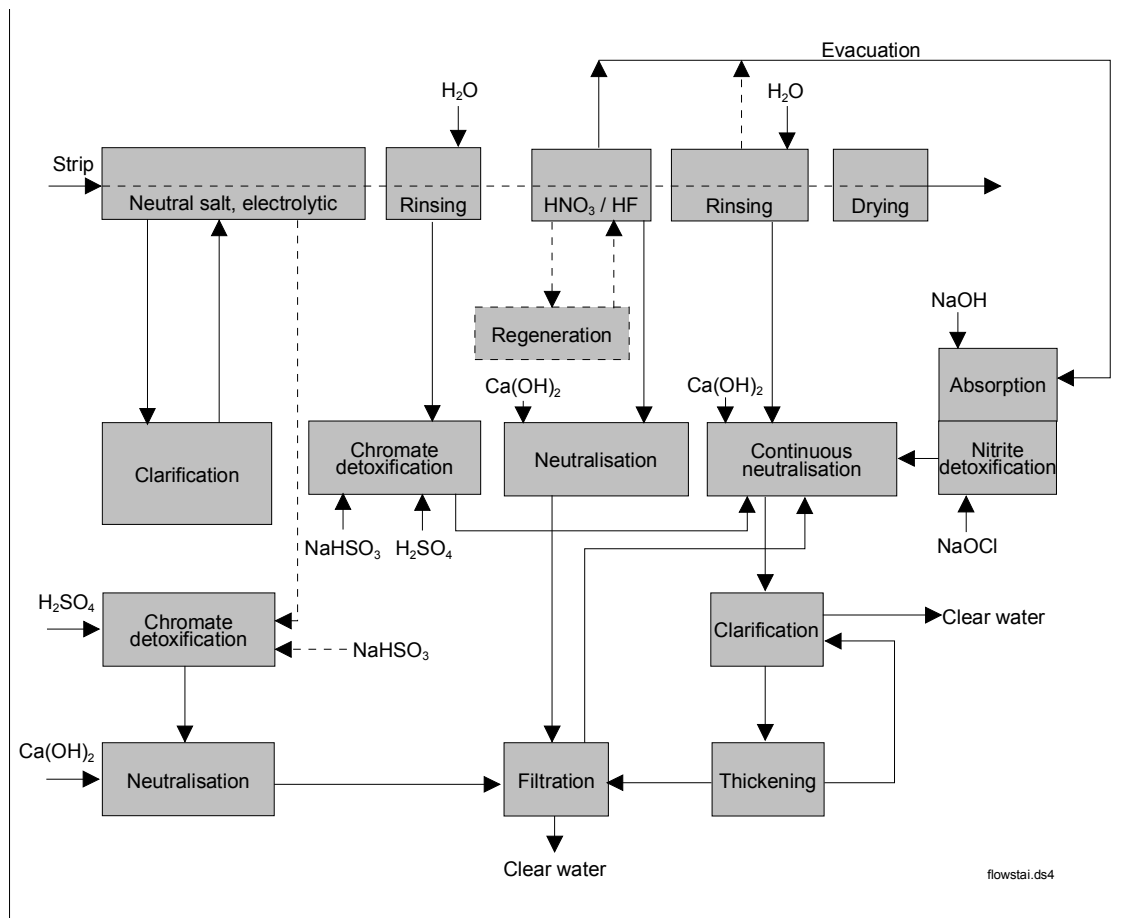


Figure A.3-7: Flow sheet for stainless steel pickling with  $\text{HNO}_3$ -HF acid (incl. recovery) [DFIU98]

Input / Consumption Level				
<b>Annealed strip</b>				
<b>Shot</b> <sup>1</sup>		1.5 - 3	kg/t	
<b>Nitric acid (HNO<sub>3</sub> 70 %)</b>		3 - 10	kg/t	
<b>Hydrofluoric acid (HF 70 %)</b>		2.5 - 7.5	kg/t	
<b>Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub> 35 %)</b>		3 - 10	kg/t	
<b>Water</b>				
<b>Energy: steam (acid heating)</b>		0.1 - 0.3	GJ/t	
Output / Emission Level				
		Specific Emission		Concentration
<b>Metal oxide and /or scale particles, shot fragments</b>				
<b>Exhaust gas from mechanical descaling</b>		350 - 450	m <sup>3</sup> /t	
<b>Dust</b>		10 - 20	g/t	< 1 – 25 <sup>2</sup> mg/Nm <sup>3</sup>
<b>Scale</b>				
<b>Spent pickle bath/ mixed acid</b>				
<b>Sludge</b>				
<b>Acid treatment sludge</b>				
<b>Exhaust gas from pickle plant: <sup>a</sup></b>				
	HF	0.2 - 3.4	g/t	0.2 – 17 <sup>3</sup> mg/m <sup>3</sup>
	NO <sub>x</sub>	3 - 4000	g/t	3 - (~1000) mg/m <sup>3</sup>
	SO <sub>2</sub>	1	g/t	1 - 10 mg/m <sup>3</sup>
<b>Waste water</b> <sup>4</sup>				
		1.0 - 9.0	m <sup>3</sup> /t	
<b>Water from neutralisation (metals, suspended solids)</b>				
<b>Gaseous emissions from storage</b>				
Note: source of data [EUROFER CR], except a: [EC Study]				
<sup>1</sup> Shot blasting is only used for hot band (pickling I)				
<sup>2</sup> 15 – 25 mg/Nm <sup>3</sup> source [EUROFER CR]; < 1 – 4.5 mg/Nm <sup>3</sup> source [FIN 28.3]				
<sup>3</sup> reported range from [EUROFER CR] 350 – 600 mg/Nm <sup>3</sup> with application of hydrogen peroxide injection and pickling tank fume exhaust absorber				
<sup>4</sup> Discharged to effluent treatment				

Table A.3-11: Consumption and emission levels for mixed acid pickling and recovery

### A.3.2.3 Cold Rolling

#### A.3.2.3.1 Low Alloy

##### Tandem Mill

Rolling oil (including additives as required) and demineralised water or equivalent water are used to prepare the rolling emulsion. Basic oils are usually naphthenic and paraffinic mineral oil fractions or vegetable fatty oils. To create a oil-in-water emulsion, anionic and nonionic emulsifier are added. The oil concentration in the emulsion can range from 1 to 25 %. To reduce friction and wear mineral oils are substituted by synthetic products, containing additional corrosion inhibitors, anti-foam agents and agents to prevent biological degradation Usual cooling/lubricant consumption is between 1800 and 3000 m<sup>3</sup>/h.

Energy is required in mill stands, emulsion-, hydraulics- and oil management for drives, fans, pumps etc.. The consumption of electrical energy is related to the steel grade rolled, the total reduction and the final gauge of the cold rolled product. Additionally, energy in form of steam



maybe needed for heating of the emulsion (if required). Oil consumption depends on the average final gauge of the cold rolled product.

Cold rolling activities result in the generation waste water which is treated in emulsion splitting plants. Effluents may contain oil and suspended solids. Oil and oil sludge from emulsion splitting plants or exhaust air absorber from mill stand are generated. Also particulate emissions can occur (roll wear or iron dust), which are collected by de-dusting systems.

Input / Consumption Level		
<b>Pickled steel strip</b>	1.002 - 1.032	t/t
<b>Cooling water</b>	5 - 6.5 (0.5) <sup>2</sup>	m <sup>3</sup> /t m <sup>3</sup> /t
<b>(River water, soft water, NaOH, inhibitor)</b> for cooling water system		
<b>Industrial + demineralised water</b>	0.014 - 0.04	m <sup>3</sup> /t
<b>Rolling oil<sup>1</sup></b>	0.3 - 2.0	kg/t
<b>Other oils (hydraulic, Morgoil...)</b>		
<b>Energy:</b>		
Steam	0.01 - 0.03	GJ/t
Electrical	0.2 - 0.3	GJ/t
Caloric	0.001 - 0.036	GJ/t
Output / Emission Level		
	Specific Emission	Concentration
<b>Cooling water</b>	5 - 6.5 (0.5) <sup>2</sup>	m <sup>3</sup> /t m <sup>3</sup> /t
<b>Waste water</b>	0.003 - 0.015	m <sup>3</sup> /t
<b>Waste air</b>	1800 - 2000	m <sup>3</sup> /t
<b>Emissions to air:</b>		
<b>Dust</b>	96	g/t
<b>Hydrocarbons</b>	7	g/t
<b>Oil<sup>a</sup></b>	0.6 - (~ 150) <sup>3</sup> Ø 19.7	g/t g/t
		10 - 50 5 - 20 0.1 - 15 (34) <sup>4</sup> mg/m <sup>3</sup> mg/m <sup>3</sup> mg/m <sup>3</sup>
<b>Oil contaminated waste (disposed)</b>	0.2	g/t
<b>Emulsion (internally recycled)</b>	5000 - 13200	kg/t
<b>Sludge cake</b>	0.9 - 1.5	kg/t
Note: Source of data [EUROFER CR], except: a [EC Study]; Production: 1600000 - 3100000 t/a		
<sup>1</sup> Consumption of rolling oil in the pickling line is also considered		
<sup>2</sup> Circulating water		
<sup>3</sup> from diagram [EC Study]		
<sup>4</sup> one extreme figure		

**Table A.3-12: Consumption and emission levels from tandem mills with emulsion system**

## Reversing Mill

Input / Consumption Level		
Pickled steel strip	1.002	t/t
Cooling water	3.2 - 3.5	m <sup>3</sup> /t
Industrial + demineralised water	0.02 - 0.06	m <sup>3</sup> /t
Rolling Oil	0.1 - 0.11	kg/t
Energy:		
Electrical	240 - 245	MJ/t
Caloric	0.023 - 0.024	MJ/t
Output / Emission Level		
	Specific Emission	Concentration
Waste air	180 - 850 m <sup>3</sup> /t	
Emisions to air		
HC	8.4 - 10.1 g/t	10 - 12 mg/m <sup>3</sup>
Oil <sup>a</sup>	0.4 - (~150) <sup>1</sup> g/t	0.1 - (~6) <sup>1</sup> mg/m <sup>3</sup>
	Ø 10.8 g/t	
Waste water	0.06 - 0.07 m <sup>3</sup> /t	
Sludge cake (disposed)	1.9 -2.0 kg/t	
Emulsion (internal recycling)	8.5 - 9.0 m <sup>3</sup> /t	
Scrap, off-cuts, etc		
Note: Source of data [EUROFER CR], except a [EC Study]; Production: 250000 - 550000 t/a		
<sup>1</sup> from diagram [EC Study]		

Table A.3-13: Consumption and emission levels from reversing mills

## A.3.2.3.2 High Alloy/Reversing Mill

As rolling oil usually mineral oil including additives is used. Energy is used on mill stands and oil circuits for drives, fans, pumps etc. From cleaning operations oil contaminated filter media (debris from roll wear, dust and steel strip) is generated. The oil from exhaust filtration system is recovered. [EUROFER CR]

Input / Consumption Level		
Stainless annealed strip	1.01 - 1.03	t/t
Cooling water (recirculating)	20 -35	m <sup>3</sup> /t
Oil (mineral)	1.5 - 6.0	l/t
Oil filtration media	1 - 2	kg/t
Energy: electrical	0.6 - 0.8	GJ/t
Output / Emission Level		
	Specific Emission	Concentration
Waste air (mill stand exhaust air absorber)	3000 - 12000 m <sup>3</sup> /t	
Oil	50 - 80 g/t	10 - 20 mg/m <sup>3</sup>
Oil <sup>a</sup>	3 - (~150) <sup>1</sup> g/t	0.1 - 16 mg/m <sup>3</sup>
	Ø 91.7 g/t	
Oil contaminated waste filter media	1.8 - 2.8	kg/t
Waste water (suspended solids, salts of iron and alloy metals, traces of oil)		
Scrap, off-cuts, etc		
Note: Source of data [EUROFER CR], except a [EC Study]; Production: 40000 - 150000 t/a		
<sup>1</sup> from diagram [EC Study]		

Table A.3-14: Consumption and emission levels from reversing mills

### A.3.2.4 Annealing of Low Alloy and Alloy Steel

#### A.3.2.4.1 Batch Annealing

##### Degreasing / Electrolytic Degreasing

Input / Consumption Level		
<b>Alkaline cleaners/detergents:</b> (caustic soda, soda ash, alkaline silicates, phosphates)		
<b>Water</b>		
<b>Energy</b>		
Output / Emission Level		
<b>Waste water:</b> (containing suspended solids, dissolved metals oil)		
<b>Alkaline fume</b>		

Table A.3-15: Consumption and emission levels from degreasing

##### Annealing

Electrical energy is required for drives, etc. and heating; mixed gas (coke-oven gas/top gas) for the HNX-hoods and natural gas or LPG for the hydrogen-high convection hoods. For protective atmosphere in the furnaces inert gas, typically nitrogen with 3 - 7 %-hydrogen or alternatively 100 %-hydrogen, is needed.

Input / Consumption Level		
<b>Cold rolled strip</b>		1 - 1.01 t/t
<b>Energy:</b>		
Electrical		0.06 - 0.12 GJ/t
Caloric		0.62 - 0.75 GJ/t
<b>Cooling water</b>		5 - 10 m <sup>3</sup> /t
<b>Inert gas (H<sub>2</sub>, N<sub>2</sub>)</b>		
Output / Emission Level		
	Specific Emission	Concentration
<b>Cooling water</b>	5 - 10 m <sup>3</sup> /t	
<b>Oil containing waste (disposed)</b>	2.04 E -4 m <sup>3</sup> /t	
<b>Waste gas</b>	200 - 250 m <sup>3</sup> /t	
<b>Emissions to air: <sup>a</sup></b>		
<b>SO<sub>2</sub></b>	Rev: (~0) - (~2) <sup>1</sup> g/t Cont: (~0) <sup>1</sup> - 41 <sup>2</sup> g/t	
<b>NO<sub>x</sub></b>	Rev: (~9) - (~900) <sup>1</sup> g/t Cont: (~0.5) - (~250) <sup>1</sup> g/t	
Note: Source of data [EUROFER CR], except a [EC Study]; Production: 175000 - 1500000 t/a Rev = Reversing mills, no differentiation batch/continuous annealing Cont = Continuous mills, no differentiation batch/continuous annealing <sup>1</sup> from diagram [EC Study] <sup>2</sup> one extreme figure: 194.4 g/t		

Table A.3-16: Consumption and emission levels from batch annealing

### A.3.2.4.2 Continuous Annealing

Chemicals for alkaline and electrolytic pre-cleaning are needed. Furthermore, wet temper rolling agents for rough passes and anticorrosive oils are consumed. Usually, natural gas, other (plant) gases or LPG are used for heating the strip. Electrical energy is used for drives, booster, overaging zone and finishing). Inert gas (nitrogen with typically about 5 %-hydrogen or alternatively 100 %-hydrogen) is used for protection of surface oxidation.

Continuous annealing mainly produces waste water (oil, suspended solids, COD) and exhaust gas from annealing furnaces (NO<sub>x</sub>, SO<sub>2</sub>, CO, CO<sub>2</sub>).

Input / Consumption Level		
<b>Cold rolled strip</b>	1.007 - 1.030	t/t
<b>Chemicals for alkaline/ electrolytic pre-cleaning</b>		
<b>Energy:</b>		
Electrical	0.173 - 0.239	GJ/t
Caloric	0.775 - 1.483	GJ/t
Steam	0.119	GJ/t
<b>Cooling water</b>	23.529	m <sup>3</sup> /t
<b>Inert gas (nitrogen/hydrogen)</b>		
<b>Wet temper rolling agent (for rough pass, electrical sheet)</b>		
<b>Anticorrosive oils,</b>		
Output / Emission Level		
	Specific Emission	Concentration
<b>Waste gas from annealing furnace:</b>	350 - 400	m <sup>3</sup> /t
<b>Emissions to air:<sup>a</sup></b>	Rev: ~0) - (~2) <sup>1</sup>	g/t
<b>SO<sub>2</sub></b>	Cont: (~0) <sup>1</sup> - 41 <sup>2</sup>	g/t
<b>NO<sub>x</sub></b>	Rev: (~9) - (~900) <sup>1</sup>	g/t
	Cont: (~0.5) - (~250) <sup>1</sup>	g/t
<b>Waste heat (steam, can be recovered)</b>	0.037 - 0.078	GJ/t
<b>Waste water (oil, suspended solids...)</b>	0.118	
<b>Cooling water</b>		
<b>Sludge cake (disposed)</b>	0.018 - 0.47	kg/t
<b>Scale dust</b>		
<b>Oil sludge from pre-cleaning</b>		
Note: source of data [EUROFER CR], except a [EC Study]; Production: 600000 t/a Rev = Reversing mills, no differentiation batch/continuous annealing Cont = Continuous mills, no differentiation batch/continuous annealing <sup>1</sup> from diagram [EC Study] <sup>2</sup> one extreme figure: 194.4 g/t		

Table A.3-17: Consumption and emission levels from continuous annealing

### A.3.2.5 Annealing and Pickling of High Alloy Steel

Table A.3-18 presents consumption and emission data of continuous furnaces for annealing hot rolled strip.

Input / Consumption Level			
<b>Hot rolled strip</b>		1.01 - 1.02	t/t
<b>Industrial + demineralised water</b>		0.015 – 0.55	m <sup>3</sup> /t
<b>Cooling water</b>		0.15 - 1.1	m <sup>3</sup> /t
<b>Energy:</b>			
Electrical		0.3 - 0.4	GJ/t
Caloric (Gas)		1.0 - 1.5	GJ/t
Steam		0.06 - 0.13	MJ/t
Output / Emission Level			
		Specific Emission	Concentration
<b>Waste gas</b>		550 - 1000	m <sup>3</sup> /t
<b>Emissions to air:</b> <sup>a</sup>			
	<b>SO<sub>2</sub></b>	0 - (~30) <sup>1</sup>	g/t
	<b>NOx</b>	0.1 - (~1500) <sup>1,2</sup>	g/t
<b>Waste water</b>		0.4 - 0.5	m <sup>3</sup> /t
<b>Sludge cake</b>		2.0 - 15.0	kg/t
Note: source of data [EUROFER CR], except a [EC Study]; Production: 56000 - 550000 t/a			
<sup>1</sup> from diagram [EC Study]			
<sup>2</sup> one extreme figure: 3820 g/t			

**Table A.3-18: Consumption and emission levels of continuous annealing furnaces**

High alloy steels are mostly treated in combined annealing and pickling lines. The amount of pickling acid required depends on the strip size (surface, volume) and the thickness of scale layer. Acid consumption depends also on whether hot band or cold rolled material is processed.

Energy requirements are: natural gas and LPG for annealing furnaces, steam for acid bath heating and electrical energy for drives, fans, pumps etc

Emissions mainly refer to waste water from neutralisation plants (metals, suspended solids), exhaust gas from furnaces (combustion products: CO, CO<sub>2</sub> NOx), exhaust gas from pickling plant fume scrubbers (containing NOx HF) and exhaust gas from mechanical descaling extraction system (dust). [EUROFER CR]

Table A.3-19 gives the consumption and emission from combined pickling and annealing lines.

Input / Consumption Level		
Stainless steel strip (hot band or cold rolled)	1.03 - 1.08	t/t
Shot <sup>1</sup>	1.5 - 3	kg/t
Cooling water (recirculated)	10 -20	m <sup>3</sup> /t
Nitric acid (HNO <sub>3</sub> 70 %)	3 - 10	kg/t
Hydrofluoric acid (HF 70 %)	2.5 - 7.5	kg/t
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> 35 %)	3 -10	kg/t
Compressed air		
Energy <sup>1</sup> : Electrical	0.15 - 0.30	GJ/t
Caloric (NG)	0.7 - 1.8	GJ/t
Steam (acid heating)	0.1 - 0.3	GJ/t
Output / Emission Level		
	Specific Emission	Concentration
Scale/shot dust		
Exhaust gas from mechanical descaling/dust	350 - 450 m <sup>3</sup> /t	
Waste water discharged to effluent treatment	1.0 - 9.0 m <sup>3</sup> /t	
Spent pickle bath/ mixed acid		
Exhaust gas from pickle plant fume scrubbers		
Exhaust gas:		
Emissions to air from furnace: <sup>a</sup>	SO <sub>2</sub> 0 - (~30) <sup>2</sup> g/t	
	NO <sub>x</sub> 0.1 - (~1500) <sup>2,3</sup> g/t	
Note: Source of data [EUROFER CR]; Production: 30000 - 300000 t/a		
<sup>1</sup> Shot blasting is only done on hot band (pickling I)		
<sup>2</sup> from diagram [EC Study]		
<sup>3</sup> one extreme figure: 3820 g/t		

Table A.3-19: Consumption and emission levels from Pickling and annealing of high alloy steel

### A.3.2.6 Tempering (Low alloy/High Alloy)

During rolling operation typically a 5 % -solutions of wet temper rolling agents, which may be nitrite based, are applied. Energy is required in form of hot water and electrical energy for mill stand, hydraulics, etc.

Input / Consumption Level			
Annealed strip	1.01 - 1.03	t/t	
Industrial and demineralised water	0.002 - 0.004	m <sup>3</sup> /t	
Cooling water	1.0 - 4.0	m <sup>3</sup> /t	
Electrical energy	0.02 - 0.15	GJ/t	
Tempering fluid concentrate	0.11 - 3	kg/t	
Anticorrosive oil	0.04 - 0.05	kg/t	
Output / Emission Level			
	Specific Emission		Concentration
Waste air	1 - 100	m <sup>3</sup> /t	
Waste water	0.002 - 0.004	m <sup>3</sup> /t	
Oil contaminated waste <sup>1</sup>	6 - 7.5 E -5	m <sup>3</sup> /t	
Tempering <sup>2</sup> /cooling fluid			
Sludge cake <sup>2</sup>	2.0 - 4.0	kg/t	
Leakage oil	4 - 5 E -5	m <sup>3</sup> /t	
Note: source of data [EUROFER CR]; Production: 300000 - 1000000 t/a			
<sup>1</sup> externally disposed			
<sup>2</sup> internally recycled			

Table A.3-20: Consumption and emission levels from tempering

### A.3.2.7 Finishing (Cutting, Inspection, Packing)

Input / Consumption Level			
Cooling water	0.5 - 0.7	m <sup>3</sup> /t	
Anticorrosive oil	0.2 - 0.4	kg/t	
Signing ink	0.5 - 80	g/t	
Film (clear)	80 -90	g/t	
Paper (blue)	9 - 80	g/t	
VCI paper	1.5 - 1.7	g/t	
FLEX-Stripes	0.05 - 0.06	m <sup>2</sup> /t	
Wood	950 - 1050	g/t	
Electrical energy	0.02 - 0.04	GJ/t	
Waste gas Output / Emission Level			
	Specific Emission		Concentration
Oil contaminated waste	1.4 - 1.6 E -4	m <sup>3</sup> /t	
Scrap	25 - 40	kg/t	
Note: source of data [EUROFER CR]			

Table A.3-21: Consumption and emission levels from finishing

### A.3.2.8 Roll Shop

Main input for the roll shop is water and grinding fluid to prepare fresh emulsions. Output resulting from grinding: spent grinding emulsions and grinding sludge. [EUROFER CR]

Input / Consumption Level			
Cooling water (circulating water)			m <sup>3</sup> /t
Grinding emulsion (fresh)		0.4 - 80	g/t
Shot grain (SBT)		40 - 50	g/t
Soluble oil concentrate		5 - 6	g/t
Chromium salt (PRETEX)		2 - 3	g/t
Condensate for chromium acid (PRETEX)		140 - 160	g/t
Waste gas Output / Emission Level			
		Specific Emission	
		25 - 70	m <sup>3</sup> /t
Waste gas <sup>1</sup>	Dust		< 1 mg/m <sup>3</sup>
	Cr		< 0.1 mg/m <sup>3</sup>
Grinding sludge		0.1 - 0.2	kg/t
Grinding wheel		0.9 - 1.0	g/t
Waste emulsion		0.035 - 0.08	kg/t
Oil contaminated waste		1.5 - 2.0 E - 4	m <sup>3</sup> /t
SBT-dust		40 - 50	g/t
Note: source of data [EUROFER CR]			
<sup>1</sup> Chroming installation			
<sup>2</sup> Cold rolled strip is used as reference value for specific consumption figures			

Table A.3-22: Consumption and emission levels from the roll shop

### A.3.2.9 Hydraulic Fluids and Lubricants Management

On several places of the cold rolling mill, hydraulic systems or oiled and greased components are in operation. These systems are generally placed in oil-tight bunds or pits to prevent the oil from penetrating into water or soil in case of leakage.

Input / Consumption Level			
Cooling water		9.0 - 10	m <sup>3</sup> /t
Demineralized water		0.05 - 0.12	m <sup>3</sup> /t
Grease, oil, hydraulic oil		1.5 - 1.8	kg/t
Rolling oil		0.45 - 2.2	kg/t
Hydraulic + lubrication oils		0.2 - 0.9	kg/t
Energy:			
	Electrical	0.2 - 0.45	GJ/t
	Steam	0.04 - 0.05	GJ/t
Waste gas Output / Emission Level			
		Specific Emission	
Waste (disposed)			
	Used oil + water + rejects	3.0 - 50	kg/t
	Used oil + water	3.2 - 3.5	kg/t
Waste water		0.05 - 0.12	m <sup>3</sup> /t
Note: source of data [EUROFER CR]			

Table A.3-23: Consumption and emission levels from hydraulic fluid and lubricant systems



### A.3.2.10 Cold Rolling Mill Waste Water Treatment Plant

The following data refer to water discharge from the cold rolling mill as a whole as available data often does not distinguish the different sources of waste water.

	Continuous C-Steel	Reversing C-Steel	Reversing Stainless Steel
<b>Specific Waste water discharge</b>	0 - 40 m <sup>3</sup> /t	0 - 6 m <sup>3</sup> /t	(~0) - 35 m <sup>3</sup> /t
<b>Waste water discharge from WW-Treatment (excl. once-through cooling)</b>	0 - 12 m <sup>3</sup> /t		
<b>Total Suspended Solids <sup>1</sup></b>	7 - 120 mg/l 2.7 - 520 g/t	(~0) - 2210 mg/l (~0) - (~160) g/t	0 - 60 mg/l 0 - (~180) g/t
<b>COD <sup>1</sup></b>	19 - 5300 mg/l 5 - 220 g/t	15 - 100 mg/l 10 - 80 g/t	10 - 2000 mg/l 10 - 275 g/t
Note: Source of data [EC Study] <sup>1</sup> Unit changed from mg/m <sup>3</sup> to mg/l			

**Table A.3-24: Waste water discharge from cold rolling mills**



### A.3.2.11 Waste and Recycling

In addition to the information on waste generation for the individual sub-process, Table A.3-25 presents an overview of the waste generated in total by cold rolling operations and of the utilisation potentials. The reference base of the hot rolling mill as a whole was chosen, because a clear distinction of waste sources and attribution of waste amounts to individual processing steps is impossible in a number of cases.

Kind of waste/Source	Average Specific Mass [kg/t]	Reported Waste <sup>1</sup> [t] (steel production) <sup>2</sup>	Utilization	Percentage <sup>3</sup>
<b>Oil recovery sludges</b>	1	13150 (14 Mt)	Recycle in-plant Externally used <sup>4</sup> Sold <sup>5</sup> Landfill	50.3 33.7 3.6 12.4
<b>Acid regeneration sludges</b>	4.2	36200 (8.5 Mt)	Recycle in-plant <sup>6</sup> Externally used <sup>7</sup> Sold <sup>5</sup> Landfill	9.8 9.4 46.0 35.0
<b>Waste water treatment sludges</b>	3.3	114000 (19.9 Mt)	Recycle in-plant Externally used or sold <sup>5</sup> Landfill	32.5 1 66.5
<b>Dry dust from air cleaning devices Stainless steel rolling</b>	5.4	8200 (1.5 Mt)	Recycle in-plant Externally used <sup>5</sup> Landfill	38.5 42 19.5
<b>Oil, emulsion, grease</b>	1.3	17700 (8.7 Mt)	Recycle Externally incineration Landfill	42.8 34.4 22.8
<b>Dismantled refractories</b>		60	Externally used <sup>5</sup> Landfill	66 34
Note: data based on [EC Study]; figures given refer to dry material <sup>1</sup> Submitted as an answer to a questionnaire activity of the EU. <sup>2</sup> Steel production of the companies that provided information on utilisation. <sup>3</sup> Percentage refers to reported mass/ answered questionnaires. <sup>4</sup> 56 % incinerated, 44 % oil recuperation in dedicated plant <sup>5</sup> No indication on further use <sup>6</sup> EAF or blast furnace <sup>7</sup> For the production of iron oxides				

**Table A.3-25: Waste generated in cold rolling mills and utilisation rates**

### A.3.2.12 Noise Issues in Cold Rolling

→ No specific information for cold rolling submitted.



### A.3.3 Wire Plant

#### A.3.3.1 Mass Stream Overview

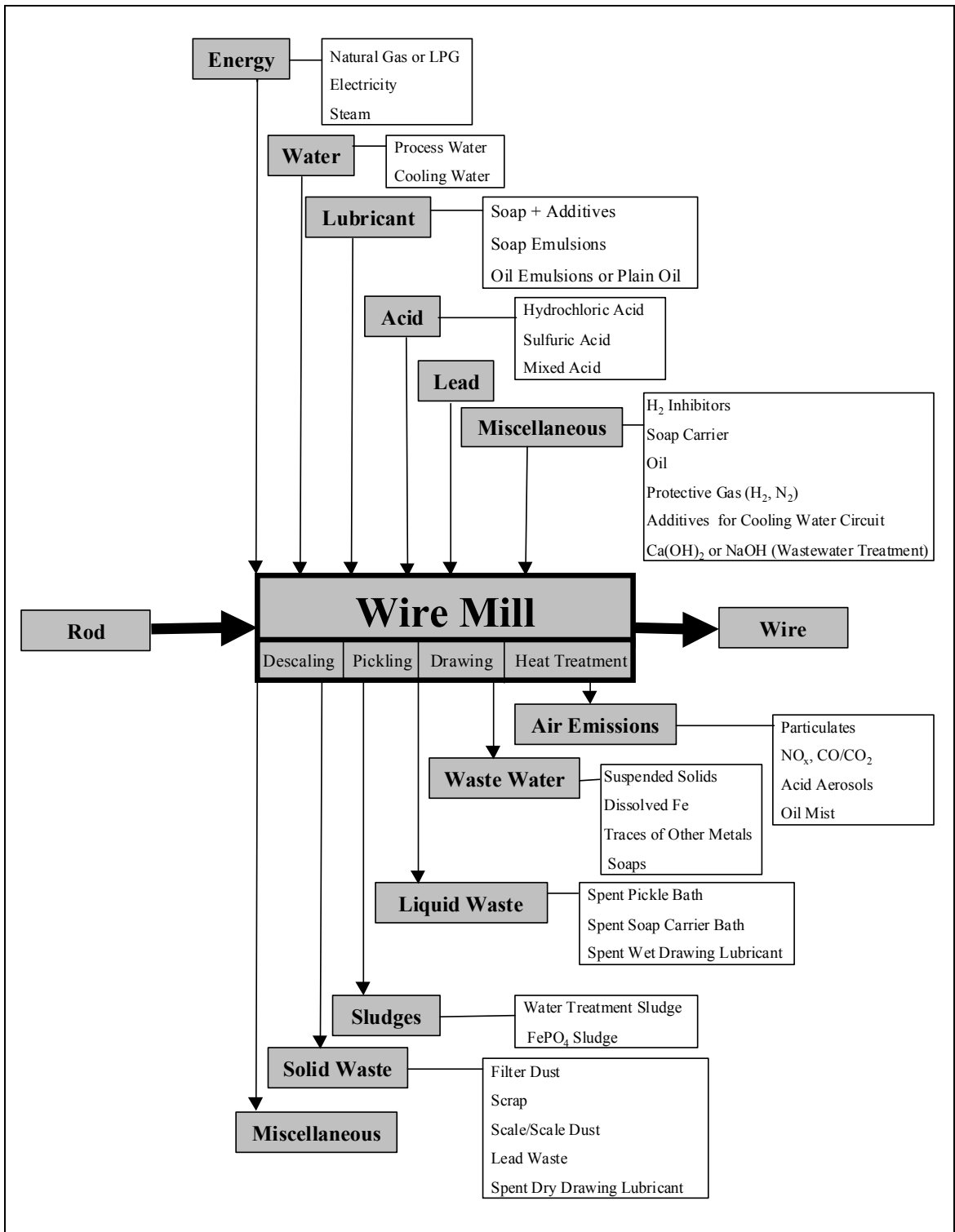


Table A.3-26: Input/Output balance for a wire mill

The subsequent chapters present input and consumption data, as well as output and emission data for individual operational steps associated with wire production (wire rod preparation, drawing, heat treatment process steps). It should be noted that specific consumption and emission data (expressed per tonne of product) can show huge variations with the wire diameter produced.

### A.3.3.2 Wire Rod Preparation

#### A.3.3.2.1 Mechanical Descaling of Wire Rod

Mechanical descaling brings about solid waste: scale, mainly consisting of iron oxide (FeO and Fe<sub>3</sub>O<sub>4</sub>) plus traces of other metal oxides, depending on the alloy elements and impurities in the wire rod. The most common wire descaling technique, wire bending, generates a relatively coarse scale, which generates only negligible amounts of dust.

Sanding, brushing and shot blasting generate a relatively fine scale and are equipped with a filter system to capture scale dust. When shot blasting is used, the scale is mixed with the fraction of the shot blasting media that is not recovered.

Scale is not contaminated with oil or water, in contrast to what is generally the case in the strip industry. Very fine scale (e.g. filter dust) represents a fire or explosion hazard.

<b>Abrasive methods:</b>		
<b>Input / Consumption Level</b>		
<b>Abrading material</b>		
<b>Output / Emission Level</b>		
	<b>Specific Emission</b>	<b>Concentration</b>
<b>Scale (iron oxide)</b>		
<b>Scale dust</b>		
<b>Wire bending:</b>		
<b>Output / Emission Level</b>		
	<b>Specific Emission</b>	<b>Concentration</b>
<b>Scale</b>	2 - 5 <sup>1</sup> kg/t	
Note: Source of data [Com BG] <sup>1</sup> depending on wire rod diameter and quality		

**Table A.3-27: Consumption and emission levels for mechanical descaling**

#### A.3.3.2.2 Chemical Descaling/Pickling of Wire Rod

In chemical descaling liquid waste is generated in form of spent HCl or H<sub>2</sub>SO<sub>4</sub> acid, largely converted to metal salts. Aerosols (small HCl or H<sub>2</sub>SO<sub>4</sub> particles) can form mechanically when the wire rod is allowed to drip off. Furthermore, fumes evaporate from the HCl bath and H<sub>2</sub> can form unless suppressed by an inhibitor. Acid fumes from the baths are evacuated. Sometimes scrubbing is needed, depending on type of acid and concentration. [Bekaert98]

Input / Consumption Level		
<b>Acid:</b>		
HCl (32 %) (no recovery)	15 – 25	kg/t
HCl (32 %) (with recovery)	n.a.	
H <sub>2</sub> SO <sub>4</sub> (98 %) (no recovery)	10 – 20	kg/t
H <sub>2</sub> SO <sub>4</sub> (98 %) (with recovery)	2.5 – 5	kg/t
<b>H<sub>2</sub> inhibitor</b>	0.01 – 0.1	kg/t
<b>Energy (mainly electricity):</b>		
Pumps, ventilation, lifting equipment etc.	n.a.	
Heating of acid (only H <sub>2</sub> SO <sub>4</sub> )	n.a.	
<b>Rinsing water</b> <sup>1</sup>	n.a.	
Output / Emission Level		
	Specific Emission	Concentration
<b>Emissions to air from</b>		
HCl pickling (acid vapour, droplets) <sup>6</sup>	n.a.	
H <sub>2</sub> SO <sub>4</sub> pickling (aerosols, droplets of acid) <sup>6</sup>	n.a.	
<b>Spent acid:</b>		
<b>HCl</b>	80 – 90 % <sup>2</sup>	
total Cl		200 - 275 g/l
Fe		100 - 160 g/l
<b>H<sub>2</sub>SO<sub>4</sub></b> <sup>3</sup>		
<b>Rinsing water</b>	10 – 20 % <sup>2</sup>	
<b>FeSO<sub>4</sub> x 7 H<sub>2</sub>O</b> <sup>4</sup>	20 – 35	kg/t
<b>H<sub>2</sub></b> <sup>5</sup>		
Note: Source of data [Com BG] <sup>1</sup> large variations from plant to plant depending on number of rinsing cascades, wire rod diameter and quality requirements <sup>2</sup> of consumed acid <sup>3</sup> No figures available for spent H <sub>2</sub> SO <sub>4</sub> if recovery by FeSO <sub>4</sub> -crystallisation is not used <sup>4</sup> from regeneration, 96 – 98 % pure; impurities: H <sub>2</sub> O, H <sub>2</sub> SO <sub>4</sub> and traces of metals depending on alloy elements in wire rod <sup>5</sup> Emission of H <sub>2</sub> is negligible if a correct H <sub>2</sub> -inhibitor is used. The use of inhibitors is normally limited to batch pickling. <sup>6</sup> Source [Stone]		

Table A.3-28: Consumption and emission levels for chemical descaling

### A.3.3.2.3 Application of Soap Carrier

Consumption and emissions associated with the application of soap carrier vary in dependence of the type of soap carrier, thickness applied and the wire rod diameter. No quantitative data is available at the moment.

When Zn-PO<sub>4</sub> coating is used, a thick FePO<sub>4</sub> sludge or cake is formed containing traces of zinc, soluble phosphates and chlorate or nitrite coming from the Zn-PO<sub>4</sub> bath. Also spent soap carrier bath may arise as liquid waste. If drying is done in gas - or fuel fired ovens, the usual combustion products are emitted. [Bekaert98]

<b>Lime and equivalent products:</b>	
<b>Consumption</b>	<b>Emissions</b>
<ul style="list-style-type: none"> <li>– lime milk (made from lime and process water)</li> <li>– steam or natural gas</li> <li>– water for compensation of heat losses</li> </ul>	<ul style="list-style-type: none"> <li>– spent lime milk baths (accumulation of impurities by dragin)</li> <li>– possible emmissions from heating.</li> </ul>
<b>Alkali-salts and mixtures of alkali salts</b>	
<b>Consumption</b>	<b>Emissions</b>
<ul style="list-style-type: none"> <li>– alkali salt (mixture)</li> <li>– water/water for compensation of heat losses</li> <li>– possibly steam</li> </ul>	<ul style="list-style-type: none"> <li>– spent soap carrier baths (accumulation of impurities by dragin)</li> <li>– possibly emissions from heating</li> </ul>
<b>ZnPO<sub>4</sub> and equivalent products</b>	
<b>Consumption</b>	<b>Emissions</b>
<ul style="list-style-type: none"> <li>– concentrated mixture of Zn, H<sub>3</sub>PO<sub>4</sub> and additive</li> <li>– water/water for compensation of heat losses</li> <li>– steam for heating</li> </ul>	<ul style="list-style-type: none"> <li>– FePO<sub>4</sub> sludge</li> <li>– rinsing water</li> <li>– <i>Bath liquid is normally never discharged.</i></li> </ul>

**Table A.3-29: Consumption and emission levels for the application of soap carrier**  
[Com BG]

### A.3.3.3 Drawing of Wire

#### A.3.3.3.1 Dry Drawing

Dry drawing activities leave spent lubricant, mainly consisting of the drawing soap itself (typically alkali-salt of natural fatty acid + additives) contaminated by degradation products, caused by heating of lubrication in the dies, soap carrier and metal particles, like Fe or Zn depending on the surfaces of the wire). From the drawing activity also soap dust arises, which can be controlled by proper encapsulation and filtering of the extracted air. Traces of soap may also contaminate the cooling tower blow down, if the drawing machine is not well maintained. Furthermore, waste arises in from broken dies. [Bekaert98]

<b>Input / Consumption Level</b>		
<b>Dry drawing lubricant</b> (preformulated alkali soap + additives)	1 - 4 kg/t	
<b>Electric energy for drawing machine...</b> <sup>1</sup>	n.a.	
<b>Cooling water</b>	n.a. (huge variation)	
<b>Output / Emission Level</b>		
	<b>Specific Emission</b>	<b>Concentration</b>
<b>Spent soap + evt. filter dust of soap filter system</b>	1 - 4 kg/t	
<b>Soap dust emission</b>	n.a.	
<b>Cooling water</b>	n.a.	
<b>Broken dies</b>	not significant	
Note: Source of data [Com BG], data per tonne of drawn wire <sup>1</sup> no figure available, huge variation, dependent on diameter, ratio initial / final diameter and type of steel.		

**Table A.3-30: Consumption and emission levels for dry drawing**



### A.3.3.3.2 Wet Drawing

Wet drawing is done in a watery emulsion of soap or oil. This emulsion is gradually contaminated by drag-in of various products from previous process steps, by dissolution or abrasion of metal from the wire surface (Fe or other metals if the wire is coated in a previous step), and by thermal or biological degradation. The result is that the wet drawing lubricant needs to be replaced from time to time; the replacement frequency can be lowered by continuous removal of some of the contaminants by decantation or filtration.

Other waste streams are broken dies and cooling tower blowdown, which could be contaminated by traces of emulsion if the heat exchanger is not properly maintained.

Cooling water contamination occurs much less frequent with wet drawing machines than with dry drawing machines.

No figures are available for wet drawing in plain oil; the percentage of wire tonnage which is drawn in oil, is rather small. If wire is drawn in plain oil, oil aerosols do not occur. All moving parts are submersed in oil; the wire is wiped at the exit of the drawing machine. [Com BG]

Input / Consumption Level		
<b>Preformulated concentrated soap emulsion or oil emulsion</b>	1 - 10	kg/t
<b>Dilution water for wet drawing lubricant</b>	20 - 250	l/t
<b>Electric energy for drawing machine...</b>	n.a.	
<b>Cooling water</b>	n.a. (huge variation)	
Output / Emission Level		
	Specific Emission	Concentration
<b>Spent Wet Drawing Emulsion</b> (including sludge removed by filtration / decantation)	20 - 250 l/t	
<b>Suspended Solids</b>		
<b>COD</b> (fatty acid soap or oil, surfactants, other additives)		20 - 80 g/l
<b>Metals</b> (Fe for wet drawing of bright wire, other metals for wet drawing of coated wire)		0.2 - 1 g/l
<b>Cooling water</b> <sup>2</sup>	n.a.	
<b>Broken dies</b>	n.a.	
Note: Source of data [Com BG], data per tonne of drawn wire <sup>1</sup> no figure available, huge variation, dependent on diameter, ratio initial / final diameter and type of steel. <sup>2</sup> Note: Cooling water contamination occurs much less frequent with wet drawing machines than with dry drawing machines.		

**Table A.3-31: Consumption and emission levels for wet drawing**



### A.3.3.4 Heat Treatment of Wire

#### A.3.3.4.1 Batch Annealing/Bell and Pot Furnaces

Emissions from batch annealing furnaces comprises the combustion products from the firing and a small flow of the protective atmosphere (purge) containing decomposition products of the lubricant. These are formed by pyrolysis/cracking of the lubricant molecules; typical decomposition products are low molecular weight olefins and alkanes.

The cooling water is not contaminated and can be used for cooling of some parts of the furnace. [Bekaert98], [CET-BAT]

Input / Consumption Level		
Energy (gas, fuel, electricity)	n.a.	
Inert gas (H <sub>2</sub> , N <sub>2</sub> , H <sub>2</sub> /N <sub>2</sub> -mixture, partially oxidized gas)	n.a.	
Cooling water	n.a.	
Oil (if applied)	n.a.	
Output / Emission Level		
	Specific Emission	Concentration
Combustion products	n.a.	
Cooling water	n.a.	
Spent inert gas <sup>1</sup>		
Note: No figures are available for annealing of wire, but they are assumed to be similar to those for annealing in a hood-type furnace used for strip, although the unit size is much smaller in the wire business. [Com BG]		
<sup>1</sup> Normally all spent protective gas is burnt.		

Table A.3-32: Consumption and emission levels for bell and pot furnaces

#### A.3.3.4.2 Continuous Annealing/Molten Lead Bath

Continuous annealing in a lead bath is composed of a lead bath followed by quenching in water. This process leads to solid wastes in the form of lead oxides and lead contaminated bath cover material. Waste water is formed as overflow of the quench bath; this stream contains some of Pb. Emissions to air occur in form of dust (bath cover material, including small amounts of Pb) and soap pyrolysis products (VOC, CO, etc.). [Com BG]

Often, this heat-treatment step is followed by continuous pickling in a HCl bath. Due to the short residence time, heated and concentrated HCl is used. HCl-fumes are removed by scrubbing from the gaseous outlet streams of the HCl-bath. Liquid waste generated are spent acids, partially converted to metal salts and contaminated by iron, lead, traces of other metals and inorganic suspended solids; quench water also contaminated by lead (magnitude mg/l). Waste waters occur as rinsing water from the rinsing cascade after the HCl-bath and from the scrubber. [Bekaert98], [Com BG]

Input / Consumption Level		
Lead	1 – 15 <sup>1</sup>	kg/t
Energy for heating the lead bath (gas, fuel)	n.a.	
Quench water	1 - 3	m <sup>3</sup> /t
Output / Emission Level		
	Specific Emission	Concentration
Lead waste (lead oxides + spent bath cover)	1 – 15 <sup>1</sup> kg/t	
Quench water overflow (containing Pb and suspended solids)	0.5 – 2.5 m <sup>3</sup> /t	n.a.
	SS	2 - 20 mg/l
	Pb	
Emissions of lead bath:	Pb	0.02 - 5 mg/m <sup>3</sup>
	Dust	1 – 30 mg/m <sup>3</sup>
	TOC	1 - 50 mg/m <sup>3</sup>
Emissions from heating the lead baths (typical emissions of standard heating process)		
Note: Source of data [Com BG], data per tonne of wire		
<sup>1</sup> extreme figures apply to fine wire		

Table A.3-33: Consumption and emission levels for lead baths

Input / Consumption Level		
HCl (expressed as 32 % HCl)	10 - 100	kg/t
Energy for heating the HCl-bath <sup>1</sup>	n.a.	
Scrubber / rinsing water	0.5 - 5	m <sup>3</sup> /t
Output / Emission Level		
	Specific Emission	Concentration
Spent HCl <sup>2</sup>	5 - 100 l/t	
	Total Cl	150 – 275 g/l
	Fe	60 - 125 g/l
Scrubber/rinsing waste water	0.5 - 5 mg/m <sup>3</sup>	
HCl (emissions from scrubber)		0 – 30 <sup>3</sup> mg/m <sup>3</sup>
Lubricant burn-off		
Waste water		
Dust		
Note: Source of data [Com BG], data per tonne of pickled wire; the figures for HCl-pickling are also +/- representative for other continuous HCl pickling process steps.		
<sup>1</sup> often the bath is heated by residual heat in the wire		
<sup>2</sup> spent acid contains Cl, Fe and other contaminants depending on previous processing steps, e.g. soap residues, pickled soap carrier, Pb...		
<sup>3</sup> small sources (< 300 g/h) can have higher concentrations, as in most countries, small sources only have to comply with a limit for mass flow		

Table A.3-34: Consumption and emission levels for in-line HCl pickling

### A.3.3.4.3 Patenting

For a patenting line consisting of a furnace with direct contact between wire and combustion gases, a lead bath and a quench bath, wastes and emissions are as follows:

Air emissions arise from the furnace. The furnace is heated to 850 - 1000 °C using natural gas (or a similar sulphur-free fuel) and with a slight O<sub>2</sub>-shortage. Fresh air is mixed with the hot exhaust gas of the oven in order to convert the CO to CO<sub>2</sub>, prior to emission into the

atmosphere. NO<sub>x</sub> and SO<sub>2</sub> are negligible in this stream: reducing atmosphere/fuel is free of sulphur.

The lead bath is used for cooling; in contrast to a lead bath used for annealing, there is no burning of residual lubricant, so the emissions to air are limited to dust (bath cover material, containing traces of Pb).

Solid waste is generated by the lead bath as lead oxides and spent bath cover material. Waste water is formed in the quench bath. Some installations need cooling water for cooling of moving parts that are in contact with the hot wire. [Com BG]

Input / Consumption Level		
<b>Lead</b>	1 - 10	kg/t
<b>Energy</b> (for heating the furnace and for heating the lead bath during start-up and stand-by periods)	n.a.	
<b>Quench water</b>	1 - 3	m <sup>3</sup> /t
<b>Cooling water</b>	0 - n.a.	
Output / Emission Level		
	Specific Emission	Concentration
<b>Lead waste</b> (lead oxides + spent bath cover)	1 - 10 kg/t	
<b>Quench water overflow</b> (containing Pb and suspended solids)	0.5 - 2.5 m <sup>3</sup> /t	n.a.
<b>SS</b>		2 - 20 mg/l
<b>Pb</b>		
<b>Stack emissions from lead bath:</b>		
<b>Pb</b>		< 0.02 - 1 mg/m <sup>3</sup>
<b>Dust</b>		1 - 30 mg/m <sup>3</sup>
<b>Stack emissions from the furnace:</b>		
<b>CO</b>		50 - 300 mg/m <sup>3</sup>
<b>NO<sub>x</sub>, SO<sub>2</sub></b>		negligible
Note: Source of data [Com BG], data per tonne of wire		

**Table A.3-35: Consumption and emission levels for patenting [Bekaert98]**

#### A.3.3.4.4 Oil Hardening & Tempering

An oil hardening and tempering line consists of a heating step under protective gas, quenching in oil or water, and reheating in a temper oven. Waste and emissions are dependent on the method of heating, the quench medium and the reheating method. This, in combination with the broad diameter range of products, makes it impossible to present general figures for an oil hardening and tempering line. [Com BG]

Input / Consumption Level	
<b>Energy for heating</b> (electricity, and/or natural gas)	
<b>Protective gas</b>	
<b>Quenching medium</b> (oil, water, additives)	
<b>Lead</b> (if applied)	
<b>Cooling water</b>	
Output / Emission Level	
Using a lead bath:	<b>lead waste</b>
Quenching with water:	<b>waste water</b>
Quenching with oil:	<b>waste quench oil</b> <b>emission to air of oil aerosols</b>
Heating with natural gas:	<b>exhaust gas of normal combustion process</b>
<b>Burnt protective gas stream</b>	

**Table A.3-36: Qualitative input / output balance for oil hardening**

### A.3.3.4.5 Annealing of Stainless Steel Wire

A quantitative mass balance cannot be given (lack of data / small tonnage when compared to plain steel/high variation due to variation in diameter and stainless steel composition).

<b>Input / Consumption Level</b>
<b>Energy:</b> gas (fuel), electricity
<b>Inert gas:</b> H <sub>2</sub> , N <sub>2</sub> , H <sub>2</sub> /N <sub>2</sub> -mixture
<b>Cooling water</b>
<b>Output / Emission Level</b>
<b>Combustion products</b>
<b>Cooling water</b>
Source [Com BG] Note: normally all spent protective gas is burnt

Table A.3-37: Qualitative input / output balance for annealing of stainless steel

### A.3.3.4.6 Stress Relieving

The most important application is stress relieving of PC-strand: reinforcement wire that will be used in prestressed concrete. Normally inductive heating is used as heating technique.

<b>Input / Consumption Level</b>
<b>Electric energy</b> for the inductive heating coil and possibly for a soaking zone
<b>Cooling water</b> for equipment and wire
<b>Output / Emission Level</b>
<b>Cooling water</b>
Source [Com BG]

Table A.3-38: Qualitative input / output balance for stress relieving

### A.3.3.5 Noise Issues in a Wire Plant

Excessive noise is primarily an internal occupational health issue, with precautions normally taken to protect employees where it is not practical to prevent or reduce noise at the source. In some instances, depending on the location of the process and noise characteristics, depending on local off-site aspects (other noise sources, nearby residential area,...), and depending on local plant aspects (noise reduction by the building structure), there can be a concern for noise off-site.

The main sources of noise in wire processes are:

- Rotating equipment, e.g. wet drawing machines; dry drawing machines; take-up units and pull-through units on coating lines.
- Air-wipes or air-brushes which clean the wire using compressed air can have a high frequency noise.
- Pay-off units of wire rod have a particular repetitive noise.
- Burners of ovens.

These operations are typically continuous operations and are operated inside a building. In this way, the impact outside the building is minimized to such an extent, that noise generated by these operations rarely is an issue when concerning noise off-site.

Case studies show that non-process sources outside the building, such as ventilation or plant utilities, are the main concern in wire plants located close to e.g. a residential area. Measures such as relocation, insulation or local enclosure can be considered for this last category of sources.





## A.4 TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BAT FOR HOT AND COLD FORMING

In this section techniques for environmental protection and energy saving measures are given for the individual processing steps. A description of each technique, the main achieved emission levels, the applicability, the monitoring of emissions, cross-media effects, reference plants, operational data, economics and driving force for the implementation are given where these data are available and pertinent.

Some of the techniques listed here aim predominantly at improving product quality and increasing yield. As these measures also have an environmental impact (reduced scrap, reduced energy consumption, less emissions) they are covered here as well, although their reduction potential may only be limited.

### A.4.1 HOT ROLLING MILL

#### A.4.1.1 Storage and Handling of Raw Materials and Auxiliaries

**Description:**

**Oil:** Spillages of oil may occur at storage tanks and from pipelines. Such spillages are drained to pump sumps, from where the oil, grease water mixture may be fed to intermediate waste oil storage tanks. Discharge of filled tanks may be carried out via authorised external companies or, in the case of integrated plant sites, by internal thermal treatment plants or via the blast furnace or coke ovens.

Accidental releases of hydrocarbons are prevented by periodic checks and preventive maintenance of seals, gaskets, pumps and pipelines.

Contaminated drainage water at the various consumers (hydraulic aggregates) should be collected and may be pumped into intermediate storage tanks. The waste oil, after separation from water, should be reused or utilized, e.g. by injection into the blast furnace or by external recycling. To allow for reuse, the separated oil has to be recovered in sufficient quantities and in a form suitable for reuse; the chemical composition and the physical properties (e.g. viscosity) of the recovered (used) oil have to be the same as of the new oil. The separated water may be further processed in a water treatment plant, e.g. with ultra filtration or vacuum evaporator (e.g. of industrial washing machines).

Complete prevention of water and scale contamination by hydrocarbons (oils and grease) is, even by applying precautionary measures, almost impossible.

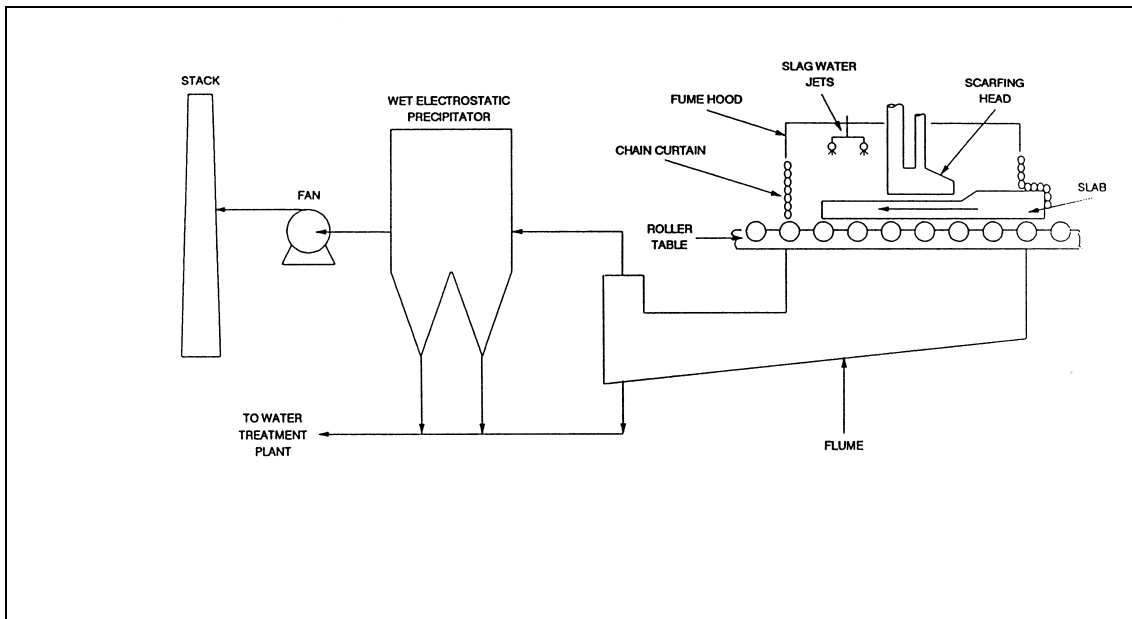
#### A.4.1.2 Surface Rectification and Conditioning of Input

##### A.4.1.2.1 Enclosed Scarfing Operation with Wastegas Cleaning

**Description:**

As shown in Figure A.4-1, scarfing takes place in a tightly closed hood, which captures the fume and dust generated by the oxy-fuel flame. The waste air is cleaned by **dry** or **wet electrostatic precipitators** or **fabric filters**. The collected dust is internally recycled within integrated steel works or disposed of by authorised companies.

Water jets are used to remove the slag from the conditioned surface. Spent water and slag are collected in a flume beneath the roller table and transferred to water treatment.



**Figure A.4-1: Scarfing abatement flowsheet (example with wet EP)**  
[HMIP]

**Main achieved environmental benefits:**

- Reduced fugitive air emissions/dust.

**Applicability:**

- New plants (difficult to implement in existing plants due to problems with structures of buildings).
- Not applicable for manual scarfing.

**Cross-media effects:**

- Increased energy consumption.
- Generation of waste / filter dust or sludge which is collected.
- Waste can be reduced by internal recycling.

**Reference plants:**

SIDMAR, Aceralia (Avilés)

**Operational data and economics:**

**Example SIDMAR:**

The scarfing machine is located in a special building (dimensions 32 m x 18 m x 9 m) with acoustic insulated sidewalls leading to a maximum noise level of 85 dBA at 1 m. The fume is captured at the 4 corners of the roof. The complete installation is operated under suction with an aspiration flow of 200000 m<sup>3</sup>/h. The aspiration is controlled automatically as a function of the place where the scarfing takes place (2/3 of fumes are aspirated above the work area). The exhaust air is cleaned by fabric filters with filter area of 3576 m<sup>2</sup> leading to an exit dust concentration of 5 – 10 mg/Nm<sup>3</sup> (continuous optical measurement in stack).

		Year of Installation	Waste Gas Volume [m <sup>3</sup> /s]	Particulate Emission [mg/m <sup>3</sup> ]	Energy Consumption <sup>1</sup> [kWh/1000m <sup>2</sup> ]	Costs EURO '000
a	Wet EP (Billet Scarfer)	1973	32	20 - 115		
b	Wet EP			< 20		
c	Wet EP	1988	approx. 60	30 - 80		n.a.
a	Dry EP (Slab Scarfer)	1986	30	20 - 115		
b	Dry EP			< 50		420
d	Bag filter	data: 1998	30	< 10		
b	Bag filter		Ø 42 max. 55	< 20	155	I <sup>2</sup> : 2200 O <sup>1,3</sup> 0.058
e	Bag filter		55.6	5 - 10		

Note: ESP = Electrostatic Precipitator; I = Investment costs; O = Operational costs  
a: [EUROFER HR]  
b: [CITEPA], levels were reported BAT levels of the air-BAT-note  
c: [Input-HR-1]  
d: [DFIU98]  
e: Company information SIDMAR  
<sup>1</sup> Reference base 1000 m<sup>2</sup>-scarfed  
<sup>2</sup> Investment costs given for complete installation, incl. civil engineering, filter (filter area: 3200 m<sup>2</sup>), hood, ventilators, motors, pipes, control measurement devices etc.  
<sup>3</sup> Operational costs for full capacity, 60 % manpower

**Table A.4-1: Operational data and achievable emission levels for dust from scarfing operation**

As the fume generated by scarfing is very corrosive, maintenance is an important issue for good performance of the abatement units. Regular inspection of precipitator electrodes, associated internals etc. is recommended to survey corrosion.

If the fume is very wet, bag filters might be problematic. [Com HR]

**Driving force for implementation:** prevention of fugitive emissions. [Com HR]

**Reference literature:**

#### A.4.1.2.2 Enclosed Grinding Operation with Waste Gas Cleaning

##### Description:

The dust created by grinding operations is collected and precipitated in **bag filters**. Manual grinding is carried out in dedicated booths, equipped with collection hoods. Machine grinding is carried out in soundproofed, complete enclosures. The abatement unit, in both cases, is either stand-alone or shop based.

The collected dust is internally recycled within integrated steelworks or disposed of by authorised companies.

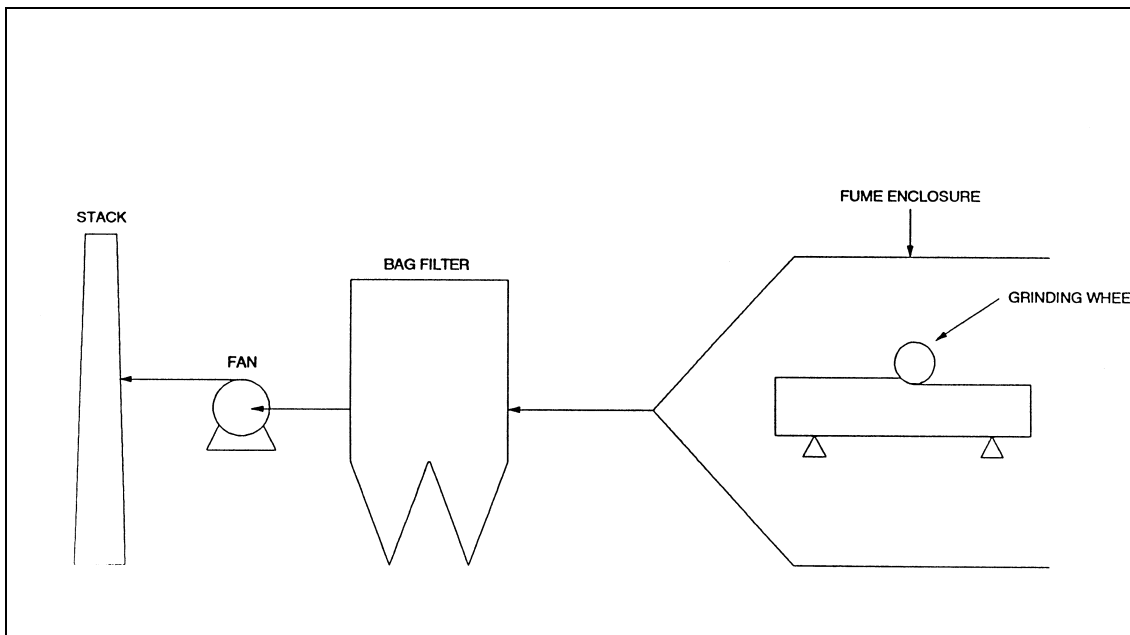


Figure A.4-2: Grinding abatement flowsheet [HMIP]

**Main achieved environmental benefits:**

- Reduced fugitive air emissions/dust.
- Noise is reduced.

**Applicability:**

- New Plants.

**Cross-media effects:**

- Increased energy consumption.
- Generation of waste / filter dust which is collected.
- Waste can be reduced by internal recycling.

**Reference plants:**

**Operational data:**

		Year of Installation	Waste Gas Volume [m <sup>3</sup> /s]	Particulate Emission [mg/m <sup>3</sup> ]	Energy Consumption <sup>1</sup> [kWh/1000m <sup>2</sup> ]	Costs EURO '000
a	Compact Cell Filter <sup>2</sup>	1980 - 1989	2.5	20 - 100		
a	Pulse Jet Filter <sup>3</sup>	1995	7	< 30		

a: [EUROFER HR], reported typical operational data and emission levels [Com2 HR]  
<sup>1</sup> Reference base 1000 m<sup>2</sup>-ground  
<sup>2</sup> Bag area 120 m<sup>2</sup>  
<sup>3</sup> Bag area 234 m<sup>2</sup>

Table A.4-2: Operational data and achievable emissions for dust reduction from grinding

**Economics:**

**Driving force for implementation:** Prevention of fugitive emissions. [Com HR]

**Reference literature:**

### A.4.1.2.3 CAQC - Computer Aided Quality Control

#### Description:

Computer aided quality control is applied to enhance the quality of the continuous casting output, thus reducing surface defects in the rolled product. A computer model observes and controls the casting conditions based on various peripheral measurements. Each change in the operation parameters leads to a new pre-setting of the machine for an optimised casting process. Changes in the casting conditions, which cannot be corrected by the control loop and may lead to surface defects, are recognised and visualised by the system so that the location of a possible fault is well known. Subsequently, selective (manual) scarfing of the damaged areas is possible instead of automatically scarfing the total slab.

#### Main achieved environmental benefits:

- Reduction of air emissions and waste from scarfing, because selected scarfing is possible.
- Energy consumption for scarfing process is reduced.
- Enhanced surface quality, reduction of scrap.

	Without CAQC	With CAQC
Machine scarfed	32 %	9 %
Inspection and selective scarfing	68 %	8 %
No inspection no scarfing		83 %

**Table A.4-3: Comparison of amount of scarfing with/without CAQC [DFIU98]**

#### Applicability:

- New and existing plants with continuous casting [Com HR].

#### Cross-media effects:

#### Reference plants:

- VA Stahl Linz, Austria.
- EKO Stahl, Germany [Com A].

#### Operational data:

#### Economics:

Only very limited data on economics were reported.

One source reported investment costs of EUR 4 m, Voest [Input-HR-1]; while another reported savings of 5 \$ per tonne of steel [Com A] in connection with implementation of CAQC.

#### Driving force for implementation:

- Improved quality of hot rolled product, increased yield.
- Reduction of slab conditioning costs [Com A].

#### Reference literature:

Aspects of modern quality control for continuous casting, 3<sup>rd</sup> European Conference on Continuous Casting, Oct. 20 – 23, 1998 [Com A]

#### A.4.1.2.4 Rolling of Wedge-type Slabs

**Description:**

Instead of flame cutting, wedge-type slabs are rolled under special settings of the hot rolling mill. The wedge is either eliminated by edging technology (automatic width control or sizing press) or by trimming during the subsequent shearing of hot strips.

**Main achieved environmental benefits:**

- Emissions and wastes normally generated by flame cutting are avoided.

**Applicability:** new plants and existing plants in case of major revamping [ComHR]

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### A.4.1.2.5 Slab Slitting

**Description:**

In order to improve caster productivity, the slabs are often cast in multiple widths. The slabs are slit before hot rolling by means of slitting devices, slit rolling or torches either manually operated or mounted on a machine. In that way, wedge-type slabs are prevented.

**Main achieved environmental benefits:**

- Emissions and waste arising from wedge correction are prevented.

**Applicability:**

**Cross-media effects:**

- Additional energy consumption [Com A].

**Reference plants:**

- Krakatau Steel [Com A].

**Operational data:**

This technique requires an improved quality of centre segregation.

Gas consumption 1.6 Nm<sup>3</sup>/t slab

Oxygen consumption 2.7 Nm<sup>3</sup>/t slab

Yield loss 1.4 0 3.0 % of slab weight, depending on slab dimensions [Com A]

**Economics:**

**Driving force for implementation:**

Higher caster capacity as twin or triple casting [Com A]

**Reference literature:**

### A.4.1.3 Reheating and Heat Treatment Furnaces

#### A.4.1.3.1 General Measures for Energy Efficiency and Low Emission Operation

##### Furnace design

The design of the furnace and the degree of insulation have a significant effect on the thermal efficiency. The furnace as a whole, the number and the installed capacity of the burners should be carefully calculated starting from several realistic production scenarios. Different heating temperatures of the stock, differences in production rhythm caused by changes in the dimensions of the stock or as a result of changes in the production rhythm of the hot mill as well as periods where hot or direct charging is applied have to be taken into account. [EUROFER HR]

The appropriate equipment should be available to limit the emissions and the energy consumption in case of a sudden line stop. This means that temperature can easily be turned down or burners switched off in certain furnace sections. In the latter case, a N<sub>2</sub>-purge might be necessary for safety reasons. [EUROFER HR], [Com HR]

Generally, the following recommendations should be considered, preferably in the design process:

- Incorporation of a stock recuperation zone in the furnace, with the unfired preheating section being large enough to ensure a maximum recovery of the heat of the flue gases.
- Radiant burners in the roof of the furnace, due to quick dissipation of energy, produce lower NO<sub>x</sub> levels.
- Return of the flue gases into the burners influences the NO<sub>x</sub> emission level.
- Insulation properties of the refractory material are important, therefore constructional measures should be taken to increase the life of the refractory material, as damage in the refractory material cannot be repaired immediately.
- Use of low thermal mass refractory material can reduce stored energy losses and reduce light-up energy and time [ETSU-G76]. Ceramic fibres are generally cheaper than pre-cast concrete modules and have good insulating properties. However, following a European Directive, their use is or will be limited because they may cause cancer by inhalation. In new condition the fibres are dust-producing when being manipulated and may cause some skin irritation. After heating, cristoballite is formed which is suspected to cause cancer. Nevertheless, new ceramic fibres are also considered suspect [Com2 HR].
- Improved air-tightness of furnaces and installation of specially designed doors, to reduce tramp air [ETSU-G76].
- Door areas and/or charge and discharge door gaps should be minimized, use of insulating refractory curtains for times when doors are necessarily open (provided that excessive mechanical damage to stock can be avoided) [ETSU-G76].
- Measures such as skid mark compensation or skid shifting, avoid skid marks and allow lower heating temperature [EUROFER HR].

##### Waste Heat Recovery

The heat contained in the gases leaving the reheating furnace normally constitutes the main energy loss. Three basic principles of heat recovery options should be considered:

- (a) Minimizing energy lost in the exhaust gases.
- (b) Recycling the exhaust gas energy back to the furnace.
- (c) Using the exhaust gas energy for other purposes ('external').

As mentioned under furnace design, energy loss in exhaust gases can be minimized by creating a large temperature gradient along the length of the furnaces, removing the exhaust gas at the

cold (discharge) end and using the heat for stock recuperation. Using exhaust gas energy outside the furnace usually implies the generation of steam, which might be used elsewhere in the plant. Utilising the exhaust gas energy within the furnace comprises basically three heat recovery systems: regenerative burners, self-recuperative burners and recuperators, which are presented in more detail later on. [ETSU-G76]

### Operation & Maintenance

The furnace should be run with 'good craftsmanship'. Even sophisticated installations can give poor results in emission and thermal efficiency if the process is not properly operated and if the installations are not maintained on a regular basis. Experience has shown that good housekeeping can lead to fuel savings of up to 10 %. [ETSU-G76]

Turbulence in the flame of the burners should be avoided. Investigations showed a marked increase of the NO<sub>x</sub> production by temperature fluctuations compared to the NO<sub>x</sub> values produced by a steady flame operating at the same mean temperature. The control system should therefore be appropriate.

Air excess is also an important factor for the control of the NO<sub>x</sub> emission level, the energy consumption and the formation of scale. The air excess should be minimized without excessive CO emission. Special care should be taken to avoid the presence of tramp air, which increases the energy consumption as well as the NO<sub>x</sub> emission. A mass spectrometer is useful in keeping the air/gas ratio at an optimal level for fuels with variable or unknown composition. [EUROFER HR]

Heat stored in the refractories is supplied during light-up period and the first production shift. During continuous operation this stored heat is usually regarded as negligible. When down-shift practices are employed (e.g. at weekends) or when furnaces are deliberately cooled for maintenance reasons, these energy losses can become an important factor as this energy has to be put in during furnace heat-up for the next production period. For two cases, stored energy losses during weekend plant shut-down were reported: 0.409 GJ/m<sup>2</sup> and 0.243 GJ/m<sup>2</sup>. During production stoppages and weekends, doors should be closed and sealed to retain the heat. The use of low thermal mass refractories can reduce light-up time, energy consumption and operating costs. [ETSU-G76]

### Choice of fuel

Integrated steel works normally utilise gases from the coke oven plant, the blast furnace or the basic oxygen furnace, sometimes in mixture with natural gas. Non-desulphurised coke oven gas and S-containing liquid fuel (including liquefied petroleum gas (LPG) and all types of oil (distillate and residual) and emulsion) are the major sources of SO<sub>2</sub> emission from re-heating furnaces. If required, desulphurisation ought to be performed at the gas producing and providing plants (e.g. coke oven battery). The use of liquid fuel is sometimes necessary to continue operations during a temporary stop in the supply of gaseous fuels, which can result in elevated sulphur oxide emission. Limiting the sulphur content in fuel oil is one measure to reduce SO<sub>2</sub> emissions. Where possible, the use of plant gases should be maximised, which minimizes the use of valuable natural resources and the need to flare the plant gases.

SO<sub>2</sub> emission is directly related to the S-content of the fuel. Due to the different ratios of the volume of the flue gases to the volume of the fuel gas for different fuels, a comparable S-content in 2 different fuels can result in marked differences in the SO<sub>2</sub> content in the flue gases.

Depending on the fuel used the following SO<sub>2</sub> levels are achieved:

- natural gas < 100 mg/Nm<sup>3</sup>
- all other gases and gas mixtures < 400 mg/Nm<sup>3</sup>
- fuel oil (< 1 % S) up to 1700 mg/Nm<sup>3</sup>



Techniques for efficient combustion are based on burner design, the method of atomisation and control of air supply. A control system is required to govern the fuel and air supplies and is important in air pollution control. It is important that the atomisation of oil fuels is efficient, and the primary consideration will be the viscosity of the fuel fed to the burners. [EUROFER HR]

With regard to NO<sub>x</sub> formation, the individual combustion gases also show a different behaviour. For instance, waste gas from coke-oven gas firing contains 50 to 100 % more NO<sub>x</sub> than the waste gas from natural gas firing.

The composition of the fuel is related to the flame temperature. Methane (natural gas) burns relatively slowly compared to fuels with a high H<sub>2</sub> - content (e.g. coke oven gas) that tends to burn more quickly with a higher NO<sub>x</sub> emission level (up to 70 % higher). The type of burner should be appropriate for the available fuel(s). [EUROFER HR]

#### A.4.1.3.2 Furnace Automation / Furnace Control

##### **Description:**

With the help of a process computer the heating process can be optimised (e.g. no unnecessary overheating of slabs during interruptions, more accurate temperature control) in accordance with material quality and dimensions. At the same time, parameters such as the proportion of combustion air, are controlled more exactly. [EUROFER HR]

**Furnace pressure control:** If the furnace pressure is below atmospheric pressure, cold air will be drawn into the chamber through doors and openings. Conversely, if it is above atmospheric pressure, hot gases will be forced out through the same openings. For reasons of energy efficiency, consistency of operation and product quality furnaces, are usually operated at a slight positive pressure compared with the outside air. [ETSU-G76] Another reason to maintain a slightly positive furnace pressure is for safety; to prevent air ingress which might provide an explosive mixture if fuel/gas were ignited, especially on start-up. [Com HR]

**Air/fuel ratio control:** Control of the air/fuel ratio is necessary to regulate the quality of the combustion, as it secures flame stability and complete combustion. Adjusting the air/fuel ratio as close as possible to stoichiometric conditions results in higher fuel efficiency and reduced exhaust gas energy losses. Measurements of the oxygen concentration in the combustion products in the furnace can be used to provide a signal to trim air/fuel ratio control systems (**Oxygen Trim Control**). [ETSU-G76]

##### **Main achieved environmental benefits:**

- Reduced energy consumption.
- NO<sub>x</sub> reduction.

##### **Applicability:**

- New and existing continuous reheating furnaces.

**Cross-media effects:** - no negative effects on other media are known.

##### **Reference plants:**

Roundwood Coil Bar Mill, Rotherham Engineering Steels Ltd, UK  
 British Steel, Teesside, UK  
 Benteler AG, Dinslaken, Germany [StuE-116-11]

**Operational data and economics:****Example Oxygen Trim Control**

A system using zirconia-based oxygen measuring cells has been installed at Rotherham Engineering Steels' walking beam furnace which is used for reheating square billets from cold to 1200 °C. The 110 t/h capacity furnace operates 6 independently controlled temperature zones. It is usually fired by natural gas, but with heavy fuel as an alternative during interruptions in gas supplies. The oxygen trim resulted in a lower average oxygen concentration in the furnace than with conventional air/fuel ratio control. Energy savings of about 2 % were achieved: although the reduction in oxygen content suggests that savings of around 4.7 % could realistically be achieved, this potential has been reduced by an increase of temperature in the heating zones. Additional benefits included improved product quality and reduced maintenance costs. [ETSU-FP15], [ETSU-G77]

Energy reductions of 2 % were equivalent to an approximate fuel cost saving of £ 26000/y, giving a simple payback time of 1 year on the initial investment of £ 26572 (reference year 1989). [ETSU-FP15]

**Example Computer-Controlled Furnace Management**

Computer-controlled furnace management installed at two pusher-type furnaces used to re-heat cold charged slabs at BS, Teeside, resulted in energy savings of 15 % for both furnaces. The former manually adjusted temperature zones switched to computer controlled (using on-line mathematical models) to provide optimal heating profiles.

Implementation of computerised furnace control at a German pipe production site, led to energy savings of 5 % and a reduction of scale generation during reheating of up to 30 %. [StuE-116-11]

	Reduction [%]		Investment cost [M ECU]	
	NOx	Energy <sup>1</sup>	New facilities	Existing facilities
<b>Furnace automation</b> <sup>2</sup>	10	10	2.0	2.0
Note: Source of data [EUROFER HR]. Basis is a furnace with a yearly capacity of 1.5 Mt fired with natural gas with standard burners and without air preheat. Investment costs can be site specific (available room, layout of the existing furnace, number of side and bottom burners)				
<sup>1</sup> In percentage terms, the energy reduction is matched by the reduction in SO <sub>2</sub> , CO and CO <sub>2</sub> emissions				
<sup>2</sup> With furnace automation is meant all measures that allow a quick adaptation of the furnace parameters to changes in the production and a tight control of the air excess				

**Table A.4-4: Typically achievable reductions and cost data for furnace automation**

**Driving force for implementation:**

**Reference literature:** [ETSU-FP15], [ETSU-G77], [ETSU-G76]

**A.4.1.3.3 Optimised Furnace Door Design****Description:**

Conventional (one-segment) furnace doors leave gaps beside the feedstock through which furnace gases escape (or tramp air may be sucked into the furnace; see negative impact of excess air). In case of escaping furnace gases, this results not only in uncontrolled (fugitive) emission, but also in a loss of waste gas which might otherwise be used for combustion air preheating. The recuperation efficiency is thus reduced.

The modern furnace door design comprises a vast number of single doors (e.g. 64 doors on a width of 15.6 m) which can be lowered down on the refractory to the left and right of the feedstock. [STuE-117-5]

**Main achieved environmental benefits:**

**Applicability:**

- New and existing continuous reheating furnaces.

**Cross-media effects:** - no negative effects on other media are known.

**Reference plants:** Stahlwerke Bremen

**Operational data:**

The change of the furnace door design (of a walking beam furnace) resulted in an increase of the air preheat temperature (recuperation) of 60 ° with a reduction in energy consumption of 0.05 GJ/t. [STuE-117-5]

**Economics:**

With the given reduction of energy consumption of 0.05 GJ/T and an investment cost of DEM 1 m (reference year 97) for 2 doors and a production of about 3.5 Mt, the return on investment was about 1 year. [STuE-117-5]

**Driving force for implementation:**

**Reference literature:**

#### A.4.1.3.4 Regenerative Burner System

**Description:** see Chapter D.2.1

**Main achieved environmental benefits:**

- Reduced energy consumption.
- Reduction of the total volume of flue gases.

**Applicability:**

- New plants.
- Existing plants, provided that space is available.

**Cross-media effects:**

- Higher NO<sub>x</sub> emission levels may occur. [EUROFER HR]
- Reduced energy consumption has a positive effect on SO<sub>2</sub> and CO<sub>2</sub>.

**Reference plants:** small part of reheating furnaces.

**Operational information and economics:**

**Example A:**

A UK plant operating a **walking beam furnace** to heat various sizes of mild steel tube (up to 200 mm diameter and 15 m long) from cold to 1050 °C, changed their firing to regenerative burners. The old 44 nozzle mix, NG fired burners were replaced by 12 pairs of regenerative burners. At the same time, the roof profile was modified to improve zone control and hot gas circulation. As a result of the plant modification the specific energy consumption was reduced from typically 3.55 GJ/t to 1.7 GJt, giving a 52 % saving in fuel use. Productivity potential was improved by 14 %. The payback period was less than three years. [ETSU-G77]

**Example B:**

Rotherham Engineering Steels revamped one of their **soaking pit** re-heating units in 1987 with dual-fuel, regenerative low-NO<sub>x</sub> burners. The original pit was feeding a billet mill with ingots; a nominal charge being about 100 t heated to about 1300 °C. About 80 % of the charged material was hot charged at about 750 °C, 20 % was charged cold coming from stock (no mixed charges of hot and cold material). The pit was dual-fuel fired by NG or heavy fuel oil by a main 6.5 MW burner in the upper part of one of the end-walls and by a 750 kW supplementary unit directly beneath. A concentric-tube recuperator provided preheated air to the main burner only. Compared with the original plant only the combustion system was changed; the structure, stock tonnage, and the thermal objectives remained essentially the same. An assembly of two regenerative burners was installed at each end of the pit. Long-term monitoring showed energy savings of 40 % for oil-firing mode. Short-term monitoring for oil-firing confirmed the same savings. Cost of the modification was £ 170000 (including £ 21500 on-site burner development) resulting in a payback period of 2.4 years (2.1 without the burner development). [ETSU-NP-54]

**Advantages and disadvantages:**

Higher NO<sub>x</sub> emissions may occur (typical value is 350 mg/Nm<sup>3</sup>), but combined with lower energy consumption and waste gas flow reduction, specific NO<sub>x</sub> emission (in g/tonne steel) is comparable with the specific NO<sub>x</sub> emission level reached with other systems. [EUROFER HR]

A drawback of regenerative systems is their sensitivity to dust. If the heating process generates substantial amounts of dust the permeability of the ceramic fillings in the regenerator drops very fast and the fillings have to be replaced consequently. This item appears to be a minor problem in re-heating furnaces in steel plants. [EUROFER HR]

Regenerative burners are usually bigger than conventional burners. Thus limited space can be an obstacle for installing regenerative burners in existing plants. To date, it has not been possible to use regenerative systems cannot be used for roof burners. [EUROFER HR]

A regenerative system might be considered for the construction of new re-heating furnaces in those cases where, due to the plant layout, the length of the re-heating furnace has to be limited. In the same way, an increase in the production capacity of an existing furnace is possible by installing a regenerative system without increasing the length of the furnace (which in most cases is a fixed specification). [EUROFER HR]

This system is particularly interesting for batch processes because batch processes generally do not contain a preheat zone. In continuous furnaces equipped with a central recuperator system, a similar thermal efficiency is reached by means of a long unheated (preheat) zone, where the heat of the flue gases is transmitted by convection to the cold stock. A thermal efficiency of the furnace of 80 % can be achieved. [EUROFER HR]

The higher investment costs (regenerative system, more expensive burners) may be compensated by the benefits of shortening the length of the furnace (new plant) and increased fuel efficiency. [EUROFER HR]

	Reduction [%]		Investment cost [M ECU]	
	NO <sub>x</sub>	Energy <sup>1</sup>	New facilities	Existing facilities
<b>Regenerative systems</b>	50	40	4.0	4.5

Notes: Source of data [EUROFER HR]. Basis is a furnace with a yearly capacity of 1.5 Mt fired with natural gas with standard burners and without air preheat. Investment costs can be site specific (available room, layout of the existing furnace, number of side and bottom burners)

<sup>1</sup> In percentage terms, the energy reduction is matched by the reduction in SO<sub>2</sub>, CO and CO<sub>2</sub> emissions

**Table A.4-5: Typically achievable reductions and cost data for regenerative systems**

**Driving force for implementation:** improved energy efficiency and monetary advantage.

**Reference literature:** [ETSU-G76], [ETSU-G77]

### A.4.1.3.5 Recuperator and Recuperative Burners

**Description:** see Chapter D.2.2

**Main achieved environmental benefits:**

- Reduced fuel/energy consumption.

**Applicability:**

- New plants.
- Existing plants in case of major revamping [Com HR].

**Cross media effect:**

- NOx emission levels increase with rising combustion air temperature.
- Reduced energy consumption has a positive effect on SO<sub>2</sub> and CO<sub>2</sub>.

**Reference plants:**

**Operational data and economics:**

Recuperator with low-NOx (2nd generation)	Reduction [%]		Investment cost [M ECU]	
	NOx	Energy <sup>1</sup>	New facilities	Existing facilities
	50	25	1.0	2.2
Recuperative burner	30	25	4.5	5.0

Notes: Source of data [EUROFER HR]. Basis is a furnace with a yearly capacity of 1.5 Mt fired with natural gas with standard burners and without air preheat. Investment costs can be site specific (available room, layout of the existing furnace, number of side and bottom burners)

<sup>1</sup> In percentage terms, the energy reduction is matched by the reduction in SO<sub>2</sub>, CO and CO<sub>2</sub> emissions

**Table A.4-6: Typically achievable reductions and cost data for recuperators and recuperative burners**

**Driving force for implementation:**

**Reference literature:**

### A.4.1.3.6 Oxy-fuel Technology

**Description:**

Normal combustion air is replaced by industrial grade oxygen.

**Main achieved environmental benefits:**

- Reduced energy consumption and CO<sub>2</sub> emission.
- Reduced CO and overall NOx emissions.

**Applicability:**

- New furnaces.
- Existing furnaces in case of major revamps.

**Cross-media effects:**

- Higher NOx emission concentrations, although overall NOx emissions are lower.
- Potential safety hazard from using pure oxygen.

**Reference plants:** several case studies (mostly for stainless steel)

At least 50 units in normal daily steel heating operation; soaking pits, car bottom furnaces, box furnaces, catenary furnaces, rotary hearth furnaces, roller hearth furnaces etc. At least 6 new furnaces operating in Sweden.

**Operational data:**

**Economics:**

- Low investment costs.
- High running cost if no increase in production is realized.

**Driving force for implementation:**

- Increased productivity.
- Fuel savings.
- Lower overall NO<sub>x</sub> emissions.

**Reference literature:**

"All Oxy-Fuel in heating furnaces", Dr. Joachim von Schéele and Dipl. Ing. Tomas Ekman, "Nordic Steel and Mining Review 2000", page 100.

#### **A.4.1.3.7 Low-NO<sub>x</sub> Burners**

**Description:** see Chapter D.2.1

Nowadays burners combining low-NO<sub>x</sub> design features and air preheating are available, e.g. regenerative low-NO<sub>x</sub> burners.

**Main achieved environmental benefits:**

- Reduction in NO<sub>x</sub> emission.

**Applicability:**

- New furnaces.
- Existing plants in case of major revamping (limitation for the replacement of existing burners may be given with respect to the size). [Com HR] Existing conventional burners can generally be converted into first generation low-NO<sub>x</sub> burners by changing burner baffle and port block. A conversion to second generation low-NO<sub>x</sub> burners is more difficult and requires a modification of the furnace lining. [EUROFER HR]

**Cross-media effects:**

- The internal flue gas re-circulation, a design feature of low-NO<sub>x</sub> burners, reduces the NO<sub>x</sub> level, but may increase energy consumption.

**Reference plants:**

EKO Stahl, Aceralia, Voest Alpine, Preussag, etc.

**Operational data and economics:**

For low-NO<sub>x</sub> burners the NO<sub>x</sub> level is less dependent on the air preheat temperature. Sometimes in industrial practice, low-NO<sub>x</sub> burners do not show best performance in NO<sub>x</sub> emission. This shows that the total NO<sub>x</sub> output is influenced by a lot of other parameters such as furnace design, type of fuel, heating temperature, operation and maintenance. [EUROFER HR] Special care is therefore necessary regarding operating conditions and control of operation.

Compared to conventional burners a reduction in the NO<sub>x</sub> emission level of approximately 30 % can be obtained. A typical value for natural gas is 300 mg NO<sub>x</sub> /Nm<sup>3</sup>.

In two cases, using COG and heavy oil, guaranteed emission levels of 330 mg NO<sub>x</sub>/m<sup>3</sup> (dry waste gas at 5 % O<sub>2</sub>) were reported. [DFIU]

### Examples

**Voest Alpine** is operating 2 pusher-type (350 t/h) and 2 heat treatment furnaces. The reduction of the NO<sub>x</sub> level can only be obtained, when the burner capacity is higher than 20 %. During an unscheduled or scheduled delay time (burner capacity < 20 %) the NO<sub>x</sub> level can be double or more. Investment costs were reported to be EUR 1 m/furnace (350 t/h). [Input-HR-1]

**EKO Stahl** operates a walking-beam furnace with a capacity of 200 t/h. The furnace is equipped with low-NO<sub>x</sub> burners and is operated with natural gas and an air preheating temperature of 450° C (waste gas volume 140000 m<sup>3</sup>/h). Levels of 400 mg/m<sup>3</sup> for NO<sub>x</sub> and <100 mg/m for CO (reference 5 % O<sub>2</sub>) are achieved as daily averages in the case of cold charging.

NO<sub>x</sub> emissions of 250 mg/m<sup>3</sup> (reference 3 % O<sub>2</sub>) with Low-NO<sub>x</sub> burners were also reported, compared to conventional burners with 300 – 500 mg/m<sup>3</sup> **ACB**

	Reduction [%]		Investment cost [M ECU]	
	NO <sub>x</sub>	Energy	New facilities	Existing facilities
<b>Low-NO<sub>x</sub> burners with internal flue gas recirculation (1st generation)</b>	40	0	0	0.8
<b>Low-NO<sub>x</sub> burners with internal flue gas recirculation and air staging (2nd generation)</b>	65	0	0.2	1.2

Notes: Source of data [EUROFER HR]. Basis is a furnace with a yearly capacity of 1.5 Mt fired with natural gas with standard burners and without air preheat. Investment costs can be site specific (available room, layout of the existing furnace, number of side and bottom burners)

**Table A.4-7: Typically achievable reductions and cost data for low-NO<sub>x</sub> burners**

### Driving force for implementation:

### Reference literature:

## A.4.1.3.8 Selective Catalytic Reduction (SCR)

### Description:

A secondary measure to reduce the NO<sub>x</sub> emissions is selective catalytic reduction. The general technical description of SCR is given in Chapter D.2.4.

### Main achieved environmental benefits:

- Reduction in NO<sub>x</sub> emission.

### Applicability:

- New and existing plants.

### Cross-media effects:

- Use of ammonia gas (transport and storage can be hazardous and subject to stringent safety regulations).
- Risk of air pollution due to ammonia slip.
- Possible increase in energy consumption [Vercaemst 27.7].
- Possible increase in waste; de-activated catalyst, which can be reprocessed by the manufacturer. This waste stream probably will be minimal.[Vercaemst 27.7], [Oekopol 7.9]

**Reference plants:**

Hoogovens Steel, walking beam furnace [Com NL]

**Operational data:**

**Example Corus/Hoogovens Hot Rolling Mill No 2 in IJmuiden:**

In IJmuiden the SCR technique is applied at the walking beam furnaces which produce about 2.3 million tonnes of hot rolled steel annually. Due to the specific construction of the flue gas channel, it was possible to build the ordinary SCR catalyst into the existing channel. The type of catalyst used is suitable to operate within the temperature range 270 - 450 °C. Short periods of temperatures up to 500 °C do not harm the catalyst. With this type of installation it is possible to get an overall reduction rate of more than 80 %. The permit of the plant describes a reduction from 800 mg/Nm<sup>3</sup> to 320 mg/Nm<sup>3</sup> and a demand to achieve more than 85 % reduction, which can probably be done. The cost efficiency of the SCR at the walking beam furnace at Corus/Hoogovens is NLG 4.20 per kg NO<sub>x</sub> reduced. [EUROFER 31.3] [EUROFER 3.4]

In IJmuiden no SCR behind a pusher type furnace is installed yet, but one is under construction. Start of operation is scheduled for June 2000. For the second pusher furnace, installation of an SCR is planned for early next year. The performance will probably be much worse than in the case of the walking beam furnace. Due to the very high temperatures of the flue gas (75 % above 520°C) an experimental type of catalyst has to be used. This type only functions properly within a temperature range of 300 - 520°C. At temperatures above 520° no ammonia can be injected any more because of potential damage to the catalyst. Unless the high temperatures are dealt with (i.e. technical solutions for this problem are found or additional measures are taken), it is estimated that the overall reduction of NO<sub>x</sub> will not be more than 30 %. [EUROFER 31.3]

Some doubts were expressed regarding the technical feasibility of SCR which may limit the applicability to reheating furnaces:

- Some practical problems are likely to be encountered in application of SCR on steel reheating/heat treatment furnaces as production rate (and therefore thermal input) and temperature profiles are not steady state. To avoid either excessive NH<sub>3</sub> slip or excess NO<sub>x</sub> in the stack, the ammonia injection rate would need to be controlled to match rapidly changing exhaust flow rates and NO<sub>x</sub> concentrations. [ETSU-GIR-45].
- SCR technology requires certain limits of temperature and volume flow, which might not be achieved by some plants [DK 30.6].
- The required flue gas temperature suitable for SCR may not be readily available. If the temperatures are too high, dilution air could be used, although furnace draughting may then not be acceptable. [ETSU-GIR-45].
- In the case of regenerative burners, the efficiency of flue gas heat recovery would be affected, unless the SCR could be incorporated midway in a regenerator bed (e.g. the bed would need to be split). [ETSU-GIR-45].
- Many plants recover the waste heat of the exhaust gases for reasons of energy efficiency. The resulting temperature of the waste gas is in the range 150 – 210 °C and needs to be reheated for the SCR catalyst to work properly. Consequently, additional energy input would be necessary [EUROFER 2.7].
- As there is only very limited experience with the application of SCR at reheating furnaces (only one plant and only for walking beam furnaces), it not verified whether the technique will work under all temperature conditions and air ratios, [EUROFER 30.6].
- With higher dust concentrations in the waste gas (e.g. if fuel oil is used as energy source) de-dusting measures would be required to protect the catalyst [EUROFER 2.7].
- In integrated steel plants, plant gases (blast furnace top gas, BOF converter gas or coke oven gas) are used as fuel. They contain usually only negligible traces of zinc or other metals, but these could still contaminate the surface of the catalyst and gradually reduce its efficiency and lifetime [EUROFER 2.7].



- A problem which can arise is the formation of acidic ammonium sulphate  $(\text{NH}_4)_2\text{SO}_4$  or bisulphate  $(\text{NH}_4)\text{HSO}_4$  particles by the reaction of excess ammonia carried over from the SCR reactor with  $\text{SO}_2$  and  $\text{SO}_3$  in the cooler flue gases downstream. Deposition of these particles can cause fouling, erosion and corrosion of downstream equipment surfaces. The formation of ammonium sulphate is minimized by use of slightly sub-stoichiometric amounts of  $\text{NH}_3$  (0.9 – 1.0 mole per mole of  $\text{NO}_x$ ) to suppress carry over. [HMIP-95-003], [ETSU-GIR-45].

**Economics:** NLG 4.20 per kg  $\text{NO}_x$  reduced [EUROFER 3.4]

**Driving force for implementation:**

**Reference literature:** [HMIP-95-003], [ETSU-GIR-45], [EUROFER 31.3]

#### A.4.1.3.9 Selective Non-Catalytic Reduction (SNCR)

##### Description:

The general description of SNCR is given in Chapter D.2.5

##### Main achieved environmental benefits:

- Reduction in  $\text{NO}_x$  emission.

##### Applicability:

- New and existing plants.

##### Cross-media effects:

- Use of ammonia gas (transport and storage can be hazardous and subject to stringent safety regulations).
- Risk of air pollution due to ammonia slip.

##### Reference plants:

**Avesta Sheffield**, walking beam furnaces

##### Operational data:

##### Example Avesta Sheffield:

At the hot strip mill for rolling stainless steel slabs to strip, there are two reheating furnaces (walking beam furnaces), each with a capacity of 100 t/h and using propane/butane gas as fuel. Furnace A, supplied by Stein Heurty, became operative operation in 1992, and furnace B, supplied by Italimpianti, in 1996.

Because this is the plant's largest point source of  $\text{NO}_x$ , action has been taken to reduce these emissions through the introduction of an SNCR installation. The installation comprises mainly a storage tank for ammonia (25 % water solution), pumps, pipes, injection lances, and a computerised measurement and control system, where ammonia is added to the exhaust gas of each furnace on the basis of continuous  $\text{NO}_x$  measurement.

The installation was put into in continuous operation in October 1999 and was regulated during the autumn. Measurements in January 2000 gave the following results ( $\text{NO}_x$  measured as  $\text{NO}_2$ ):

	<b><math>\text{NO}_x</math> content (mg/MJ fuel)</b>	<b>Reduction (%)</b>	<b><math>\text{NO}_x</math> [mg/Nm<sup>3</sup>]</b>
Furnace A	74	70	205
Furnace B	62	30	172 (ammonia slip 5 mg/Nm <sup>3</sup> )

The measurement results are averages of continuous measurements made during 32 hours at Furnace A and 42 hours at Furnace B. They are considered normal and expected to remain at these levels in continuous operations.

The reason why the reduction is lower at Furnace B is that the nitrogen oxide content without ammonia is lower than in Furnace A.

The following cost information was given to the Swedish Environment Court in December 1999 in a report on the possibilities of reducing the emissions of nitrogen oxides from these furnaces:

The capital investment (including installation and running-in costs as well as the cost of all equipment): SEK 6.3 m (EUR 0.76 m)<sup>2</sup>

Operating costs (mainly ammonia and maintenance): SEK 1.4 m per year (EUR 0.169 m per year)

Total capital and operating costs: SEK 3.3 m per year (EUR 0.40 m per year)

With the NO<sub>x</sub> reduction mentioned above, the emissions of nitrogen oxides can be reduced by 60 tonnes per year, corresponding to a specific cost of SEK 55 (EUR 6.63) per kg NO<sub>x</sub> reduced (measured as NO<sub>2</sub>). [EUROFER 17.4]

Other sources report efficiency of NO<sub>x</sub> removal by SNCR of typically 50 – 60 % with 20- 30 ppm NH<sub>3</sub> slip [ETSU-GIR-45], but even higher reductions of up to 85 % are reported in connection with ammonia injection on a natural gas-fired regenerative burner. Others reported on the use of ammonia and urea injected into the flue of a burner (operating at 900 °C air preheat) burning a mixture of blast furnace and coke oven gases. For both reagents, the maximum reduction was of the order of 80 %. These data derive from test furnaces not exceeding 600 kWth, which in this case was a 1/3 scale version of a soaking pit furnace. [HMIP-95-003]

Some doubts were expressed regarding the technical feasibility of SNCR which may limit the applicability to reheating furnaces. Problems in applying SNCR to reheating furnaces due to large variations in process conditions (waste gas temperature, volume flow etc.) and or non-availability of a suitable temperature window are probably the same as for the application of SCR (see above):

- The temperature window for SNCR is about 850 – 1100 °C (depending on the reagent). For those regenerative systems which have furnace temperatures well in excess of 1000 °C, the appropriate SNCR temperature range is liable to be found within the regenerator bed, which may militate against the use of the method. Control systems would be complicated if there were a need to 'follow' a temperature window which can change its location within the furnace/burner as thermal inputs and production rates are altered. [HMIP-95-003], [EUROFER HR]
- A potential drawback of the SNCR technique is the formation of ammonium sulphate by the carry over of excess NH<sub>3</sub>. The use of clean gaseous fuels such as natural gas in conjunction with SNCR should avoid the reported problems of adhesive and corrosive compounds that can otherwise occur. This may not be the case with sulphur-containing steelwork gases. [HMIP-95-003]

**Economics:** The economic data of the Swedish plants shows that the cost of 6.63 euro per kg of NO<sub>x</sub> reduced gives rise to additional costs of 0.33 euro in the manufacture of 1 tonne of rolled steel. Based on a price of about 400 euro per tonne of hot wide strip, the relative expenditure comes to 0.08 %. Annual production of the two plants was estimated to be 1.2 million tonnes of rolled steel. [Germany 7.4]

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<sup>2</sup> The costs in EUR were calculated using an exchange rate of EUR 0.12 for 1 SEK.

**Driving force for implementation:**

The SNCR units were fitted as a result of local regulatory issues. The site has a total annual mass emission limit for NO<sub>x</sub> and there was a desire to increase production. The increased throughput could not be realised unless some emission reductions were achieved and the SNCR installation was then found to be the best solution.

**Reference literature:** [HMIP-95-003], [ETSU-GIR-45], [EUROFER 17.4]

**A.4.1.3.10 External Flue Gas Recirculation (FGR)**

**Description:** see Chapter D.2.3

**Main achieved environmental benefits:**

- Reduction in NO<sub>x</sub> emission.

**Applicability:**

- New and existing furnaces.
- In practice, for retrofitting, there may be physical difficulties in installing ductwork and problems of accessibility.
- Potentially difficult to control in cases where composition and hence waste gas volumes are variable (e.g. on integrated sites where mixed plant gases are used).

**Cross-media effects:**

- Potential increase in fuel consumption (as long as waste gas flow and temperature are not affected by FGR, combustion efficiency and fuel consumption will remain the same, but this implies an increase in air-preheat temperature).

**Reference plants:****Operational data:**

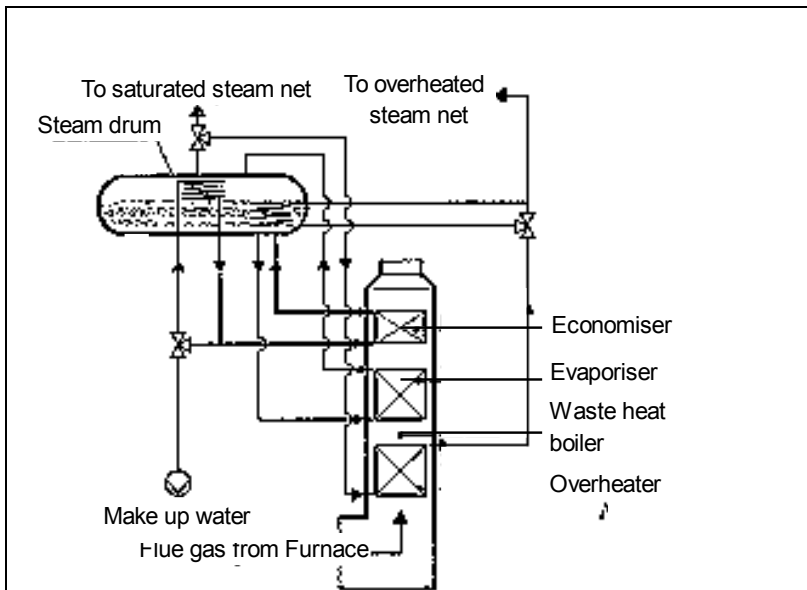
For a COG fired steel slab reheater with a capacity of at least 140 t/h NO<sub>x</sub> reductions of 51.4 %, 69.4 % and 79.8 % (from a base level of 657 mg/m<sup>3</sup>) for 10 %, 20 %, and 30 % FGR respectively, are reported. [ETSU-GIR-45]

Data given for increases in fuel consumption (and hence for CO<sub>2</sub> emission) for different burner designs range from 1.1 to 9.9 % (FGR ranging from 10 – 50 %). [ETSU-GIR-45]

**Economics:****Driving force for implementation:****Reference literature:****A.4.1.3.11 Waste Heat Boiler****Description:**

A waste heat boiler can be installed between furnace exit and chimney (decreasing the effectiveness of a recuperating system) or between the recuperator and the stack. In the waste heat boiler, the heat content of the waste gas is used to generate steam. The waste gas temperature after the waste heat boiler is lowered to about 200 °C. The generation of steam by this method at this point saves generating this energy elsewhere (e.g. in the power plant or heating station). As a result, considerable energy and emission reductions can be achieved.

The steam generated can be used within the rolling mill for heating systems or outside the rolling mill to produce electrical energy in the power plants and for municipal long-distance heating systems. [EUROFER HR]



**Figure A.4-3: Schematic of waste heat boiler**  
[EUROFER HR]

**Main achieved environmental benefits:**

- Efficient energy use.
- Saves resources, as no fuel is consumed at other stages for producing the steam and emissions are reduced.

**Applicability:**

- New plants.
- Existing plants, provided required space is available.

**Cross-media effects:**

**Reference plants:**

Voest Alpine (2 boilers), Svenskt Stål AB

**Operational data and economics:**

**Example Voest:**

Steam temperature:	320 °C
Steam pressure:	18 bar
Waste gas temperature behind water heat boiler:	200 °C
Energy recovery:	0.17 GJ/t (12 % of fuel consumption)
Investment costs:	4.5 M Euro/ heat boiler (65t/h)

	Reduction <sup>1</sup> [%]		Investment cost [M ECU]	
	NOx	Energy <sup>2</sup>	New facilities	Existing facilities
<b>Waste heat boiler</b>	15	15	4.0	4.0
Notes: Source of data [EUROFER HR]. Basis is a furnace with a yearly capacity of 1.5 Mt fired with natural gas with standard burners and without air preheat. Investment costs can be site specific (available room, layout of the existing furnace, number of side and bottom burners)				
<sup>1</sup> Waste heat boilers have a negligible effect when combined with recuperators or with regenerative systems				
<sup>2</sup> The energy reduction in terms of percentage has an equal effect on the reduction in SO <sub>2</sub> , CO- and CO <sub>2</sub> emissions				

**Table A.4-8: Typically achievable reductions and cost data for waste heat boilers**

Installation of a waste heat boiler is only sensible when there is a special requirement for steam, i.e. some users. Only a marginal effect can be expected from the installation of a waste heat boiler when it is combined with effective recovery of the waste heat by the use of recuperators or of a regenerative system and with the proper furnace design. [EUROFER HR]

**Driving force for implementation:** - reduced energy consumption, monetary advantage.

**Reference literature:**

#### **A.4.1.3.12 Optimised Skid Design to Reduce Skid Marks**

##### **Description:**

##### **SMC - Skid Mark Compensation Device**

The slabs heated in the **pusher-type furnace** lean on water-cooled supporting pipes which cause local undercooling (skid marks) on the bottom side of the slabs and must be compensated for during the residence time in the soaking hearth to avoid thickness variations of the finished product.

The soaking time can be reduced if the skid marks are reheated by application of suitable methods, e.g. local inductive heating (skid mark compensation device). Losses due to the cooling system and the hearth wall are almost constant over time, regardless of whether the furnace is operated under full load or partial load.

**Main achieved environmental benefits:** The reduction of the residence time on the hearth and, consequently, of the throughput time, results in energy savings. But it was also reported that SMC requires high energy input for inductive heating. [Com2 HR]

##### **Furnace Skid Riders**

An additional measure to reduce the formation of skid marks is the use of so-called skid riders. These are fixtures for the water-cooled furnace rails made from special material (metal alloy or ceramics), which reduce temperature dissipation.

**Main achieved environmental benefits:** - As in SMC, a reduction of the temperature compensation, combined with an increased throughput and reduced energy consumption, is possible.

##### **Skid Shifting**

In modern **walking beam furnaces**, the material supporting skids are not straight all along the furnace. Mainly the last section of skids, near the furnace exit side, is shifted with an offset designed to distribute and therefore to decrease the skidmarks.

**Main achieved environmental benefits:** - Quality is enhanced and waste output reduced.

##### **Applicability:**

- Furnace skid riders and skid shifting: only applicable to new installations as they have to be considered at design stage.
- Skid mark compensation device: new and existing installations.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

Reported reduction for skid shifting, skidmark compensation or furnace skid riders was 1 % for energy consumption and 1 % NO<sub>x</sub> emission. [EUROFER HR]

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.1.3.13 Reduction of Energy Loss through Stock Transportation Device**

**Description:**

In re-heating furnaces water cooling is used to protect some components and maintain their physical strength; examples include doors, lintels and the stock transport mechanism or support system. Water-cooled components represent a significant source of energy loss. In particular, the loss through stock transport systems in continuous (walking beam) furnaces, can account for 6 to 12 % of the fuel input under typical operating conditions. Close to the end of a furnace operating campaign, when insulation of the cooled components begins to degrade, the loss can be as high as 20 to 25 %. [ETSU-G76], [Com2 HR]

Losses from stock supporting structures can be minimized at the design stage by optimizing/reducing the **number of cooled beams and supports** and by using **suitable insulation**. [ETSU-G76]

**Main achieved environmental benefits:**

- Reduction in water cooling losses of 26.7 GJ/h (equivalent to a fuel saving of 44.5 GJ/h) were reported [ETSU-G76].

**Applicability:**

- New furnaces and existing furnaces.
- For existing furnaces, optimisation can be done during refractory maintenance [Com2 HR].

**Cross-media effects:**

- 46 % reduction in water use [ETSU-G76].
- Reduced energy consumption of pusher mechanism [ETSU-G76].
- Reduced skid marks, improved quality [ETSU-G76].

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

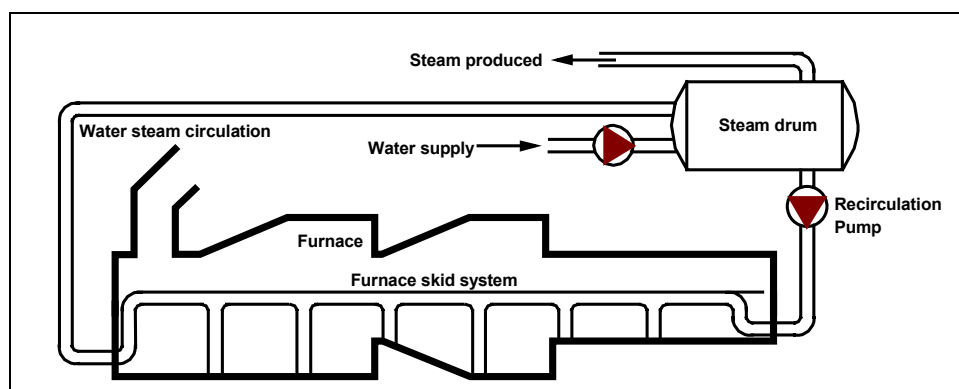
**Reference literature:**

#### **A.4.1.3.14 Evaporative Furnace Skid Cooling**

**Description:**

Skid cooling energy losses can be used to generate steam. A closed, forced cooling circuit, which circulates a mixture of approx. 95 % water and 5 % saturated steam can be installed in re-

heating furnaces. Steam produced by cooling the supporting beams (skids) of rolling stock is extracted from the circuit and fed to other consumers for further use. [EUROFER HR]



**Figure A.4-4: Typical schematic of evaporative furnace skid cooling** [EUROFER HR]

**Main achieved environmental benefits:**

- Efficient energy use, saves resources as no fuel is consumed at other stages for producing the steam, emissions are reduced.

**Applicability:**

- New and existing installations.
- Only sensible when there is a specific requirement for steam. [ETSU-G76].

**Cross-media effects:** - no negative effects on other media are known.

**Reference plants:** Svenskt Stål AB, EKO Stahl

**Operational data and economics:**

**Example EKO Stahl [Input-HR-1]**

- average working pressure in the boiler: 23 bar
- average temperature of cooling water: 222 °C (at 23 bar)
- possible steam production for the turbine: 10 – 41 t/h (depending on the situation of the refractory material and the working conditions of the furnace)
- generator capacity: 4.16 MW
- steam production (cold charging): Ø 18 t/h
- steam production (hot charging): Ø 22 t/h
- recovered energy: n.a.

Reported general reduction potentials and cost data are given in the following table.

	Reduction <sup>1</sup> [%]		Investment cost [M ECU]	
	NOx	Energy <sup>2</sup>	New facilities	Existing facilities
<b>Evaporative furnace skid cooling</b>	7	7	4.0	4.0

Notes: Source of data [EUROFER HR]. Basis is a furnace with a yearly capacity of 1.5 Mt fired with natural gas with standard burners and without air preheat. Investment costs can be site specific (available room, layout of the existing furnace, number of side and bottom burners)

<sup>1</sup> Evaporative furnace skid cooling has a negligible effect when combined with recuperators or with regenerative systems

<sup>2</sup> The energy reduction in terms of percentage has an equal effect on the reduction in SO<sub>2</sub>, CO and CO<sub>2</sub> emissions

**Table A.4-9: Typically achievable reductions and cost data for evaporative furnace skid cooling**

Only a marginal effect can be expected from evaporative furnace skid cooling when it is combined with good insulation of the skids.

**Driving force for implementation:**

**Reference literature:**

#### A.4.1.3.15 Feedstock Preheating

##### Description:

The heat in the waste gas of heating furnaces can be used to preheat the feedstock by blowing the hot waste gas from top and bottom onto the slab. Even after regenerative burners and a waste heat boiler, the waste gas can have enough energy to heat the slabs up to 400 °C. Figure A.4-5 shows the example of a slab preheater installed upstream of a pusher-type heating furnace.

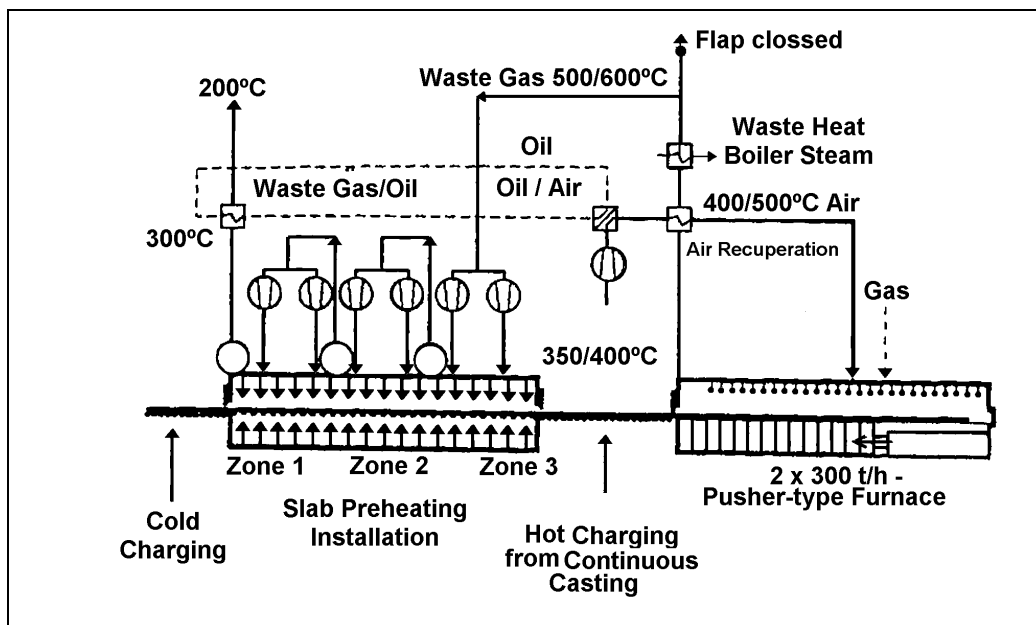


Figure A.4-5: Principle of slab preheating by waste gas  
[StuE-113-10]

##### Main achieved environmental benefits:

- Reduced energy consumption in the heating furnace (20 %).

##### Applicability:

- New and existing continuous reheating furnaces (for cases where stock recuperation is not already incorporated in the furnace).

**Cross-media effects:** - no negative effects on other media are known.

**Reference plants:** Preussag Stahl, Salzgitter



**Operational data:****Example:**

The preheater shown in Figure A.4-5 is installed up-stream of 2 pusher-type furnaces. The furnaces have capacities of 300 t/h and are fired by regenerative burners. The heat from the waste gas of the furnace is first used for heat recovery in a waste heat boiler. After that it still has a temperature of 500 – 600 °C and is used in the preheater to heat the slabs to up to 400 °C. The waste gas leaving the preheater still has a temperature of 300 °C and is used to preheat the combustion air for the regenerative burners of the heating furnace to about 150 °C (by means of a oil heat exchangers). The waste gas is discharged at a temperature of 200 °C. [StuE-113-10]

As an alternative to preheaters, the heat of waste gas can be used in very long walking beam furnaces in the un-fired long preheating zone. [StuE-113-10]

**Economics:****Driving force for implementation:****Reference literature:****A.4.1.3.16 Heat Conservation Box / Thermal Covers****Description:**

Hot boxes or insulated chambers are used to promote heat retention in the steel and to provide a link between the source of hot stock and the furnace. Semi-finished products, which cannot be charged immediately (because of programme co-ordination and for bridging gaps caused by interruptions) are stored in this unheated, heat-insulated box instead of being stored in open stockyards. Heat losses of the slabs are reduced and the charge temperature is maintained at a high level. On average, the storing time for slabs is 8 hours. The temperature of insulated stored slab is approximately 220 °C higher than that of open stored slabs. [EUROFER HR], [ETSU-G76].

Another method for reducing the furnace operating temperature and preventing heat loss between the furnace and the rolling mill is insulated shields (heat retaining covers) installed between the furnace discharge and the rolling stands. Heat losses during transport from the casting machine to the re-heating furnace can be prevented by the same kind of measures. [DFIU98], [ETSU-G76]

**Main achieved environmental benefits:**

- Reduced energy consumption in re-heating.
- Thermal covers for the transport of slabs between a continuous caster and a re-heating furnace can save about 0.33GJ/t [DFIU98].

**Applicability:**

- New and existing installations.
- All continuous casting plants with adjacent rolling mill [Com A].
- same limitations may apply as for hot charging [Input-HR-1].

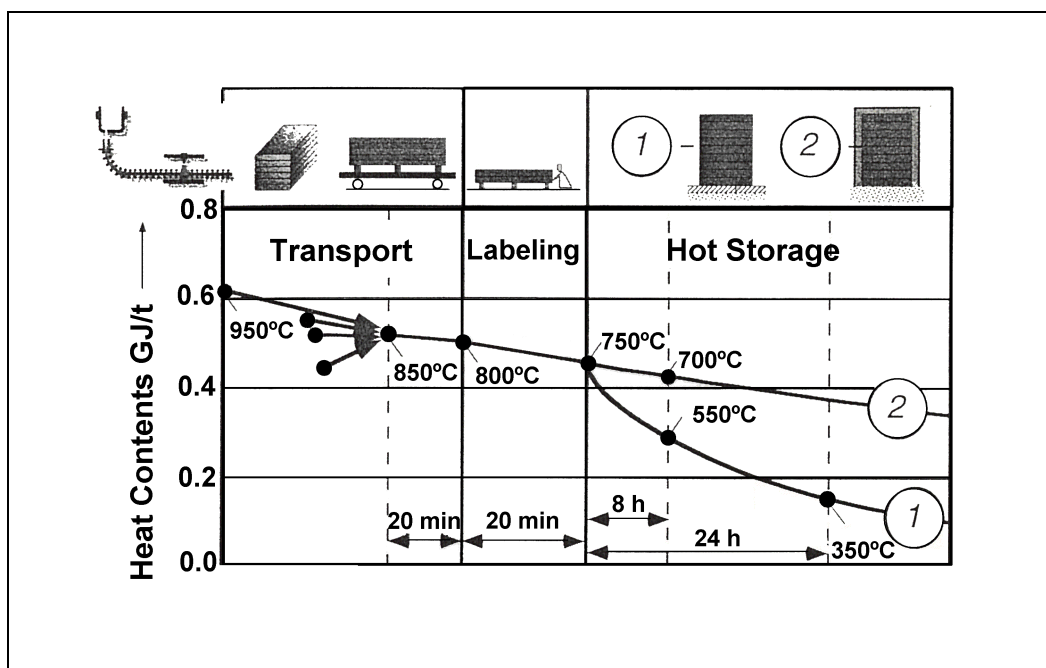
**Cross-media effects:** - no negative effects on other media are known.

**Reference plants:**

- VA Stahl Linz, (max. 5000 t), Austria [Input-HR-1].
- HADEED, Saudi Arabia [Com A].
- Stahlwerke Bremen [STuE-117-5].

**Operational data:****Example**

An investigation on potential measures to increase the charging temperature of continuous cast slabs to a heating furnace was done at Stahlwerke Bremen using numerical modelling. The results based on computer simulation and measurements for that installation showed that the core temperature of slab immediately after casting was about 950 °C. On the way to the stockyard of the hot rolling mill the slabs cooled down by 200 ° to 750 °C: during the storage time of 24 h the temperature of the slabs dropped further, leaving a remaining charging temperature to the heating furnace of about 350 °C. By optimizing the synchronisation of the continuous caster and the rolling schedule, the storage time could be reduced to a third. Additionally, the slabs were covered with thermal covers with a 50 mm mineral wool lining. It was proven that during an 8 hour storage, starting from 750 °C, a charging temperature of 700 °C could be maintained. Compared to the old charging practice (350 °C) this represented an additional energy input to the furnace of 0.26 GJ/t resulting half from the shorter storage time and half from the thermal insulation. [StuE-117-5]



**Figure A.4-6: Modified storage to increase charge temperature**  
[StuE-117-5]

**Economics:**

Return on investment in 1 year at VA Stahl Linz [ComA].

Investment costs 2 M Euro, Voest [Input-HR-1].

**Driving force for implementation:**

- Increased furnace- and rolling mill capacity.
- Increased hot charging rate in connection with CAQC. [Com A].

**Reference literature:**

Ideas and Concepts for Hot or Direct Charging, Paper No. 50, 7<sup>th</sup> International Continuous Casting Conference, May 20 – 22, 1996 [Com A].

### A.4.1.3.17 Hot Charging / Direct Rolling

#### Description:

Contrary to the conventional process (storage and cooling of the material), the residual heat from the continuous-cast slabs, blooms, beam blanks or billets is utilized by charging them directly (with their residual heat content) into the heating furnaces. Hot charging refers to charging temperatures of 300 to 600 °C; direct rolling to charging temperatures of 900 to 1000°C. These techniques can only be applied if the surface quality is good enough so that cooling and scarfing is not required and if the manufacturing programs of the steel making plant and the hot rolling mill can be adequately tuned. Control computers are used to co-ordinate the production of both departments according to customers' orders and to prepare the rolling schedules.

Figure A.4-7 presents a possible material flow in a plant allowing both cold charging and warm or hot charging. An optimised production planning and control system to synchronise the production schedules of a steelworks and a rolling mill can achieve a hot charging share of over 60 % at about 800°C. A soaking furnace placed before the rolling mill may be required.

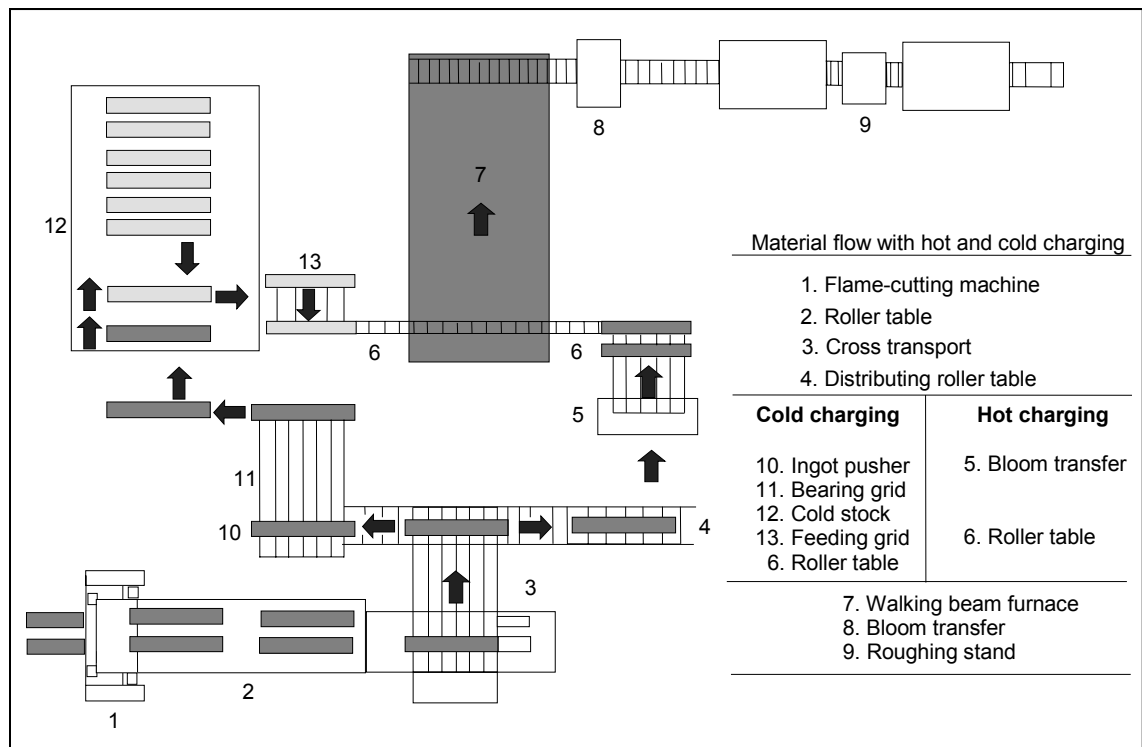


Figure A.4-7: Material flow: cold versus hot charging [DFIU98]

#### Main achieved environmental benefits:

- Reduction in energy consumption (fuel savings).
- Reduction in SO<sub>2</sub>, CO and CO<sub>2</sub> emissions.

#### Applicability:

- New and existing installations.
- Application may be limited at some existing plants because of plant layout and operational logistics. Important technological parameters are mill type and configuration, proximity of the caster to furnace and rolling mill (time required for the transfer of the stock from the steel plant to the reheating furnace) as well as steel specifications. Sometimes application to furnaces with unfired preheating zones is not possible. The implementation of hot charging

or direct rolling depends furthermore on the installation of equipment to allow a higher furnace throughput, temperature normalisation (e.g. edge heaters), schedule free rolling, potential to align the production schedule of the steel plant (caster) and the production schedule of the rolling mill, high quality slabs (surface quality) etc. [DFIU98], [ETSU-G77].

#### Cross-media effects:

- Reduced stock residence time in the furnace.
- Higher production rates (e.g. 10 - 25 %).
- Improved yields and product quality due to reduced scaling and decarburisation.
- Waste reduction in following processes, e.g. descaling.
- Temperature of exhaust gas may increase [ETSU-G77].

#### Reference plants:

EKO Stahl, [Input-HR-1]

Rotherham Engineering Steels, [ETSU-CS-263]

Stahlwerke Thuringen [StuE-118-2]

#### Operational data:

Table A.4-10 illustrates the influence of hot charging on energy consumption and production time for hot charging. In the examples shown, production potential was increased by 10 % for a hot charging temperature of 400 °C and by 25 % for a charging temperature of 700 °C.

Charging Temperature			
	20 °C	400 °C	700 °C
<b>Specific energy consumption (fuel)</b>	1.55 GJ/t	1.25 GJ/t	0.94 GJ/t
<b>Percentage Reduction</b>	0 %	19 %	39 %
<b>Heat to steel</b>	0.80 GJ/t	0.56 GJ/t	0.37 GJ/t
<b>Residence time in furnace<sup>1</sup></b>	100 min	90 min	75 min

<sup>1</sup> Example based on: billets, mild steel, top-fired pusher furnace, discharge temperature 1200 °C

**Table A.4-10: Effect of hot charging on fuel consumption and residence time [ETSU-G77]**

#### Examples

##### EKO Stahl hot charging of slabs [Input-HR-1]

- percentage of hot charging: 4.63 – 31.65 %, Ø in 1998 14.64 %
- average charging temperature of slabs: 700 – 900 °C
- fuel consumption (natural gas): 17 Nm<sup>3</sup>/t
- energy saving: 0.6 GJ/t

##### Rotherham Engineering Steels hot charging of blooms [ETSU-CS-263]

- percentage of hot charging: 66.4 %
- charging temperature of blooms: ~ 700 °C
- specific energy consumption (SEC): 1.1 GJ/t during productive periods  
1.23 GJ/t including light-up energy  
energy saving: ~ 0.67 GJ/t (compared with a walking-beam type furnace with similar structural energy loss, efficiency of 67 % and SEC 1.9 GJ/t)

##### Stahlwerke Thuringen hot charging beam blanks [StuE-118-2]

- percentage of hot charging: > 60 %

**British Steel, Scunthorpe hot charging concast blooms [Input-HR-1]**

- charging temperature of blooms: ambient up to concast exit temperature ~ 1300 °C
- energy savings of about 33 %
- specific energy consumption (SEC): 1.35 GJ/t (2.1 GJ/t without hot charging)

Energy savings for hot charging at 300 °C of 15 % were reported in [EUROFER HR].

**Imatra Steel, Imatra Hot charging of blooms**

- engineering steel grades, billets / heavy bars 74 / 26 %
- percentage of charging via hot route 91 – 93 %
- direct hot charging 700 – 900 °C
- charging via hot buffer (natural gas fired) 700 °C
- soaking temperature 1250 - 1290 °C
- specific energy consumption 0.87 GJ/t (average for production 1998 (98 % including hot buffer, cold charging, weekends and light-up energy).
- natural gas + 2 % electricity)

Hot buffer is used:

- to eliminate effects of short stoppages in rolling mill
- to balance the production speed difference when rolling bars (the casting speed cannot be lowered to match the speed of the old rolling mill)
- for slow preheating of cold blooms at weekends.

**Economics:**

Type of investment	Investment cost	
	New facilities (M ECU)	Existing facilities (M ECU)
Hot charging (at 300 °C)	1.5	2.0
Notes: Source of data [EUROFER HR]. Basis is a furnace with a yearly capacity of 1.5 Mt fired with natural gas with standard burners and without air preheat. Investment costs can be site specific (available room, layout of the existing furnace, number of side and bottom burners)		

**Table A.4-11: Investment costs for hot charging**  
[EUROFER HR]

**Driving force for implementation:** - reduced energy consumption.

**Reference literature:**

**A.4.1.3.18 Near Net Shape Casting / Thin Slab Casting****Description:**

'Near net shape casting' or thin slab casting comprises an improved continuous casting technology in which the thickness of the produced slab is reduced as far as possible to the required end-product shape.

The technical solutions available differ mainly in the thickness of the slabs, ranging from 15 up to 80 mm (conventional thickness ranges 150 - 300 mm), in the reheat technique and the linkage between caster and hot rolling mill. Available thin slab casting techniques include:

- **Compact Strip Production (CSP):** using funnel type moulds with a casting thickness of approx. 50 mm.

- **Inline Strip Production (ISP):** the cast strand of about 60 mm thickness undergoes a soft reduction (on liquid core) with rolls below the mould, followed by a shaping of the solidified strand creating slab thickness of about 15 mm.
- **Continuous Thin Slab Casting and Rolling (CONROLL):** using straight parallel moulds with casting thickness of 70 - 80 mm.
- **Direct Strip Production (DSP):** 90 mm caster mould and soft-reduction to 70 mm.

The casting machines may be linked to all main configurations of hot rolling finishing mills, e.g. finishing train, planetary mills, Steckel mills etc.

Figure A.4-8 and Figure A.4-9 show as examples the schematics of the CSP and the ISP process.

Furnaces of different design – chieving uniforme incoming slab temperature - are the linkages between the caster and the hot rolling mill. Depending on the type of thin slab production plant, tunnel furnaces or 'cremona boxes' are used. The main target of these facilities is to equalise and homogenise the temperature of the continuous cast slabs of different cross sections and length of around 50 m up to 300 m nowadays [Com2 HR] and to regulate the feed to the finishing rolling mill. Dependent on the casting strands, 1 or 2 furnaces are installed, connected by a shuttle device.

Firing of continuous furnaces and combustion systems is in general comparable with the common systems of reheat furnaces.

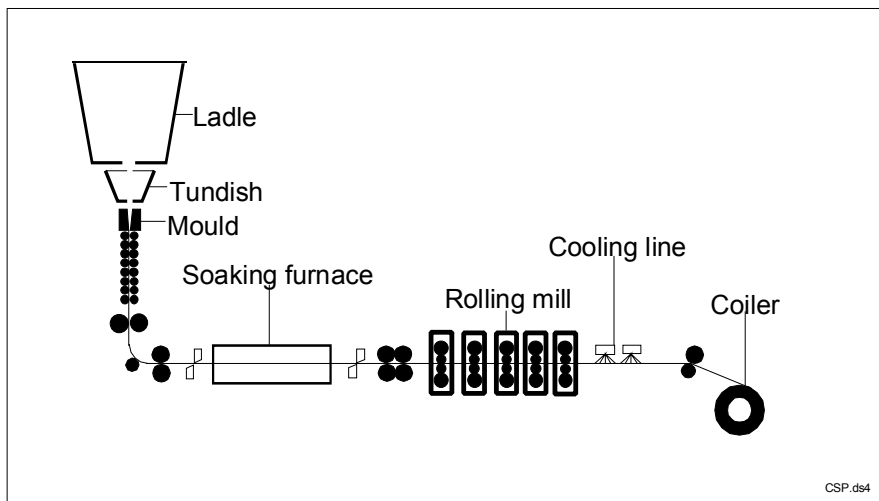
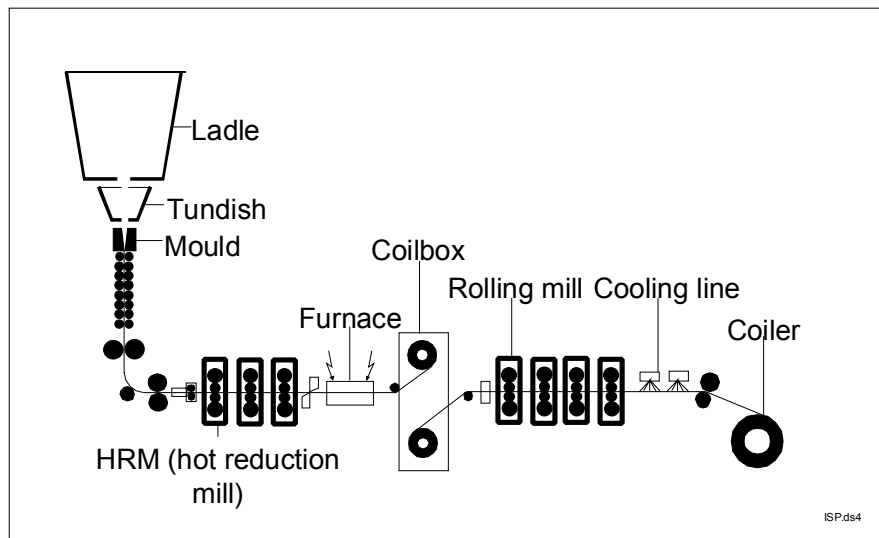


Figure A.4-8: Schematic of the CSP process [DFIU98]



**Figure A.4-9: Schematic of the ISP process [DFIU-99]**

**Main achieved environmental benefits:**

- Reduced energy consumption.

**Applicability:**

- Applicable for new plants.
- For the production of low carbon steel, higher strength unalloyed and micro-alloyed structural steel and C-steel > 0.22 % [STuE-118-5].
- For production of high quality stainless steel (austenitic, grades, ferritic grades as well as martensitic grades (BHM, 142Jg. 1997, Heft 5, 210 – 214)) [Com A].

**Cross-media effects:** - no negative effects on other media are known.

**Reference plants:**

	Slab dimensions [mm]	Capacity [Mt/a]	Rolled Thickness [mm]	Start Date
<b>Compact Strip Production</b>				
<b>Nucor</b> Crawfordsville, USA	50 x 900 - 1350 50 x 500 - 1350	0.8 1	1.6 1.6	7/89 4/94
<b>Nucor</b> Hickman, USA	50(75) x 1220 - 1560 50(75) x 1220 - 1560	1 1	1.5 1.5	8/92 5/94
<b>Nucor</b> , Berkeley County, USA	50 x 1680	1.5	1.2	3/97
<b>Geneva Steel</b> Provo, USA	150-250 x 3200 max or 50 x 1880 max	1.9	plate	7/94 - 95
<b>AST</b> , Terni, Italy	50 x 1000 - 1560	-	-	12/92
<b>Hylba SA</b> , Monterrey, Mexico	50 x 790 - 1350	0.75	1.2	11/94
<b>Hanbo Steel</b> Asan Bay, Korea	50 x 900 - 1560 50 x 900 - 1560	1 1	1.5 1.5	6/95 12/95
<b>Gailatin Steel</b> , Warsaw, USA	50 x 1000 - 1560	1	2.1	2/95
<b>Steel Dynamics</b> , Butler, USA	40-70 x 990 - 1560	1.2	1.2	1/96
<b>Nippon Denro Ispal</b> Calcutta, India	50 x 900 - 1560	1.2	1.2	8/96
<b>Amalgamated Steel Mills</b> Malaysia	50 x 900 - 1560	2	1.2	10/96
<b>Ac. Compacta Bizkaya</b> Bilbao, Spain	53 x 790 - 1560	0.91	1.3	7/96
<b>Acme Metals</b> Riverdale, USA	50 x 900 - 1560	0.9/1.8	1.25	10/96
<b>Inine Strip Production</b>				
<b>Arvedi ISP Works</b> Cremona, Italy	60* x 1070 - 1250 *(red. to 40 during solidification)	0.5	1.2	1/92
<b>Posco</b> , Kwangyang, Korea	75* x 900 - 1350 *(red. to 60 during solidification)	1 0.8	1.0 1.0	1996 1996
<b>Nusantara Steel Corp</b> Malaysia				?
<b>Saldanha</b> , South Africa		(1.4) <sup>1</sup>		?
<b>Ipsco</b> , USA		(1) <sup>1</sup>		?
<b>Pohang Iron and Steel</b> South Korea		(2) <sup>1</sup>		
<b>Hoogovens Staal</b> <sup>2</sup> Ijmuiden, NL	70 – 90 x ??	(1.3)	1 – 2.5	
<b>CONROLL</b>				
<b>Avesta</b> , Sweden	80-200 x 660–2100	-	-	12/88
<b>Armco</b> , Mansfield, USA	75-125 x 635-1283	0.7/1.1	1.7	4/95
<b>Voest Alpine</b> , Linz, Austria				?
<b>Direct Strip Production</b>				
<b>Algoma</b> , CAN <sup>3</sup>	90* x 200 *(red. to 60 during solidification)		1	11/97

Note: Source of data [Jahrbuch Stahl 1996], reference year of information 1995  
<sup>1</sup> Source [StuE-116-11], ordered plants, reference year of information 1996  
<sup>2</sup> Source [Steel News, march 1998]  
<sup>3</sup> Source [algoma.com]

Table A.4-12: Thin slab casting plants (by July 1995)



**Operational data:**

The production of 1 to 3 mm thick strip by conventional slab casting - with a charging temperature for the furnace of 20 °C and discharge at 1200 °C - requires a specific energy of 1.67 GJ/t. A thin slab casting line - with a charging temperature for the furnace of 960 °C and discharge at 1150 °C - has a specific energy consumption of 0.50 GJ/t.

**Grades cast by thin slab casting (commercial production):**

- Plain carbon steels outside peritectic range (CSP).  
(0.065 - 0.15 %C) (CSP).
- High alloyed and stainless (CSP).
- Unalloyed structural steels (ISP).
- Alloyed structural steels (ISP).
- Line pipe steels (HSLA) (ISP).
- Oil field pipe steels (ISP).
- High alloyed austenitic and ferritic steels (ISP)
- Stainless steels CONROLL [Near-Net-Shape].
- Low and ultra-low carbon steel (CSP) [StuE-118-5], [AC-Kolloq].
- C-steel grades with > 0.22 %.
- High strength (micro- and unalloyed) structural steel.
- Deep steel drawing grades.
- Microalloyed Nb steels.
- Cu alloyed structural steels [Near-Net-Shape].

	<b>Conventional production route Typical Consumption</b>	<b>Thin slab production route Typical Consumption</b>
<b>Electrical energy <sup>1</sup> (deformation energy)</b>	72 - 115 kWh/t  average 94 kWh/t (reported by members of shadow group)	approx. 70 kWh/t (deformation only) approx. 77 kWh/t (incl. Coil box)
<b>Reheating energy (fuel consumption) <sup>2</sup></b>	approx. 1300 - 1900 MJ/t	approx. 300 - 650 MJ/t
Note: source of data [EUROFER HR] <sup>1</sup> Depends on the degree of deformation; temp. of intermediate strip; material hardness <sup>2</sup> fuel consumption depends on the furnace design and thickness of ingoing slab		

**Table A.4-13: Comparison of consumption figures for conventional and thin slab production route**

**Economics:**

Thin slab casting technique effectively opened the flat rolled market to mini mills, which up to that time had been bound more or less to the production of long products. Implementation of this technology shrinks the size of the caster and eliminates the roughing mill, resulting in capital cost saving. Hot band, in the non-critical surface segment, can now be economically produced with capacities of 0.8 - 1.0 Mt/year (with one-strand casters).

**Driving force for implementation:**

- Due to reduction in energy consumption and processing time, economic/monetary advantage.

**Reference literature:**

### A.4.1.3.19 Near Net Shape Casting/ Beam Blank Casting

**Description:**

Another – more common - form of 'near net shape casting' is applied in the field of long product rolling of structural steel. Instead of the traditional bloom with a rectangular or square cross section the continuous caster produces an H, I or double T shaped beam blank.

**Main achieved environmental benefits:**

- Reduced energy input in reheating and rolling.

**Applicability:**

- New plants or existing plants in case of a major revamp.

**Cross-media effects:** - no negative effects on other media are known.

**Reference plants:**

Northwestern Steel & Wire, USA [StuE-114-8]

Chaparral Steel, USA [StuE-114-8]

Kawasaki Steel, Nucor-Yamato, Yamato Steel Tung Ho Steel [StuE-114-9]

Stahlwerke Thuringen [StuE-118-2]

**Operational data:**

**Economics:**

**Driving force for implementation:**

- Increased yield in the continuous caster due to reduced material to be cropped.
- Increased specific heat transfer in the reheating furnace.
- Reduced time in the rolling process, increase in productivity [Com HR].

**Reference literature:**

### A.4.1.4 Descaling

#### A.4.1.4.1 Material Tracking

**Description:**

Automation of the respective train areas and peripheral sensors allow exact determination of the entry into and the delivery of the materials from the descaling equipment and allow the operator to open the valves of the pressure-water pipes accordingly. As a result, the water volume can be continuously adjusted to the requirement.

**Main achieved environmental benefits:**

- Reduced water consumption.
- Reduced energy consumption.

**Applicability:**

- Roughing, finishing and plate mills.
- New and existing hot rolling mills for flat products.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### A.4.1.4.2 Use of High-pressure Storage Equipment

**Description:**

Appropriately sized high-pressure storage vessels are used to temporarily store the high-pressure water and to reduce the starting phase of the high-powered pumps. In addition, it is possible to keep the pressure at a constant level when several simultaneous descaling processes are performed. This method helps to keep the energy consumption within reasonable limits and, in the case of several descaling processes at the same time, helps to ensure optimum cleaning and high-quality products due to the constant system pressure.

**Main achieved environmental benefits:**

- Reduced energy consumption.

**Applicability:**

- Roughing, finishing and plate mills' descaling systems.
- New and existing hot rolling mills for flat products.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### A.4.1.5 Edging

##### Sizing Press

**Description:**

In conventional vertical rolling, width reduction is limited to the slab edges with only little effect on the centre part of the slabs. Material thickness increases at the edges, forming dog-bone shaped cross sections. In the following horizontal rolling a significant return in width - side spreading - takes place, resulting in low width reduction efficiency.

In-line size presses, due to the forging effect on the slab, increase also the material thickness in the middle of the slab. The shape of the cross section is nearly rectangular and side spreading during horizontal rolling passes is reduced.

With the introduction of a sizing press prior to the rougher the width intervals of the caster and the number of wedge type slabs are reduced. Caster productivity and hot charging rate may therefore be increased. [EUROFER HR]

**Main achieved environmental benefits:**

- Reduced energy consumption.
- Reduced trimming and cropping scrap.

**Applicability:**

- Roughing and plate mills.
- New hot rolling mills for flat products.
- With limitations for existing mills.

**Cross-media effects:**

**Reference plants:** Sollac Fos, Thyssen Bruckhausen

**Operational data:**

**Economics:**

**Driving force for implementation:** - Improved yield.

**Reference literature:**

#### A.4.1.5.1 Automatic Width Control Comprising Short Stroke Control

**Description:**

In conventional edging the width of the slab is reduced independently of the actual width and temperature of the material, therefore generating width variations along the transfer bar, especially under high width reductions. With the aid of an AWC system the edging process is performed via computer models. For the strip ends (head and tail) the edging values are reduced across a defined length and thus the formation of so-called tongues at the strip head and/or fish tails occurring in conventional rolling are avoided.

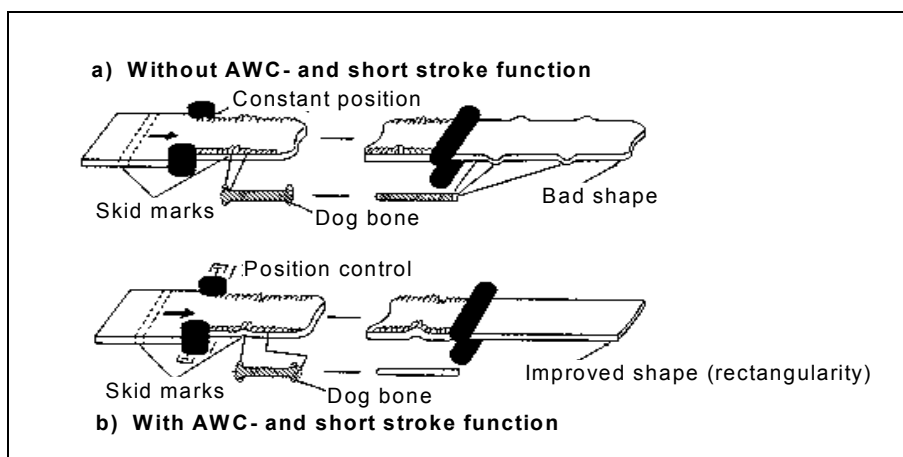


Figure A.4-10: AWC-operation

**Main achieved environmental benefits:**

- Reduced trimming, head and tail scrap.

**Applicability:**

- Roughing, finishing and plate mills.
- New and existing hot rolling mills for flat products.

**Cross-media effects:**

- Increased product quality, improved yield, therefore less material has to be recycled; energy consumption and emissions are reduced.

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:** - Improved yield.

**Reference literature:**

### A.4.1.6 Roughing

#### A.4.1.6.1 Process Automation

**Description:**

The use of computers allows the adjustment of the thickness reduction per pass. In other words, slabs and blooms are reduced to a rough strip by applying the lowest possible number of passes, even in the case of short interruptions resulting in temperature losses of the material.

**Main achieved environmental benefits:**

- Reduced energy consumption.
- Furnace discharge temperature can be decreased.
- Number of roll passes is optimised.

**Applicability:**

- Roughing and plate mills.
- New and existing hot rolling mills for flat products.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### A.4.1.7 Transport of Rolled Stock from Roughing Mill to Finishing Train

#### A.4.1.7.1 Coil Box

**Description:**

The intermediate product produced in the roughing train (transfer bar) is wound up to a coil without a mandrel by means of appropriately arranged, electrically driven pinch/bending rolls and cradle rolls. After completion of coiling, the coil is placed on an uncoiling device, decoiled, and passed to the finishing stand. During the uncoiling process and finishing rolling the coiler is free to receive the next rough strip. In this way, bottlenecks in the production flow can be avoided.

This equipment has the advantage that the temperature distribution across the length of the transfer bar remains constant and the loads during finishing rolling are reduced. On the other hand, the additional energy requirement for the coiling operations must be considered. When modernising existing mills, product range may be increased.

In the event of a cobble downstream, the coiled bar may be held for a longer period than would otherwise be possible. For longer mill break-downs the coiled transfer bar might be stored in so called heat recovery furnaces. Both measures thereby improve the yield.

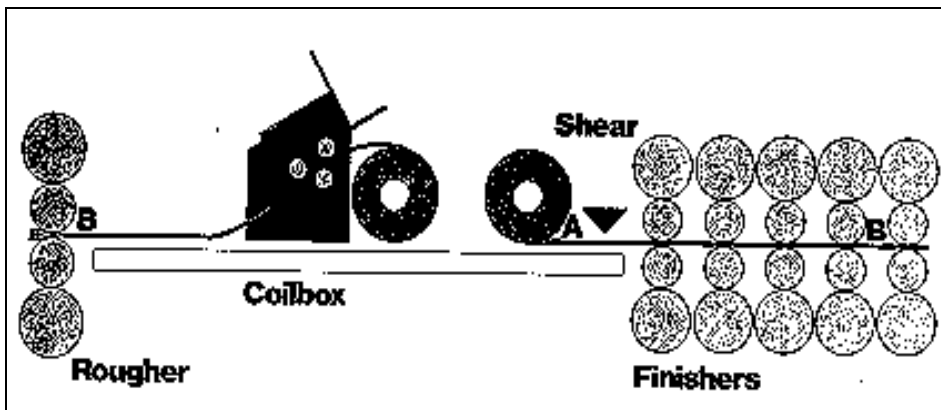


Figure A.4-11: Coil box arrangement  
[EUROFER HR]

**Main achieved environmental benefits:**

- Reduced energy consumption.
- Less rolling force required (temperature in stock is higher and more uniform).

**Applicability:**

- Run-out table of roughing mills.
- New and existing hot rolling mills for flat products.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

In some cases a coil box can limit the maximum mill production. [Com HR]

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### A.4.1.7.2 Coil Recovery Furnace

**Description:**

Coil recovery furnaces were developed as an addition to coil box installations, so that in case of longer rolling interruptions the coils could be restored to rolling temperature and returned to the rolling sequence, which results in a yield improvement. Temperature losses are minimized and even rolling breaks of up to 2 hours can be covered.

Heating and cooling temperature models determine the correct heating cycle for each coil, taking into account the temperature profile of the coil at the start of heating. This profile is determined from data from the mill computer on the temperature at the roughing pass, the elapsed time before and after coiling, as well as bar size and grade. Coils saved using the recovery furnace are rolled into prime hot band, providing they are rolled within 2h. Coils held for longer periods are processed to 'non-surface critical' products. (The furnace can be built with an inert gas system.)

**Main achieved environmental benefits:**

- Reduced energy consumption.

**Applicability:**

- In combination with coil boxes at roughing stands.
- New and existing hot rolling mills for flat products.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:** - Improved yield.

**Reference literature:**

#### **A.4.1.7.3 Heat Shields on Transfer Tables**

**Description:**

To minimize temperature loss in a bar while it is conveyed from rougher to finishing mill and to decrease the temperature difference of head and tail end on entering the finishing train, the transfer roller table can be equipped with heat shields. These are insulated covers applied to the conveyor. For those sizes where the rolled products reach the limit of capacity of the rolling train, this equipment achieves lower rolling loads.

**Main achieved environmental benefits:**

- Reduced energy consumption.
- Reduced temperature loss.

**Applicability:**

- Transport roller table between roughing and finishing mills.
- New and existing hot rolling mills for flat products.

**Cross-media effects:**

**Reference plants:**

**Operational data:** Heat shields on transfer tables involve high maintenance costs as the shields are easily damaged by cobbles. [Com2 HR]

**Economics:**

**Driving force for implementation:** -Improved yield

**Reference literature:**

#### **A.4.1.7.4 Strip Edge Heating**

**Description:**

In order to raise the temperature of the cooler strip edges to the overall temperature level and achieve a constant temperature profile across the strip width, the transfer roller table is equipped with additional gas or inductive heating devices.

**Main achieved environmental benefits:**

- Reduced energy consumption in finishing rolling.
- Reduced wear occurring on the work rolls (less grinding sludge).

**Applicability:**

- Transport roller table between roughing and finishing mills.
- New and existing hot rolling mills for flat products.

**Cross-media effects:**

- Energy used for edge heating.

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:** -Improved yield.

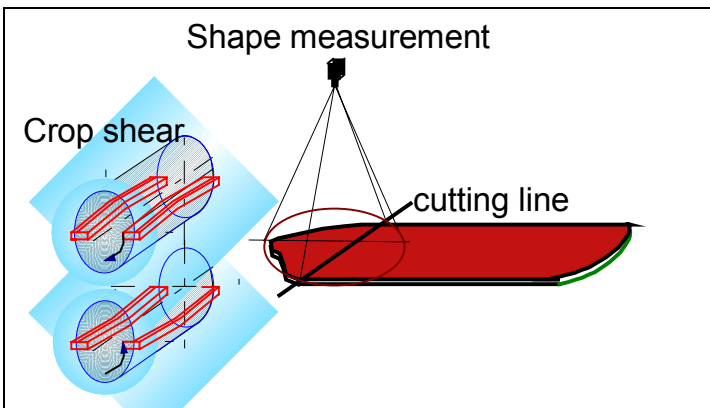
**Reference literature:**

## A.4.1.8 Rolling

### A.4.1.8.1 Crop Optimisation System

**Description:**

By the use of CCD-cameras, combined with a width measurement subsequent to the roughing train, the real crop shape of the ingoing rough strip is identified. An automatic system ensures that the cutting action of the shears is limited to cut off materials outside of the rectangular area of the transfer bar.



**Figure A.4-12: Crop optimisation system**  
[EUROFER HR]

**Main achieved environmental benefits:**

- Scrap (head and tail) reduction.

**Applicability:**

- At entry of finishing trains.
- New and existing hot rolling mills for flat products.

**Cross-media effects:**

**Reference plants:** Sidmar

**Operational data:**

**Economics:**

**Driving force for implementation:** - Improved yield.

**Reference literature:**



### A.4.1.8.2 Work Roll Lubrication System

**Description:**

Rolling oils are supplied to the roll gap via nozzles in order to reduce the friction between material and roll, to lower the drive power requirements, to decrease rolling forces and to improve the surface quality of rolled material.

**Main achieved environmental benefits:**

- Reduced energy consumption by reduced rolling load.
- Reduced roll wear (especially at the strip edge areas) resulting in a longer lifetime of work rolls and reduction of grinding sludge.

**Applicability:**

- Finishing stands.
- New and existing hot rolling mills for flat products.

**Cross-media effects:**

- Contamination of water system with rolling oils.

**Reference plants:** large number of plants.

**Operational data:**

**Economics:**

**Driving force for implementation:** - Higher mill productivity and increased pickling rate.

**Reference literature:**

### A.4.1.8.3 Forced Interstand Strip Cooling

**Description:**

To permit acceleration of the finishing train and still attain a constant finishing temperature, forced interstand cooling of the strip by water sprays or water curtains is employed.

**Main achieved environmental benefits:**

- The formation of scale and oxide fumes is suppressed.
- Decreased wear rate of the work rolls in succeeding stands and reduced grinding sludge.

**Applicability:**

- Between finishing stands.
- New and existing hot rolling mills for flat products.

**Cross-media effects:**

- Generation of waste water.

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### A.4.1.8.4 Interstand Strip Tension Control

**Description:**

Normally loopers are used for controlling strip tension between finishing stands. Various looper designs (hydraulic, low inertia, and tension measuring devices) are available. Additionally, so-

called looper-less techniques have been developed but their successful operation depends largely on the measurement accuracy of processing parameters. Improved looper systems combined with computer models for calculating the strip tension and appropriate electronics controller facilitates the independent control of both tension and looper height. This mainly avoids necking of the strip after threading and unstable operation.

Automatic systems for controlling the strip width when leaving the finishing mill train and/or approaching the coilers (with feedback to the computer models of the finishing train) supports the tension control system.

**Main achieved environmental benefits:**

- Trimming scrap is reduced by avoiding 'necking' during threading and unstable operation.

**Applicability:**

- Finishing trains.
- New and existing hot rolling mills for flat products (part of mill automation systems).

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:** - Improved yield.

**Reference literature:**

#### **A.4.1.8.5 Strip Profile and Flatness Control**

**Description:**

The cross sectional profile and flatness of the hot band is of importance for subsequent processing and is dependent on a number of operating conditions including the pass schedule practice.

The principle purpose of strip profile and flatness control in rolling mills is to achieve the desired strip profile without exceeding the required flatness tolerances. In application to hot rolling mills, strip profile and flatness control systems are commonly designed to achieve the following targets:

- Strip crown control range from approx. 0 - 75  $\mu\text{m}$ .
- Strip crown tolerances.
- Strip flatness of approx. 10 I-Units (I-Unit:  $\Delta L/L = 10^{-5}$  m).
- Reduction in edge drop.

To maintain good strip flatness in hot strip mills, there are only certain maximum changes in the strip crown to thickness ratio that are possible in one rolling pass without introducing undesirable disturbances to strip flatness, known as 'flatness deadband'. Different actuators are developed for an objective selection of strip profile and flatness:

- Work roll and backup roll bending systems.
- Flexible body adjustable crown rolls.
- Flexible edge adjustable crown rolls.
- Roll crossing systems.
- Axially shifting systems with non cylindrical rolls.
- Axially shifted cylindrical rolls.
- Automatic gauge control.

In hot strip mills each stand is usually equipped with a roll bending system that can be either crown in, crown out or both. If that is not sufficient to reach the crown requirements the stands can be equipped with additional actuators such as CVC-rolls, UPS-rolls, roll crossing systems or others. A computer mill set up model, sometimes comprising neural networks, calculates the required settings of profile and flatness actuators under consideration of thermal crown of the roll body to obtain desired strip crown and flatness.

Downstream of the mill stands, profile measuring devices (sensors) are installed to monitor the actual crown. The actual crown is compared to the target and the difference is used to produce changes mainly in the roll bending forces. Flatness control loops lead to nearly constant stripcrown-to-thickness ratio. Shapemeter devices are installed either at the end of the finishing train or between mill stands to monitor the actual flatness. Detected flatness errors are again used to adjust roll bending forces.

**Main achieved environmental benefits:**

- Reduced scrap.

**Applicability:**

- Finishing and plate mills.
- New and existing hot rolling mills for flat products (part of automatic process control).

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:** - Improved yield.

**Reference literature:**

#### **A.4.1.8.6 Work Roll Cooling**

**Description:**

In the mill stands a wide variety of water spray nozzle types and spray header configurations are used to cool the work rolls. This is important to avoid damage and cracks of the rolls (which means less grinding operations and waste generation) and reduces the formation of scale.

**Main achieved environmental benefits:**

- Reduced scale formation.
- Reduced roll wear and reduced grinding sludge.

**Applicability:**

- Roughing, finishing and plate mills.
- New and existing hot rolling mills for flat products.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### A.4.1.8.7 Finishing Train Automation - Process- and Basic Automation

**Description:**

High quality materials can be produced by using process computers supported by appropriate control loops (basic automation - level I) for production planning and control of furnaces and roughing mills. In the event of short rolling interruptions the implemented flexible software models allow pass schedule changes up to the last moment (just before grabbing in the first stand).

**Main achieved environmental benefits:**

- Reduced scrap from short mill breakdowns.

**Applicability:**

- Finishing mill.
- New and existing hot rolling mills for flat products.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:** - Increased yield.

**Reference literature:**

#### A.4.1.8.8 Reduction of Fugitive Emissions / Oxide Removal System

**Description:**

Oxide particles are released due to the rolling operation. The air borne particles are released as fugitive emissions, mainly at the exit side of mill stands (where the speed of the mill stands is the highest). They may be suppressed by **water sprays** or removed by **exhaust systems** (suction hoods, dust hoods or suction lines).

**Water sprays**

With the spray water, the suppressed oxides are led to the roller table flumes and further to the water treatment, where they are recovered in settling basins and filters.

**Exhaust system**

Another option is to install an exhaust system, where dust hoods are installed between the mill stands (mainly behind the last 3 finishing stands) to collect the dust and oxides. Via suction pipes at the mill drive side the oxide-dust mixture is drawn off and routed to pulse jet filters (dry type, bag filter) or wet type filters. The separated dust and oxides are transported into buckets via screw conveyors and are recycled in integrated steel plants.

**Main achieved environmental benefits:**

- Fugitive emissions of particles are reduced.

**Applicability:**

- Finishing mills.
- New and existing hot rolling mills for flat products.

**Cross-media effects:**

- Water sprays result in waste water, oxides have to be recovered from the waste water.
- Dry systems consume energy but, like exhaust/bag filters, have the advantage that they avoid the need to recover the oxides from waste water and the collected dust can be recycled internally. [Com2 HR].

**Reference plants:**

**Water sprays** WSM Avilés, Aceralia; Sidmar, Hoogovens

**Exhaust System** Voest Alpine

**Operational data and economics:**

		Particulate Emission [mg/m <sup>3</sup> ]	Capacity [Mt/a]	Costs EURO '000
a	Water sprays			IC: 50
a	Hood and Bag filter <sup>1</sup>	< 50	3	IC: 280

a: [CITEPA], level was reported BAT level of the air-BAT-note  
IC: Investment costs

**Table A.4-14: Achieved emission levels and operational data for oxide removal systems**

**Examples Water sprays:**

Water sprays are installed in the last finishing stand. The equipment comprises 6 nozzles in the upper part and 8 nozzles in the lower part at each stand. The water is sprayed at a flow-rate of 22 l/min and a pressure of 8 bar. The total water flow of the spraying system is 35 m<sup>3</sup>/h. Costs given for 1994: 50000 ECU.

Sampling location Sampling Duration: 3 h	Concentration of particulate matter	
	without spraying	with spraying
Above the finishing mill	6.02 mg/Nm <sup>3</sup>	2.35 mg/Nm <sup>3</sup>
Roof	2.77 mg/Nm <sup>3</sup>	0.63 mg/Nm <sup>3</sup>

**Table A.4-15: Typical reduction of fugitive emissions by water spraying [Input-HR-1]**

The measuring system does not correspond to any standard, because the emissions are more or less diffuse. The sampling points were chosen valuing from where the emissions came due to aspiration in the workshop because there were no well defined flows.

**Example Exhaust System:**

Investment costs of 1 M Euro (Voest) were reported in [Input-HR-1]. Another source [EUROFRER HR] reports approx. investment costs of 1.45 M ECU and operating cost of 0.15 M ECU/t (sludge and dust removal /disposal not included) for suction plants for finishing train.

**Driving force for implementation:** - reduction of emissions of ferrous oxides. [Input-HR-1]

**Reference literature:**

#### **A.4.1.8.9 Prevention of Hydrocarbon Contamination**

**Description:**

Reduction of oil and lubricant losses is a preventive measure against the contamination of process waters and the included scale. The use of **modern design bearings** and **bearing seals** for work-up and back-up rolls and the installation of **leakage indicators** in the lubricant lines (pressure monitoring equipment e.g. at hydrostatic bearings) can reduce the hydrocarbon content (oil) of scale and waste water and reduces the oil consumption by 50 to 70 %. [EUROFER HR]

Contaminated drainage water at the various consumers (hydraulic aggregates) should be collected and can be pumped into intermediate storage tanks. The waste oil, after separation from water, can be used as a reducing agent in the blast furnace or can be recycled off-site. The

separated water may be further processed either in the water treatment plant or in dressing plants with ultra filtration or vacuum evaporator. [Com2 HR]

**Main achieved environmental benefits:**

- Prevention of oil (hydrocarbon) contamination of water and scale.
- Reduced amount of oily scale.

**Applicability:**

- New plants and existing plants in case of major revamps (less applicable to older plants).

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.1.8.10 Hydraulic Coilers Comprising Step Control**

**Description:**

In conventional coiling the strip is in contact with the wrapper rollers during at least 3 turns of the mandrel and penetrates the overlaying winding. These parts of the hot band have to be removed for subsequent processing in the cold rolling mill.

Hydraulically operated coilers comprising step control systems lift the wrapper rollers automatically, commanded by sensors, when the strip head passes the individual roller.

**Main achieved environmental benefits:**

- Amount of crop scrap in the subsequent processes is reduced.

**Applicability:**

- Hot strip mills.
- New and existing hot rolling mills for flat products.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:** - Increased yield.

**Reference literature:**

#### **A.4.1.8.11 Shape Rolling / Plan View Control**

**Description:**

During conventional plate rolling by maintaining a constant plate thickness during each rolling pass, a distinct distortion of the plate plan view from true rectangular shape takes place.

Employing shape controlled rolling, tapered thickness profiles or dog bones will be produced during rolling. Supported by measurements (load or shape) the amount of dog bone formation or tapering is computed and the correction signals are sent to the roll adjusting system. The plan view control is mainly employed as an addition to the automatic gauge system. The term 'shape rolling or plan view control' is applied to various techniques developed in recent years. All of them are based on the same principle that employs rolling a plate of variable thickness during

the intermediate passes, which results in closely rectangular final plate shape and a reduction in trimming scrap.

**Main achieved environmental benefits:**

- Reduced scrap.

**Applicability:**

- Plate mills.
- New plants and, with limitations, existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:** - Increased yield.

**Reference literature:**

#### **A.4.1.8.12 On Line Heat Treatment (Accelerated Cooling)**

**Description:**

Cooling devices of various design (e.g. water curtains, water pillows, etc.) are arranged behind the rolling mill stand. By controlling the cooling water volume under consideration of sheet temperatures, in-line treatment, such as normalising or quenching, can be applied.

**Main achieved environmental benefits:**

- Reduced energy consumption and emissions from subsequent heat treatment furnaces.

**Applicability:**

- Plate mills.
- New plants and with limitations for existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.1.8.13 Thermo Mechanical Rolling Operation**

**Description:**

In a 'thermo-mechanical rolling operation', the properties of hot rolled plates or sections are influenced to reduce the need for subsequent heat treatment. Slabs or blooms/beam blanks from the re-heating furnace are rolled to an intermediate thickness, followed by a holding period (during which water sprays may be applied) to cool down to a desired temperature and are then finally rolled. Thermo-mechanical rolling achieves a technological parameter, usually attributed to smaller grain size, using less alloying additives and without or with reduced need for subsequent heat treatments, such as normalising.

**Main achieved environmental benefits:**

- Reduced of energy consumption.
- Reduction of emissions from heat treatment.

**Applicability:**

- Plate and section mills.
- New and existing plants, provided sufficient rolling power is available [Com HR].

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### **A.4.1.9 Cooling Lines**

#### **A.4.1.9.1 Optimized Water Pumps for Laminar Flows**

**Description:**

→ No description and technical information submitted..

### **A.4.1.10 Subsequent Sheet Production**

#### **A.4.1.10.1 Leveller Dust Removal**

**Description:**

By the strip bending effect of levelling rollers, scale is broken from the strip surface and fugitive dust is generated. Suction hoods can be installed which collect the air born particles near the leveller and lead them via suction pipes to a filter plant, usually equipped with fabric filters. [Com HR]

**Main achieved environmental benefits:**

- Reduction of fugitive particle emissions.

**Applicability:**

- Shearing and rewinding lines.
- New installations for subsequent treatment equipment for flat products.

**Cross-media effects:**

- Waste generation.
- Collected dust particles are recycled into the steel production.
- Increased energy consumption [Com2 HR].

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**



### A.4.1.11 Roll Shop

#### A.4.1.11.1 Good Operational Practice for Roll Shops

**Description:**

**Use of solvents**

- As far as technically acceptable for the degree of cleanliness required, water based degreasing should be applied.
- If organic solvents are used, preference should be given to non-chlorinated solvents.

**Wastes**

- Grease removed from roll trunnions is collected and disposed of properly (e.g. by incineration).
- Grinding sludge is treated by magnetic separation for recovery of metal particles which are recycled into the steelmaking process.
- Mineral residues from grinding wheels are deposited in landfills.
- Steel and iron turnings are recycled into the steelmaking process.
- Worn grinding wheels are deposited in landfills.
- Worn rolls which are unsuitable for further reconditioning are recycled into the steelmaking process or returned to the manufacturer.
- Cooling liquids and cutting emulsions are treated for oil/water separation. Oily residues are disposed of properly (e.g. by incineration).
- Waste water effluents from cooling and degreasing as well as from emulsion separation are recovered by the hot rolling mill water treatment plant.

**Main achieved environmental benefits:**

- Reduction of overall environmental impact.

**Applicability:**

- New and existing roll shops.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### A.4.1.12 Water Treatment

#### A.4.1.12.1 Reduction of Water Consumption and Discharge

**Description:**

Implementation of semi-closed and closed loop water systems, with discharge as low as possible. For further description refer to Chapter A.2.1.15

**Main achieved environmental benefits:**

- Reduction of waste water and pollutant discharge.

**Applicability:**

- In some cases upgrading existing plants from 'wet mills' (once-through) to mills with semi- or closed circuits, may not be possible due to insufficient space being available to accommodate a fully equipped water treatment plant at economically justifiable investment costs.

**Cross-media effects:**

- Increased energy consumption and consumption of chemicals.
- Waste (sludge) generation.

**Reference plants:**

Semi-closed: .....

Closed: Stahlwerke Bremen, ...

**Operational data:**

Table A.4-16 shows the emission levels achieved with semi-closed and closed water circuits. For comparison the levels achieved by an open system are also given.

Parameter	Open circuit	Semi closed circuit	Closed circuit
<b>Suspended solids (SS)</b>	≤ 40 mg/l	≤ 40 mg/l	≤ 40 mg/l
<b>Specific emission of SS</b>	approx. 800 g/t	approx. 480 g/t	0 - 40 g/t
<b>Water consumption</b>	100 %	approx. 60 % <sup>1</sup>	approx. 5 % <sup>1</sup>
<b>COD (O<sub>2</sub>)</b>	≤ 40 mg/l	≤ 40 mg/l	≤ 40 mg/l
<b>Specific emission of COD</b>	approx. 800 g/t	approx. 480 g/t	approx. 38 g/t
<b>Hydrocarbons (HC)</b> (related to mineral oil)	≤ 5 mg/l	≤ 5 mg/l	≤ 5 mg/l
<b>Specific emission of HC</b>	approx. 100 g/t	approx. 60 g/t	approx. 5 g/t

Notes: Source of data [EUROFER HR]. Based on a production of approx. 3.0 Mt. Waste water treatment consisting of a combination of individual measures as described in the following chapter (no detailed information available)  
<sup>1</sup> Compared with open-circuit, absolute values for water consumption depends on the individual plant situation.

Table A.4-16: Typically achieved effluent levels for different water treatment systems

**Economics:**

Process	Investment costs	Operating costs	Water volume flow/consumption
<b>Open circuit treatment plant</b>	ECU 9.4 - 14.4 million	ECU 0.5 - 0.65 / t	4000 m <sup>3</sup> /h
<b>Semiclosed circuit treatment plant</b>	ECU 13.0 - 14.5 million	ECU 0.6 - 1.15 / t	2500 m <sup>3</sup> /h
<b>Closed circuit treatment plant</b>			m <sup>3</sup> /h
•with cooling tower	ECU 25.0 up to 40.0 million	ECU 1.45 / t	additional water consumption (cooling tower) and/or cooling water in large quantities for heat exchangers
•with heat exchanger	ECU 43.2 million	ECU 1.6 - 1.75 / t	

Notes: Source of data [HR]. Basis is a production of about 3.0 Mt/year hot rolled products. Investment costs exclude costs for building ground and shops, but include the necessary infrastructure. Operating costs are typical examples only; sludge and dust removal (disposal) is not considered).

Table A.4-17: Estimated costs for different water treatment plants

**Driving force for implementation:****Reference literature:**

### A.4.1.12.2 Treatment of Scale and Oil Bearing Process Water

#### Description:

Scale and oil bearing waste water from hot rolling (and often from continuous casting) is treated by a sequence of cleaning steps, for example scale pits, settling tanks, cyclones, filtration etc. creating quite complex waste water treatment systems. The first step, usually, is a scale pit to remove the coarse scale by sedimentation. This is followed by several secondary or fine cleaning steps aiming at separating and abating oil and the remaining scale.

For a detailed description of the individual treatment devices refer to Chapter D.9.1.

As there are numerous options for combining the individual cleaning steps, the treatment of scale and oil bearing process waters and the achievable emission levels are described by means of examples of water treatment systems implemented in hot rolling mills.

#### Main achieved environmental benefits:

- Reduction of pollutant discharge to water, especially suspended solids, oil, grease etc.

#### Applicability:

- New and existing plants.

#### Cross-media effects:

- Oil and sludge arise as waste in waste water treatment. [Com D].

#### Reference plants:

Stahlwerke Bremen (D), SSAB (S), BSW (D).

#### Operational data:

##### Example A: SSAB

The major portion of scale and oil is separated in two scale pits near the rolling mill. The water treatment plant has three basins for gravimetric separation of scale and surface separation of oil and grease. The final cleaning is done in ten sand filters. The rate of water circulation has gradually been increased over the past years to reduce water discharge to river to below 200 m<sup>3</sup>/h (former: 3500 m<sup>3</sup>/h, recirculation rate approx. >95 %). Additionally, primary measures have been taken to reduce leakage of e.g. grease, lubricants and hydraulic oils from machine equipment. Hoses have been changed, better couplings have been installed and routine inspections are carried out. [SSAB]

Achieved discharge values are 0.4 mg/l for oil (0.7 t/a) and 3.8 mg/l for suspended solids (6t/a) (reference year 1994, monthly mean value?) [SSAB]

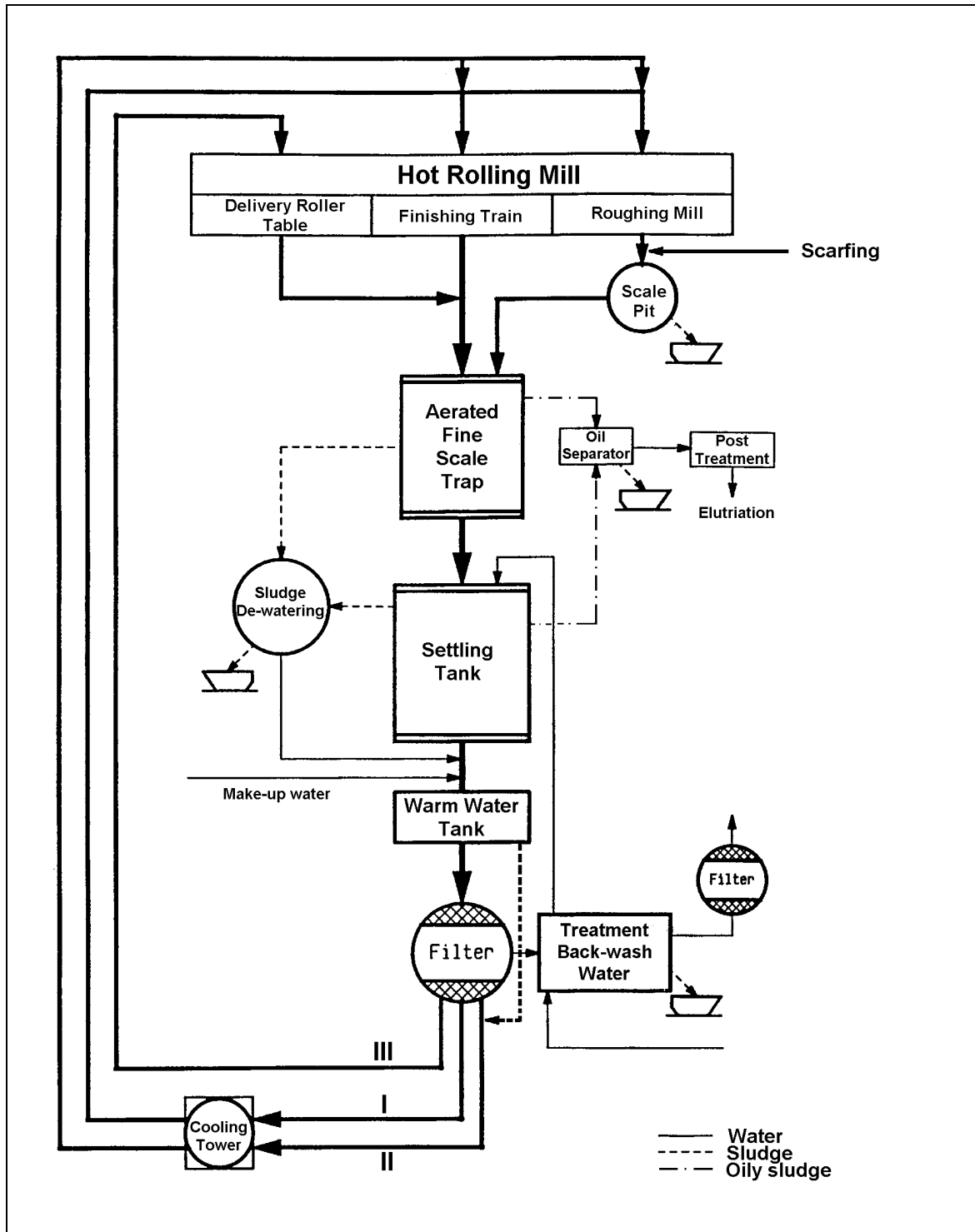
##### Example B: Stahlwerke Bremen

Figure A.4-13 shows the water circuit and the water treatment system installed at Stahlwerke Bremen. The system treats an average water flow of 18000 m<sup>3</sup>/h; about 3500 m<sup>3</sup>/h of which is from the roughing mill and about 14500 m<sup>3</sup>/h from the finishing train including water from the delivery roller table, the coiler and the mist extraction system. The coarse scale is removed from the roughing mill process water in scale pits before it is treated together with the stream from the finishing train in aerated fine scale traps followed by settling tanks. Before the water is recirculated and split into different quality streams, it is cleaned in sand filters. These consist of 3 groups of pressure filters; operating at full production capacity, the filtering speed is 21.4 m/h. The reduced concentration of suspended solids, iron and hydrocarbons is shown in Table A.4-18. [Dammann], [UBA-Kloeckner-82]

Substance	Scale pits, aerated fine scale trap, settling tank	Sand/Gravelfilter		
	Outlet [mg/l]	Inlet <sup>1</sup> [mg/l]	Outlet [mg/l]	Reduction [%]
<b>Suspended solids</b>	40 – 70	36	3.5 ~ 3.8	90
<b>Iron</b>	10 – 20	7.7	0.85	90
<b>Hydrocarbons</b>	1 - 2	1.7	0.5 ~ 0.6	65

Note: Source of data [UBA-Kloechner-82]  
<sup>1</sup> average inlet concentration

Table A.4-18: Pollutant concentration in the water circuit



Stream I: 4600 m<sup>3</sup>/h for machine cooling (highest quality, oil < 10 mg/l)  
 Stream II: 7400 m<sup>3</sup>/h roughing mill and finishing train (medium quality, oil ~15 mg/l)  
 Stream III: 6000 m<sup>3</sup>/h delivery roller table (lowest quality, oil < 20 mg/l)

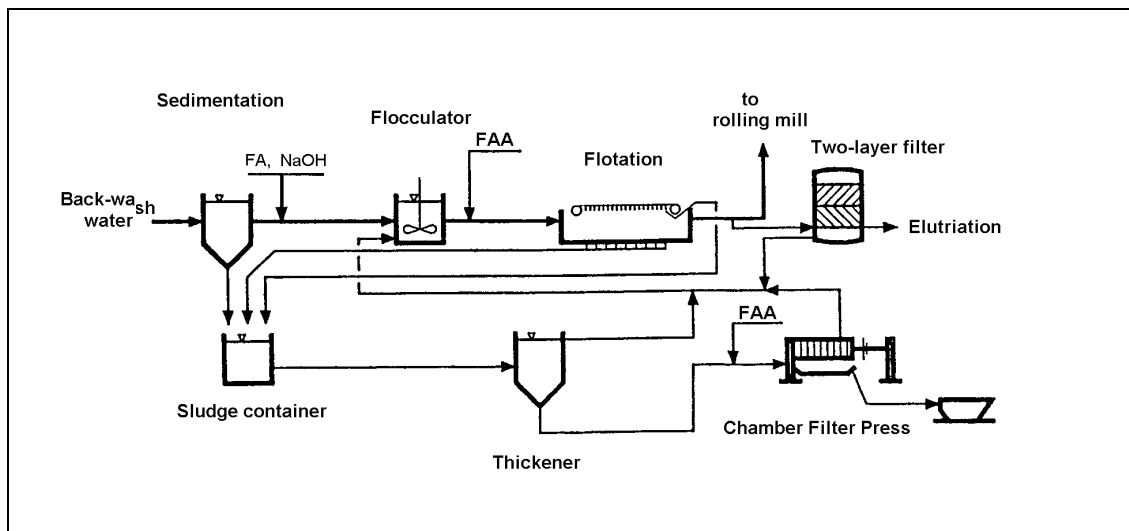
**Figure A.4-13: Example of a water recirculation system for a hot rolling mill [UBA-CS-8007]**

To make-up for evaporation losses and elutriation water, water from the LD steel plant or – in case of production stop - roughly filtered water from a river is added to the system. The amount of elutriation water, which needs to be withdrawn from the system to avoid salt built-up, is

mimimised by reuse for back-washing sand filters and by partial reuse in slag processing. [Dammann], [UBA-Kloeckner-82]

From filter back-washing about 750 m<sup>3</sup>/h arise which are treated as shown is in Figure A.4-14. About 92 % of the solids settle in the sedimentation step; the remaining suspended solids (approx. 50 mg/l) and the hydrocarbons (average 1.5 mg/l) are treated by flocculation and flotation. The water is then recirculated to the water system. The partial stream which has to be discarded is treated in two-layer filters. The concentration of suspended solids and hydrocarbons are well below the emission limit values set by authorities (10 mg/l SS and 1 mg/l HC). Achieved emission levels are shown in Table A.4-19.

For maintaining the water circuit, biocides, corrosion inhibitors and dispersing agents are added. When needed (e.g. once a day) flash chlorination is done.



FA = flocculation agent FAA = filtration aiding agent

Figure A.4-14: Treatment of back-washing water [UBA-CS-8007]

Substance	Concentration in mg/l	Type of sampling	Measurements in 1998 Operator/Comp. authority
Fe	0.13	Qualified random sample	12/6
Oil	< 0.1	Qualified random sample	12/6
Suspended solids	< 3	Qualified random sample	12/6
Cr	< 0.01	Qualified random sample	12/6
Ni	0.02	Qualified random sample	12/6
Zn	0.03	Qualified random sample	12/6

Note: Source of data: Senator für Bau und Umwelt Bremen. Plant: Stahlwerke Bremen. Mean values of the qualified random samples from 1998. Waste water volume: 1620404 m<sup>3</sup>

Table A.4-19: Concentration of effluents from treatment of back-washing water [Com2 D]

**Example C: SIDMAR**

The water circuit installed at Sidmar consists basically of 3 systems: the 3 bar-system for cooling the supporting rolls, the roll table and the motors; the 12 bar-system for cooling of the

work rolls and for feeding of the descaling pump system and the 150 bar-system for descaling at the furnace exits and in the roughing and finishing mill. The total flow is up to 13000 m<sup>3</sup>/h.

Oil and scale bearing water from the 150 bar-system is cleaned in a first step by scale pits followed by gravity sand filters. The process water from the roughing mill contains mainly large scale, less than 20 % of the oil and grease consumption, does not require colling and can be reused in the 3 bar-system without further treatment. Water from the finishing mill contains fine scales and over 80 % of the oil and grease consumption. Following the decanters and the sand filters this water needs to be cooled before it is reused in the 3 bar-system. The reused channel water contains less than 5 mg/l suspended solids and less than 0.2 mg/l hydrocarbons.

Due to evaporation losses and high contents of Na, Cl, etc., about 500 m<sup>3</sup>/h of refreshing water is needed, which is taken from the cold rolling mill. The elutriated water exits to the steel mill.

The reutilisation rate of the described system is over 95 %.

Efficiency of the waste water treatment and thus the pollutant concentration discharged depends among others on the combination of individual cleaning operations. Table A.4-20 lists more example water treatment sequences and achieved emission levels.

Results of waste water treatment		
Before Treatment	Treatment	After treatment [mg/l]
<b>Oil/Grease:</b> 10 -200 mg/l 0.7 - 2.73 kg/t  <b>Suspended solids (SS):</b> 120 – 2000 mg/l 0.13 - 4.57 kg/t	<b>Example E</b> Sedimentation + flocculation, flotation + sand filter	Oil: 50 SS: 50
	<b>Example F</b> Sedimentation + flocculation + cooling + sand filter	SS: < 10 Oil: <5 Fe: 12 Ni, Cr, Cu, Zn, Pb, Cd: < 0.1
	<b>Example G</b> Sedimentation + flocculation + cooling + magnetic filtration <sup>1</sup>	Reduction: SS: 90 % (down to 3 - 9 mg/l) Oil: 50 - 90 %
	<b>Example B'</b> Sedimentation + aerated sinter removal + flotation + sand filter, blow down: biological polishing	Reduction: SS (>63 µm): > 99 % 31 < SS <63 µm): 20 - 80 %:
	<b>Example H</b> Cyclones, settling basin, sand filter, cooling towers	Oil: 50 (= 20 g/t) SS: 50 (= 20 g/t) COD: 100
Note: Source of data [EC Haskoning] <sup>1</sup> Concentration before treatment: 30 - 100 mg suspended solids/l		

**Table A.4-20: Pollutant reduction for several waste water treatments**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.1.12.3 Cooling Water Treatment**

**Description:**

In order to operate closed cooling water cycles the cooling water has to be re-cooled and treated.

Cooling is carried out either by evaporation in cooling towers or by heat exchangers. In pressure-cooled counterflow **cooling towers** the water to be cooled is sprayed on grids in the cooling tower cells and flows over blocks into the cooling tower tray. Fans arranged laterally or on top draw off ambient air which passes the water in counterflow. Thus cooling is achieved by evaporation of water. The cooling efficiency is controlled by means of the air volume. Desalting is controlled via a measurement of the electrical conductivity. If required, the necessary amount of dispersants, sodium hypochlorite and biocide (prevention of growth of bacteria and fungi) and acid or alkali (pH-value) is added.

In **plate heat exchangers** plates with flow-through channels are screwed to a package. From each plate, alternatively hot waste water and cold cooling water is pumped through these channels. The heat is transferred via the plate wall.

In **hybrid cooling towers**, a plate heat exchanger is installed in the upper part of the tower. In the lower part, the water is cooled by evaporation. Due to the heat exchanger, the air with 100 % moisture is heated and condenses as fog some time later and with less intensity.

**Main achieved environmental benefits:**

- Reduced water consumption as water can be re-used in the process.

**Applicability:**

**Cross-media effects:**

- Addition of dispersants and of biocides [Com HR].
- Increased energy consumption as a result of recirculation pumping requirements. [Com2 HR].

In the planning and installation of circuit-type water treatment plants with cooling towers the geographical situation of the respective mill has to be taken into consideration. Due to the water evaporation in the recooling process the climatic conditions can be affected by the constant formation of fog and by the so-called industrial snow, especially in central Europe.

**Reference plants:**

**Operational data:** refer to Table A.4-16 [Com2 HR]

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### **A.4.1.13 Waste/By-product Treatment and Recycling**

#### **A.4.1.13.1 Internal Recycling of Dry or Drained Oxides**

**Description:**

Dry or drained oxides, which mostly consist of the coarse fraction - also resulting from the grinding or scarfing operations -, can be selectively recycled by magnetic and mechanical separation (sieves). Thus part of the oxide can be directly reused in the sinter plant, in the blast furnace or in the steel plant.

**Main achieved environmental benefits:**

- Reduced waste.
- Use of iron content.

**Applicability:**

- Certain recycling options require pretreatment by briquetting [Com D].



**Cross-media effects:**  
**Reference plants:**  
**Operational data:**  
**Economics:**  
**Driving force for implementation:**  
**Reference literature:**

#### **A.4.1.13.2 Recycling Technologies for Oily Mill Scale**

##### **Description:**

The direct utilisation of oily mill scale in metallurgical processes is restricted depending on the oil content. Coarse scale with a particle size of 0.5 – 5 mm and a oil content below 1 % can be returned to the sinter strand without any pre-treatment. High oil contents (> 3 %) result in increased emissions of VOC and potentially dioxins and can lead to problems the waste gas purification systems (e.g. glowfires in the electrostatic precipitators). Because of that the residues and waste have to be pre-treated before reuse. Fine scale sludge consists mainly of very small scale particles (< 0.1 mm). Because the fine particles absorb oil to a very high degree (5 – 20 %) this scale normally cannot be returned to the sinter strand without any pre treatment. The high oil content of the sludge combined with incomplete burning can result in oil vapour formation which can lead to fire in the following waste gas treatment systems. [Com A]

##### **Examples for treating oily mill scale are:**

##### **Briquetting and Converter charging**

The scale containing sludge is formed to briquettes under addition of binders. The produced, moulded bodies are of adequate consistency to be charged in the converter. Briquettes cooling effect is sufficient for converter charging. Additives such as anthracite can be included to make the briquettes thermally neutral.

##### **CARBOFER**

Oily mill scale sludge is mixed with lime and coal dust and, optionally, iron or carbon bearing flue dust to obtain a dry mixture that is suitable for pneumatic injection into a reactor of the iron and steel making process, such as the blast furnace or the electric arc furnace. A fully recovery of the injected materials can be expected. [Com HR]

##### **Washing (PREUSSAG method/de-oiling)**

A stirring device is charged with preconditioned sludge (scale, oil, water) under addition of washing water reagents. After rinsing the created suspension, solids, water and oil is separated. Result is oil free ( $\leq 0.2$  %) ferrous material.

##### **Flotation (THYSSEN method/de-oiling)**

Scale containing sludge is conditioned with reagents and deoiled in a 3-stage flotation process. The result is a Fe-product, an oily-product and a mixture of these.

##### **Revolving tubular furnace (de-oiling)**

Scale, containing oil and water, is dewatered and deoiled by temperatures of approx. 450 - 470 °C. The furnace may be heated directly or indirectly. The result is an oil free ferrous product (~ 0.1 %) plus emissions to air by additional usage of energy.

##### **2-layer sintering technology**

Process steps:

Prestraining of the charge (mill scale, flue dust, etc.)

Premixing the charge in the bunker followed by an intensive mixing procedure

charging the waste mixture - approx. 10 m behind ignition - onto the already sintered primary charge, resulting in secondary ignition.

**Direct utilization in the blast furnace (VOEST-ALPINE STAHL method)**

Scale is shot into the bottom of the blast furnace via a sludge burning lance. This is a very economic way to utilize the energy of the hydrocarbons and to reduce the iron oxide (scale) without needing an extra furnace and without producing extra environmental pollution, but it is only possible for blast furnaces equipped with a sludge or waste oil burning lance. It is important to inject the sludge at the bottom and not at the top of blast furnace to ensure that the hydrocarbons are burnt and not only evaporated. Special attention has to be taken on the emissions, to control, that really all hydrocarbons are burnt and to ensure, that the coincineration of these wastes in the blast furnace will not result in higher emissions.

**Main achieved environmental benefits:**

- Reduced waste.
- Using iron contents as raw material.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

- De-oiling methods consume washing agents or flocculating agents and result in oily waste water or residues from flotation.
- Thermal treatments result in emissions to air and increased energy consumption.

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

## A.4.2 COLD ROLLING Mill

### A.4.2.1 Storage and Handling of Raw Materials and Auxiliaries

### A.4.2.2 Pickling

#### A.4.2.2.1 Reduction of Waste Water Volume Contaminant Loading

**Description:**

General techniques for the reduction of waste water volume and contaminant loading include:

- Reduction of iron oxide formation during hot rolling and steel handling (e.g. by high pressure descaling, fast cooling, short storage time, corrosion free storage and transport). The acid consumption during pickling is proportional to the amount of iron oxide removed from the steel surface. Although the potential for a reduction in oxide formation is limited, control of the cooling rate can modify the structure of the scale. This can influence the pickling speed and thus reduce energy consumption for the process. Fast cooling of the hot rolled strip may be limited however for quality reasons.
- Partial or full replacement of wet pickling processes by waste water free mechanical treatment (mechanical descaling). For stainless steel mechanical descaling can only be applied at one part of the process and only partial replacement is viable. [Com2 CR] However, it should be recognised that there is an energy penalty associated with the use of mechanical descaling equipment.
- Reduction of acid consumption and regeneration costs by adding adequate chemicals (inhibitors) for pickling of low alloy and alloy steel (not applicable to stainless steel). However, inhibitors can have a detrimental effect on surface quality (due to the formation of rust).
- Reduction of acid concentration by using high pickling temperatures. Although a balance has to be reached between acid concentration and pickling temperature. The optimum is a function of acid losses, pickling efficiency and energy consumption. Increasing the pickling temperature leads to a rise in NO<sub>x</sub> generation for stainless steel pickling and therefore avoiding excessive NO<sub>x</sub> formation needs to be considered in the balance.
- Reduction of acid concentration by using electrical processes.
- Minimization of waste water volume by use of cascading flow.
- Minimization of waste water volume by using improved pickling and rinsing equipment (mechanical pre-treatment, closed tanks to reduce gas scrubber effluents, spray type treatment instead of dip treatment, squeegee rolls for removal of adhering bath liquor to reduce carry-over of pickle liquor and rinsing water, etc.).
- Internal recycling and mechanical filtering of pickle liquor and rinsing water for lifetime extension.
- Regeneration of pickling acid. Regeneration of waste acids reduces the volume of waste requiring neutralisation. However, the concentration and the volume of waste acid has to reach a certain level to be suitable for regeneration processes.
- Side-stream ion exchange or electro dialysis for bath regeneration.

- Careful selection of raw materials to minimize contamination of waste streams.
- Reduction of the formation of oxide dust (during de-coiling, levelling or in the entry accumulator) by the use of adequate suction heads.
- Indirect heating of acid. The most common way to heat the acid is the use of heat exchangers. Direct heating by steam injection dilutes the waste acid, which therefore cannot be regenerated.

#### A.4.2.2.2 Reduction of Dust Emission at the Decoilers

**Description:**

Iron oxide dust is formed by stretching the strip during the decoiling operation. The formation of dust can be prevented by the use of **water curtains**. This wet method requires a separator system to remove the iron oxide from the spraying water. This can either be a stand-alone system or it is integrated in the global water treatment system of the plant.

In some cases the water spray method leads to an undesired build-up of iron oxide particles on the rolls in the pickling line and hence to roll marks on the strip. In these cases **an exhaust system**, usually equipped with **fabric filters**, is used as an alternative to prevent the dispersion of the dust.

**Main achieved environmental benefits:**

- Prevention of fugitive dust emissions.
- Reduction of air emissions.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

- Consumption of energy.
- Generation of waste water or waste (filter dust).

**Reference plants:**

**Operational data and economics:**

Investment costs were reported to be 50000 euro for water sprays and 280000 euro for exhaust system with fabric filter (for a 3 Mt/a plat). [CITEPA]

**Driving force for implementation:**

**Reference literature:**

#### A.4.2.2.3 Mechanical Pre-descaling

**Description:**

Mechanical descaling techniques, like **shot blasting**, **stretcher leveller**, **temper mill** or **leveller**, are used to break and remove the major portion of the hot rolling scale. As the amount of iron oxide that has to be removed from the steel surface in the chemical pickling section is reduced, the acid consumption is reduced.

Mechanical descaling facilities are equipped with extraction systems and abatement devices (generally **fabric filters**) to control the release of particulate material.

**Main achieved environmental benefits:**

- Reduction of acid consumption.
- Increased effectiveness of the pickling process.

**Applicability:**

- New plants and with limitations –due to available space- for existing plants.
- Mechanical descaling for stainless steel grades can only be applied prior the initial pickling step. In later pickling steps this would influence the surface quality of the finished product.

**Cross-media effects:**

- Increased energy consumption.
- Generation of particulate emissions, which have to be captured and abated.
- Generation of waste (filter dust).
- Due to increased effectiveness of the pickling operations, pickling bath temperatures can be lowered, resulting in lower evaporation losses. Reducing the loading on the acid pickling and hence the consumption of acids decreases the generation of acidic wastes.

**Reference plants:**

**Thyssen Stahl**, Krefeld, Germany (horizontal shot blasting for hot and cold strip, fabric filter) [Met-Plant-Int-1-94]

**Operational data:**

	Concentration [mg/Nm <sup>3</sup> ]	Specific Emission [kg/t product]	Reduction rate <sup>1</sup> [%]	Waste Gas Volume	Method of analysis
<b>Example A: shot blasting unit of stainless steel plant</b>					
Dust	15 – 25 <sub>1</sub>	0.01 - 0.02	> 95	350 – 450 m <sup>3</sup> /t	BS 3405
Cr, Mn, Ni	reliably below the limit of 5 mg/m <sup>3</sup> <sup>2</sup>				
<b>Example B: shot blasting unit of the annealing and pickling line for hot rolled steelbands</b>					
	4.5/< 1/2.6			13800/15200/18200 Nm <sup>3</sup> /h	
Note: Source of data for example A [EUROFER CR]; example B [FIN 28.3]					
<sup>1</sup> [CITEPA] reports below 20 mg/m <sup>3</sup> for V=135000 m <sup>3</sup> /h and max capacity of 225 t/h.					
<sup>2</sup> Source of data [Met-Plant-Int-1-94]					

**Table A.4-21: Dust emission levels achieved at shot blasting unit using fabric filters**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### A.4.2.2.4 Optimised Rinsing Procedure/ Cascade Rinsing

**Description:** see also Chapter D.8

An optimised rinsing operation aims at reducing the waste water generated and at minimizing contamination of the rinsing water. A common method to reduce the volume of waste water and sludge from waste water treatment is to install a (counter-current) cascading flow system in combination with squeegee rolls in the rinsing plant. Furthermore, spent rinsing water can be reused in the plant, e.g. for make-up water in pickling baths. Squeeze rolls and wiper rolls are installed behind the pickling baths, as well as before and behind the rinsing baths. Adhering bath liquor from the strip surface is removed to reduce carry-over of pickle liquor from the pickling bath and of concentrated rinsing water from one cascading flow step to the next.

A typical cascade rinse system utilizes some three to six compartments with wringer rolls to reduce carry-over between compartments. Fresh or condensate water to be added to the last compartment is allowed to cascade counter-currently over a weir to the preceding compartment. The excess, i.e. dragout, overflows from the first compartment to a storage tank from where it is usually passed to the regeneration plant. Portions from the intermediate tanks are taken for acid vapour absorption in the absorption columns of the regeneration plant or for fresh acid dilution in the pickling tanks.

**Main achieved environmental benefits:**

- Reduced water consumption.
- Reduction of waste water volume and sludge from waste water treatment.
- Reduction of acid consumption.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:** Jenn An, Taiwan

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### A.4.2.2.5 Turbulence Pickling

**Description:**

Recent developments in pickling techniques aim mainly at improving the process itself; enhancing efficiency, pickling speed and quality and making the process easier to control. Figure A.4-15 shows the development from deep pickling tanks via shallow tanks to turbulent pickling where the acid is sprayed onto the strip at the narrow gap between the pickling tanks.

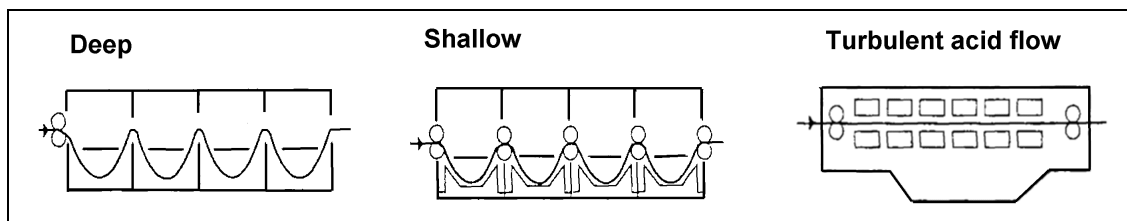


Figure A.4-15: Different type of pickling tanks

**Main achieved environmental benefits:**

- Increased efficiency.
- Reduction energy consumption, reduction in acid consumption.

**Applicability:**

- New pickling plants and existing in connection with major revamping.

**Cross-media effects:**

- As the process is more efficient, lower temperatures are possible for the acid bath, leading to a reduction in acid consumption [Metall94].
- As turbulence pickling is easier to control ( and may be equipped with additional process models) a more effective control of the pickling effect is possible, leading to less over-pickling and thus reduction in pickling loss (20 – 30 %, 0.8 – 1.2 kg/t respectively) [Metall94].
- New acid consumption and/or regeneration capacities for spent acid are reduced [Metall94].

**Reference plants:**

Stahlwerke Bochum AG (Germany); BHP (Australia); Sumitomo Metals (Japan); Sidmar (Belgium); Thyssen Stahl (Germany); ILVA (Italy); ALZ (Belgium), Avesta (Sweden); Allegheny Ludlum (USA) [Metall94]

**Operational data:**

**Economics:** reduced investment and operational costs

**Driving force for implementation:** improvement of pickling process efficiency, improved quality, monetary advantage

**Reference literature:****A.4.2.2.6 Cleaning and Reuse of Acid Pickle Liquor****Description:**

Side-stream mechanical filtering, acid recovery and internal recycling can be used for cleaning and extending the lifetime of the pickling liquor. The liquor is filtered, e.g. in deep bed media filters, to remove particulates. Cooling of the acid by means of heat exchangers might be necessary prior to the adsorption unit in which a physio-chemical adsorbent (like a resin) removes free acid from the waste stream. Once the unit is saturated the free acid is desorbed by a fresh water stream and recycled to the pickling process.

**Main achieved environmental benefits:**

- Reduced acid consumption (waste water volume and sludge).

**Applicability:**

- New and existing plants.

**Cross-media effects:**

- Increased energy consumption.

**Reference plants:**

Allegheny Ludlum, USA

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### A.4.2.2.7 Hydrochloric Acid Regeneration by Spray Roasting

#### Description:

See Chapter D.6.10.1.2 for regeneration process description and chapter D.6.3 for emission abatement.

#### Main achieved environmental benefits:

- Reduced consumption of fresh acid (from 12 - 17.5 kg/t to 0.7 - 0.9 kg/t; HCl conc. 33 %).
- Reduced waste water volume and sludge.

#### Applicability:

- New plants and existing plants depending on size.

#### Cross-media effects:

- Consumption of energy and water.
- Generation of air emissions (combustion product and acid), which have to be reduced by e.g. wet scrubbers.
- Generation of waste water, which has to be treated (see A.4.2.2.28).
- Specific emission of suspended solids of 2.86 g/t product (in treated waste water).
- Reduction of new acid to be produced (supplier).
- Generates a sellable solid by-product: iron oxide, which can be reused in the ferrite industry or in color- and glass production.

#### Reference plants: [Karner-1]

Company	Year of contract	Capacity [t/h]	Remarks
Hoesch Stahl AG; Dortmund, FRG	1989	9000	
Ornatube Enterprise; Kaohsiung; Taiwan	1989	900	
Shanghai Cold Strip; China	1989	2900	
China Steel; Kaohsiung, Taiwan	1989	1900	
Sidmar S.A.; Gent, Belgium	1990	11000	
Anshan Iron & Steel; China	1991	2 x 6000	high-purity oxide
Benxi Iron & Steel; China	1992	5000	
Karaganda Met. Komb.; Kazakhstan	1992	2 x 10000	
MMK; Magnitogorsk, Russia	1993	11000	
Baoshan Iron & Steel; China	1994	2 x 2900	high-purity oxide
Hanbo Steel; Korea	1994	11000	

#### Operational data:

Table A.4-22 and Table A.4-23 present data on consumption and emissions associated with HCl spray roasting.



Input / Consumption Level		
Spent acid	0.7 - 0.9	kg/t
Cooling water (in)	0.07 - 0.09	m <sup>3</sup> /t
Industrial + demineralised water	0.09 - 0.15	m <sup>3</sup> /t
Energy:		
Electrical energy	4 - 15	MJ/t
Caloric energy (natural gas)	102 - 119	MJ/t
Output / Emission Level		
Specific Emission		
Solid by-product: Fe <sub>2</sub> O <sub>3</sub>	5.1 - 5.4 (5.6 Sidmar)	kg/t
Recycled acid (20 %)	23 - 40	kg/t
Cooling water (out)	0.07 - 0.09	m <sup>3</sup> /t
Waste gas	24 -38	m <sup>3</sup> /t
Waste water (discharge)	0.04 - 0.07	m <sup>3</sup> /t

Note: Source of data [EUROFER CR]

**Table A.4-22: Consumption and emission levels for HCl spray roasting**

	Concentration [mg/Nm <sup>3</sup> ]	Specific Emission [kg/t product]	Reduction rate <sup>1</sup> [%]	Method of analysis
Dust	20 - 50	n.a.	n.a.	EPA
SO <sub>2</sub>	50 - 100	n.a.	n.a.	SO <sub>4</sub> detection by Ion Chromatography (NBN T95-202)
NO <sub>2</sub> <sup>2</sup>	300 - 370	0.014	> 90	NO <sub>3</sub> detection by Ion Chromatography (NBN T95-301), Luminiscence
CO	150	0.006	> 90	Umwelt-BA EM-K1
CO <sub>2</sub>	180000	6855	> 90	Infrared
HCl	8 - 30	3.05 E-4	> 98	Ion chromatography (ASTM D 4327-84), Potentiometric titration (NEN 6476)

Note: Source of data [EUROFER CR]  
<sup>1</sup> Reduction rate based on mass flow of constituent before/after abatement measure  
<sup>2</sup> (3 % O<sub>2</sub>)

**Table A.4-23: Emissions to air from HCl spray roasting**

Plant supplier claim pollutant concentrations of less than 2 mg/m<sup>3</sup> of HCl and free Cl<sub>2</sub>. [Karner-1]

For a countercurrent packed water scrubber with final alkaline scrubbing HCl emission levels of <15 mg/m<sup>3</sup> with investment cost of 1175 kECU and operating costs of 6 kECU/a (electricity 300 kWh, V=10000 m<sup>3</sup>/h) were reported by [CITEPA].

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.2.8 Hydrochloric Acid Regeneration by Fluidised Bed**

**Description:**

See Chapter D.5.10.1.1 for regeneration process description and Chapter D.5.3 for emission abatement.

**Main achieved environmental benefits:**

- Reduced consumption of fresh acid.
- Reduced waste water volume and sludge.

**Applicability:**

- New plants and existing plants depending on size.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

The economics of a modern pickling plant, including the fluidized bed process, involve the following factors:

- Raw acid consumption.
- Utilisation of rinse and scrubber water.
- Production of clear, iron-free hydrochloric acid.
- Production of iron oxidem which can be used in different industries.

Generally, the capital costs of a pickling plant, including fluidised bed process, are favorable compared with the operation costs and resulting benefits. Overall economics will vary from one installation to another, due to local differences in acid cost, waste pickle liquor regeneration cost and the cost involved in modernizing existing facilities or constructing new facilities. [Rituper-1]

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.2.9 Effluent-free HCl Strip Pickling Plant**

**Description:**

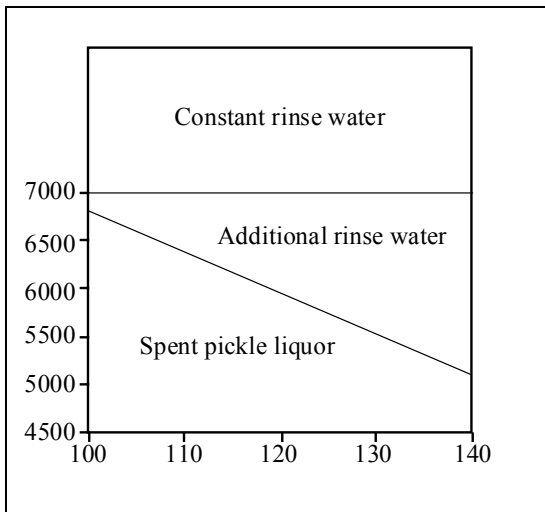
In determining the waste water from pickling operation: spent pickle liquor; rinse waste water; and scrubber water have to be taken into account. Using the fluidized bed process, the pickle liquor recycled between the pickling tanks and regeneration unit, results in a nearly zero consumption of raw acid apart from some small amount of evaporation loss. [Rituper-1]

Since the fluidized bed process operates at approximately 850 °C, additional rinse and scrubber water from the pickle line can be utilized in the regeneration plant. In accordance with the energy balance of the venturi scrubber, a certain amount of water is necessary for cooling the reactor off-gas by evaporation. [Rituper-1]

The quantity of rinse and scrubber water, which can be utilized in the fluidized bed process, depends on the iron content of pickle liquor. An example of rinse water utilization is shown in Figure A.4-16 A portion of the rinse water is used for absorption, with the remainder directly added to the venturi scrubber. [Rituper-1]

In the example shown in Figure A.4-16, a total of 5943 l/h of rinse water can be used for the absorption of HCl. Depending on the iron content of the pickle liquor, approximately 500 l/h of

rinse water at 105 g/l Fe<sup>++</sup> and approximately 1750 l/h of rinse water at 130 g/l Fe<sup>++</sup> can be used in addition.



**Figure A.4-16: Dependence of rinse water utilisation on iron content [Rituper-1]**

This example shows that an economical effluent-free pickling line operation can be achieved considering spent pickling liquor as well as rinse water quantities and concentrations.

This process is capable of operating a completely closed, effluent-free pickling, plant and has already been installed in several modern facilities. These facilities are operating with hydrochloric acid consumption of less than 0.2 kg acid/tonne of pickled material. One example of effluent-free strip pickling line in operation is illustrated in Figure A.4-17. [Rituper-1]

**Main achieved environmental benefits:**

- No water discharge/pollution.

**Applicability:**

- New plants and existing plants depending on size.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

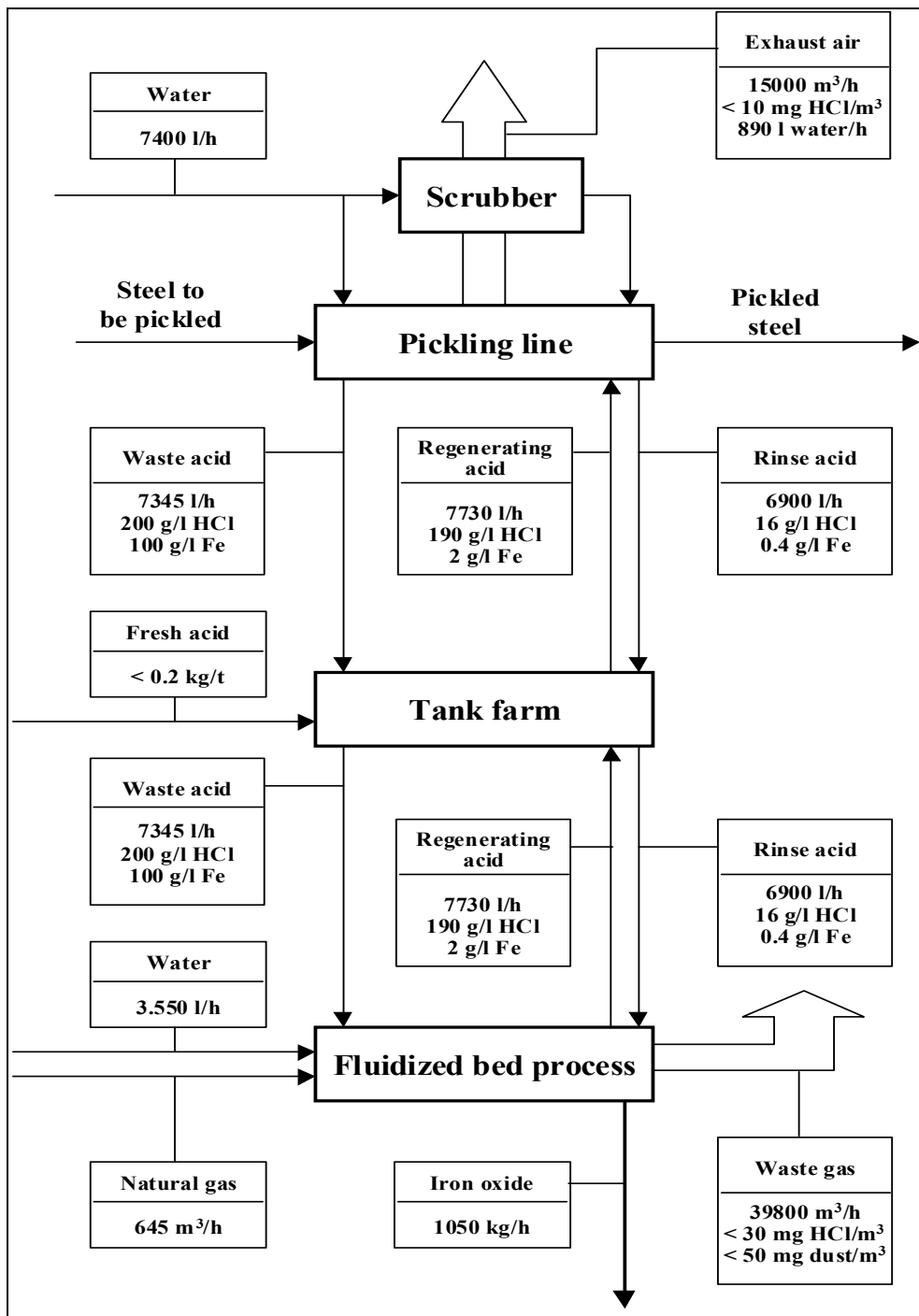


Figure A.4-17: Example of effluent-free HCl pickling and acid regeneration [Rituper-1]

#### A.4.2.2.10 Sulphuric Acid Recovery by Crystallization

**Description:** see Chapter D.6.9.1 and D.6.3 for reduction of air emissions (scrubbing).

**Main achieved environmental benefits:**

- Reduced consumption of fresh acid.
- Reduced waste water volume and sludge.

**Applicability:**

- New plants and existing plants depending on size.

**Cross-media effects:**

- Increased energy consumption.
- Emissions to air from recovery.

**Reference plants:****Operational data:**

Table A.4-35 presents data on consumption and emissions associated with H<sub>2</sub>SO<sub>4</sub> vacuum crystallisation.

Input / Consumption Level	
Spent acid	7 - 10 kg/t
Cooling water (in)	2 - 3.5 m <sup>3</sup> /t
Industrial + demineralised water	0.2 - 0.4 m <sup>3</sup> /t
Energy:	
Electrical energy	1 - 20 MJ/t
Caloric energy	100 - 200 MJ/t
Output / Emission Level	
	Specific Emission
Solid by-product: Fe-sulphate	26 - 30 kg/t
Recycled acid (20 %)	0 - 10 kg/t
Cooling water (out)	2 - 3.5 m <sup>3</sup> /t
Waste gas	70 - 90 m <sup>3</sup> /t
Waste water (discharge)	0.2 - 0.4 m <sup>3</sup> /t
Note: Source of data [EUROFER CR]	

**Table A.4-24: Consumption and emission levels for H<sub>2</sub>SO<sub>4</sub> vacuum crystallisation**

	Concentration [mg/Nm <sup>3</sup> ]	Specific Emission [g/t product]	Reduction rate <sup>1</sup> [%]	Method of analysis
SO <sub>2</sub>	8 - 20	0.5 - 1.5	> 95	Infrared
H <sub>2</sub> SO <sub>4</sub>	5 - 10	0.3 - 0.6	> 95	Titration
Note: Source of data [EUROFER CR]				
<sup>1</sup> Reduction rate based on mass flow of constituent before/after abatement measure				

**Table A.4-25: Emissions to air from H<sub>2</sub>SO<sub>4</sub> vacuum crystallisation**

**Economics:****Driving force for implementation:****Reference literature:**

#### A.4.2.2.11 Mixed Acid Regeneration by Spray Roasting

**Description:** see Chapter D.5.10.1.2 and D.5.3

**Main achieved environmental benefits:**

- Reduction in fresh acid consumption (from 2.5 - 7. kg/t HF and 3 - 10 kg/t HNO<sub>3</sub> down to 0.8 - 1.2 kg/t HF), reduction of new acid to be produced (supplier) [Com Karner].
- Reduction of neutralisation sludge [Com Karner].

**Applicability:**

- New and existing plants [Com Karner].

**Cross –media effects:**

- Consumption of energy and chemicals.
- Generation of air emissions, which have to be reduced/controlled.
- Generation of waste water, which has to be treated.
- Generation of usable by-product mixed oxide [Com Karner].

**Reference plants:** [Com Karner]

Company	Capacity [l/h]	Year of Start
Acerinox, Spain	3000	1992
Yieh United, Taiwan	4500	1994
Posco, Korea	4500	1994
Columbus, South Africa	4500	1995

**Operational data:**

Table A.4-26 presents data on consumption and emissions of mixed acid regeneration by spray roasting.

Input/Consumption Level	
Spent acid	25 - 100 kg/t
Cooling water (in)	1.5 - 9 m <sup>3</sup> /t
Urea (for Denox)	0.4 - 1 kg/t
Caustic soda	
Energy:	
Electrical energy	5 - 20 MJ/t
Caloric energy (natural gas)	60 - 230 MJ/t
Output/Emission Level	
Solid by-product: mixed oxide	1.7 - 5 kg/t
Recycled acid (HF 6 %, HNO <sub>3</sub> 10 %)	26 - 108 kg/t
Cooling water (out)	1.5 - 9 m <sup>3</sup> /t
Waste gas:	25 - 100 m <sup>3</sup> /t
NO <sub>x</sub>	< 100 ppm (= 200 mg/m <sup>3</sup> calc. NO <sub>2</sub> )
HF	< 2 mg/Nm <sup>3</sup>
Dust	< 10 mg/Nm <sup>3</sup>
Waste water	0.003 - 0.01 m <sup>3</sup> /t

Note: Source of data [Com-Karner], example Pyromars

**Table A.4-26: Consumption and emissions of mixed acid regeneration by spray roasting**

**Economics:** savings due to reduced acid consumption and sellable by-product

**Driving force for implementation:**

**Reference Literature:**

W. Karner, W.Hofkirchner, Modern pickling and acid regeneration technology, MPT-Metallurgical Plant and Technology No.2, 1996, 92 -100

#### A.4.2.2.12 Mixed Acid (HNO<sub>3</sub> and HF) Recovery by Ion Exchange

**Description:** see Chapter D.5.9.3

**Main achieved environmental benefits:**

- Reduction of waste and fresh acid consumption.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

Input / Consumption Level	
Spent mixed acid	0.05 - 0.2 m <sup>3</sup> /t
Water	0.05 - 0.2 m <sup>3</sup> /t
Energy: Electrical energy	2 - 5 MJ/t
Output / Emission Level	
	Specific Emission
Recovered mixed acid	0.05 - 0.2 m <sup>3</sup> /t
Free HF recovery rate:	75 - 85 %
Free HNO <sub>3</sub> recovery rate:	80 - 85 %
Metals removal rate:	50 - 55 %
Metal containing weak acid solution	0.05 - 0.2 m <sup>3</sup> /t

Note: Source of data [EUROFER CR]

**Table A.4-27: Consumption and emission levels for mixed acid recovery by ion exchange**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### A.4.2.2.13 Mixed Acid (HNO<sub>3</sub> and HF) Recovery by Diffusiondialysis

**Description:** see D.5.9.4

**Main achieved environmental benefits:**

- Reduction of waste and fresh acid consumption.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:** Swedish plant.

**Operational data:**

**Example**

Thanks to the filtration of the used acids, a membrane cleaning does become necessary very seldom. By means of a corresponding pretreatment of the process solution it was reached, that a diffusion dialysis plant, installed in Sweden in 1989, for regeneration of stainless steel pickling

acid (HF/HNO<sub>3</sub>, 300 l/h) has been operating until today (1993) without any membrane cleaning with perfect results. [OSMOTA]

**Economics:**

**Driving force for implementation:**

**Reference literature:**

**A.4.2.2.14 Mixed Acid Recovery by Evaporation**

**Description:** See Chapter D.5.10.4 and D.5.10.5.

**Main achieved environmental benefits:**

- Reduction of fresh acid consumption by recycling both free and bounded HNO<sub>3</sub> and HF.
- No nitrates in waste waters.
- No dust emissions [Com2 FIN].

**Applicability:**

- New and existing plants.

**Cross-Media effects:**

- Consumption of energy and H<sub>2</sub>SO<sub>4</sub>.
- Generation of metal sulfates, which can be neutralised to metal hydroxides [Com2 FIN].

**Reference plants:**

Company	Capacity (l/h)	Year of Start
Outokumpu, Finland	1500	1984
Outokumpu, Finland	3000	1997



**Operational data:**

Input/Consumption Level	
Spent acid	15 – 30 litres / t
H <sub>2</sub> SO <sub>4</sub> (95 %)	4.0 – 6.0 kg / t
Cooling water	3.8 – 5.8 kg / t
Energy:	
Electricity	2.3 – 3.5 MJ / t
Steam	16 – 24 kg / t
Propan	3.2 – 4.8 MJ / t
Output/Emission Level	
Cooling water	3.8 – 5.8 kg / t
Recycled acid:	14 – 20 litres / t
130 g/l HNO <sub>3</sub>	
55 g/l HF	
Metal sulphate:	5.0 – 7.6 kg / t
Fe	0.6 – 0.8 kg / t
Cr	0.09 – 0.13 kg / t
Ni	0.08 – 0.12 kg / t
SO <sub>4</sub>	1.9 – 2.9 kg / t
H <sub>2</sub> SO <sub>4</sub>	1.7 – 2.5 kg / t
Waste gas:	
Dust	None
HF	< 2 mg / l
NO <sub>2</sub>	< 100 mg / l
The data above is based on measurements during plant operation.	

**Table A.4-28: Consumption and emission levels for mixed acid recovery by evaporation [Com2 FIN]**

**Economics:**

- Savings due to reduced consumption of acids.
- Easy to maintain constant composition of pickling acids.
- No need to acid neutralization [Com2 FIN].

**Diving force for implementation:**

- Total regeneration of acids [Com2 FIN].

**Reference literature:**

B.Nyman, T.Koivunen, The Outokumpu process for pickling acid recovery, Iron Control in Hydrometallurgy, Toronto, 19 - 22 Oct 1986, p 519-536, John Wiley & Sons.

#### **A.4.2.2.15 Electrolytic Pre-pickling for High Alloy Steel**

**Description:**

Pre-pickling is done in an initial neutral electrolyse tank using an aqueous solution of sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) at a processing temperature (max. 80 °C) prior to the mixed acid baths. Electrolytic pre-pickling facilities are fully sealed; fumes are extracted and led to a scrubber unit before release.

Recent developments include also alkaline electrolytic pre-pickling in combination with neutral pre-pickling and acidic pickling /acidic electrolysis. [Hitachi]

**Main achieved environmental benefits:**

- Reduction of the load on the mixed acid and hence a reduction in NO<sub>x</sub> and nitrate releases.
- Wet scrubbing techniques using packed towers are generally employed to reduce the emissions to air from pre-pickling facilities.

**Applicability:**

- New pickling lines and existing in case of major revamps provided sufficient space is available.

**Cross-media effects:**

**Reference plants:**

Allegheny Ludlum, USA

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.2.16 Cleaning and Reuse of Electrolytic Pickle Liquor**

**Description:**

During the pickling process non soluble salts and metallics are formed and must be removed from the electrolytic sodium sulfate solution to maintain proper operation.

Therefore, a small side stream of the electrolyte is cleaned. Particulates in the solution are removed in inclined plate clarifiers by gravity settling. The clarified solution is returned to the electrolysis; while the sludge stream is sent to a chromium reduction unit.

**Main achieved environmental benefits:**

- Reduced electrolyte lifetime, reduced waste.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

Allegheny Ludlum, USA

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.2.17 External Use of Spent Acid Pickle liquor**

**Description:** sell for external regeneration / sell for external use in water treatment

→ *no information submitted.*

**Main achieved environmental benefits:**

**Applicability:**

**Cross-media effects:**

**Reference plants:**  
**Operational data:**  
**Economics:**  
**Driving force for implementation:**  
**Reference literature:**

#### A.4.2.2.18 Reduction of Emissions from Pickling/Closed HCl and H<sub>2</sub>SO<sub>4</sub> Pickling Tanks with Exhaust Gas Scrubbing

**Description:** see Chapter D.5.2 and D.5.3 ff

The various working steps of the pickling process are carried out in totally enclosed equipment or in equipment fitted with hoods. The acid fumes generated are extracted and passed through gas scrubbers (absorption towers) for cleaning. Recycling water, e.g. from rinsing, is used as absorbent. Partial flow of the scrubbing water has to be discharged via the neutralisation plant.

**Main achieved environmental benefits:**

- Reduction of emissions to air, especially of fugitive acid fumes.

**Applicability:**

- New plants and existing plants.

**Cross-media effects:**

- Increased energy consumption.
- Generation of acidic waste water, which can be used in the process, e.g. as rinse water for HCl regeneration, or require neutralisation followed by water treatment (associated with consumption of chemicals and generation of water treatment sludges).

**Reference plants:** Jenn An, Taiwan [Danieli].

**Operational data:**

##### HCl Pickling

	HCl Pickling	
	Dust	HCl
<b>Specific Waste Gas Volume [m<sup>3</sup>/t]</b>	25 - 400	
<b>Energy Consumption [MJ/t]</b>	0.5 - 1.5	
<b>Concentration [mg/Nm<sup>3</sup>]</b>	10 - 20	10 - 30 <sup>1</sup>
<b>Specific Emission [g/t]</b>		0.258
<b>Reduction rate<sup>2</sup></b>		> 98 %
<b>Method of analysis</b>	EPA	Ion chromatography (ASTM D 4327-84) Potentiometric titration (NEN 6476)

Note: Source of data [EUROFER CR]  
<sup>1</sup> [EUROFER 6.9] reports upper level of 30 mg/Nm<sup>3</sup> when including continuous measurements.  
<sup>2</sup> Reduction rate based on mass flow of constituent before/after abatement measure

**Table A.4-29: Emission levels achieved for HCl pickling by absorption towers**

Other sources reported the following achieved emission levels:

**USA** [EPA-453]

**Packed scrubber + mesh demister:**

HCl emission values: 2.7 / 2.8 / 21.2 mg/m<sup>3</sup>, respectively 99.5 / 97.8 / 97.0 % efficiency.

**Plate scrubber + mesh demister:**

HCl emission values: 3.5 mg/m<sup>3</sup>, respectively 99.96 % efficiency.

**Plate scrubber + chevron demister:**

HCl emission values: 12.9 / 13.4 mg/m<sup>3</sup>, respectively 99.0 % efficiency.

[Co-or] reported HCl emission values as low as 1 mg/m<sup>3</sup>, with an average of 15.4 and a maximum of 30 mg/m<sup>3</sup>

[CITEPA]:

**water wall + mist arrestor:**

HCl emissions 10 – 15 mg/m<sup>3</sup>, investment costs: 450 kECU, operating costs: 14 kECU/a, electricity hourly consumption: 100 kWh.

**Counter current water packed scrubbing:** HCl emissions 10 – 15 mg/m<sup>3</sup>, investment costs: 625 kECU, operating costs: 14 kECU/a, electricity 80 kWh.

[Rituper] reported emission levels < 10 mg/m<sup>3</sup>.

**H<sub>2</sub>SO<sub>4</sub> Pickling**

	H <sub>2</sub> SO <sub>4</sub> Pickling	
	SO <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>
Specific Waste Gas Volume [m <sup>3</sup> /t]	50 - 110	
Energy Consumption [MJ/t]	1 - 2	
Concentration [mg/Nm <sup>3</sup> ]	8 - 20	1 - 2
Specific Emission [g/t]	0.4	0.05
Reduction rate <sup>1</sup>	> 95 %	> 95 %
Method of analysis	Infrared	Titration
Note: Source of data [EUROFER CR]		

**Table A.4-30: Emission levels achieved for HCl pickling by absorption towers**  
**Economics:**

Counter-current water scrubbing in packed columns	
Production capacity	900000 t/a
Energy consumption (electrical)	0.68 kWh/t
Volume flow	10.6 Nm <sup>3</sup> /s
Investment cost	625 EUR '000
Operating costs	14 EUR '000

**Table A.4-31: Estimated costs for counter-current water scrubbing in packed columns**  
[CITEPA]

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.2.19 Reduction of Emissions from Pickling/Closed Mixed Acid Pickling Tanks with Exhaust Gas Scrubbing**

**Description:** see Chapter D.5.2, D.5.3 (fabric filter) and D.5.8.3. scrubbing with H<sub>2</sub>O<sub>2</sub>, NaOH, urea ...

**Main achieved environmental benefits:**

- Reduction of emissions to air, especially of fugitive acid fumes (HF and NO<sub>x</sub>).

**Applicability:**

- New plants and existing plants.

**Cross-media effects:**

- Scrubbing with H<sub>2</sub>O<sub>2</sub> results in a nitric acid by-product with a concentration that allows recycling to the pickling process.
- Reduction of nitric acid consumption.
- Reduced waste water volume and waste water treatment sludge.
- In case of H<sub>2</sub>O<sub>2</sub> or urea injection in the pickling bath, scrubbing water can be reused as make up water in the pickling tanks.
- Scrubbing with sodium hydroxate results in a sodium nitrate waste which is disposed of.

**Reference plants:**

**Thyssen Stahl**, Krefeld, Germany [Met-Plant-Int-1-94]

**Allegheny Ludlum**, USA

**Operational data:**

[CITEPA] reported emission figures of 0.2 – 2 mg/m<sup>3</sup> (max 17 mg/m<sup>3</sup>) for HF and 5 - 1000 mg/m<sup>3</sup> for NO<sub>x</sub>.

Industry reported the lower end of the emission range to be 350 mg/Nm<sup>3</sup> for NO<sub>x</sub>. [Com2 CR]

**Economics:****Driving force for implementation:****Reference literature:**

#### A.4.2.2.20 Suppression of NO<sub>x</sub> from Mixed Acid Pickling by Addition of H<sub>2</sub>O<sub>2</sub> (or Urea) to Pickling Bath

**Description:** see Chapter D.5.8.1

**Main achieved environmental benefits:**

- Reduction of NO<sub>x</sub> emission.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

- Reduction in acid consumption.
- Consumption of hydrogen peroxide (3 to 10 kg/t).

**Reference plants:**

**Thyssen Stahl**, Krefeld, Germany (urea addition) [Met-Plant-Int-1-94]

**Operational data:**

Addition of hydrogen peroxide suppresses the formation of gaseous NO<sub>x</sub> emissions by reforming HNO<sub>3</sub> in the pickle tank. Thus it is possible to reuse the acid part leading to a reduction of acid consumption of up to 25 %.

	Concentration [mg/Nm <sup>3</sup> ]	Specific Emission [g/t product]	Reduction rate <sup>1</sup> [%]	Method of analysis
NO <sub>x</sub>	350 - 600	80 - 300	75 - 85	Chemiluminescence
HF	2 - 7	1 - 1.5	70 - 80	Titration

Note: Source of data [EUROFER CR]

<sup>1</sup> Reduction rate is a combination of H<sub>2</sub>O<sub>2</sub> injection and exhaust absorber system.

**Table A.4-32: Achievable emission levels by H<sub>2</sub>O<sub>2</sub> injection**

For NO<sub>x</sub> suppression using urea addition to the pickling bath (plus gas washer), it was reported that emissions were reliably below the NO<sub>x</sub> limit value of 850 mg/m<sup>3</sup>. Higher ammonia contents in the waste water were reduced by aeration. [Met-Plant-Int-1-94]

**Economics:**

For a 70 % reduction of NO<sub>x</sub>, hydrogen peroxide addition cost of 4 kECU/kg NO<sub>x</sub> were reported. [CITEPA]

For shallow bath turbulent pickling, the required dose rate of hydrogen peroxide may increase dramatically. [Com2 CR] Hence for large pickling installations where the dose rate for hydrogen peroxide would be excessive, other NO<sub>x</sub> reduction measures, e.g. SCR system, can be more appropriate.

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.2.21 NO<sub>x</sub> Reduction from Pickling by Selective Catalytic Reduction**

**Description:** for more detailed description see Chapter D.2.4

The technique of Selective Catalytic Reduction (SCR) can be applied to the emissions from mixed acid pickling. This comprises heating the NO<sub>x</sub> laden exhaust gas from the pickling tanks to 280 - 450°C and injecting ammonia or urea. The gas stream is then passed over a catalyst and the NO<sub>x</sub> reacts with the ammonia to form nitrogen and water.

SCR can be coupled with an additional HF reduction step which is either wet absorption or lime treatment. [Com CR] In the latter, the waste gas is treated with lime prior to the SCR. HF reacts with the lime to form fluor-spar, which, because of its high degree of purity, can be used as secondary raw material. [CITEPA]

**Main achieved environmental benefits:**

- Reduction of NO<sub>x</sub> (reduction efficiency of up to 95 % with a typical range of 70 – 90 %. The achieved NO<sub>x</sub> level depends on the initial concentration).
- If coupled with lime treatment, reduction of HF emissions.

**Applicability:**

- New plants and major modernisation of existing plants.

**Cross-media effects:**

**Reference plants:** 3 units in Outokumpu Tornio Plant, Finland [Com2 FIN]

**Operational data:**

**Economics:** High capital cost, therefore only for large installations [Com CR]

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.2.22 NO<sub>x</sub> Reduction from Pickling by Non-Selective Catalytic Reduction**

**Description:** for more detailed description see Chapter D.2.5

**Main achieved environmental benefits:**

- Reduction of NO<sub>x</sub>.

**Applicability:**

- New plants and mayor modernisation of existing plants.

**Cross-media effects:**

- Energy consumption to heat exhaust gas to operating temperature for SNCR

**Reference plants:** not applied for mixed acid pickling.

**Operational data and Economics:**

To heat the exhaust gases from a process operating at ambient temperature up to the temperature required for SNCR to operate (in the range of 900 - 1000°C) means, that the running costs would be very high. Furthermore, the removal efficiency is lower than can be achieved by the SCR technique, which requires a temperature of some 500 -600°C less than SNCR for effective operation. [Com3 EUROFER] As there are other, NOx reduction measures readily available, which are more suitable and more efficient, SNCR was not selected as BAT for NOx reduction from mixed acid pickling.

**Driving force for implementation:****Reference literature:****A.4.2.2.23 Nitric Acid Free Pickling of Stainless Steel**

**Description:** for more detailed description see Chapter D.5.8.2

**Main achieved environmental benefits:**

- Reduction of NOx.

**Applicability:**

- New plants and mayor modernisation of existing plants.

**Cross-media effects:**

**Reference plants:** not applied for pickling of strip [Com2 CR]

**Operational data:****Economics:****Driving force for implementation:****Reference literature:****A.4.2.2.24 Optimized Oil Use for Low Alloy and Alloy Steel****Description:**

When oiling the sheet (with rolling oil or anticorrosive oil), optimisation of the oil spray chambers or the oiling machines leads to a reduction in oil consumption. An electrostatic oiling machine has the advantage that the oil flow can continuously be adapted to the required oil film thickness at the actual line speed.

If the pickled sheet (product) is to be used for cold rolling, oiling with rolling oil may not be required at the pickling line. On the other hand oiling with anticorrosive oil is not necessary if the next process step follows immediately.

**Main achieved environmental benefits:****Applicability:****Cross-media effects:****Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.2.25 Magnetic Pumps (Low Alloy and Alloy Steel)**

**Description:**

Mechanical pumps need a constant gland water flow on the mechanical seals. Substitution of mechanical by magnetic pumps reduces the water needs.

**Main achieved environmental benefits:**

- Reduction of water consumption.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.2.26 Acid Heating by Heat Exchangers**

**Description:** see Chapter D.6

The use of heat exchangers avoids the dilution of the pickling acid that can occur with direct steam injection.

**Main achieved environmental benefits:**

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.2.27 Acid Heating by Submerged Combustion**

**Description:** see Chapter D.6

**Main achieved environmental benefits:**

**Applicability:**

- New and existing plants.



**Cross-media effects:**  
**Reference plants:**  
**Operational data:**  
**Economics:**  
**Driving force for implementation:**  
**Reference literature:**

#### A.4.2.2.28 Treatment of Acidic Waste Water

##### Description:

Acidic waste water from rinsing and from fume absorbers of the pickling tank exhaust system, if it cannot be used in the pickling tanks, and the waste water from flushing (plant cleaning) require treatment prior to discharge. The waste water is neutralised (e.g. with alkaline waste waters from other plant operations), dissolved metal ions are transformed into hydroxides or sparingly soluble salts and subsequently eliminated by sedimentation, in many cases by adding flocculants. The precipitated metal sludge is de-watered in filter presses and disposed of.

##### Main achieved environmental benefits:

- Reduction of volume and contaminant load to water.

##### Applicability:

- New and existing plants.

##### Cross-media effects:

- Generation of a large quantity of sludge.
- The sludge, mainly consisting of iron hydroxide and water, can be recycled for iron production as long as it is not contaminated by unacceptable metals (e.g. zinc) or by other constituents. Care should be taken to avoid mixing of waste water streams or sludges which can make recycling difficult.
- Neutralisation can also create large amounts of neutral salts (e.g. NaCl, CaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, CaSO<sub>4</sub>), most of which are very soluble in water and are discharged with the treated water. Removal is only possible by very special, and in most cases uneconomical, treatment (reverse osmosis, electrodialysis or evaporation followed by ion exchange and concentrate evaporation with salt drying). Even if these salts are removed, their mixed composition limits re-use and disposal to landfill may be restricted by their solubility.

##### Reference plants:

##### Operational data:

	Concentration [mg/l]	Specific Emission [g/t product]	Reduction rate <sup>1</sup> [%]	Method of analysis
Suspended solids	50	2.86	> 90	DIN 38409-H2
Fe total	2	0.114	> 90	DIN 38406
Zn total	0.06 - 1			"
Ni total	0.1 - 0.5			"
Cr total	0.02 - 0.5			"
Cr <sup>VI</sup>	0.01 - 0.1			"
Temperature	< 30 °C			Thermometer
pH	6.5 - 9.5			DIN38404-C5
Note: Source of data [EUROFER CR]. Data based on weekly, volume proportional 24-h sampling				
<sup>1</sup> Reduction rate based on mass flow of constituent before/after abatement measure				

**Table A.4-33: Pollutant concentration in water discharge of HCl pickling and regeneration plants [EUROFER CR]**

Substance	Concentration in mg/l <sup>1)</sup>	Type of sampling	Measurements in 1998 Operator/Comp. authority
Fe	0.41	Qualified random sample	12/6
Oil	< 0.28	Qualified random sample	12/6
Suspended solids	< 10	Qualified random sample	12/6
Cr	< 0.01	Qualified random sample	12/6
Ni	0.03	Qualified random sample	12/6
Zn	0.02	Qualified random sample	12/6

Note: Source of data: Senator für Bau und Umwelt Bremen. Plant: Stahlwerke Bremen.  
<sup>1)</sup> Mean values of the qualified random samples from 1998. Waste water volume: 264528 m<sup>3</sup>

**Table A.4-34: Pollutant concentration in water discharge of HCl pickling and regeneration plants [Com2 D]**

	Concentration [mg/l]	Specific Emission [g/t product]	Reduction rate <sup>1</sup> [%]	Method of analysis
Suspended solids	40 - 50	16 - 20	> 90	DIN 38409-H2
Fe total	1.4 - 2	0.3 - 0.5	> 95	DIN 38406
Zn total	0.15 - 1			"
Ni total	0.1 - 0.5			"
Cr total	0.5			"
Cr <sup>VI</sup>	0.01 - 0.1			"
Temperature	< 30 °C			Thermometer
pH	6.5 - 9.5			DIN38404-C5

Note: Source of data [EUROFER CR]. Data based on weekly, volume proportional 24-h sampling  
<sup>1</sup> Reduction rate based on mass flow of constituent before/after abatement measure

**Table A.4-35: Pollutant concentration in water discharge of H<sub>2</sub>SO<sub>4</sub> pickling and regeneration plants**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### A.4.2.3 Rolling

#### A.4.2.3.1 Continuous instead of Conventional Discontinuous Rolling for Low Alloy and Alloy Steel

**Description:** see Chapter A.2 Continuous Rolling

**Main achieved environmental benefits:**

- Reduction in oil consumption.
- Reduction of electricity consumption.

**Applicability:**

- Applicable for installations with a high production capacity and the same kind of products.
- New installations or major modernisation of existing installations.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

- Continuous rolling coupled or full continuous can have a lot of advantages compared to discontinuous rolling.
- Improvement of the material yield due to the better control of gauge for coil ends.
- Improvement on quality yield.
- Reduction in roll change frequencies.

**Economics:****Driving force for implementation:**

- Improved quality and increased yield.

**Reference literature:****A.4.2.3.2 Pickling Plant Coupled with the Tandem Mill****Description:**

The coupling of an existing pickling line with an existing tandem mill is only beneficial when the capacities of the two individual installations are well balanced.

**Main achieved environmental benefits:**

- Reduced scrap (minimization of defects).

**Applicability:**

- For new installations or major modernisation of existing plants.

**Cross-media effects:****Reference plants:****Operational data:****Economics:****Driving force for implementation:**

- Reduced processing time, minimization of defects, increased yield.

**Reference literature:****A.4.2.3.3 Optimal Choice of Rolling Oil and Emulsion System****Description:**

The proper choice of a tandem mill oil is important for quality reasons (good distillation properties, easy removal in degreasing lines). Besides that, to limit the oil consumption, a tandem mill oil must satisfy a number of performance criteria:

- Good lubrication characteristics allow a decrease in the oil consumption.
- An easy separation caused by accidental leakages from the hydraulic system or from the Morgoil bearings is necessary. If separation is not possible, a partial or a complete renewal of the emulsion is necessary.
- The actual process parameters (cold reduction, gauge, rolling forces, speed, roughness) and the available emulsion preparation station determine the requirements on the stability of the emulsion and on the dispersion of the oil in the emulsion.
- The quality of the oil has to remain unaffected by longer periods of line stop conditions (stability of the emulsion, formation of bacteria) in order to avoid a need for the premature disposal of the emulsion.

**Main achieved environmental benefits:**

- Reduction in oil consumption.
- Reduced disposal of waste emulsion.

**Applicability:**

- New plants and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.3.4 Continuous Monitoring of Emulsion Quality**

**Description:**

The quality of the emulsion can be downgraded by a lot of accidents, which are difficult to monitor: carry-over of acid from the pickling line, contamination from the emulsion cooling water, contamination with hydraulic or Morgoil oil, destruction of the emulsion properties by bacteria, or concentration of iron fines. These accidents very often result in a partial or a complete renewal of the tandem emulsion. A regular or, if possible, a continuous measurement of the important emulsion characteristics (oil concentration, pH, saponification index, acid concentration, concentration of possible pollutants, concentration of iron fines etc.) offers the possibility to detect and to cure anomalies in the emulsion quality.

**Main achieved environmental benefits:**

- Reduction in oil/emulsion consumption.
- Reduction of waste emulsion to be treated and disposed of.

**Applicability:**

- New plants and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.3.5 Prevention of Contamination**

**Description:**

A regular control of the seals and of the pipings helps to prevent leakage and thus contamination of the rolling emulsion with hydraulic oil or Morgoil oil.

**Main achieved environmental benefits:**

- Reduced emulsion consumption.
- Reduced waste water treatment and discharge.

**Applicability:**

- New plants and existing plants.

**Cross-media effects:**  
**Reference plants:**  
**Operational data:**  
**Economics:**  
**Driving force for implementation:**  
**Reference literature:**

#### **A.4.2.3.6 Optimized Emulsion/Oil Use**

The residual oil concentration left on the strip leaving the mill, which is responsible for the major part of the oil consumption, is a function of the oil concentration in the last stand. Therefore oil concentration in the last stand should be limited to the minimum required for lubrication and the carry-over of emulsion from the previous stands, where the oil concentration is higher, should be lower than the minimal working concentration. The possible measures (separating the emulsion cellars, shielding of the mill stands) are specific for each installation.

**Main achieved environmental benefits:**

- Reduction of oil consumption.

**Applicability:**

- New and existing plants.

**Cross-media effects:**  
**Reference plants:**  
**Operational data:**  
**Economics:**  
**Driving force for implementation:**  
**Reference literature:**

#### **A.4.2.3.7 Cleaning and Reuse of Emulsion**

**Description:** see Chapter D.3.1

Rolling emulsions from the mill stands are sprayed onto the rolls for cooling, lubrication and cleaning. Contamination of the rolling emulsion occurs due to the pick up of particulate matter, steel slivers, scale and dust. Nowadays emulsions systems are operated as circulation systems, in which cleaning devices are integrated to maintain emulsion quality and thus minimize damage to the surface finish of the strip.

Settling tanks, separators, mesh filters, magnetic filters etc. are used to remove impurities from the emulsion. Only a partial flow needs to be discarded from the circuit and is treated in emulsion splitting plants and finally discharged.

**Main achieved environmental benefits:**

- Reduced consumption of new cold rolling emulsion.
- Reduced waste water volume.

**Applicability:**

- New and existing plants.

**Cross-media effects:**  
**Reference plants:**  
**Operational data:**  
**Economics:**

**Driving force for implementation:**

**Reference literature:**

### **A.4.2.3.8 Treatment of Spent Emulsion**

**Description:** see Chapter D.3.2

The partial flow of the emulsion circuit cleaning system that is discarded, is de-oiled in an emulsion splitting plant and/or split into oil sludge and water, and the purified water is then discharged. The separated, oil-containing sludge may be e.g. used in the blast furnaces in an integrated steel work.

Figure A.4-18 shows an example of an emulsion splitting system using electrolytic splitting.

**Main achieved environmental benefits:**

- Reduced emissions to water.

**Applicability:**

- New plants and existing plants.

**Thermal Treatment:**

**Cross-media effects:**

- High energy consumption.
- Waste gas treatment required.
- Little COD in effluent [Woll].

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

**Chemical Treatment:**

**Cross-media effects:**

- Generation of additional oil-containing neutralisation sludges [Com D].
- Consumption of chemicals [Woll].
- COD in effluent [Woll].

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

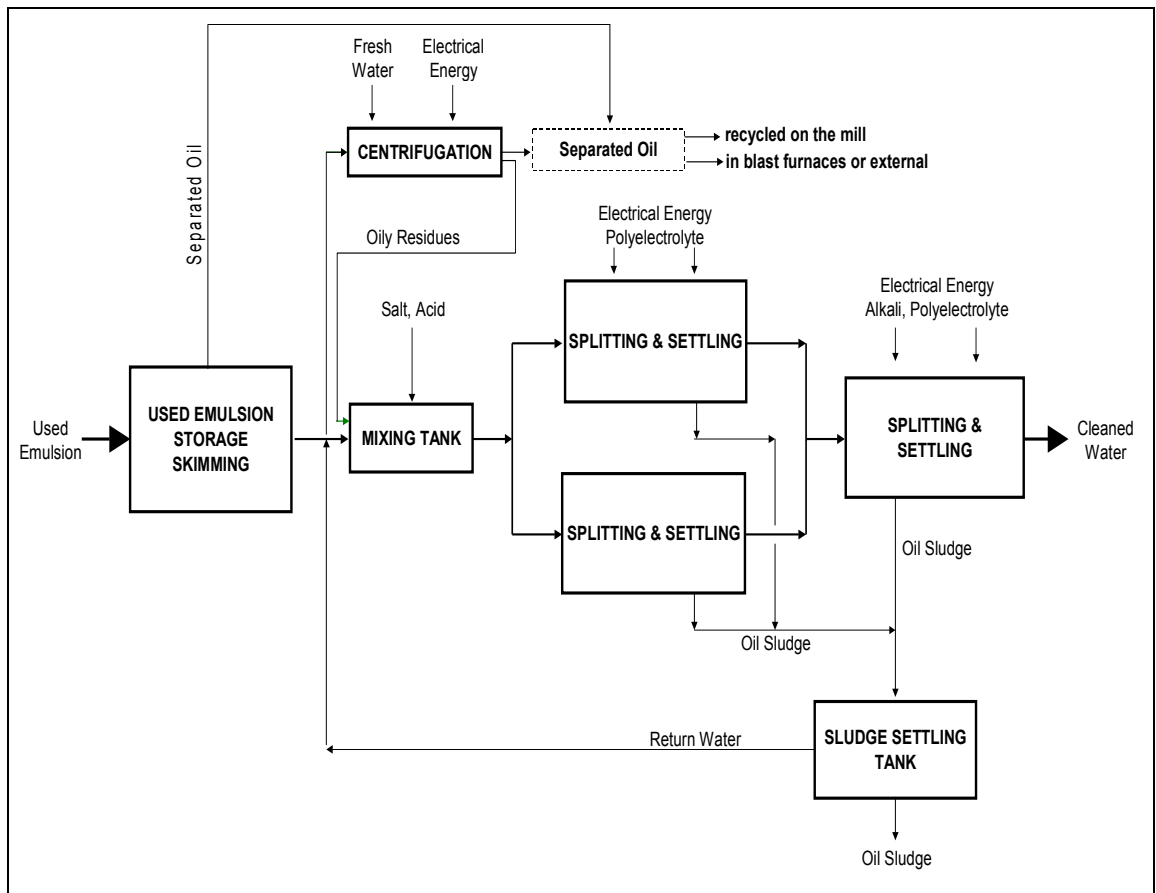
**Reference literature:**

**Electrolytical Treatment:**

**Cross-media effects:**

**Reference plants:**

**Operational data:**



**Figure A.4-18: Spent emulsion splitting system  
[EUROFER CR]**

Input / Consumption Level				
	Tandem Mill		Reversing Mill	
Spent emulsion	5 -13	kg/t	0.06	m <sup>3</sup> /t
Industrial water	0.5 - 1	kg/t		kg/t
Salt	0.025 - 0.05	kg/t	0.125 (NaCl)	kg/t
Polyelectrolyte	0.003 - 0.005	kg/t	0.012	kg/t
Al-Anodes	0.003 - 0.006	kg/t	0.012	kg/t
Electrical energy	5 - 10	MJ/t	3 - 3.5	MJ/t
Output / Emission Level				
Purified waste water	5 - 13	kg/t	0.06	m <sup>3</sup> /t
Water (-> coke plant)				
Oily sludge (disposal)	0.1 - 0.3	kg/t	1.9	kg/t
Oily sludge (internal recycling)	2.5 - 3.5	kg/t		
Oil (+/- 20 % water, → blast furnace)	1.3 - 2	kg/t		
	Concentration [mg/l]	Specific Emission [kg/t product]	Reduction rate <sup>1</sup> [%]	Method of analysis
Settleable solids	7 - 10	5.8 - 8 E -5	> 90	DIN 38409-H9
Σ Hydrocarbons	6 - 18	5.2 - 18 E -5	> 90	DIN 38409-H18
Chlorides	800 -1400	6.7 - 10 E -3		DIN 38405-D1
Sulfide	0.004 - 0.4	3.3 - 330 E -8		DIN 38405-D26
NO <sub>2</sub> <sup>-</sup>	8 -10	8 - 9 E -5		DIN 38405-D19
Pb total	0.03 - 0.3	2.65 - 27 E -7	> 90	DIN 38406
As total	0.075 - 0.1	6.2 - 7.5 E -7	> 90	DIN 38406
Zn total	0.08 - 1.6	6.6 - 132 E -7	> 90	DIN 38406
Ni total	0.4 - 0.5	3.3 - 4 E -6	> 90	DIN 38406
Cr total	0.008 - 0.4	6.6 - 2500 E -8	> 90	DIN 38406
Cu total	0.06 - 0.4	5 - 33 E -7	> 90	DIN 38406
AOX	0.1 - 0.4	8.3 - 32 E -7		DIN 38409-H14
BTX	0.02 - 0.08	1.7 - 6.6 E -7		DIN 38407-F9
Temperature	28 °C			Thermometer
pH	7.6			DIN 38405-C5
Notes: - Source of data [EUROFER CR] - Data based on weekly, volume proportional 24-h sampling				

Table A.4-36: Operational data for electrolytic emulsion splitting

**Economics:****Driving force for implementation:****Reference literature:****Ultrafiltration:****Cross-media effects:**

- No chemical addition required [SIDMAR].
- No oily sludge is generated [SIDMAR].
- Nearly 100 % oil removal efficiency, independent of influent oil content [SIDMAR].

**Reference plants:** SIDMAR**Operational data:****Economics:** saves costs**Driving force for implementation:****Reference literature:**



### A.4.2.3.9 Extraction of Oil Mist Emissions and Oil Separation

#### Description:

Emulsion fumes from the mill stands are extracted and passed through separators for cleaning. Eliminators containing baffle packing and impingement plates or mesh pads to separate the oil from the extracted airflow and in some cases electrostatic precipitators are used. The separated emulsion can be returned to the emulsion system.

#### Main achieved environmental benefits:

- Reduction of emulsion fumes, efficiency > 90 %.

#### Applicability:

- Rolling and strip grinding operations.
- New plants and existing plants.

#### Cross-media effects:

- Oil recovered from the separators may be recircled, although in some cases the return of the oil from the emulsion filters might be impossible due to the poor quality of the oil (bacteria) [Com HR].

#### Reference plants:

#### Operational data:

		<b>Tandem Mill</b>	<b>Reversing Mill Low alloy</b>	<b>Reversing Mill High alloy</b>
<b>Emulsion Fume Exhaust Separator</b>		n.a.	Steel fabric droplet separator	Steel fabric droplet separator
<b>Volume</b>	[m <sup>3</sup> /t]	1850 - 2000	175 - 850	3000 - 12000
<b>Energy Consumption</b>	[MJ/t]	5 - 10	12 - 13	n.a.
<b>Achieved Emission Levels</b>				
<b>Pollutant</b>		<b>Dust<sup>2</sup></b>	<b>Hydrocarbons<sup>1</sup></b>	<b>Hydrocarbons<sup>1</sup></b>
<b>Concentration</b>	[mg/m <sup>3</sup> ]	10 - 50	5 - 20	10 - 12
<b>Specific Emission</b>	[g/t]	96	7	8.4 - 10.1
<b>Reduction Rate<sup>3</sup></b>	[%]	> 90	> 90	> 90
				<b>Oil</b>
				10 - 20
				50 - 80
				n.a.

Note: Source of data [EUROFER CR]

<sup>1</sup> as organic carbon, method of analysis Umwelt-BA EM-K1, EPA S 008

<sup>2</sup> method of analysis EPA

<sup>3</sup> Reduction rate based on mass flow of constituent

Table A.4-37: Achievable emission levels for emulsion fume separation at rolling mills

#### Economics:

#### Driving force for implementation:

#### Reference literature:

### A.4.2.3.10 Cooling Water Cycles/Special Cooling Water systems

#### Description:

The heat generated during cold rolling is usually rejected via plate heat exchangers to cooling water circuits. Water from these circuits may be recirculated to minimize consumption by rejecting the heat via evaporative cooling towers or secondary cooling circuits.

**Special cooling water system:**

The risk of contaminating the cooling water with oils can be minimized.

**Reuse of cooling water:**

Saving natural resources and energy in the cooling water cleaning system.

**Main achieved environmental benefits:****Applicability:****Cross-media effects:****Reference plants:****Operational data:****Cooling Water System**

Input / Consumption Level		
Cooling water (re-circulating)	8400	m <sup>3</sup> /t
River water	7000	m <sup>3</sup> /t
Soft water <sup>1</sup>	2.5 E -4	m <sup>3</sup> /t
NaOH	1.25 E -8	m <sup>3</sup> /t
Inhibitor	2.5 E -7	m <sup>3</sup> /t
<b>Energy:</b>		
Electrical	0.004	GJ/t
Caloric <sup>2</sup>	0.282	GJ/t
Output / Emission Level		
	Specific Emission	Concentration
Cooling water (re-circulating)	8400	m <sup>3</sup> /t
Waste water (system drain water)	2.5 E -4	m <sup>3</sup> /t
Settleable solids (volume)	2 - 5	ml/l
Hydrocarbons (oil, grease)	2 - 5	mg/l
Chlorides	50	mg/l
Fe total	2	mg/l
Temperature	35	°C
pH	6.5 - 9.5	
Electric conductivity	1.1	mS/cm
Notes: Source of data [EUROFER CR] Data based on weekly, volume proportional 24-h sampling		
<sup>1</sup> only in case of system drainage		
<sup>2</sup> energy removed from tandem mill by cooling water		

**Table A.4-38: Consumption and emission levels for the cooling water system of a tandem mill**

**Economics:****Driving force for implementation:****Reference literature:**

## A.4.2.4 Annealing

### A.4.2.4.1 Implementation of Degreasing Bath Cascades

→ No description and technical information submitted

### A.4.2.4.2 Hot Water Pre-degreasing

→ No description and technical information submitted

### A.4.2.4.3 Cleaning and Reuse of Degreasing Solution

**Description:** see Chapter D.4.3

High oil contents make the degreasing solution unusable and cleaning measures are applied to extend the life span of the bath. Measures to clean the degreasing bath and to extend the lifetime are:

**Magnetic separators** to remove the mixture of iron fines and oil.

#### **Mechanical cleaning**

Usually the emulsions of degreasing agents and oil/grease from the metal surface are unstable and after some time they float on the surface of the bath. They can be removed by skimmers. Suspended particles are removed by sedimentation in gravity separators. Mechanical cleaning can extend the lifetime of degreasing baths 2 – 4 times.

**Adsorption of surfactants and oil** (precipitation followed by filtration).

#### **Ultrafiltration**

##### **Main achieved environmental benefits:**

- Consumption of chemicals for new alkaline baths can be drastically reduced.
- Reduction of waste water treatment and discharge.

##### **Applicability:**

- New plants and existing plants.

##### **Cross-media effects:**

- Oil and grease arise as waste in the cleaning of degreasing solutions. This waste may be used for energy recovery or has to be disposed of by incineration.

##### **Reference plants:**

##### **Operational data:**

Table A.4-39 presents input/output data and effluent data for degreasing solution cycle of a continuous annealing line, which is maintained by cleaning via **ultrafiltration**.

Input / Consumption Level				
Degreasing solution		50 - 60 kg/t		
Demineralised water		0.3 - 0.4 kg/t		
Degreaser		0.04 - 0.05 kg/t		
Tempering fluid concentrate		0.15 - 0.2 kg/t		
Electrical energy		4 -5 MJ/t		
Output / Emission Level				
Cleaned degreasing solution		40 - 50 kg/t		
Sludge		0.4 - 0.5 kg/t		
	Concentration [mg/l]	Specific Emission [g/t product]	Reduction rate <sup>1</sup> [%]	Method of analysis
Suspended solids (filterable)	20 - 40	2.35 - 4.7 E -4	> 90	DIN 38409-H2
Σ Hydrocarbons (oil, grease)	5 - 8	5.9 - 9.4 E -5	> 90	DIN 38409-H18
Fe total	1 -2	1.2 - 2.4 E -5	> 90	DIN 38406
Temperature	30 °C			Thermometer
pH	6.5 - 9.5			
Note: Source of data [EUROFER CR]. Data based on weekly, volume proportional 24-h sampling				
<sup>1</sup> Based on mass flow of constituent				

Table A.4-39: Operational and effluent data for degreasing bath cleaning by ultrafiltration

Economics:

Driving force for implementation:

Reference literature:

#### A.4.2.4.4 Treatment of Spent Degreasing Bath and Alkaline Waste Water

**Description:** see also Chapter D.4.4 and D.4.5

Partial flows from the degreasing solution cleaning circuit, rinsing water from the electrolytic degreasing and waste water from the skin pass mill stand, which cannot be reused in the mills, have to be treated prior to discharge. Prior to treatment of the waste water with flocculants, the oil content has to be removed, e.g. by ultrafiltration. [Com2 D] Then the waste water is usually neutralised with lime or HCl in a neutralisation plant, passed through filters and finally discharged. The sludge is dewatered in filter presses and discharged for landfill deposit. The oil sludge from the ultrafiltration plants can be used in the blast furnaces. [EUROFER CR]

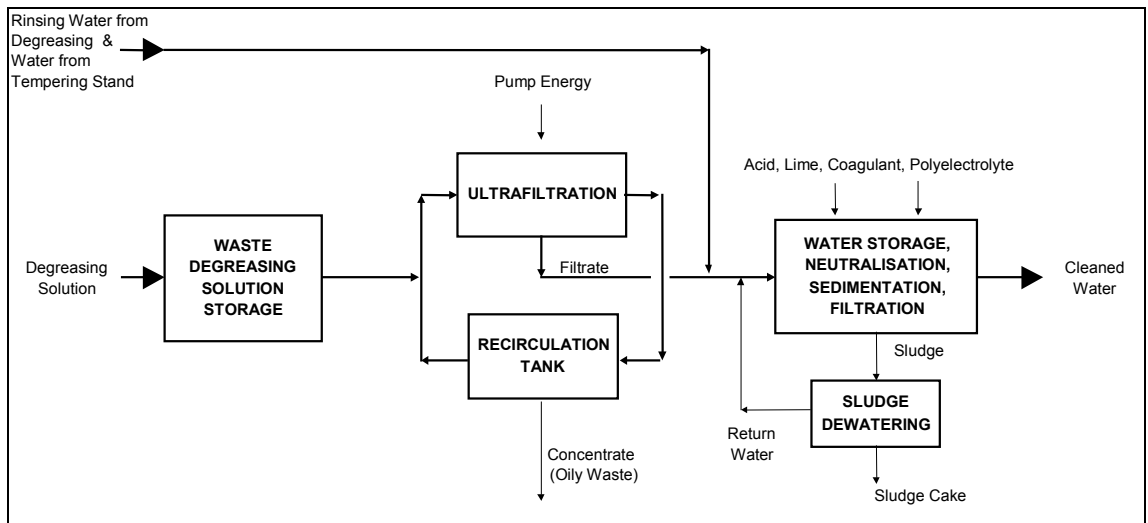


Figure A.4-19: Spent degreasing solution flow (example of a continuous annealing line) [EUROFER CR]

**Main achieved environmental benefits:**

- Reduced emissions, especially oil, to water.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

- Energy and raw material consumption.

**Reference plants:****Operational data:**

Table A.4-40 presents input/output data and effluent data for alkaline (degreasing) waste water treatment by ultrafiltration (continuous annealing line).

Input / Consumption Level				
Raw waste water		12 - 15 kg/t		
Citric acid		occasionally kg/t		
Electrical energy		1 - 1.5 MJ/t		
Output / Emission Level				
Purified waste water		12 - 15 kg/t		
Sludge		kg/t		
	Concentration [mg/l]	Specific Emission [g/t product]	Reduction rate <sup>1</sup> [%]	Method of analysis
Suspended solids (filterable)	20 - 40	2.35 - 4.7 E -4	> 90	DIN 38409-H2
Σ Hydrocarbons (oil, grease)	5 - 8	5.9 - 9.4 E -5	> 90	DIN 38409-H18
COD	5000 - 6000	5.9 - 7.1 E -5	> 50	DIN 38409-H44
Temperature	30 °C			Thermometer
pH	6.5 - 9.5			
Note: Source of data [EUROFER CR]. Data based on weekly, volume proportional 24-h sampling				
<sup>1</sup> Reduction rate based on mass flow of constituent				

Table A.4-40: Operational and effluent data for alkaline waste water treatment

**Economics:****Driving force for implementation:****Reference literature:**

#### A.4.2.4.5 Extraction System for Degreasing Facilities

**Description:**

Fumes from degreasing baths and the pre-cleaning section of continuous annealing lines are extracted by an exhaust system and passed through gas scrubbers for cleaning. Recycled water is used as an absorbent. Partial flow of the scrubbing water has to be discharged via the water treatment facilities of the degreasing line or, respectively, the continuous annealing plant.

**Main achieved environmental benefits:**

- Reduced fugitive emissions of degreasing fumes.

**Applicability:****Cross-media effects:****Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.4.6 Special Cooling Water Systems and Water Reuse**

→ No description and technical information submitted

#### **A.4.2.4.7 Batch Annealing with 100 % Hydrogen**

**Description:**

Batch annealing 100 % hydrogen may be used instead of hydrogen/nitrogen.

**Main achieved environmental benefits:**

- Reduction in specific energy consumption (reduced from 700 MJ/t when annealing under  $H_2N_2$  to 422 MJ/t under 100 % hydrogen atmosphere) [EUROFER CR].

**Applicability:**

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.4.8 Continuous Instead of Batch Annealing**

**Description:** Continuous annealing instead of conventional batch annealing can be used for some parts of the product range.

**Main achieved environmental benefits:**

**Applicability:** For new installations or major modernisation of existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.4.9 Preheating Combustion Air/Use of Regenerative or Recuperative Burners for Annealing Furnace**

**Description:** see Chapters D.1.1 and D.1.2

**Main achieved environmental benefits:**

- Reduction in energy consumption.

**Applicability:**

- New and existing furnaces.

**Cross-media effects:**

- Potential increased NO<sub>x</sub> emission level (concentration).

**Reference plants:** - British Steel Stainless, Sheffield.

**Operational data:****Example**

The 'old' annealing furnace for stainless strip was operated with 3 individually controlled zones, but at the same temperature of about 1100 °C, heated by electric elements mounted in the sidewalls. Maximum throughput was 1 t/h. In 1989 structural modification were done to increase capacity and to improve circulation of furnace gas. The 3 zones remained, but the first two were equipped with two pairs of 5.5 therm/h integral bed burners (IBB), in the third zone a self-recuperative burner was installed.

NO<sub>x</sub> emissions were measured at burner firing rates of 21 – 84 % of maximum and ranged from 225 – 317 ppm corrected to 3 % oxygen (460 – 650 mg/m<sup>3</sup>).

Assuming a mean throughput of 100 t/week and 46 production weeks per year, the primary energy consumption was reduced by 50.6 % (taking into account the primary energy consumption at power station for the former electrical heating system). Payback period in that case study was 5.5 years, but payback time depends to large extend on the energy costs (fuel, gas, electricity etc.). Calculated payback periods for other scenarios were reported: 2.5 years for £2.93/GJ gas and £ 11.77/GJ electricity. [ETSU-FP-64]

**Economics:**

**Driving force for implementation:**

**Reference literature:**

**A.4.2.4.10 Reduction in NO<sub>x</sub> Emission by Low-NO<sub>x</sub> burner**

**Description:** see Chapter D.2.1

The generation of NO<sub>x</sub> resultant from the combustion processes can be reduced by selection of low-NO<sub>x</sub> burners.

**Main achieved environmental benefits:**

- Reduced NO<sub>x</sub> emissions.

**Applicability:**

- New and existing furnaces.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

	Concentration [mg/m <sup>3</sup> ]	Emission [kg/t product]	Reduction <sup>1</sup> [%]	Method of analysis
Dust	5 - 10			EPA
SO <sub>2</sub>	60 - 100	9 - 14 E -03		Infrared, UV-fluorescence
NO <sub>2</sub> <sup>2</sup>	150 - 380	25 - 110 E -02	60	Chemiluminescence (NBN T94-303)
CO	40 - 100	15 - 40 E -03	87	Umweltbundesamt-EM-K1, IR-spectrometry
CO <sub>2</sub>	200000 - 220000	31200	0	IR-absorptions-spectrometry
Notes: Source of data [EUROFER CR] m <sup>3</sup> are based on standard conditions; (waste gas 10000 – 16000 m <sup>3</sup> /h, 200 - 250 m <sup>3</sup> /t) <sup>1</sup> reduction rate based on mass flow of constituent <sup>2</sup> reference 3 % O <sub>2</sub> , mg/m <sup>3</sup> dry				

Table A.4-41: Achievable emission levels with low-NOx burners on batch annealing furnaces

	Concentration [mg/m <sup>3</sup> ]	Emission [kg/t product]	Reduction <sup>1</sup> [%]	Method of analysis
Dust	10 - 20	0.16 – 0.32		EPA
SO <sub>2</sub>	50 - 100	0.08 – 1.6		Infrared, UV-fluorescence
NO <sub>2</sub> <sup>2</sup>	400 - 650	0.14 - 0.22	60	Chemiluminescence (NBN T94-303)
CO	50 - 120	0.08 - 0.2	87	Umweltbundesamt-EM-K1, IR-spectrometry
CO <sub>2</sub>	180000 - 250000	62.5 - 86.8	0	IR-absorptions-spectrometry
Notes: Source of data [EUROFER CR] m <sup>3</sup> are based on standard conditions; (waste gas 350 – 400 m <sup>3</sup> /t) <sup>1</sup> reduction rate based on mass flow of constituent <sup>2</sup> reference 3 % O <sub>2</sub> , mg/m <sup>3</sup> dry				

Table A.4-42: Achievable emission levels with low-NOx burners on continuous annealing furnaces

**Economics:**

Investment costs of 100 kECU (for continuous annealing furnace, capacity: 540000 t/a) were reported. [CITEPA]

**Driving force for implementation:****Reference literature:****A.4.2.4.11 Preheating the Feedstock****Description:****Preheating the material in the continuous annealing line with waste gas:**

This can either be done by a direct contact between the strip and the flue gases or the heat can be transferred to the strip by the protective gas heated by the waste gas in heat exchangers. A direct contact is only possible in controlled circumstances (depending on temperature of the gas and of the strip, oxidation potential of the gas, moisture, contamination of the gas with particles). The result is a reduction of energy consumption.

**Main achieved environmental benefits:**

- Reduced energy consumption.



**Applicability:**  
**Cross-media effects:**  
**Reference plants:**  
**Operational data:**  
**Economics:**  
**Driving force for implementation:**  
**Reference literature:**

#### **A.4.2.4.12 Heat Utilisation for Heating Degreasing Bath**

→ No description and technical information submitted

### **A.4.2.5 Tempering**

#### **A.4.2.5.1 Optimisation of Emulsion System**

**Description:**

**a) Use of low pressure sprays for the emulsion**

Atomisation of the temper rolling emulsion has to be minimized by the use of the appropriate type of spray nozzles at the appropriate pressure.

**b) Adapt the number of emulsion jets to the width of the strip**

Since the temper rolling emulsion is not recycled, optimisation of the spray patterns reduces emulsion consumption.

**Main achieved environmental benefits:**

- a) Reduced oil emissions.
- b) Reduced oil consumption.

**Applicability:**

- New plants and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.5.2 Change to Dry Temper Process**

**Description:**

**Main achieved environmental benefits:**

- No oil consumption.

**Applicability:**

- New plants and existing plants.

**Cross-media effects:**

- Generates emissions to air.
- Requires an exhaust system and generates waste (filter dust).

**Reference plants:**  
**Operational data:**  
**Economics:**  
**Driving force for implementation:**  
**Reference literature:**

### A.4.2.5.3 Cleaning of Temper Mill Emulsion

**Description:**

The used temper mill emulsion has to be cleaned before disposal. This emulsion is generally treated together with the tandem mill emulsion and the other oily residues in the emulsion treatment system.

**Main achieved environmental benefits:**

- Reduced emissions to water.

**Applicability:**

- New plants and existing plants.

**Cross-media effects:**

- Energy and raw material consumption.

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### A.4.2.5.4 Reduction of Oil Mist and Dust

**Description:**

Oil mist and dust are extracted via an exhaust system, equipped with wet or dry filters. Also oil mist eliminators (mechanical) and cyclones may be applied.

**Main achieved environmental benefits:**

- Reduced oil emissions.

**Applicability:**

- New plants and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

	Concentration [mg/Nm <sup>3</sup> ]	Specific Emission [g/t product]	Reduction rate <sup>1</sup> [%]	Specific Volume [m <sup>3</sup> /t]	Method of analysis
<b>Example: Steel fabric droplet separator</b>					
Hydrocarbon	5 - 15	0.273	> 90	90 - 110	Umwelt-BA EM-K1
Note: Source of data [EUROFER CR]					

Table A.4-43: Achievable emission levels for fabric droplet separators

Oil mist emissions reported by [CITEPA]:  $\sim 10 \text{ mg/m}^3$

**Economics:**

**Oil mist eliminator:** investment costs: 375 kECU (125 for oil abatement, 250 for dust), operating costs: 6 kECU/a, electricity: 70 kWh [CITEPA]

**Cyclone:** investment costs: 25 kECU, operating costs: 2.5 kECU/a electricity 45 kWh [CITEPA]

**Driving force for implementation:**

**Reference literature:**

## A.4.2.6 Finishing

### A.4.2.6.1 Capture and Abatement of Oil Mists from Oiling Operation

**Description:**

Oil emissions that arise from spraying oil mist on strips for conservation reasons, can be reduced by extraction hoods, followed by mist eliminator (baffle-type) and electrostatic precipitator. The oil captured in the mist eliminator can be recircled into the oiling process.

**Main achieved environmental benefits:**

- Reduction of fugitive oil mist emissions.
- Reduced oil consumption.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:** Stahlwerke Bremen.

**Operational data:**

**Example**

By the described measure it is possible to capture the mist arising from oiling almost completely (visual judgement: all visible emissions are captured). The mist eliminator efficiency was reported to be 72 %. Measurements of the waste gas showed concentrations of oil droplets after the mist eliminator, but before the EP, of up to  $296 \text{ mg/m}^3$  (average  $104 \text{ mg/m}^3$ ). The maximum concentration measured after EP was  $6.3 \text{ mg/m}^3$  with an average emission of  $3.0 \text{ mg/m}^3$ . The efficiency of the EP was between 97 and 98 %. The carbon contents of the unabated waste gas was measured 17.5 to  $21.3 \text{ mg/m}^3$ ; behind the EP around 10.6 to  $11.9 \text{ mg/m}^3$ . [UBA-Kloekner-82]

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### A.4.2.6.2 Electrostatic Oiling

→No description and technical information submitted

### A.4.2.6.3 Optimization of Oil Spray

→No description and technical information submitted

**Main achieved environmental benefits:**

- Reduced oil consumption.

**Applicability:**

- New plants and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.6.4 Dust Reduction from Levelling and Welding**

**Description:**

Particulate emissions from welding and levelling are captured by hoods and abated by fabric filters. [CITEPA]

**Main achieved environmental benefits:**

- Reduction of emissions to air, especially fugitive dust.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

- Increased energy consumption.
- Generation of waste (filter dust).

**Reference plants:**

**Operational data and economics::**

Dust emission 5 – 30 mg/m<sup>3</sup> were reported in [CITEPA] for an installation operated 5 % of the time to reduce emissions from welding (discontinuously) and continuously for dust reduction from levelling. The hourly electricity demand was 110 kWh (0.64 kWh/t). [CITEPA]  
Investment costs of 625 kECU (for collection devices, pipes, filters, fans, electrical equipment, motors hood) and operating costs of 10 kECU were reported. [CITEPA]

Other sources [Vanroosb 3.4] reported for an installation that is filtering the exhaust gases from the stretcher leveller, the welding machine and the leveller the decoiler dust emission values of: 16 - 7 - 39 - 22 - (change of bags) - 24 - 29 - 35 - 39 mg/Nm<sup>3</sup>.

Each emission value is the result of 6 isokinetically taken samples on 6 different places in the cross section of the chimney. There are therefore 2 sampling points at 90 ° of each other. Each sampling campaign takes about 6 hours. Sampling frequency is about 6 times per year.

**Installation data:**

Filter area	687 m <sup>2</sup>
Number of filter bags	441
Dimensions filter bags	Dia 120 mm x length 4030 mm
Type of filter bags	PE/PE - weight 550 g/m <sup>2</sup> - thickness 1.9 mm - density 0.29 g/cm <sup>3</sup> - air permeability 150 l/dm <sup>2</sup> ; min at 196 Pa (20 mm water column)
Number of exhaust fans	3 x 55 kW - 1470 rev/min
Gas flow (design)	90000 m <sup>3</sup> /h
Pressure drop (design)	120 daPa
Cleaning cycle	50 msec at a pressure of 4 - 6 bar [Vanroosb 3.4]

Bags are changed when it is observed that the bags present cracks. This change takes about 50 manhours and requires a stop of the pickling line of at least 2 shifts - the cost is about 400000 BEF (10000 EUR). [Vanroosb 3.4]

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.6.5 Optimised Finishing Operation**

→No description and technical information submitted

**Main achieved environmental benefits:**

- Scrap reduction.

**Applicability:**

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.2.7 Roll Shop**

##### **A.4.2.7.1 Cleaning and Reuse of Grinding Emulsion**

→No description and technical information submitted

##### **A.4.2.7.2 Exhaust System (PRETEX/SBT)**

→No description and technical information submitted

##### **A.4.2.7.3 Reduction and Recycling of Scrap**

→No description and technical information submitted

**Description:**

Internal recycling options for scrap (from trimming, finishing, etc.).  
Good process control helps to reduce material losses [Com D].

**Main achieved environmental benefits:**

**Applicability:**

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### A.4.3 Wire Mill

#### A.4.3.1 Storage and Handling of Raw Materials and Auxiliaries

**Description:**

All storage tanks for both fresh and spent acid must be equipped with an efficient and sealed secondary containment and if required also with protective shields. This secondary containment must be completely protected with an acid-resistant coating which must be regularly controlled on potential damage and cracks.

Furthermore the loading and unloading area for the acids must be designed in such a way that any potential leak is directly discharged to the waste water treatment plant or can be collected separately.

**Main achieved environmental benefits:**

**Applicability:**

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### A.4.3.2 Mechanical Descaling

##### A.4.3.2.1 External Recycling of Scale

**Description:**

The bulk of descaling in wire industry is done by reverse bending, leading to a scale which consists mainly of metal oxides and which is oil- and water-free. Due to bending and torsion of the wire, the scale breaks and drops into collection containers. All wire companies can keep scale separated from other waste streams to allow recovery of the iron content by recycling to the primary iron and steel industry. Whether recycling is done or not, depends to a large extent on the interest of the local steel industry, that has not much to win by the recycling of this small amount of rather difficult to handle secondary raw material. [CET-BAT]

In some exceptional cases where abrasives are used (e.g. shot-blasting, sanding etc.), scale gets mixed with other products. Recovery of shot-blasting media from scale is a common practice with both economical (less consumption) and environmental (less waste) benefits. Infinite recovery is not possible and not desired (quality loss, higher degree of dust formation). [CET-BAT]

**Main achieved environmental benefits:**

- Reduction of waste [CET-BAT].

**Applicability:**

- New and existing plants.
- Technically possible for all scale from mechanical descaling of wire (rod).
- Limitation of recycling not due to technical factors, but due to acceptance by the potential recycler [CET-BAT].

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### A.4.3.3 Chemical Descaling / Pickling of Wire Rod

#### A.4.3.3.1 Optimum Range of Operation for HCl Pickling Baths

**Description:** see Chapter D.5.1

As chemical pickling of wire rod is mostly done in batch operation as pickling is done in job galvanizing, in principle the same good operational practice and reduction measures can be applied.

**Main achieved environmental benefits:**

- Reduction of acid emissions to air.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

The acid concentration chosen according to the VDI-guideline is lower than typically used for wire rod pickling (see A.3.3.2.2. for typical process conditions). This results in:

- Lower conversion of the acid from HCl to FeCl<sub>2</sub>, which implies a higher consumption of fresh HCl [Com2 BG].
- Reuse of spent acid as secondary raw material becomes very difficult; for reuse for the production of FeCl<sub>3</sub>, a minimum concentration of 10 % Fe is requested; this high Fe-concentration can only be achieved with a high conversion of HCl and with a high initial concentration of HCl [Com2 BG].
- Increased pickling time, which implies investment in more and/or bigger pickling tanks. Increased bath surface leads to more g/h HCl-evaporation. [Com2 BG].

**Reference plants:**

**Operational data:**

**Economics:** Due to increased pickling time, investment in more and/or bigger pickling tanks may be necessary. [Com2 BG]

**Driving force for implementation:**

**Reference literature:**

#### A.4.3.3.2 Pickling Tank Fume Control

**Description:** see Chapter D.5.2

Vapour and aerosols coming off pickling tanks can be controlled by a variety of collection system designs, e.g lateral extractors or hoods and covers installed above or around a single pickling bath or a group of pickling baths. The air above the baths is extracted and sent to a stack. In case of continuous, in-line pickling the same measures as for pickling in cold rolling mills can be applied.

**Main achieved environmental benefits:**

- Reduction of fugitive emissions from pickling (acid vapour and aerosols).

**Applicability:**

**Hoods**

- New pickling lines or in case of major revamps of existing plants.
- Retrofitting of existing open baths by adding a cover or a hood over a pickling bath or a group of pickling baths, is only possible at extremely high costs. It requires a completely new internal transport system, requires to change the way the pickling process is controlled, (as the operator has no visual control anymore, a switch to an automated system is imposed), and generally requires some changes to building and infrastructure.

**Lateral Extraction**

- New and existing plants.

**Cross-media effects:**

- Extraction (large volumes) may cause more emission as, due to vapour pressure, the extracted vapour over the bath is replaced to yield equilibrium.

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

Improvement of working environment, protection of installation and equipment

**Reference literature:**

### **A.4.3.3.3 Treatment of Extracted Air from Pickling Tank Fume Control**

**Description:**

The type of treatment and the necessity depend largely on the type of acid (HCl, H<sub>2</sub>SO<sub>4</sub>, others,...) and the way the pickling bath is operated (heated or not, use of inhibitors or surfactants, degree of agitation). Available abatement techniques are packed or plate scrubbers and entrainment separators (demisters).

For **H<sub>2</sub>SO<sub>4</sub>** or **H<sub>3</sub>PO<sub>4</sub>** baths, even when heated, the acid vapour pressure is very low, so treatment of the extracted air is not needed unless droplets are emitted. In this case the entrained acid droplets can be removed from the exhaust gas by **dry fume filters**. The removed acid can be returned into the pickling tank. Only little water is needed to, occasionally, wash the filter medium. [CET-BAT]

For **HCl pickling baths**, depending on the concentration of the HCl, the bath temperature, the number of wire rod coils treated per time unit or the presence of additives, wet scrubbers are used to reduce the emission of HCl vapour and aerosols. Plate scrubbers can operate on small amounts of scrubbing water compared to packed scrubber, resulting in a small volume of quite strong acid effluent. This effluent can be recirculated into the pickling tank. [CET-BAT], [N.Stone 2]

**Main achieved environmental benefits:**

- Reduction of acid vapour, droplets and aerosol emissions.

**Applicability:**

- New and existing plants with pickling tank fume extraction.

**Cross-media effects:**

**Reference plants:**

Most installations for pickling of wire rod, built in the last +/- 10 years, have scrubbers on the exhaust from the HCl baths. [CET-BAT]

**Operational data:**

Typical emission limits are: < 20 to < 30 mg/Nm<sup>3</sup>. This can be reached without significant problems with a demister (for H<sub>2</sub>SO<sub>4</sub>) or with a scrubber (for HCl). [CET-BAT]

**Economics:**

**Driving force for implementation:**

**Reference literature:**



#### A.4.3.3.4 Cascade Pickling

**Description:**

Cascade pickling is performed in two or more baths in series. The acid flows (continuously or discontinuously) in counter flow from one bath to the next. This allows to achieve a very efficient use of the acid while still reaching good pickling quality. [CET-BAT]

**Main achieved environmental benefits:**

- Reduced consumption of fresh acid.
- Reduced spent acid (waste).

**Applicability:**

- New and existing plants.
- Existing plants available space might be a limiting factor.

**Cross-media effects:****Reference plants:****Operational data:****Economics:**

Costs include:

- larger building, including larger acid proof floor surface and larger secondary containment
- extra tank, circulation pump, possibly extra exhaust system
- more complex process control software for follow-up of pickling bath composition and level
- often, different types of wire rod require different contact times. If this is the case, also specific process control software for scheduling and follow-up of the movements of the different rolls is required.

Estimation: 0.2 - 0.4 M Euro depending on capacity.

**Driving force for implementation:****Reference literature:**

#### A.4.3.3.5 Minimizing Carry-out from Pickling

**Description:**

Minimizing carry-out requires sufficient time for the acid to drip of the wire rod coils. This can be done by lifting the wire rod coil slowly from the last acid-bath of the cascade and then allowing several seconds of dripping time above the acid bath before moving the wire rod coil to the first bath of the rinsing cascade. Dripping off can be enhanced e.g. by vibrating the wire rod coil.

**Main achieved environmental benefits:**

- Reduced carry-out of acid, reduced consumption of fresh acid.
- Reduced spent acid (waste).
- Reduced pickling loss.

**Applicability:**

- New and existing plants.

**Cross-media effects:****Reference plants:****Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### **A.4.3.3.6 Separation and Reuse of Free Acid Fraction**

**Description:** see also Chapter D.5.9

Various methods are available to separate free acid from bounded acid. The free acid output stream is reused in the pickling process. This technique has no added value when cascade pickling of wire rod is applied, as cascade pickling allows to convert nearly all acid to metal salts (no or only little free acid). In other words, separation and reuse of the free acid fraction is an alternative to cascade pickling (see A.4.3.2.2).

For  $\text{H}_2\text{SO}_4$ , **crystallisation** of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and reuse of the liquid phase (containing  $\text{H}_2\text{SO}_4$ ) is a common technology that is economically viable if  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  can be marketed as a by-product.

For HCl, **evaporation** of HCl is a technically available but rarely used because of the important investment and energy costs.

Other methods described in literature, such as acid **retardation** or **membrane processes**, are generally not feasible (short lifetime of membranes in the presence of additives to the acid and impurities in technical acid as well as blocking of membrane pores by  $\text{FeCl}_2$ ).

**Solvent extraction** is not considered as separation method because of the use of dangerous chemical products in the extraction process. Any malfunctioning of the recovery unit brings solvent where it is not supposed to be, resulting in hazwaste or spills to the waste water that are not removed in a typical waste water treatment station. [CET-BAT]

**Main achieved environmental benefits:**

- Reduced consumption of fresh acid.
- Reduced spent acid (waste).

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### **A.4.3.3.7 Regeneration of Spent Acid**

**Description:** see also D.5.10

**Roasting of hydrochloric acid:** heating of spent acid in presence of oxygen; vapour phase process at elevated temperature. All acid is converted to free acid; metals are converted to metal oxides. Oxidation chamber and acid recovery unit have to be made from extremely corrosion resistant materials. HCl can be upgraded to a quality suited for chemical pickling; metal oxides are either dumped or used as secondary raw material. [CET-BAT]

A viable roasting plant has a capacity of an order of magnitude higher than the output of spent acid of a typical wire plant. [CET-BAT]

**Main achieved environmental benefits:**

- Reduction of acidic waste.

**Applicability:**

- Regeneration plants require a minimum capacity, a minimum amount of spent acid to be treated which is far beyond the spent acid generated at a single wire plant.
- Wire industry depends on outside contractors for the recycling of spent acid.

**Cross-media effects:****Reference plants:****Operational data:****Economics:****Driving force for implementation:****Reference literature:****A.4.3.3.8 Reuse of Spent Acid as Secondary Raw material****Description:**

The chemical industry uses spent acid as a secondary raw material for the production of  $\text{FeCl}_3$  and, to a minor extent, for pigments. The possibility to recycle spent acid for the production of valuable chemicals is available in many regions in Europe. Some contractors impose or have to impose strict limits for some metal impurities in the spent acids. A few contractors have recently developed and patented special processes to remove e.g. Zn or Pb from some types of spent acid. [CET-BAT]

**Main achieved environmental benefits:**

- Reduction of acidic waste.

**Applicability:**

- New and existing plants.

**Cross-media effects:****Reference plants:****Operational data:****Economics:****Driving force for implementation:****Reference literature:****A.4.3.3.9 Minimize Rinsing Water Consumption by Cascade Rinsing****Description:** see Chapter D.8

The wire rod coil is rinsed several times in separate tanks, each time in cleaner water. Only to the last bath, fresh rinsing water is supplied. Each bath flows over to the previous one.

**Main achieved environmental benefits:**

- Reduction of water consumption (by an order of magnitude less than single step rinsing) [CET-BAT].

**Applicability:**

- New and existing plants.

**Cross-media effects:****Reference plants:****Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### **A.4.3.4 Shot Blast Descaling: Separation of Scale and Blast media**

**Description:**

Shot blasting is possible as in-line or bulk processing. It involves the propulsion of thousands of steel shot particles per second, towards the surface of the material. This causes the scale to break and fall off the base metal. The shot blast or blast cleaning system consists of:

1. A cabinet to house and contain the descaling operation.
2. A series of blast wheels of varying power depending on required line speeds, production requirements, etc.
3. A reclaim system to return used shot or media to a recycling system.
4. A recycling system where media is cleaned and small particles of dust and scale are removed.
5. A storage area within the system where shot is stored before being distributed once again to the blast wheels.
6. A dust collection system.

The blast cabinet is a confined enclosure where the blast descaling operation takes place. A series of blast wheels are mounted to the cabinet and propel the media, usually steel shot, by centrifugal force towards the wire.

The reclaim system provides a means to retrieve the used shot and dust from the descaling operation and brings it to the recycling system.

Recycling of the shot media involves separating the good reusable media from the contaminants and dust gathered in the mix. By passing the collected media through an air wash separator, the fine dusts and smaller contaminants are drawn from the system by a vacuum effect leaving the cleaned shot particles to be returned to a storage system. From this storage system, the media will be distributed through a series of controls or valves back to the blast wheels. By synchronizing the entire system, a continuous flow of media is directed toward the work to achieve the desired results in the fastest and most expedient manner.

***Stream descaling***

This method involves pre-descaling of wire rod by bending and torsion and fluidization of the scale obtained in this descaling. In a special chamber the fluidized scale is then blown onto the wire rod surface by means of jet pumps and compressed air. The rod is descaled to its metallic surface. The scale is transported to a dust collection system (cyclone, cloth filter) by the compressed air. Coarse scale is returned to the jet pumps and used again. The fine scale is utilized as a component in the production of paints.

This method is reported to be applicable to low carbon steel wire rod and high carbon steels. Initial investment costs and space requirements are reported to be very low. Another advantage is that no other media as shot or grit is needed.

**Main achieved environmental benefits:**

- Scale is collected separately and can be reused.
- Consumption of shot-blasting media is reduced.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Stream descaling:** Wire Factory in Gliwice, Poland application low carbon wire, reduced production costs (planned or implemented?)

**Operational data:****Economics:****Driving force for implementation:****Reference literature:****Stream descaling:**

'A new Method of mechanical Descaling of Carbon Steel Wire Rods', Conference Proceedings – Wire association International Incorporated, 65<sup>th</sup> Annual Convention Atlanta, 1995.

**A.4.3.5 Dry Drawing****A.4.3.5.1 Control of Air Emissions from Drawing Machines / Treatment of Extracted Air****Description:**

A hood or cover is installed above parts of the drawing machine that are in contact with the wire. The cover needs to be designed in a way that it can be removed easily for frequent tasks, such as threading a wire through the machine, fixing a broken wire, adjusting or replacing a die or adding soap. The air within the cover is extracted.

The extracted air can be treated by a filter or similar device to capture soap dust.

**Main achieved environmental benefits:**

- Reduction of emissions to air, especially of fugitive soap dust [CET-BAT].

**Applicability:**

- New plants.
- Technical problems expected in existing plant due to design reasons.

**Cross-media effects:****Reference plants:**

All recent dry drawing machines are for a large extend enclosed [CET-BAT].

**Operational data:****Economics:****Driving force for implementation:**

The goal is to limit the spread of lubricant-dust over the area around the drawing machine. 100 % elimination of soap dust is impossible (e.g. soap dust leaving the drawing machine with the drawn wire). This is mainly done to improve the working environment. [CET-BAT]

**Reference literature:****A.4.3.5.2 Closed Loop for Cooling Water****Description:**

The drawing operation heats both wire and drawing die through friction of the wire. So both the dies and the wire (indirectly, through cooling of the capstans in contact with the wire) are water cooled. In order to reuse the cooling water, the water circuit is equipped with a wet cooling tower, an air cooler or similar device. [CET-BAT]

**Main achieved environmental benefits:**

- Reduced water consumption.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### A.4.3.6 Wet Drawing

#### A.4.3.6.1 Closed Loop for Cooling Water

**Description:**

The drawing operation heats both wire and drawing die through friction of the wire. This heat is taken up by the lubricant. The lubricant on its turn is cooled, often this is done indirectly with cooling water. [CET-BAT]

**Main achieved environmental benefits:**

- Reduced water consumption.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### A.4.3.6.2 Cleaning of Drawing Lubricant / Coolant

**Description:** see also Chapter D.3.1

Wire drawing lubricants, water-miscible oil emulsions or straight oils, accumulate metal fines during operation. As the contents of fines increases, operational problems develop, such as wire-drawing breaks, capstan wear and poor quality of wire, requiring replacement of the lubricant. **Media filtration** and/or **centrifuges** are used to clean the lubricant and to prolong the life-cycle. [El-Hindi]

**Main achieved environmental benefits:**

- Reduction of waste drawing lubricant [El-Hindi].

**Applicability:**

- New and existing plants.

**Cross-media effects:**

- Generation of waste filter media [El-Hindi].

**Reference plants:****Operational data:**

Cleaning of drawing lubricant, can improve the operational behavior as it reduces wire-drawing breaks and improves the wire quality (thus reducing also operational problems downstream). [El-Hindi]

**Economics:****Driving force for implementation:**

**Reference literature:** [El-Hindi]

**A.4.3.6.3 Treatment of Waste Drawing Lubricant: Oil and Oil emulsions**

**Description:** see Chapter D.3.2

**Main achieved environmental benefits:**

- Reduced disposal volume.
- In case of incineration, thermal utilisation of waste.

**Applicability:**

- New and existing plants.

**Cross-media effects:****Reference plants:****Operational data:**

- Reduced waste disposal costs.

**Economics:****Driving force for implementation:**

**Reference literature:**

**A.4.3.6.4 Treatment and Disposal of Waste Drawing Lubricant: Soap Emulsions****Description:**

For soap emulsions based on a fatty acid alkali soap the treatment depends on the amount of waste lubricant. In case the quantities are small compared to other waste waters of the plant, the spent lubricant is mixed with other waste waters. The soaps are bounded in the filter cake during almost all existing water treatment methods for acidic waste waters. If a biological treatment is used, the fatty acid soaps are well biodegradable. [CET-BAT]

If the quantities are comparably big, the spent lubricants are treated separately by coagulation and precipitation, coagulation and flotation, membrane filtration, evaporation or other suited methods. [CET-BAT]

**Main achieved environmental benefits:**

- Reduced emissions to water.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

- Generation of sludge and filter cake from water treatment.

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### **A.4.3.7 Batch Annealing of Wire**

#### **A.4.3.7.1 Burn Purge of Protective Gas**

**Description:**

In order to keep an over-pressure in the "pots" or "bells", a fraction of the protective gas is continuously purged.

This gas stream contains - apart from the components of the actual protective gas, decomposition products of the lubricant. These are formed by pyrolysis / cracking of the lubricant molecules; typical decomposition products are low molecular weight olefins and alkanes.

These volatile organic components and the combustible components in some types of protective gasses (CO, H<sub>2</sub>), should be converted to harmless products. As the purge is a very small flow of combustible gas, this is simply done in an open flame. [CET-BAT]

**Main achieved environmental benefits:**

- Reduced emissions to air.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### **A.4.3.8 Continuous (In-line) Annealing of Low Carbon Wire**

#### **A.4.3.8.1 Lead-bath: Good Housekeeping**

**Description:**

The most important house-keeping methods are:

- Maintain a protective layer (particulate material) or cover on the lead-bath to minimize loss of lead by oxidation and drastically reduce energy losses of the lead bath.
- Prevent formation of dust while removing impurities from the lead-bath.
- Keep containers with lead contaminated waste in a separate area, protect this waste from any contact with wind or rain.
- Minimize drag-out of lead with the wire by maintaining a suited surface condition on the half-product (both economically and environmentally attractive).



- Minimize drag-out of lead with the wire by using an anthracite gravel wipe or similar immediately after the lead bath.
- Apply a method that minimizes / eliminates the spread of lead dust that is possibly dragged out with the wire. In many production lines, this is done by coupling the in-line heat-treatment to in-line pickling. Other methods are: coating of the wire with a suitable product or adapted packaging of the wire. [CET-BAT]

**Main achieved environmental benefits:**

- Reduce emissions from lead bath (Pb from bath itself, CO and TOC from incomplete burning of residues on the wire [CET-BAT]).

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

By good house-keeping methods, it is perfectly possible to run a lead-bath at very low emissions of below 5 mg Pb/Nm<sup>3</sup>, 100 mg CO /Nm<sup>3</sup> and 50 mg TOC /Nm<sup>3</sup>. [CET-BAT]

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.3.8.2 Recycling of Pb-containing Residues**

**Description:**

Some Pb-containing residues originate from the Pb-bath (waste bath cover material, lead oxides). These residues should be stored separately and protected from rain and wind. The wire industry depends on subcontractors for the final disposal or recycling of these residues. Normally Pb-containing waste is recycled by the non-ferro industry (Pb-smelters). [CET-BAT]

**Main achieved environmental benefits:**

- Reduced waste disposal.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### A.4.3.8.3 Operation of Quench Bath and Treatment of Waste Water from Quench baths from In-Line Annealing

#### Description:

As the water quality requirements for this bath are generally low, it is advised to use recuperated water for this purpose or to operate the quench bath in closed loop. [CET-BAT]

Waste water from a quench bath should be treated in such a way that contamination (mainly contamination with insoluble  $Pb(OH)_2$  and  $PbCO_3$ ) is removed in a satisfactory way prior to discharge. [CET-BAT]

#### Remark:

1) Each site has to determine its own waste water treatment facility in such a way that it can handle the mix of waste waters that originates at that site. This mix is different for each site, and is highly dependent on the product range of that site (use of acid or not, availability of recycling services for spent acid or not, use of wet drawing emulsions or not, use of plating baths or not + type of plating baths,...) and on the local environmental requirements.

2) If a heat treatment without protective atmosphere is used (e.g. a heat treatment involving the use of a molten Pb-bath), then also acid pickling is used  $\Rightarrow$  at least spent rinsing water containing acid and iron has to be treated. In this case, most wire plants use a traditional physico-chemical waste water treatment, in other words neutralisation with lime milk followed by precipitation of Fe and Pb + other heavy metals, followed by decantation and filter-pressing of the cake. [Com BG2]

#### Main achieved environmental benefits:

- Reduced emissions to water.

#### Applicability:

- New and existing plants.

#### Cross-media effects:

- Generation of waste/sludges from waste water treatment.

#### Reference plants:

#### Operational data:

#### Economics:

#### Driving force for implementation:

#### Reference literature:

### A.4.3.9 Continuous (In-line) Annealing of Stainless Steel Wire

#### A.4.3.9.1 Burn Purge of Protective Gas

Refer to A.4.3.5.1

#### A.4.3.10 Patenting

##### A.4.3.10.1 Optimised Operation of the Oven

#### Description:

A slightly substoichiometric mixture is used in the burners. In this way, all  $O_2$  is excluded from the oven atmosphere, in order to minimize the formation of iron oxides at the wire surface.

Excessive formation of iron oxide leads to high losses of wire material and to excessive consumption of pickling acid, and leads to excessive dragout of lead. [CET-BAT]

Excess CO must be converted to CO<sub>2</sub> by adding air in a controlled way to the hot exhaust of the oven. The CO-content of the oven atmosphere and the exhaust gas must be controlled regularly, e.g. after every major change in the product mix or at least every month. [CET-BAT]  
Because of the heating method, NO<sub>x</sub> formation is not an issue. [CET-BAT]

**Main achieved environmental benefits:**

- Reduced consumption in following process steps (e.g. acid).
- Reduced CO-content.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **A.4.3.10.2 Lead-bath: Good Housekeeping**

Refer to A4.3.6.1

#### **A.4.3.10.3 Recycling of Pb-containing Residues**

Refer to A.4.3.6.2

#### **A.4.3.10.4 Operation of Quench Bath and Treatment of Waste Water from Quench Baths of Patenting Line**

Refer to A.4.3.6.3

#### **A.4.3.11 Oil Hardening and Tempering**

##### **A.4.3.11.1 Burn Purge of Protective Gas**

Refer to A.4.3.5.1

##### **A.4.3.11.2 Extraction of Oil Mists from Quench Baths and Abatement**

**Description:**

Evacuation of the oil mist and removal of the oil mist from the extracted air.

**Main achieved environmental benefits:**

- Reduction of fugitive air emissions, especially oil emissions.

**Applicability:**

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### **A.4.3.12 Heat Treatment of wire (different processes)**

#### **A.4.3.12.1 Inductive Heating of Wire**

**Description:**

The wire to be heated is guided through a coil; in this coil a magnetic field is generated. Typically, applied frequencies are 5 - 50 kHz (mid-frequent heating). Exceptionally, high-frequent heating (well above 50 kHz) is used. This magnetic field induces an electric current in the wire; the wire is heated through the Joule effect of the induced current. The induced current is mainly in a small layer towards the outside of the wire section; this phenomenon is called the "skin-effect".

The applicability of inductive heating is highly dependent on wire material, wire diameter and required temperature increase:

- Material is preferably magnetic.  
Steel and certain steel alloys are magnetic. Most types of stainless steel are non-magnetic. Most metal coatings are non-magnetic.
- Wire diameter is preferably high, e.g. above 2 - 3 mm.  
The smaller the diameter, the higher the frequency should be in order to maintain a sufficient skin-effect.
- Above the "Curie-temperature", a magnetic material loses its magnetic properties. Steel loses its magnetic properties at approx. 760 °C.

Applications outside this range are available. However, expensive high-frequency equipment has to be used and energetic efficiency is on average lower.

The vast majority of the applications of inductive heating are found in single wire lines. Induction heating in a single wire line concept can be used for austenitising and tempering. Austenitising is the first step of several thermal treatment operations: patenting (see A.2.3.4.4), oil hardening (see A.2.3.4.5) and tempering (described in A.2.3.4.5. and A.2.3.4.6).

An exact control of the wire temperature is a necessity for these thermal treatments.

Induction heating in a multi-wire line concept can be used for preheating of the wires (e.g. to the Curie-temperature). Another application is diffusion of Cu and Zn coatings on a steel wire in order to obtain a brass coated wire.

**Main achieved environmental benefits:**

Air emissions from combustion are avoided in the plant.

**Applicability:**

The applicability of inductive heating in a single wire line concept is quite wide and includes applications where exact temperature control is required.

Use of inductive heating in a multi-wire line concept is limited to applications where exact temperature control is not an issue, e.g. preheating.

Applicability is dependent on wire properties. See above.

**Cross-media effects:**

Consumption of fuel (typically NG or LPG) is replaced by consumption of electricity. When taking into account the fuel consumption of electricity generation, this cross-media effect is negligible.

Typical electrical energy efficiencies of mid-frequency inductive heating are in the range 60 - 85 %. Typical energy efficiency of a NG-based heating method for similar applications is 25 - 45 %. Taking into account the efficiency of NG-based electricity generation, e.g. a STAG reaching 50 – 55 %, one can conclude that there is hardly any difference in primary fuel consumption.

Cooling water is needed to cool the induction coil.

**Reference plants:****Operational data:****Economics:****Driving force for implementation:****Reference literature:**

*not enough information to make BAT decision?*

**A.4.3.13 In-line Pickling**

See Part B



## A.5 BEST AVAILABLE TECHNIQUES FOR HOT AND COLD FORMING

In understanding this chapter and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- Identification of the key environmental issues of hot and cold forming. The diversity of the processing steps in this part of the ferrous metal processing sector means that all media are affected. Among the most important issues are air emissions (especially NO<sub>x</sub>) from furnaces; energy consumption of furnaces, effluents containing oil and solids, acidic wastes and waste water; acidic and oil mist emissions to air and oil-containing wastes.
- Examination of the techniques most relevant to address those key issues.
- Identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide.
- Examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques.
- Selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this chapter that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous chapter. These give a rough indication about the

magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this chapter are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

This chapter discusses the best available techniques for reducing the environmental impacts from hot and cold forming. Where possible, the structure follows the logic of the production line and identifies BAT for individual processing stages. However, some measures, especially primary or preventive measures, cannot be assigned to one single process step and have to be allocated to the plant as a whole. As far as possible and wherever the data available allowed, emission levels, efficiencies or recirculation rates are given as an indication of the improvement that can be expected by implementation of the techniques. For a number of techniques the obvious positive effect cannot be described by an exact number, but some of these techniques are nevertheless considered as BAT.

Unless stated otherwise the emission figures presented in the following BAT chapters are daily mean values. For emissions to air they are based on standard conditions of 273 K, 101.3 kPa and dry gas.

Discharges to water are indicated as daily mean value of a flow-rate-related 24-hours composite sample or a flow-rate-related composite sample over the actual operating time (for plants not operated in three shifts).

## A.5.1 Hot Rolling Mill

For **storing and handling of raw materials and auxiliaries** the following techniques are considered to be BAT:

- Collection of spillages and leakages by suitable measures, e.g. safety pits and drainage.
- Separation of oil from the contaminated drainage water and reuse of recovered oil.
- Treatment of separated water in the water treatment plant.

In general, the best way to reduce the environmental impact from **surface rectification and conditioning of input** is to avoid the need for rectification. The improvement of surface quality of cast products to reduce the need for surface rectification is therefore considered BAT.

Furthermore, the following measures were identified as BAT for surface rectification and conditioning of input:



For **machine scarfing**:

- Enclosures for machine scarfing and dust abatement with fabric filters.  
There was agreement that this technique constitutes BAT, but there were different opinions on the associated emission level and the TWG recorded a split view. One plant reported achieved dust emission levels of 5 - 10 mg/m<sup>3</sup>. Some Member States argued (without supporting data for this type of installation) that fabric filters in general can achieve below 5 mg/Nm<sup>3</sup> and that this is the level that should be associated with BAT. Others pointed out that < 20 mg/Nm<sup>3</sup> is the appropriate level.
- The use of an electrostatic precipitator, where fabric filters cannot be operated because of very wet fume. There were no dust emission data available for individual plants, but reported current emission levels ranged from < 20 mg/Nm<sup>3</sup> to 20 - 115 mg/m<sup>3</sup>. Based on information submitted by TWG members on generally achievable dust levels for electrostatic precipitators<sup>3</sup> in the application of oxide and dust removal in the FMP sector, an associated dust level of 15 – 20 mg/Nm<sup>3</sup> was proposed by the EIPPCB. Interventions were made by an industrial NGO that the BAT-associated level was 20 - 50 mg/m<sup>3</sup>; while Member States claimed that generally achievable levels of electrostatic precipitators are < 10 mg/Nm<sup>3</sup> and that this should be the BAT-associated emission level. The TWG was unable to reach agreement on the BAT-associated level and a split view was recorded.
- Separate collection of scale/swarf from scarfing. The oil-free scale should be kept apart from oily millscale for easier reuse in metallurgical processes.

For **grinding**:

- Enclosures for machine grinding and dedicated booths, equipped with collection hoods for manual grinding and dust abatement for the extracted air by fabric filters.  
There was consensus among TWG members that these techniques constitute BAT, but no agreement was reached as to what the associated emission level is. Emission data taken from various sources lead to a reported current dust emission range for grinding of 1 – 100 mg/m<sup>3</sup>. Industry reported data for the application of fabric filters with resulting dust levels of < 30 mg/Nm<sup>3</sup> and 20 – 100 mg/Nm<sup>3</sup> (for different filter types). Taking into account the better range of the reported emission levels and the information submitted by TWG members on generally achievable dust levels for fabric filters<sup>4</sup> in the application of oxide and dust removal in the FMP sector, a BAT-associated level of < 20 mg/Nm<sup>3</sup> was proposed. Some Member States opposed, saying (based on very limited data) that fabric filters in general can achieve below 5 mg/Nm<sup>3</sup> and that this should be the BAT-associated level.

Additionally, for all surface rectification processes:

- Treatment and reuse of water from all surface rectification processes (separation of solids).
- Internal recycling or sale for recycling of scale, swarf and dust.

Air emissions from **reheating and heat treatment furnaces** basically comprise NO<sub>x</sub>, SO<sub>2</sub> and dust. For dust, no specific abatement measures are applied. Generally, dust emissions are in the range of 4 – 20 mg/m<sup>3</sup>, but figures as low as 2.2 mg/Nm<sup>3</sup> have been reported.

For reducing air emissions, especially NO<sub>x</sub>, from reheating and heat treatment furnaces and to reduce the energy consumption, the general measures described in Chapter A.4.1.3.1 should be taken into account at the design stage. Special attention should be paid to energy efficiency and waste heat recovery, e.g. by adequate furnace insulation, insulation of skids, adequate stock

<sup>3</sup> Reduction efficiency 95 – 99 %, grain size > 0.1 µm and input dust content up to 100 mg/m<sup>3</sup>, dust output levels for EP 15 – 20 mg/Nm<sup>3</sup> reference [EUROFER HR]

<sup>4</sup> Reduction efficiency 95 – 99 %, grain size (> 0.1 µm) > 0.5 µm and input dust content up to 500 mg/Nm<sup>3</sup>; dust output levels for FF 1 – 20 mg/Nm<sup>3</sup> [EUROFER HR].

recuperation zone etc, and to air emission reduction, e.g. by choice of burners and placement of burners.

Additionally, the following measures, which can also be applied to existing furnaces, are considered BAT for reheating and heat treatment furnaces:

- Avoiding excess air and heat loss during charging by operational measures (minimum door opening necessary for charging) or structural means (installation of multi-segmented doors for tighter closure).
- Careful choice of fuel (in some cases, e.g. coke oven gas, desulphurisation maybe necessary) and implementation of furnace automation and control to optimise the firing conditions in the furnace. Depending on the fuel used, the following SO<sub>2</sub> levels are associated with BAT:
  - for natural gas < 100 mg/Nm<sup>3</sup>
  - for all other gases and gas mixtures < 400 mg/Nm<sup>3</sup>
  - for fuel oil (< 1 % S) up to 1700 mg/Nm<sup>3</sup>

There was a split view in the TWG on whether the limitation of < 1 % sulphur content in fuel oil can be considered as BAT. Some experts considered this limit enough to be BAT, whilst others expressed the view that the resulting emissions of up to 1700 mg SO<sub>2</sub>/Nm<sup>3</sup> cannot be regarded as such. They considered a lower S content or the application of additional SO<sub>2</sub> reduction measures to be BAT.

- Recovery of heat in the waste gas- by feedstock preheating
  - by regenerative or recuperative burner systems
  - by waste heat boiler or evaporative skid cooling (where there is a need for steam)

Energy savings of 40 - 50 % can be achieved by regenerative burners, with reported NO<sub>x</sub> reductions potentials of up to 50 %. Energy savings associated with recuperators or recuperative burners are about 25 %, with reported achievable NO<sub>x</sub> reductions of about 30 % (50 % in combination with low-NO<sub>x</sub> burners).

- Second generation low-NO<sub>x</sub> burners with associated NO<sub>x</sub> emission levels of 250 - 400 mg/Nm<sup>3</sup> (3 % O<sub>2</sub>) without air preheating and reported NO<sub>x</sub> reduction potential of about 65 % compared to conventional burners. It should be noted that in evaluating the efficiency of NO<sub>x</sub> reduction measures it is important to also pay attention to specific emission levels, not only to the achieved concentration. In some cases, NO<sub>x</sub> concentrations may be higher, but the NO<sub>x</sub> mass emitted may be equal or even lower. Unfortunately, the figures available at present for NO<sub>x</sub> concentrations and specific NO<sub>x</sub> emissions are very limited.

Reheating furnaces do not operate in stable conditions during start-up and shut-down; during these phases the emission levels may increase.

- Limiting the air preheating temperature.  
Higher NO<sub>x</sub> concentrations may arise in the case of reheating furnaces operating with combustion air preheating. Only very limited data were submitted on NO<sub>x</sub> concentrations in connection with air preheating. The following data, taken from available UK reports<sup>5</sup>, give an indication of the NO<sub>x</sub> emission levels that may be expected with increasing air preheating temperature (refer also to Part D.2.2):

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<sup>5</sup> See also Part D.3.2, for more detailed information see references [HMIP-95-003] [ETSU-GIR-45]

Air preheating Temperature [°C]	NOx [mg/Nm <sup>3</sup> ] <sup>6</sup>
100 - 200	< 400
300	up to 450
400	up to 600
500	up to 800
700	up to 1500
800	up to 2300
900	up to 3500
1000	up to 5300

With increasing air preheating temperature, a significant rise in NOx concentrations is inevitable. Thus, limiting the preheating temperature may be seen as a NOx reduction measure. However, the advantages of reduced energy consumption and reductions in SO<sub>2</sub>, CO<sub>2</sub> and CO have to be weighed against the disadvantage of potentially increased emissions of NOx.

Regarding further NOx reduction measures, information on actual application of SCR and SNCR at reheating furnaces was received at a very late stage of the work. It was confirmed that one plant is applying SCR at its walking beam furnaces, achieving below 320 mg/Nm<sup>3</sup> with a reduction rate of about 80 % and that another plant has installed SNCR after its walking beam furnaces achieving NOx levels of 205 mg/Nm<sup>3</sup> (~ 70 % reduction rate) and 172 mg/Nm<sup>3</sup> (~30 % reduction rate) with an ammonia slip of 5 mg/Nm<sup>3</sup>.

Based on this information, some members of the TWG stated that these techniques are BAT for the sector as a whole; while other members thought the available information on technical details and on economics was not sufficient enough to allow for a final decision on whether SCR and SNCR are BAT or not and therefore a split view was recorded.

Furthermore, the following measures to minimize the energy requirements are considered to be BAT:

- Reduction of heat loss in intermediate products; by minimizing the storage time and by insulating the slabs/blooms (heat conservation box or thermal covers) depending on production layout.
- Change of logistic and intermediate storage to allow for a maximum rate of hot charging, direct charging or direct rolling (the maximum rate depends on production schemes and product quality).

For new plants, near-net-shape casting and thin slab casting are considered BAT, to the extent that the product to be rolled can be produced by this technique. A great variety of qualities is already produced by these techniques and rapid developments are taking place. The list given in Chapter A.4.1.3.16 should therefore not be seen as final.

In reducing water and energy consumption, material tracking is considered BAT for **descaling**.

Large amounts of heat contained in continuous cast products or in intermediate products are lost during handling and storage. To reduce unwanted energy loss during **transport of rolled stock** from roughing mill to finishing train, coil boxes or coil recovery furnaces and heat shields for

<sup>6</sup> Rough estimate as taken from diagram; 3 % oxygen, dry gas, standard conditions

transfer bars are considered to be the best available techniques, although a potentially higher risk of surface defects (rolled-in scale) and potential damages caused by curled transfer bars was reported for heat retention shields. Coil boxes may also result in increased surface defects.

During rolling in the **finishing train** fugitive emissions of dust occur. Two techniques have been identified as BAT for the reduction of these emissions:

- water sprays followed by waste water treatment in which the solids (iron oxides) are separated and collected for reuse of iron content.
- Exhaust systems with treatment of extracted air by fabric filters and recycling of collected dust. The reported current dust emission level ranged from 2 – 50 mg/Nm<sup>3</sup>. Taking into account the better range of the reported emission levels and the information submitted by TWG members on generally achievable dust levels for fabric filters<sup>7</sup> in the application of oxide and dust removal in the FMP sector, a BAT associated level of < 20 mg/Nm<sup>3</sup> was proposed. Some Member States opposed, saying (not supported by data) that fabric filters in general can achieve below 5 mg/Nm<sup>3</sup> and that this should be the BAT-associated level. The TWG was unable to reach agreement on the BAT associated level and a split view was recorded.

For tube mills, collection hoods and fabric filters for fugitive emissions from rolling stands are not considered BAT, due to low rolling speeds and resulting lower emissions.

For reducing fugitive dust emissions from **levelling and welding**, suction hoods and subsequent abatement by fabric filters was identified as BAT. There were no emission data available for levelling and welding, but following the general approach on what is achievable by fabric filters (see above) a BAT-associated dust level of < 20 mg/Nm<sup>3</sup> was proposed. Some Member States expressed the view (without supporting data) that fabric filters in general can achieve below 5 mg/Nm<sup>3</sup> and that this should be the BAT-associated level. The TWG was unable to reach agreement on the BAT associated level and a split view was recorded.

Best available operational and maintenance techniques for **roll shops** are:

- Use of water-based degreasing as far as technically acceptable for the degree of cleanliness required.
- If organic solvents have to be used, preference is to be given to non-chlorinated solvents.
- Collection of grease removed from roll trunnions and proper disposal, such as by incineration.
- Treatment of grinding sludge by magnetic separation for recovery of metal particles and recirculation into the steelmaking process.
- Disposal by incineration of oil- and grease-containing residues from grindingwheels [Com D]
- Deposition of mineral residues from grinding wheels and worn grinding wheels in landfills.
- Treatment of cooling liquids and cutting emulsions for oil/water separation. Proper disposal of oily residues, e.g. by incineration.
- Treatment of waste water effluents from cooling and degreasing as well as from emulsion separation in the hot rolling mill water treatment plant.
- Recycling of steel and iron turnings into the steelmaking process.
- Recycling of worn rolls which are unsuitable for further reconditioning, into the steelmaking process or returned to the manufacturer.

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<sup>7</sup> Reduction efficiency 95 – 99 %, grain size (> 0.1 µm) > 0.5 µm and input dust content up to 500 mg/Nm<sup>3</sup>; dust output levels for FF 1 – 20 mg/Nm<sup>3</sup> [EUROFER HR].

For **cooling** (machines etc.) separate cooling water systems operating in closed loops are considered BAT.

Hot rolling leads to a large amount of **scale- and oil-containing process water**. The minimization of consumption and discharge by operating closed loops with recirculating rates of > 95 % is considered BAT.

Treatment of this process water and pollution reduction in the effluent from these systems as described by examples in Chapter A.4.1.12.2 or by other combinations of the individual treatment units (as in D.10.1) are considered BAT. The following release levels from the waste water treatment are associated with BAT:

SS:	< 20 mg/l	
Oil:	< 5 mg/l	(oil based on random measurements)
Fe:	< 10 mg/l	
Cr <sub>tot</sub> :	< 0.2 mg/l	(for stainless steel < 0.5 mg/l)
Ni:	< 0.2 mg/l	(for stainless steel < 0.5 mg/l)
Zn:	< 2 mg/l	

As the volume and contamination of waste water from tube mills are quite similar to other hot rolling operations, it was noted that the same techniques and the same associated BAT levels apply for tube mills.

Recirculation to the metallurgical process of mill scale collected in water treatment is BAT. Techniques are described in Chapter A.4.1.13.2.. Depending on oil content, additional treatment may be required. All oily waste/sludge collected should be de-watered to allow for thermal utilisation or safe disposal.

Throughout the plant the following techniques for **prevention of hydrocarbon contamination** of water have been identified and are considered to be BAT:

- Preventive periodic checks and preventive maintenance of seals, gaskets, pumps and pipelines.
- Use of bearings and bearing seals of modern design for work- and back-up rolls as well as the installation of leakage indicators in the lubricant lines (e.g. at hydrostatic bearings). This reduces the oil consumption by 50 - 70 %.
- Collection and treatment of contaminated drainage water at the various consumers (hydraulic aggregates), separation and use of oil fraction, e.g. thermally utilized by blast furnace injection. Further processing of the separated water either in the water treatment plant or in dressing plants with ultra filtration or vacuum evaporator.

## A.5.2 Cold Rolling Mill

At the entry side of pickling lines, **decoiling** of the hot rolled strip leads to fugitive dust emissions. For the reduction of these emissions two techniques have been identified as BAT:

- Water curtains followed by waste water treatment in which the solids are separated and collected for reuse of iron content.
- Exhaust systems with treatment of extracted air by fabric filters and recycling of collected dust.

There were no emission data available for decoiling, but following the general approach on what is achievable by fabric filters (see above), a BAT-associated dust level of  $< 20 \text{ mg/Nm}^3$  was proposed. Some Member States expressed the view (without supporting data) that fabric filters in general can achieve below  $5 \text{ mg/Nm}^3$  and that this should be the BAT-associated level. The TWG was unable to reach agreement on the BAT associated level and a split view was recorded.

To reduce the environmental impact from **pickling**, general measures to reduce acid consumption and waste acid generation as described in chapter A.4.2.2.1. should be applied as far as possible and be considered preferably already at design stage, especially the following techniques that are considered BAT:

- Prevention of steel corrosion by appropriate storage and handling, cooling etc.
- Mechanical pre-descaling to reduce the load on the pickling step. If mechanical descaling is applied, BAT is a closed unit, equipped with an extraction system and fabric filters. For shot blasting, dust emission levels of  $< 1 \text{ mg/Nm}^3$ ,  $2.6 \text{ mg/Nm}^3$  and  $4.5 \text{ mg/Nm}^3$  have been achieved [FIN 28.3].
- Use of electrolytic pre-pickling.
- Use of modern, optimised pickling facilities (spray or turbulence pickling instead of dip pickling).
- Mechanical filtration and recirculation for lifetime extension of pickling baths.
- Side-stream ion-exchange or electro-dialysis (for mixed acid) or other method for free acid reclamation (described in chapter D.6.9) for bath regeneration.

For **HCl pickling**, BAT is considered to be:

- The reuse of spent HCl

or

- The regeneration of the acid by spray roasting or fluidised bed (or equivalent process) with recirculation of the regenerate to the pickling process is considered BAT. Depending on site circumstances, the high acid consumption and amounts of waste acid generated and the savings generally obtained from regeneration *may* justify the investment in a regeneration plant. The acid regeneration plant needs to be equipped with an air scrubbing system as described in Chapter 4, to reduce emissions, especially acid emissions. Achievable reduction efficiencies of  $> 98 \%$  were reported. Some sources report achieved HCl concentrations by applying caustic scrubbing of  $< 2 \text{ mg/Nm}^3$ . The TWG agreed that the following emission levels are associated with acid regeneration (waste gas treatment by scrubbers or adsorption towers):

Dust	20 -50	$\text{mg/Nm}^3$
HCl	2 – 30	$\text{mg/Nm}^3$
SO <sub>2</sub>	50 - 100	$\text{mg/Nm}^3$
CO	150	$\text{mg/Nm}^3$
CO <sub>2</sub>	180000	$\text{mg/Nm}^3$
NO <sub>2</sub>	300 - 370	$\text{mg/Nm}^3$

The recovered solid by-product Fe<sub>2</sub>O<sub>3</sub> is a saleable product and is externally reused.

For **H<sub>2</sub>SO<sub>4</sub> pickling** processes, recovery of the free acid by crystallisation is considered BAT. The recovery plant needs to be equipped with air scrubbing devices; emission levels associated with this process are:

H <sub>2</sub> SO <sub>4</sub>	5 - 10	$\text{mg/Nm}^3$
SO <sub>2</sub>	8 - 20	$\text{mg/Nm}^3$

For **mixed acid pickling**, free acid reclamation (e.g. by side-stream ion exchange or dialysis) or acid regeneration (e.g. by spray roasting or evaporation process) is considered BAT. While free acid reclamation is applicable to virtually all plants, the applicability of regeneration processes may be limited for site-specific reasons. The emissions associated with BAT are:

	<b>Spray Roasting</b>	<b>Evaporation Process</b>	<b>Free Acid Reclamation</b>
<b>Dust</b>	< 10 mg/Nm <sup>3</sup>	none	
<b>HF</b>	<2 mg/Nm <sup>3</sup>	<2 mg/Nm <sup>3</sup>	none
<b>NO<sub>2</sub></b>	< 200 mg/Nm <sup>3</sup>	< 100 mg/Nm <sup>3</sup>	
<b>Waste water</b>	0.003 – 0.01 m <sup>3</sup> /t	not available	0.05 – 0.02 m <sup>3</sup> /t (metal-containing weak acid solution)
<b>Other output</b>	mixed oxide	metal sulphate filter cake	

All three processes are equally considered BAT. Despite the disadvantage of higher air emissions and energy consumption, spray roasting was selected because of its high acid recovery rate and associated low fresh acid consumption. Furthermore the waste water is only a fraction of that produced by reclamation processes. Metals are basically bound in a solid by-product. This mixed iron-chromium- nickel oxide can be reused in metal production.

The evaporation process also provides a very high acid recovery rate and thus low fresh acid consumption, but with much lower energy consumption than spray roasting. The metal sulphate filter cake, however, needs to be disposed of.

For the reduction of **air emissions from the pickling tanks**, totally enclosed equipment or equipment fitted with hoods and scrubbing of extracted air are considered BAT with associated emission levels:

**HCl pickling:** Dust 10 - 20 mg/Nm<sup>3</sup>  
HCl 2 – 30 mg/Nm<sup>3</sup> (reduction efficiency > 98 %)

**H<sub>2</sub>SO<sub>4</sub> pickling:** H<sub>2</sub>SO<sub>4</sub> 1- 2 mg/Nm<sup>3</sup>  
SO<sub>2</sub> 8 - 20 mg/Nm<sup>3</sup> (reduction efficiency > 95 %)

For **mixed acid pickling** of stainless steel, in addition to enclosed equipment/hoods and scrubbing, further NO<sub>x</sub> reduction measures are required. The following techniques are considered to be BAT:

- Scrubbing with H<sub>2</sub>O<sub>2</sub>, urea etc.;
- or
- NO<sub>x</sub> suppression by adding H<sub>2</sub>O<sub>2</sub> or urea to the pickling bath;
- or
- SCR.

Emission levels of 200 - 650 mg/Nm<sup>3</sup> for NO<sub>x</sub> (reduction 75 - 85 %) and 2 – 7 mg/Nm<sup>3</sup> for HF (reduction 70 - 80 %) are associated with these techniques. Some sources reported achievable emission levels for HF of < 2 mg/Nm<sup>3</sup>, but as there was some recognition of difficulties in measuring HF, especially at low levels, it was concluded that the BAT-associated level is the range given above.

As an alternative, implementation of nitric acid-free pickling (e.g. H<sub>2</sub>O<sub>2</sub> based) with enclosed equipment or equipment fitted with hoods and scrubbing is considered BAT. However, this technique is not applicable to all applications.

For **heating of acids** the direct injection of steam is not considered BAT as it leads to unnecessary dilution of the acid. BAT is indirect heating by heat exchangers or, if steam for heat exchangers has to be produced first, by submerged combustion.

The following measures have been identified as BAT for the minimization of acidic waste water:

- Cascade rinsing systems with internal re-use of overflow (e.g. in pickling baths or scrubbing).
- Careful tuning and managing of the 'pickling-acid regeneration-rinsing' system. Some sources report a possible waste water-free operation.
- in any case where acidic water blow-down from the system cannot be avoided, waste water treatment is required (neutralisation, flocculation, etc.). Associated release levels of the waste water treatment are:  
SS: < 20 mg/l  
Oil: < 5 mg/l (oil based on random measurements)  
Fe: < 10 mg/l  
Cr<sub>tot</sub>: < 0.2 mg/l (for stainless steel < 0.5 mg/l)  
Ni: < 0.2 mg/l (for stainless steel < 0.5 mg/l)  
Zn: < 2 mg/l

There was agreement in the TWG that there are exceptional cases for stainless steel where the levels of Cr<sub>tot</sub> and Ni cannot be kept below 0.5 mg/l.

For **emulsion systems** the following techniques are considered to be BAT:

- Prevention of contamination by regular checking of seals, pipework etc. and leakage control.
- Continuous monitoring of emulsion quality.
- Operation of emulsion circuits with cleaning and reuse of emulsion to extend lifetime.
- Treatment of spent emulsion to reduce oil content, e.g. by ultrafiltration or electrolytic splitting.

During **rolling and tempering**, fugitive emissions of emulsion fumes occur. To capture and reduce these emissions the best technique available is the installation of an exhaust system with treatment of extracted air by mist eliminators (droplet separator). Reduction efficiencies achieved are > 90 % and associated emission levels of hydrocarbons 5 - 15 mg/Nm<sup>3</sup>.

For installations operating with a **degreasing** step, the following techniques are considered BAT:

- Implementation of a degreasing circuit with cleaning and reuse of the degreaser solution. Appropriate measures for cleaning are mechanical methods and membrane filtration as described in Chapter A.4.
- Treatment of spent degreasing solution by electrolytic emulsion splitting or ultrafiltration to reduce the oil content. The separated oil fraction should be reused, e.g. thermally; the separated water fraction requires treatment (neutralisation etc.) prior to discharge.
- Extraction system to capture degreaser fume and scrubbing of extracted air.



The main environmental issues for **annealing furnaces** are air emissions from combustion processes and efficient energy use. The best available techniques to reduce emissions at continuous annealing furnaces are low-NO<sub>x</sub> burners with reduction rates of 60 % for NO<sub>x</sub> (and 87 % for CO) and with an associated emission level of 250 – 400 mg/Nm<sup>3</sup> (without air preheating, 3 % O<sub>2</sub>). The NO<sub>x</sub> emission level for batch annealing furnaces without the application of low-NO<sub>x</sub> burners and without air preheating is in the range of 150 – 380 mg/Nm<sup>3</sup> (without air preheating, 3 % O<sub>2</sub>). Generally the emissions levels to expect from annealing furnaces are:

	Batch Furnaces	Continuous Furnaces	
Dust	5 - 10	10 - 20	mg/Nm <sup>3</sup> .
SO <sub>2</sub>	60 - 100	50 - 100	mg/Nm <sup>3</sup> .
NO <sub>x</sub>	150 - 380	250 - 400	mg/Nm <sup>3</sup> .
CO	40 - 100	50 - 120	mg/Nm <sup>3</sup> .
CO <sub>2</sub>	200000 - 220000	180000 - 250000	mg/Nm <sup>3</sup> .

Oxygen reference level 3 %

The best available measures to increase the energy efficiency are:

- Combustion air preheating by regenerative or recuperative burners.  
Higher NO<sub>x</sub> concentrations may arise in the case of annealing furnaces operating with combustion air preheating. No data was submitted on NO<sub>x</sub> concentrations in connection with air preheating, but the figures given for reheating furnaces may serve as an indication. Limiting the preheating temperature may be seen as a NO<sub>x</sub> reduction measure. However, the advantages of reduced energy consumption and reductions in SO<sub>2</sub>, CO<sub>2</sub> and CO have to be weighed against the disadvantage of possible increased emissions of NO<sub>x</sub>.

or

- Preheating of stock by waste gas.

For **finishing**, the steel strip may be oiled for protection; this can lead to oil mist emissions. The best techniques to reduce these emissions are:

- Extraction hoods followed by mist eliminators and/or electrostatic precipitators. Data submitted for one plant showed an achieved average oil droplet concentration of 3.0 mg/Nm<sup>3</sup> applying mist eliminator and electrostatic precipitator.

or

- Electrostatic oiling.

Further finishing operations, **levelling and welding**, generate fugitive dust emissions. BAT to reduce these emissions are extraction hoods with dust abatement by fabric filters. Emission data available from one plant range from 7 – 39 mg/Nm<sup>3</sup>; data from another plant (part time operation) from 5 – 30 mg/Nm<sup>3</sup>. Taking into account the better range of the reported emission levels and the information submitted by TWG members on generally achievable dust levels for fabric filters<sup>8</sup> in the application of oxide and dust removal in the FMP sector, a BAT-associated level of < 20 mg/Nm<sup>3</sup> was proposed. Some Member States opposed, saying (not supported by data) that fabric filters in general can achieve below 5 mg/Nm<sup>3</sup> and that this should be the BAT-associated level. The TWG was unable to reach agreement on the BAT associated level and a split view was recorded.

<sup>8</sup> Reduction efficiency 95 – 99 %, grain size (> 0.1 µm) > 0.5 µm and input dust content up to 500 mg/Nm<sup>3</sup>; dust output levels for FF 1 – 20 mg/Nm<sup>3</sup> [EUROFER HR].

For **cooling** (machines etc.), separate cooling water systems operating in closed loops are considered BAT.

For the **roll shops** of cold rolling mills the same principles as for roll shops in hot rolling mills are applicable.

**Metallic by-products**, scrap from cutting, heads and tails are collected at different stages in the rolling mill. Collection and recirculation into the metallurgical process is BAT.

### A.5.3 Wire plant

**Pickling** operations, especially when concentrated or heated acid is used, lead to emissions of acidic vapors. Techniques to reduce the emissions depend on the acid used and on the way pickling is done (batch or continuously). Batch (discontinuous) pickling, used for preparation of wire rod, is described below. Continuous pickling of wire is typically used in combination with other operations such as hot dip coating of wire. See B.5.4.

For batch pickling, the following techniques are considered to be BAT:

- HCl pickling: close monitoring of bath parameters: temperature and concentration and operating within the limits given in Part D/Chapter D.6.1 'Open Pickling Bath Operation'. Where operation in compliance with the conditions described in D.6.1 is not possible, extraction and scrubbing is considered BAT.
- In the case of pickling baths with high vapour emission, e.g. heated or concentrated HCl-bath: installation of lateral extraction and possibly treating of the extraction air for both new and existing installations. The BAT-associated level for HCl emission is 2 – 30 mg/Nm<sup>3</sup>.

To reduce acid consumption, amounts of acidic wastes and waste water, the following techniques are considered to be BAT:

- Cascade Pickling (for installations above a capacity of 15 000 tonne wire rod per year. For small scale applications, the investment in a second tank, piping and process control equipment is not justified.)

or

- Reclamation of free acid fraction and reuse in pickling plant.
- External regeneration of spent acid. (On-site regeneration of spent acid, which is described as BAT for hot/cold rolling (see section A.5.2), is not feasible for wire pickling plants. These regeneration plants require a certain waste acid throughput for economic operation. The volumes of waste acid available in a wire plant are far below this threshold for economic operation).
- Recycling of spent acid as secondary raw material.
- Non-acid descaling, e.g. shot blasting, if quality requirements allow.
- Countercurrent cascade rinsing [CET-BAT]

To reduce fugitive soap dust emissions from **dry drawing**, enclosing the drawing machine (and connecting to a filter or similar device when necessary), is considered to be BAT for all new machines with drawing speed  $\geq 4$  m/s.

In some categories of wire drawing machines where the drawing speed is limited ( $< 4$  m/s), the spread of lubricant-dust is limited, even without a cover. In these cases, the added

environmental value of a hood or cover is very limited. Examples of such drawing machines are mono-blocs (machines with only 1 die) and multi-wire drawing machines that are coupled to another operation.

Equipping existing drawing machines with a cover with acceptable dust capture efficiency that would still allow efficient operation and maintenance of the machine is technically impossible for design reasons.

For **wet drawing** lubricants, the following measures are considered to be BAT:

- Cleaning and reuse of drawing lubricant.
- Treatment of spent lubricant to reduce oil content in the discharge and/or to reduce waste volume, e.g. by chemical breaking, electrolytic emulsion splitting or ultrafiltration.
- Treatment of discharge water fraction.

Not to use once-through cooling water systems is considered BAT. The best available techniques to reduce cooling water consumption are closed cooling-water loops for **dry and wet drawing**.

Burning of the protective gas purge is considered to be BAT for all **batch annealing furnaces, continuous annealing furnaces for stainless steel and furnaces used in oil hardening and tempering**.

For **continuous annealing of low carbon wire and patenting**, the following measures are considered to be BAT:

- Good housekeeping measures, as described in chapter A.4.3.7 for the lead bath with associated emission levels of Pb < 5 mg/Nm<sup>3</sup>, CO < 100 mg/Nm<sup>3</sup> and TOC < 50 mg/Nm<sup>3</sup>
- Separate storage of Pb-containing wastes, protected from rain and wind
- Recycling of Pb-containing wastes in non-ferrous metals industry
- Closed loop operation of quench bath.

For quench baths in **oil-hardening lines**, evacuation of the oil mist and removal of the oil mists, when appropriate, are considered BAT.



## **A.6 EMERGING TECHNIQUES FOR HOT AND COLD FORMING**

### **A.6.1 Hot Rolling Mill**

#### **A.6.1.1 Scarfing and Grinding**

Stainless Steel

- Increased power for grinding machines (speeding up the process and therefore reducing emission/t steel processed).
- In line installations within the casting plant to reduce energy consumption by grinding when hot charging [HR].

#### **A.6.1.2 Reheating Furnace**

##### **A.6.1.2.1 Flameless Burner**

The “**flameless burner**” or “**diffused flame**” is the most recent development. In this burner type the burner only provides the air supply. The gas is supplied via separate inlets in the furnace. Maximum recirculation of the flue gases is achieved.

A NO<sub>x</sub> emission level of approximately 100 mg/Nm<sup>3</sup> could be realised. Until now no industrial realisation of the flameless burner exists in a reheating furnace. Combustion control may be a problem. [HR]

##### **A.6.1.2.2 Ultra Low-NO<sub>x</sub> Burner**

In the ultra low-NO<sub>x</sub> burners a high gas flow is achieved. The complete mixing of the fuel and the combustion air (and the flue gases) takes place in the furnace, which has the effect that there is no anchoring of the flame to the burner. As a result this type of burners can only be used at furnace temperatures beyond the spontaneous ignition temperature of the fuel/air mixture. NO<sub>x</sub> levels of 100 - 200 mg/Nm<sup>3</sup> can be achieved. The NO<sub>x</sub> levels are less dependent of the air preheat temperature. [HR]

##### **A.6.1.2.3 Water Injection**

The objective of diluent addition as a means of NO<sub>x</sub> control is to ensure that temperatures are reduced significantly in the pollutant forming regions so as to limit formation by the thermal mechanism. In principle, various species can be employed as diluents depending on their availability. In practice, water injection is the most viable diluent for reheating and heat treatment furnaces. The quality of water required for use on reheating furnaces is very much lower than that needed for NO<sub>x</sub> reduction on gas turbines. Steam or nitrogen may be available at some sites but these are likely to be more expensive than water in terms of additional capital costs and less effective in terms of the required diluent/fuel mass ratio.

The most effective method of water injection is usually one in which the water is mixed with the fuel immediately prior to combustion; this being more easily engineered and better able to achieve uniform flame temperatures than methods which seek to dilute the air supply.

A system which limits NO<sub>x</sub> formation by using water injection to limit peak flame temperatures in regenerative burners has been described by Wills and Volgt (1993). In this arrangement, water and air are supplied through the centre of the fuel gas inlet pipe, which is concentric with the hot combustion air supply from the regenerator. A 'two fluid' atomiser sprays fine water droplets into the gas before the end of the supply pipe, and shortly after the combustion of the gas/water mist/hot air mixture is initiated and then stabilised.

At least one burner manufacturer (Stordy Combustion Engineering, 1994) would offer water injection as a NO<sub>x</sub> control technique, and there may well be other suppliers.

Data on the performance of water injection systems on laboratory test rigs for natural gas and BFG/COG showed reductions up to 60 – 80 %.

In principle, diluent injection could be widely applicable as a retrofit method provided intimate mixing of diluent and either fuel or combustion air is possible. At present, information on the application of diluent injection seems confined to short duration experiments on test rigs.

It is possible that flame stability will be reduced, as will flame thrust. The increase in water vapour content of the combustion products could affect scaling of steel being heated.

There will be additional capital costs over and above those of the basic burner. These will certainly include pipework, pumps, injectors and a Water injection control system. Depending on the source of water, there may be a requirement for treatment plant and storage. For other diluents there will be similar requirements for pipework and controls.

#### **A.6.1.2.4 Shell de-NO<sub>x</sub> Process**

**Description:** SCR with catalyst operation at lower temperatures 120 °C [Com NL].

#### **A.6.1.2.5 Regenerative Active Coal Process**

No information submitted.

#### **A.6.1.2.6 Degussa H<sub>2</sub>O<sub>2</sub> Process**

No information submitted.

#### **A.6.1.2.7 Bio-de-NO<sub>x</sub> Process**

No information submitted.

### **A.6.1.3 Descaling**

#### **A.6.1.3.1 Rotor Descaling**

Instead of descaling headers (rings) equipped with nozzles, rotary heads equipped with 1 to 2 nozzles are used. Due to the rotation of the head, combined with the advance movement of the rolling stock, a good cleaning effect is achieved with low water volumes. However, this method is up to now more or less only as test installation available and not really proved in practical operation.

**Main achieved environmental benefits:**

- Reduced water consumption.
- Reduced energy consumption.

**Applicability:**

- Roughing, finishing and plate mills.
- New and existing hot rolling mills for flat products.

**Installations:**

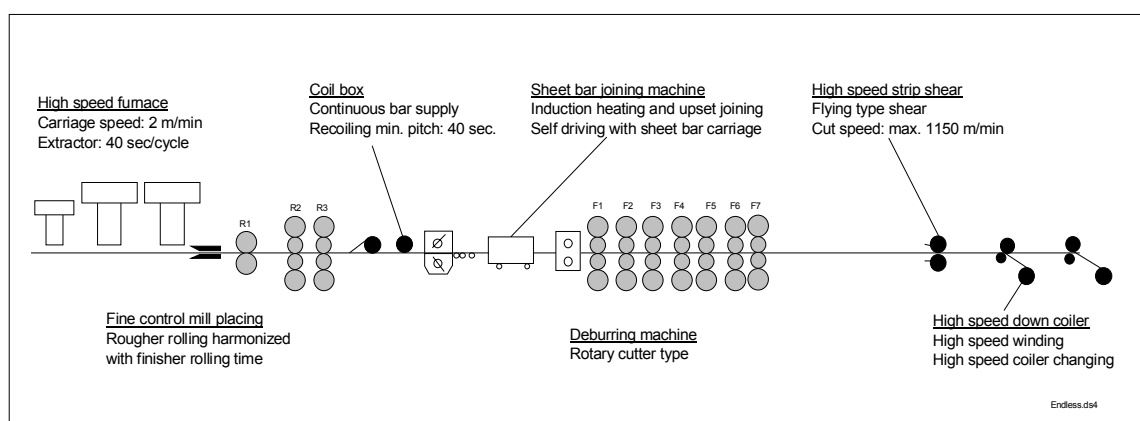
Boehler Edelstahl (97?)  
Huta Bailden, Polen (98?)

**A.6.1.4 Hot Rolling and Water Treatment****A.6.1.4.1 Endless Rolling**

The hot strip production of gauges  $\leq 1.0$  mm by means of the conventional rolling mill concepts will be difficult. The final rolling speeds which are necessary to ensure the desired final rolling temperature increases by the decrease of final strip thickness and that by a decrease of the allowable transport speed on the run out table.

One procedure to overcome these problems is the so called „endless rolling“ where the transfer bars are welded together before they enter the finishing train in order to form an endless strip and divided to desired specific coil weight after the finishing mill. [HR]

This process has been implemented in one plant in Japan. It has the potential to increase the overall productivity of the mill, to reduce yield losses and improve the steel quality leading to an overall reduction in specific energy use. The implementation of endless rolling requires particular care in order to join the bars properly in an economic manner. Also the control systems need to be adapted to new tasks, as mill idle times for pre-setting are no longer provided. Figure A.6-1 shows a diagrammatic view of the endless hot rolling process at Kawasaki Steel Chiba Works. [DFIU-99]



**Figure A.6-1: Diagrammatic view of the endless hot strip rolling process**

Reported benefits at the plant mentioned have been an increase in strip quality (slight thickness change over the entire length of strip, a slight width change over the entire length of strip:  $\pm 3 - 6$  mm, little coiling temperature fluctuation over the entire length of strip: deviation  $\pm 15 - 30$  °C), an increase in productivity (increase 20 %, decrease in unexpected roll change

time of 90 %) and an increase in yield (decrease in shape rejects from head and tail end of 80 % and decrease in surface defects due to pincher marks of 90 %).[DFIU-99]

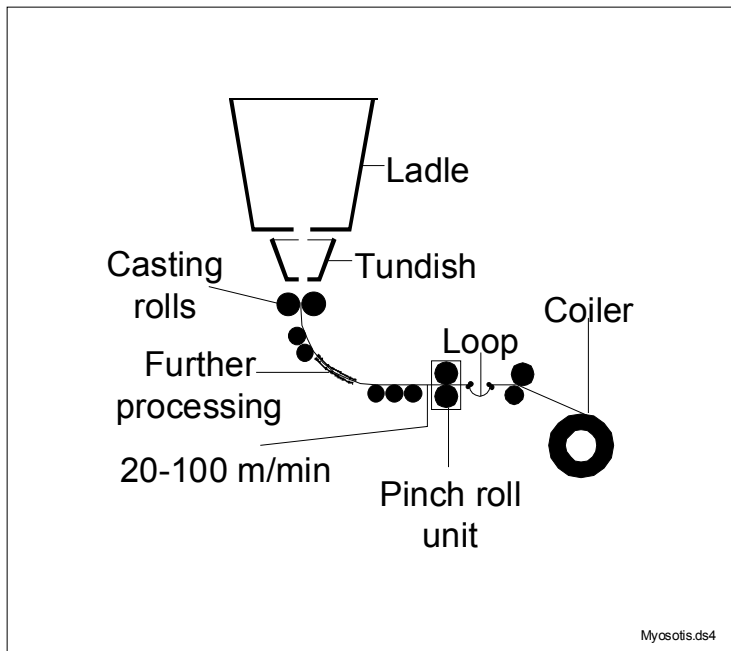
### A.6.1.4.2 Strip Casting Procedure

Over the last years several companies have been working on the development of technologies for strip casting. While thin slab casting and directly connected rolling technologies are basically an improvement of the conventional rolling technology, the direct strip casting is a new technology. By direct casting of strip, which can be subsequently cold rolled, the process chain from liquid steel to the final product can be shortened substantially. Table A.6-1 lists a comparison of characteristic parameters for the slab casting, thin slab casting and strip casting process.

Technology	Continuous casting	Thin slab casting	Strip casting
Product thickness	150 - 300mm	20 - 60mm	2 - 4mm
Solidification time	>600s	about 60s	<1s
Casting speed	1 - 2.5m/min	4 - 6m/min	30 - 90m/min
Average heat flux in the mould	1 - 3MW/m <sup>2</sup>	2 - 3MW/m <sup>2</sup>	8 - 10MW/m <sup>2</sup>
Metallurgical length	>10m	>5m	<0.5m
Melt weight in the caster	>5000kg	about 800kg	<400kg

**Table A.6-1: Comparison of selected parameters of different casting technologies [DFIU-99]**

A lot of research has been and is still being done in order to develop strip casting plants on an industrial scale. Figure A.6-2 and Figure A.6-3 show principles of two techniques (pilot plants), which have been developed by a co-operation of several firms.



**Figure A.6-2: Double-roller pilot plant [DFIU-99]**



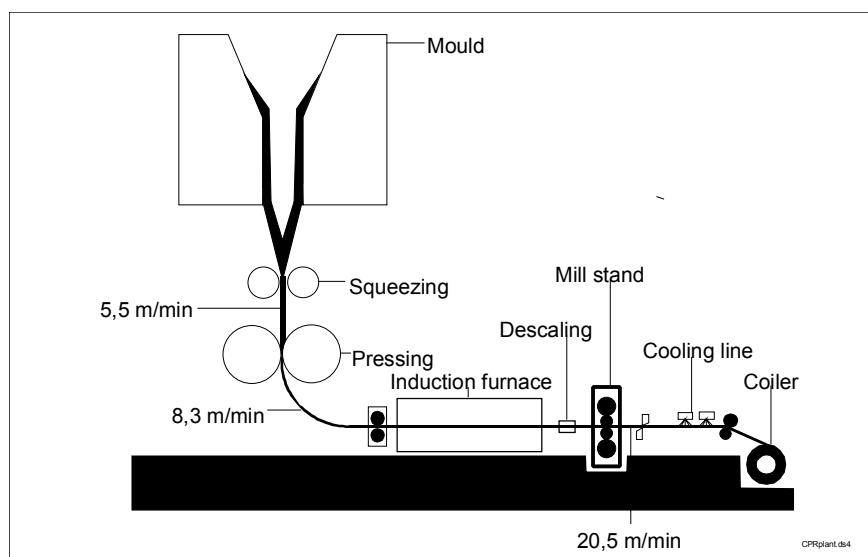


Figure A.6-3: Casting Pressing Rolling (CPR) pilot plant [DFIU-99]

	Typ <sup>1</sup>	Stand <sup>2</sup>	Thickness [mm]	Width [mm]	Year of Start	Remarks
<b>BHP</b> , Mulgrave, Aus	R/B	HM	1 - 2	160	1995	
<b>BHP, IHI</b> , Port Kembla, AUS	2-R	Pilot	2	1900		
<b>Voest Alpine</b> , Linz, A	1½-R	HM	1.15	330	1986	slanted & vertical
<b>CRNC-IMI</b> , Boucherville, CAN	2-2	HM	3	100	1990	horizontal feeding
<b>CRNC-Projet Bessemer</b> , Boucherville, CAN	2-R	HM	2-5	200	1992	vertical feeding
<b>Shanghai Metal Research Inst.</b> Shanghai, CHN	2-R	HM				
<b>Cleim</b> , Le Creusol, F	1½-R	HM	12	200	1968-1974	stopped
<b>IRSID</b> , Maizières, F	2-R	HM	2-5	200		
<b>IRSID</b> , Maizières, F	1-R	HM	0.2	200		
<b>Myosotis</b> , Isbergues, F			2.5			
<b>Myosotis</b> , Isbergues, F			2-6	865		
<b>ZFW</b> , Dresden, D	2-R	HM	0.15-2	30-110		stopped
<b>Thyssen</b> , Oberhausen, D	1-R	HM	0.10-0.30	270		
<b>RWTH/Thyssen</b> , Aachen, D	2-R	HM	0.3-2.5	150		
<b>Max Planck</b> , Düsseldorf, D	2-R	HM	13	110		
<b>Krupp Stahl</b> , Siegen, D	1½-R	HM				stopped
<b>Krupp Stahl</b> , Unna, D	1½-R	In-pilot	1.5-4.5	700-1050		stopped
<b>Clausthal Uni.</b> Clausthal, D	B	HM	5-10	150-300	1989-1995	
<b>CSM</b> , Rome, I	2-R	HM	3-25	150		
<b>CSM</b> , Terni, I	2-R	Pilot	2-5	400		
				750-800		

Table A.6-2: Development projects in strip casting [Jahrbuch Stahl 1996]

NSC/MHI, Kawasaki, JAP	2-R	HM	0.5-3	100		
NSC/MHI, Hikari, JAP	2-R	In-Pilot	1.5-6	1330		stopped
Kawasaki, Chiba, JAP	2-R	HM	0.2/0.8	250-500		
Kawasaki, Chiba, JAP	2-R	Pilot				stopped
Kobe, Kakogawa, JAP	2-R	HM	1-3	100		stopped
		HM	1.5/5	300		stopped
Nippon Metal, Sagamihara, JAP	1½-R		1-4	650		stopped
Nippon, Naoetsu, JAP	1-R	HM				
Stainless Nippon Yakin, Kawasaki, JAP	2-R	Pilot	1-2.5	600		
Nisshin + Hitachi, Yamaguchi, JAP	2-R	HM	0.8/5	300		
	2-R	HM	2.1	600		
Nisshin + Hitachi, Hitachi, JAP	2-R	HM	2.3	80		
Nisshin + Hitachi, Hitachi, JAP	2-R			200		
Pacific Metals, Hachinoe, JAP	2-R	Pilot	2-7	1050		
Pacific Metals, Hachinoe, JAP	2-R	HM				
Waseda Uni., Tokyo, JAP						
POSCO RIST Davy, Pohang, KOR	2-R	HM	2-6	350		
POSCO RIST, Davy, Pohang, KOR	2-R	Pilot	3	1050-1300	1994	
Inst. of Ind. Sc. & Techn. Pohang, KOR	2-R	HM	1-5	250-350		status unknown
VNIMETMACH, Moscow, RUS	2-R		0.1-0.35	150		
MEFOS, Lulea, S	6	Pilot	5-10	450	1991	
ASEA-Royal Institute, Stockholm, S	2-R	HM		(900)		
British Steel, Teesside, UK	2 R	HM	1-3	76	1986	
BS-Avesta, Sheffield, Teesside, UK	2 R	Pilot	2.3-5.5	400	1990	
British Steel, Teesside, UK	2 R	Indust. pilot	2-7	1550	under study	
Consortium <sup>3)</sup> , Bethelhem, USA	2-R	HM	0.5-2	300	1982	stopped
	1-R	HM	0.5-0.8	75	<1988	stopped
ARMCO-Westinghouse, Middletown, USA	1-R	HM	1.25-1.75	(25 µm)-1.75		stopped
National-Batelle, Columbus, USA	1-R	Pilot	1-3	660-1220		1220 mm not yet tried
Allegheny/VA, Breckenridge, Lockport, USA						

Table A.6-2 cont.: Development projects in strip casting  
[Jahrbuch Stahl 1996]

### A.6.1.4.3 By-product Recycling

#### Technologies for Recycling without Deoiling

##### Blast furnace injection

Process steps:

Sludge and scale dewatering (drying) at low temperatures, thus the hydrocarbons remain in the dried substance.

Adding of granulators to bring the mixture into a friable condition.

BF injection via special designed equipment. Oily sludges can also be injected in liquid form.

#### Deoiling Techniques

##### Thermocon process (Thermal physical Process for deoiling \*)

Oily sludges are batchwise (40 - 45 t/charge) processed.

The materials are charged into a special container and heated up to approx. 130 °C.

The actually chemical-physical effect utilized, is steam distillation.

Steam including water and hydrocarbons sucked from the container is heated up to approx. 500 °C and afterwards burned by approx. 1000 °C.

##### CED - process (Chemnitzer Entsorgungsdienst) (\*)

The process is based on the thermal deoiling principle.

Contrary to the thermocon method, CED is a continuous process.

The scale is transported through heated pipes by means of screws.

Moistness with oil is distilled and afterwards condensed.

##### DCR - process (Dispersion by Chemical Reaction) (\*)

Scale with liquid additive and the DCR reagent (e.g. quicklime) is homogenised within a mixing apparatus. The hydrocarbons are bounded by the generated  $\text{Ca}(\text{OH})_2$ . Pulverised oil is separated from the ferrous material via combined sieving and sorting device.

##### TRF process (Tubular-Rotor Filter) (\*)

Cleaning of the oily scale in a washing device by a water-tenside-emulsion.

The waste washing water is cleaned from tenside- / oilmixture by using the so called Tubular-Rotorfilter.

The fractionated oil is thermal utilized.

##### HD - process (High pressure method) (\*)

Scale is cleaned from oil by shooting a water scale mixture under high pressure (approx. 150 - 180 bar) and from a short distance (200 - 400 mm) onto a baffle plate.



## **A.6.2 Cold Rolling Mill**

### **A.6.2.1 Pickling**

#### **A.6.2.1.1 Hydro-abrasive Pre-descaling (Ishi Clean)**

Iron containing sludge is mixed with a circulating high pressure water jet and is sprayed onto the strip surface to remove the scale.

#### **A.6.2.1.2 Pre-descaling by Ferromagnetic Abrasive**

Splintered, ferromagnetic abrasive material is aligned by a magnetic field and is mechanically pressed onto the strip surface.

### **A.6.3 Wire Plant**

Acid regeneration process such as electrodialysis / bipolar membrane technology are under development or being tested. This technology which converts all acid again to free acid and metals to hydroxides is much too young / not proven / too expensive

From analogy with more traditional membrane processes, a short membrane life is expected.

## A.7 CONCLUDING REMARKS

The following conclusions and recommendations concern timing of the work, sources of information, availability and quality of data, consensus amongst experts of the TWG and recommendations for future work.

### Timing of work

The drawing up of this BREF took about 2 ½ years. The major steps have been:

- First TWG meeting (kick-off meeting) 11 – 12.12.97
- Submission of relevant information and data by TWG:
  - for Chapters 2 February – October '98
  - for Chapters 3 April – October '98
  - for Chapters 4 July – October '98
- First draft December 1998
- First consultation round 16.12.98 – 12.2.99
- Evaluation of comments and redrafting:
  - (*response to comments, clarification and request for additional information*) May – July '99
- Submission of missing information/data: September – November '99
- Second draft December 1999
- Second consultation 17.12.99 - 17.02.00
- Second TWG meeting 22 – 24.03.00
- Submissions on controversial issues that came up during the 2<sup>nd</sup> TWG meeting: 28.03.00 – 19.07.00
- Consultation on 'new' chapters (*revised Chapters 5, Chapter 7 Conclusions & Recommendations, Executive Summary, Chapter 4: SCR and SNCR*) 21.07.00 – 18.08.00
- Final draft

### Sources of information

65 reports dealing with the various aspects of the ferrous metals processing sector were submitted. These reports contain very different kinds of information (statistical data, description of production technologies, information on certain environmental measures including case studies and emission/consumption data). They have been prepared from different points of view; most of them only focusing on single aspects or media, only very few covering all environmental aspects.

During the period of work on the Ferrous Metals Processing BREF, industry shadow groups on hot rolling, cold rolling and continuous coating and the European General Galvanizers Association (EGGA) provided reports and papers on their sectors regarding the applied production techniques and some environmental measures. Germany submitted a report on 'BAT in the German Ferrous Metals Processing Industry'.

The availability of such documents is essential for the quality of the document, but their usefulness is potentially compromised if they are not sent in early in the process. Delays in submitting crucial information, especially on the techniques to be considered in the determination of BAT, have led to delays in issuing drafts of this BREF.

### Best available techniques

BAT have been identified for all three sub-sectors of ferrous metals processing and for the individual production steps. They are described in detail in the three Chapters 5 providing background and, where necessary, justification for selection as BAT and for the reported BAT-associated emission levels. The executive summary includes all these BAT conclusions.

### **Level of consensus**

Part A of this BREF contains several split views. There were three areas in which the TWG could not reach an agreement:

- BAT-associated dust levels for application of fabric filters/electrostatic precipitators
- SCR and SNCR NO<sub>x</sub> reduction measures for reheating furnaces
- S-content in fuel oil

On dust emissions, the TWG agreed that capturing and fabric filters are BAT, but there were two general points of view on what is achievable with fabric filters. Industry proposed, based on their experience and knowledge of achieved dust levels, the higher level of 20 mg/Nm<sup>3</sup>. Some Member States and environmental NGOs considered below 5 mg/Nm<sup>3</sup> to be the appropriate associated level for fabric filters, but there were only very few figures and for most applications no data presented to support this view (see also recommendations for future work).

Information and data on SCR and SNCR in reheating furnaces was received at a very late stage of the work; during and after the second TWG meeting. Some TWG members considered these techniques to be BAT, while others thought the available information on technical details and on economics was not sufficient to allow a final decision to be made on whether or not SCR and SNCR are BAT. As this controversy was raised almost at the end of this exercise, there was no time to resolve the outstanding issues (see also recommendations for future work).

Another point of dissent was the issue of limiting S-content in fuel oil. Although a level of S < 1% can lead to emissions as high as 1700 mg SO<sub>2</sub> /Nm<sup>3</sup>, some TWG members thought that this should be BAT. Others regarded a lower S-limit in the fuel oil or additional SO<sub>2</sub> reduction measures as BAT.

Parts B and C of this BREF enjoy a high level of consensus. No split views had to be noted. All parties in the information exchange process consider them an acceptable result.

### **Recommendations for future work**

A lack of data and information on the performance of techniques to be considered in the determination of BAT, especially on achieved emission and consumption levels and on economics, was noted as a flaw of this BREF document. For future BREF reviews, all TWG members and interested parties should continue to collect these data and information and should make them available earlier rather than later in the process.

For quite a number of the techniques to be considered in the determination of BAT, no information or only a technical description is available. Information on reference plants and actual performance data are scarce. For the revision of this document the missing information should be provided. Some of the techniques concerned are the following:

Part A:

- Optimized water pumps for laminar flows
- Implementation of degreasing bath cascades
- Hot water pre-degreasing
- Heat utilisation for heating degreasing bath
- Electrostatic oiling
- Optimization of oil spray
- Optimized finishing operation
- Cleaning and reuse of grinding emulsion
- Exhaust system (PRETEX/SBT)
- External use of spent acid pickle liquor



## Part C:

- Storage and handling of raw materials and auxiliaries
- Capture/treatment of emissions from tube finishing operations

## Part D:

- Implementation of degreasing bath cascades
- Hot water pre-degreasing
- Adsorption of surfactants and oil (precipitation followed by filtration)
- Electrolytic pickling
- Treatment of rinsing water using ion exchange, electrolytic iron removal, reverse osmosis, oxidizing iron removal

Several techniques are presented in the Chapters 6 ‘Emerging Techniques’. The progress in development and the suitability for application in the FMP sector should be checked for a potential move of these techniques to Chapter 4 ‘Techniques to be considered in the determination of BAT’ and/or to Chapter 5 ‘Best Available Techniques’.

The criticism was made that the presentation of some techniques was too positive, having been derived mainly from suppliers’ information, and that only the advantages were presented. This mainly concerns reclamation and regeneration processes for spent treatment baths, e.g. for spent pickling liquors or spent degreasing or flux baths. Here industry is requested to provide the information and results they have achieved with certain techniques, together with descriptions of any problems they have experienced.

There is a need for more emission and consumption data generally, but of particular interest are figures on NO<sub>x</sub> emissions (concentrations and specific emissions) both for furnaces that use air preheating and those that do not. Such data would make possible both a more thorough evaluation of the efficiency of reduction measures and a comparison of the advantages and disadvantages of energy savings vs. NO<sub>x</sub> emissions.

More data are required on achieved dust emission levels for the various production steps of hot and cold rolling (Part A), where a split view on the BAT-associated dust level had to be stated in the BREF. Especially, those parties advocating the lower level of 5 mg/Nm<sup>3</sup> should seek to provide data to substantiate their view.

It was reported that the number of installations applying SCR (pusher type furnaces) is likely to increase. When this BREF is reviewed, there should be more information available on the performance and applicability of SCR and SNCR for reheating furnaces. Existing SCR and SNCR installations will have a longer operating history to draw on, which should help to answer the criticism that the information available was based on too short an operating period. Possibly the disagreement on whether these techniques constitute BAT can be resolved then.

During the 2<sup>nd</sup> TWG meeting the point was raised that inductive heating was BAT for several applications in furnaces. In this BREF, inductive heating is included as a technique to be considered, but it was stated that the information available was not sufficient to decide whether the technique is BAT. More information and data should be collected to enable this decision to be made.

Another issue raised was the dioxin content of dust from batch galvanizing and potential risks of dioxin build-up when these dusts are recycled. Efforts should continue to compile information and data of actual dioxin contents in dusts for normal plant operation. Available data should be provided to the IPPCB and the TWG to allow a judgement on this problem and enable an evaluation of the potential risk.

A revision of this BREF document is recommended for the year 2005.



## **PART B**

# **Continuous Hot Dip Coating Lines**



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## **Best Available Technique Reference Document on Ferrous Metals Processing**

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## B.1 GENERAL INFORMATION ON CONTINUOUS HOT DIP COATING LINES

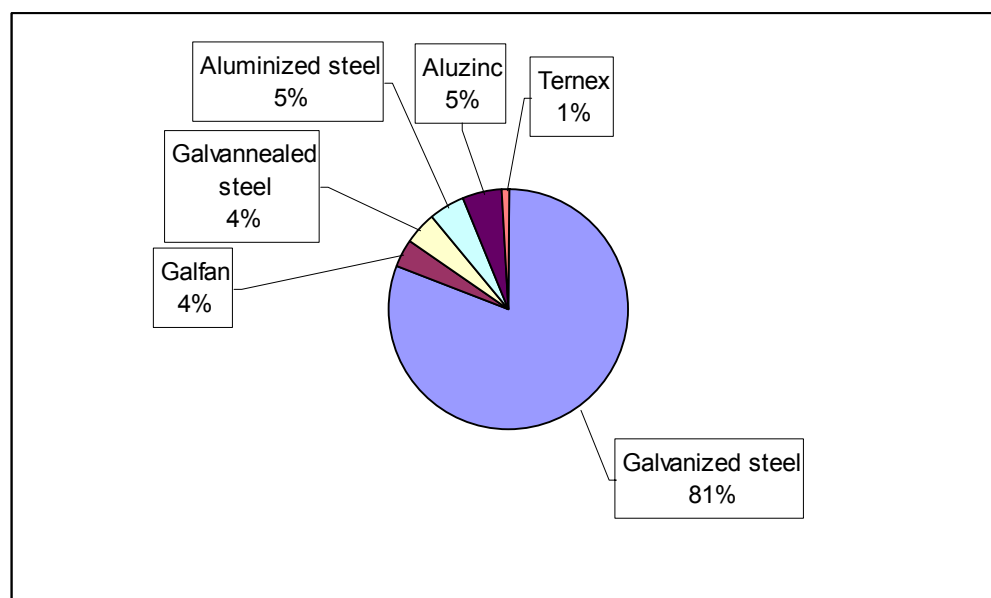
The production of continuous hot dip coating lines in EU 15 was 15 Mt in 1997. The number of continuous plants in EU Member States - operating, under construction and planned - is shown in Table B.1-1.

	Number of Continuous Coating Lines
<b>Austria</b>	4
<b>Belgium</b>	6
<b>Denmark</b>	-
<b>Finland</b>	2 (+ 1 under construction)
<b>France</b>	14
<b>Germany</b>	10
<b>Greece</b>	1
<b>Ireland</b>	-
<b>Italy</b>	8
<b>Luxembourg</b>	3
<b>Netherlands</b>	1 (+1 projected)
<b>Portugal</b>	1
<b>Sweden</b>	2
<b>Spain</b>	4 (2 under construction)
<b>United Kingdom</b>	7
<b>Total</b>	<b>63</b>

Note: Source of data [EUROFER CC]

**Table B.1-1: Number of continuous coating lines in EU 15**

The vast majority of coatings applied, as shown in Figure B.1-1, was zinc. Aluminium coatings and, especially terne coatings, played only a minor role.



Note: Source of data [EUROFER CC]

**Figure B.1-1: Production share for different hot dip coatings**

The hot dip galvanizing production for western European companies in 1997 is shown in Table B.1-2.

<b>Company</b>	<b>Production [1000 t]</b>
<b>Usinor</b>	2124.7
<b>Cockerill Sambre</b>	1917.1
<b>Thyssen</b>	1661.2
<b>British Steel S.P.</b>	1568.0
<b>Krupp-Hoesch</b>	1310.0
<b>Riva</b>	1024.0
<b>Aceralia</b>	722.5
<b>Arbed</b>	680.8
<b>Hoogovens Ijmuiden</b>	375.0
<b>Lucchini</b>	600.0
<b>Rautaruukki</b>	572.5
<b>Voest-Alpine</b>	520.0
<b>Preussag</b>	520.0
<b>SSAB</b>	505.0
<b>Others</b>	595.5
<b>TOTAL</b>	<b>14696.3</b>
Note: Source of data [EUROFER CC]	

**Table B.1-2: Hot-dip galvanizing companies and their production**

Table B.1-3 shows the shares of galvanised products consuming industries in EU.

<b>Sector</b>	<b>Consumption [1000 t]</b>
<b>Transport</b>	2570
<b>Construction</b>	4759
<b>White Lines</b>	364
<b>Others</b>	4547
<b>Total</b>	12231
Note: Source of data [EUROFER CC]	

**Table B.1-3: Main consuming industries for galvanized products**

## B.2 APPLIED PROCESSES AND TECHNIQUES IN CONTINUOUS HOT DIP COATING LINES

### B.2.1 Continuous Hot Dip Coating Process Overview

In the hot dip coating process, the steel is continuously passed through molten metal. An alloying reaction between the two metals takes place, leading to a good bond between coating and substrate.

Metals suitable for the use in hot dip coating are those, which have a melting point low enough to avoid any thermal changes in the steel product, like for example aluminium, lead, tin, and zinc.

The principal hot dip coatings for steel sheet are shown in Table B.2-1. Wire is hot dip coated with zinc (galvanized) or tin. Zinc coating is mainly applied as corrosion protection. Tin gives the wire a shine appearance and also provides a solder adhesive layer.

Coating Base	Bath	Coating	
		Type	Name
Zinc base	Zn	Zn	Galvanised
	Zn	Zn-Fe	Galvannealed
	Zn	Lead free	
	Zn-Al	99 %Zn, 1 %Al	Crackfree
	Zn-Al	95 %Zn, 5 %Al	Galfan
Aluminium Base	Al-Zn	55 %Al, 43.5 %Zn, 1.5 % Si	Galvalume
	Al	Al	Type I
	Al-Si	Al 87 %, Si 13 %	Type II
Lead base	Pb-Sn	8.25 % Sn	Terne
		75 - 92 % Pb	

Note: Source of data [EUROFER CC], [Com-CC-2]

**Table B.2-1: Main hot dip coatings for steel sheet**

In general **continuous coating lines for sheet** comprise the following steps:

- Surface cleaning by means of chemical and/or thermal treatment.
- Heat treatment.
- Immersion in a bath of molten metal.
- Finishing treatment.

**Continuous wire galvanizing plants** involve the following steps:

- Pickling.
- Fluxing.
- Galvanizing.
- Finishing.

## B.2.2 Galvanizing of Sheet (Zinc and Zinc Alloy Coating)

In continuous hot dip galvanizing steel strip is coated with a zinc or zinc alloy layer as corrosion protection. Figure B.2-2 shows the layout of a continuous galvanizing line (without pickling). Plant layouts may vary in the design of the entry section (with/without pickling or alkaline degreasing), in the design of the annealing furnaces (vertical or horizontal) or the post-dipping treatment (galvannealing etc.)

Hot dip galvanizing of cold rolled strip is more common than galvanizing hot rolled strip. The processing is similar, except that for hot rolled products additional descaling (pickling) is necessary.

### B.2.2.1 Pickling

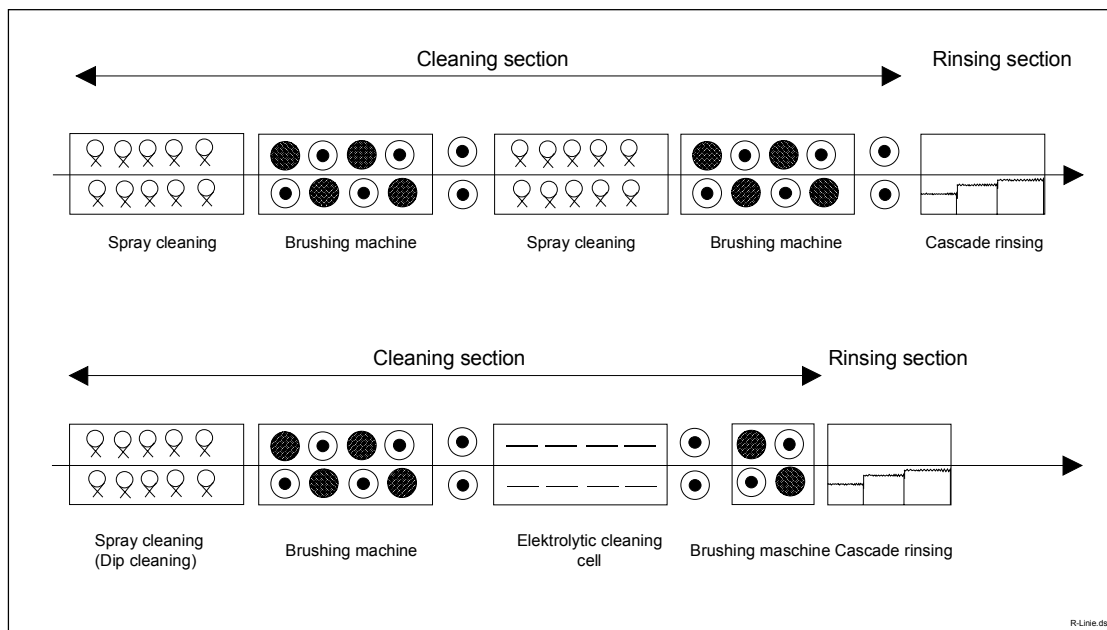
Pickling operation for descaling is only necessary for galvanizing hot rolled products to remove hot mill scale. Pickling of unannealed cold rolled coil is done for activation. Both processes are done in hydrochloric acid, followed by rinsing. The technology is the same as the pickling process described in the cold rolling section of this BREF.

### B.2.2.2 Degreasing

It is essential that the surface of the steel coil is free of impurities such as grease, oil or abraded iron fines to ensure the entire surface is exposed to the coating product and strong adherence is achieved. Although degreasing is not necessary when the strip is subsequently heat treated, it is often applied in any case. The cleaning process involves several or all of the following steps:

- Alkaline degreasing via immersion or by spraying; maybe coupled with brushing.
- Alkaline degreasing by an electrolytic system; maybe coupled with brushing.
- Rinsing with water with intermediate brushing between rinsing tanks.
- Drying.

Figure B.2-1 show two possible layouts for modern degreasing lines.



**Figure B.2-1: Degreasing line layouts**  
[DFIU]

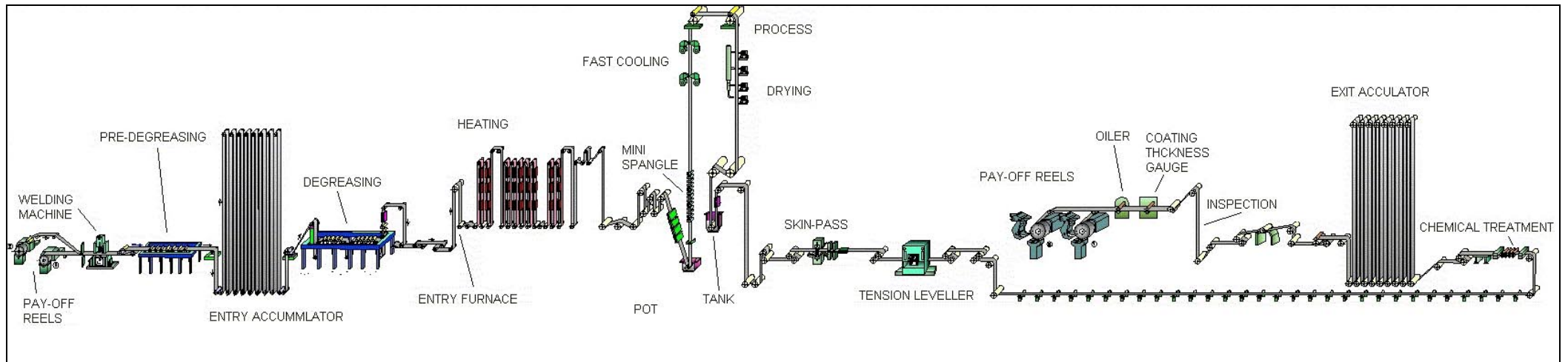


Figure B.2-2: Typical layout for a hot dip zinc coating line  
[Com-CC-2]

The degreasing agent is usually a non-siliceous alkaline solution with a concentration of 25 g/l and a temperature between 70 and 95 °C. Aqueous systems are now standard and solvent degreasing is obsolete. [ERM95], [Com-CC-2]

The same aqueous solution containing mainly sodium hydroxides, orthophosphates and surfactant compounds is used in spray degreasing and in electrolytic degreasing. Once the solution in the electrolytic degreasing section has reached a certain oil level, it is re-used on the spraying section (cascade use). It is also possible that the solution is treated in an emulsion separation centre and then biological treated [Com-CC-2] When the solution has reached the maximum oil content it is regenerated, usually off-site. [EUROFER CC]

Fumes generated in degreasing and brushing are collected and scrubbed prior to release, using water or caustic soda solution and/or led through a demister for cleaning. [Com-CC-2] Spent degreasing agent and waste water from the rinsing and brushing operations are sent to waste water treatment before release. [EUROFER CC]

### **B.2.2.3 Heat Treatment**

Hot and cold rolled steel coil are passed through a furnace with controlled atmosphere prior to galvanization to degrease and dry the surface, to improve the adhesive properties of the surface, to obtain the required mechanical properties of the steel and to allow the steel to reach the required temperature before dipping. The following types of furnaces are used:

#### **Sendzimir Furnace**

This type of furnace is no longer used in modern coating lines, but some older plants might still operate this horizontal continuous furnace, which comprises a directly heated preheating furnace (oxidizing zone) and indirectly heated reduction and holding zones with reducing H<sub>2</sub>/N<sub>2</sub> atmospheres, followed by cooling zones. In the preheating part of the furnace, the temperature is 450 - 550 °C. The strip is cleaned by burning off the oil the oil emulsion residues. In the reduction zone, at a temperature of 980 °C and in an inert atmosphere the oxides are reduced. The holding zone allows for recrystallisation and normalisation. The strip is then cooled to a temperature slightly above that of the molten metal (ca. 500 °C) and is fed into the zinc bath, under protective gas, by means of a so-called snout.

#### **Direct Flame Furnace (D.F.F)**

The direct flame furnace (Non Oxidizing Type) can be divided into different sections:

- A warming-up section where the strip is preheated using the gas flow coming from the furnace, temperature raises from 20 °C to approximately 250 °C).
- The furnace itself, where the coil is heated directly by means of a naked flame, reaching a temperature between 560°- 750 °C.
- The annealing zone where electric or radiant elements heat the strip up to 830 °C and maintain this temperature under reducing atmosphere (HNx atmosphere, 3 –20 % hydrogen).
- Two cooling areas, with different cooling rates, where the temperature of the steel is reduced by jet cooling down to 450°- 480 °C.
- The exit area where the steel goes towards the galvanising bath.

This type of furnace cleans the coil surface and does not require any prior degreasing of the metal, but air emissions are generated as the remaining oil from the surface is burnt. Furthermore combustion products, H<sub>2</sub> and N<sub>2</sub> arise from the furnace (fired by natural gas or desulphurised coke gas). [EUROFER CC], [Com-CC-2]

### **Radiant Tube Furnace (R.T.F.)**

The radiant tube furnace is a variation with indirect heating. The combustion gases circulate through radiant tubes and do not get in contact with the strip. The soaking zone can be fitted with radiant tubes or electric heating. Alkaline degreasing and radiant tubes or electric heating are required for very high quality standards and for improving the adherence of the following metallic coating. The fast cooling areas are similar to those of a D.F.F. The annealing furnace is combined with an alkaline degreasing equipment. [EUROFER CC], [Com-CC-2], [Com2 CC]

Fuels used are desulphured coke oven gas and natural gas. Energy conservation is a primary consideration in modern furnace designs. Recuperative features, such as infrared waste gas preheaters, preheating of combustion air in direct fired and radiant tube furnace burners, preheating of furnace atmosphere gas and installation of waste heat boilers are generally incorporated when feasible.

### **B.2.2.4 Hot Dipping (Galvanizing)**

The galvanizing bath consists of one or more tanks, usually made of ceramic material. These pots, which can be either fixed or mobile, contain the molten metal at a temperature of 440° - 490 °C, through which the strip is passed. The bath contains zinc and any other required additive (i.e. antimony, lead or aluminium). The bath contains a sufficient amount of molten zinc in order to prevent the wide fluctuations in the operating temperature that may appear under maximum operating conditions. Most pots are nowadays heated by electrical induction systems. However, natural gas as fuel for heating the pots is an alternative when considering the environment as a whole and taking environmental aspects of power generation into account. [EUROFER CC], [Com-CC-2]

As the steel passes through the molten zinc bath the surface is coated, to some extent with layers of different iron-zinc alloys, but due to the high speed of the steel strip (max. 180 m/min) and the short exposure time, the coating mainly consist of zinc.

Temperature control of the bath is essential, as a high temperature will increase the rate of oxidation at the surface of the molten bath, resulting in increased ash generation. A low bath temperature will increase the viscosity of the molten coating metal, thus inhibiting the formation of a thin coating layer. The bath temperature is therefore optimized to meet the individual quality requirements of the final coated product.

The strip leaves the bath with some amount of liquid zinc on the surface. In order to achieve the exact thickness of coating required, the strip passes through a series of jets placed above the surface of the bath. By blowing air or nitrogen the excess of zinc is removed from the steel. The system is usually controlled by an automatic gauge, which measures the thickness of the coating using X-ray measurement technology or a similar technique.

Special galvanising processes to produce one-sided coatings are also applied. Examples are the Monogal process in which the zinc coating after normal galvanising is brushed off by rotating metal brushes and processes in which the zinc is applied by carrier rolls.

On leaving the bath, the strip is gradually cooled by air coolers, followed by a water quench tank and a drier.

### B.2.2.5 Galvannealing

Galvannealing is a special post-treatment applied in some installations in which the strip, after galvanizing, is heated to a temperature that allows the formation of a zinc-iron alloy (10 % iron). Galvannealing yields in a particularly smooth appearance of the product.

Galvannealing is the alloying of the zinc layer by the diffusion of iron (Fe) from the steel substrate. The Fe diffusion is obtained by maintaining the steel at a temperature of about 500 °C, for low carbon steel, to a temperature of about 540°C, for new generation High Strength Steel, during a sufficient time. Such furnaces are divided in two zones: a heating zone and a soaking zone. The available space for the furnace is limited. For a same available surface, a very quick heating from the zinc bath temperature (460°C) to the soaking temperature allows to apply a longer soaking time. Some furnaces are equipped with induction heating system in the heating zone and electrical elements or radiant tubes in the soaking zone. Induction heating technique is characterised by a short heating time, a short reaction time, and an accurate regulation of the temperature and no emissions on the site. The alloying and surface qualities are improved.

Other galvannealing furnaces are equipped in the heating zone and in the soaking zone with radiant tubes characterised by a longer heating time. In that case the site emissions and the energy consumption are improved by the use of low-NOx burners and regenerative or recuperative burner systems. [Com2 CC]

Figure B.2-3 shows the schematic of view of the coating section and the galvannealing furnace.

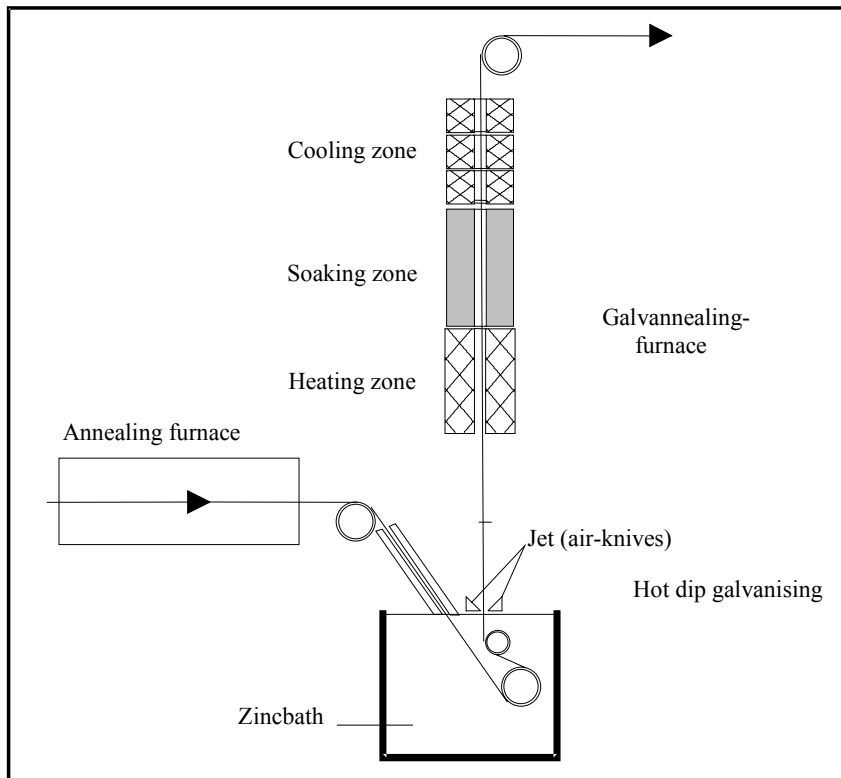


Figure B.2-3: Schematic Coating Section of a Galvannealing Line [DFIU 99]



### B.2.2.6 Post Treatments

Following the coating, the steel strips are usually subjected to post-treatment in order to prevent surface damages and flaws, like white rust caused by water condensation in case of insufficient air access. Voluminous corrosion products as zinc hydroxides (white rust) affect further processing, such as e.g. painting. The formation of condensate during transportation and storage is to be generally prevented. [Com-CC-2]

The resistance against white rust is considerably increased by the application of post treatment, like oiling, passivation, phosphating, organic coating or a combination of such treatment. In addition, the processing properties are significantly improved depending on application (e.g. oiling: deformation aid, phosphating: direct painting ensured, in combination with oiling: deformation aid). [Com-CC-2]

#### Oiling

To apply a wet film of oil on the surface of the strip dip spray, wingrolls or electrostatic oiling machines are used. The oiling coat is between 0.25 - 3 g/m<sup>2</sup>/side [Com-CC-2]

#### Passivation

Passivation is a treatment with solvents containing chromic acids, applied by spraying or applicator-rolls. For hot dip metal-coated strip, a coat of 10 - 35 mg/m<sup>2</sup> per side is applied. Coat thickness is therefore extremely thin (few nanometer only). During passivation, Cr<sup>6+</sup> is mainly converted to Cr<sup>3+</sup>. Almost all of the installations have a little heater after the treatment to make sure that the temperature rise over 120 °C which is necessary for a chemical reaction of excess Cr<sup>6+</sup> with the additives of the passivating solution and become into Cr<sup>3+</sup>. The strip is treated with solutions between 0.5 – 2 % of Cr<sup>6+</sup> and temperatures between 70-120 °C. [Com-CC-2], [Com2 D]

#### Phosphating

In phosphating a phosphate coat of approx. 1 - 1.8 g/m<sup>2</sup> is applied. The phosphating procedure is more or less a precipitation reaction of zinc phosphate crystals at the surface of the metal coat caused by an increase in pH-value at the metal surface due to a pickling reaction. Tri-cation phosphation process could be used (the hopeite crystal Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> · 4 H<sub>2</sub>O incorporates approx. 1 % Ni and 5 % Mn). Thus, this process forms the same chemical structure of the phosphate coat as the high-quality phosphating processes for cars and household appliances do. [Com-CC-2]

### B.2.2.7 Finishing

To give the steel a special surface appearance, smoothness etc. as required by the customers or to meet width tolerances, the following operations may be applied:

#### Mini or No Spangle Treatment

If the cooling rate of the top layer of pure zinc is sufficiently low, large crystals will form resulting in a 'spangled' appearance. Sometimes smaller zinc spangles or even no-spangle effect is requested. In that case the strip is either cooled more rapidly or the number of points of spangling are increased by steam spraying, steam spraying with a chemical additive (usually phosphate based) or spraying with zinc powder. [ERM95]

#### Mat Mill

The strip is skin-passed to obtain a mat finish surface.

Skin pass treatment can be done in three different ways: dry, wet (only water) or wet (with water and detergent). The 'temper mill' solution generated in the later process must be collected and sent to a waste water treatment plant when it is spent.

### **Edge cutting**

For certain applications, an edge cutting must be done in order to obtain the width tolerance needed and to avoid little dog bone defects. There are two places to realise this process:

In the pickling line before cold rolling.

In the hot dip coating process.

A perfect product schedule tries to reduce this process to the minimum to increase the line yield. [Com-CC-2]

### **B.2.2.8 Cooling Water Circuits**

In coating plants, cooling water is required to discharge excessive heat from furnaces. Part of the heat energy is emitted directly to the air (with the waste gases), via the coated strip or the shop air. The rest is transferred to the cooling water. The main cooling water consumers are the furnace (roll bearings) and final cooling of the strip.

A coating plant is supplied with cooling water re-circulated from central cooling water systems. In these systems, pumps convey the cooling water to the consumers; the heated water is returned and re-cooled again in plate heat exchangers with industrial water (e.g. from the river).

Due to the insertion of the closed re-cooling water circuits, the industrial water, even in case of leakage of a cooler, does not get into touch with the equipment of the consumers; so that, penetration of chemicals or oil into the industrial water and pollution of the sewage system is prevented.

There are several variants of re-cooling, two of them are:

- re-cooling with industrial water in heat exchangers and
- re-cooling by evaporation in cooling towers.

Compared to re-cooling in towers, re-cooling in plate exchangers offers the advantage that considerable amounts of chemicals for cooling water treatment (such as corrosion inhibitors, hardness stabilisers, dispersants and biocides) can be saved, and are not discharged into the sewage system. Another advantageous feature is that it is not necessary to do discharges of partial flow with a high salt content caused by the evaporation, as it happened in the case of cooling towers. [EUROFER CC]

#### **Typical configuration of a cooling loop with cooling towers**

The little discharge that is necessary for keeping low salt concentration of water to the sewer system is mostly made continuously. Algicide (for avoiding the saturation of the contact zone between the water and the air) is dosed. The frequency is variable depending on the weather (between 1 and 3 times per week).

Other chemicals could be necessities depending on the composition of the water used in the circuit (hardness, etc).

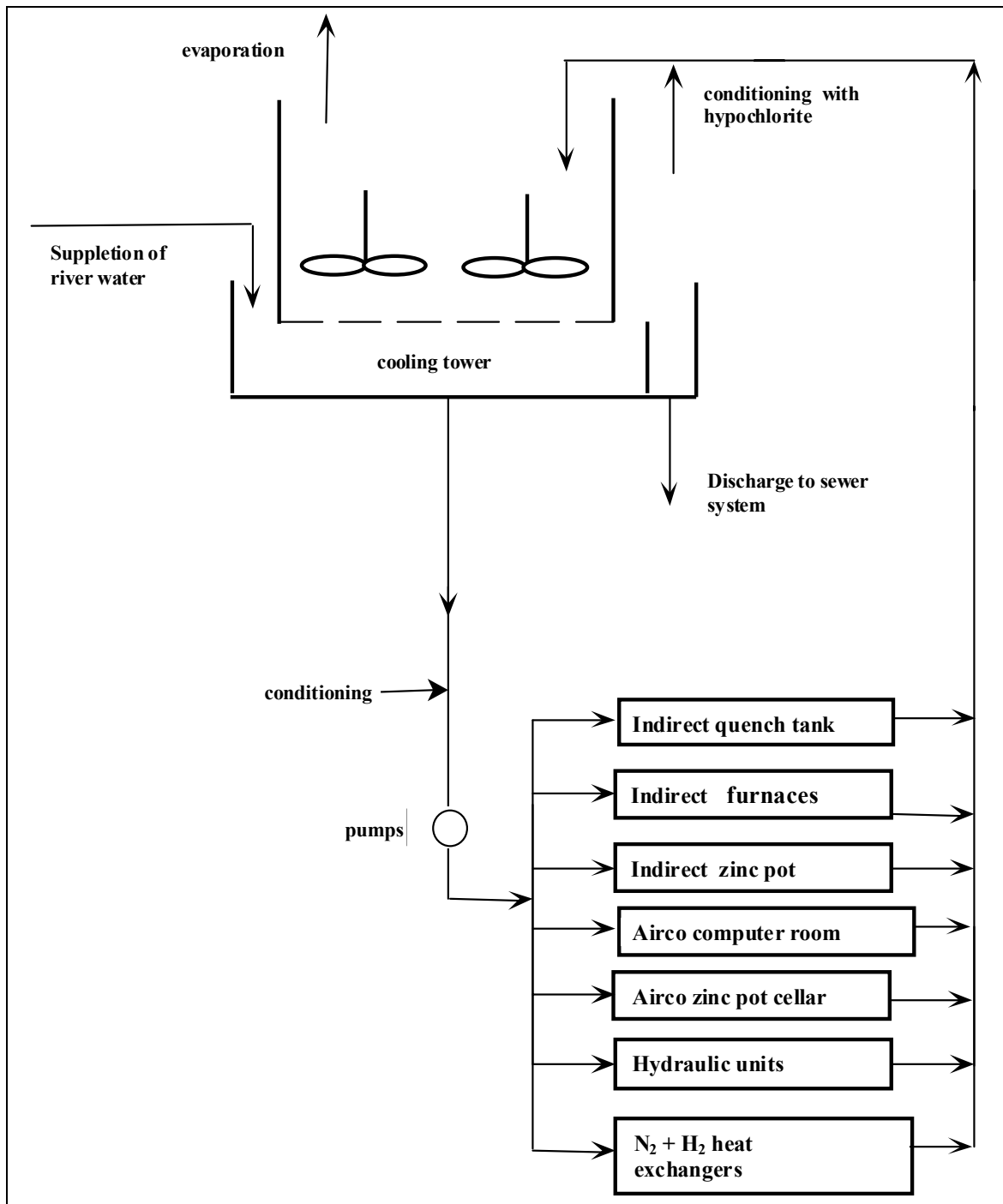
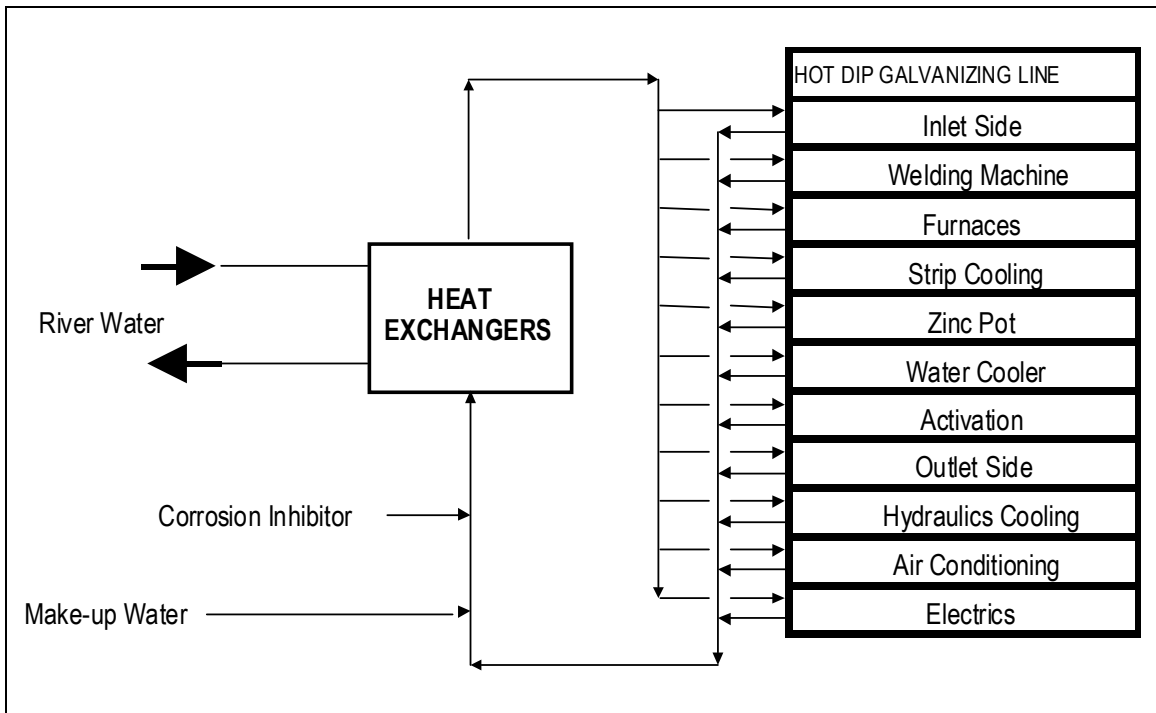


Figure B.2-4: Typical configuration of a cooling loop with cooling towers  
[CC 11/99]

**Configuration for recycling water using plate heat exchanger:**

Cooling water is recirculated in several closed cooling systems and heated by the heat expelled from the process (machine cooling, gas cooling, etc.). The cooling water is recooled by river water in heat exchangers. The river water on the secondary side of the heat exchanger is never in contact with the strip or harmful media and is therefore not contaminated. The water becomes only heat loaded and can be drained back to the river. The main cooling water consumers are the preheating and annealing furnaces, the zinc pots, several roll coolings, the immersed water coolers, the activation section, the electrical equipment, the hydraulics and air conditioning. All heat which is not removed by the cooling water has to be discharged either by waste gas or to the ambient air.

With this system, addition of algaecide and scale-preventer is avoided. The outlet water is only thermal loaded. This could be advantageous if the water of the system has no contact with pollution. There are discharges in case of system drain only.



**Figure B.2-5: Cooling water system with heat exchangers**  
[CC 11/99]

### B.2.2.9 Water Circuits/Water Management

Process water is water which is used for make-up of chemical solutions or which is in direct contact with the strip (e.g. water for direct strip cooling). It may be contaminated by the process and has then to be treated as waste water. The following process water streams are used at galvanizing lines and are finally discharged as waste water:

- Make-up water (usually deionized water) for concentrate preparation of the chemical strip treatment sections (pre-treatment, electrolytic treatment, post treatment). The different concentrates are sprayed onto strip or the strip is running through the concentrate bath. The concentrates are usually recirculated by pumps. They are clarified or filtered in recycling plants during recirculation. Only a small flow is discharged as high concentrated waste water to the water treatment plant.
- Rinsing water (usually deionized water) for chemical treatment sections (pretreatment, electrolytic treatment, post treatment). The rinsing water is used for removing of remaining concentrate from the strip. The water sprayed onto strip in a cascade of rinsing sections, with the water flowing countercurrently to the strip. It is finally discharged as low concentrated waste water to the water treatment plant.
- Make-up water for the water cooler. In the water cooler the strip is cooled first by recirculated spray water and finally by running through a water bath with an immersed turn back roll. The water will be contaminated by abrasion dust and has to be discharged from time to time to the skin pass mill water treatment plant.
- Spray water for the skin pass mill. The water is used for keeping the working rolls clean. It is sprayed onto the rolls and contaminated by Zn-containing abrasion dust and lubricating oil and is discharged to the skin pass mill water treatment plant.

### B.2.3 Aluminizing of Sheet

Most aluminium coated steel coil is produced by some variation on the hot dip galvanizing process. Figure B.2-6 shows the schematic line of production for applying aluminium coatings. The production line usually includes a passivation section, which is either in-line or is off line in a separate process unit.

Due to affinity of aluminium for oxygen it is extremely important to ensure against the formation of an oxide layer which would prevent diffusion of the aluminium into the steel substrate. The steel is sometimes spray or chloride gas pickled prior to annealing [ERM95]. The formation of an oxide layer can then be prevented by using a number of methods, like:

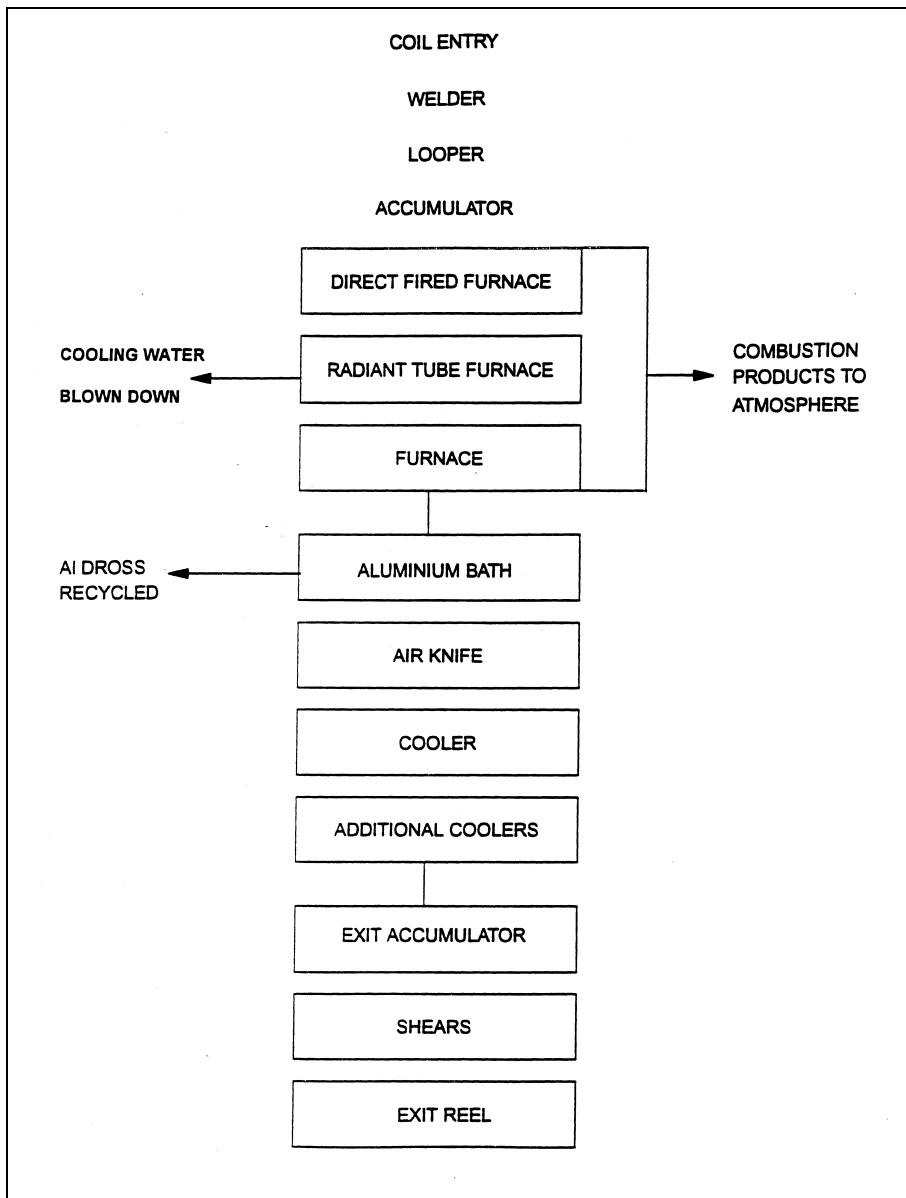
- Passing the washed and pickled steel through a furnace with a hydrogen atmosphere to eliminate oxygen (the absorbed hydrogen further protects the substrate as it passes into the molten aluminium bath).
- Dipping the pickled steel in a molten aluminium bath that is kept saturated with hydrogen injected by submerged jets.

The aluminium bath is generally maintained at temperatures of about 690 °C. The coated coil can then be further heat treated at 820 - 930 °C, which converts the aluminium coating completely to steel-aluminium alloy if required. [ERM95]

Following the coating the strips may be subjected to post-treatment in order to prevent surface damages and flaws, as white rust caused by condensation in case of insufficient air access.

**Passivation:** spray treatment with solvents containing chromic acids. For hot dip metal-coated strip, a coat of 10 - 35 mg/m<sup>2</sup> per side is applied. Coat thickness is therefore extremely thin (few nanometer only). During passivation Cr<sup>6+</sup> is partly converted to Cr<sup>3+</sup>. The strip is treated with solutions between 0.5 – 2 % of Cr<sup>6+</sup> and temperatures between 50 -120 °C.

**Anti-finger print:** wringer rolls treatment of a polymer base coating on the strip surface. A coat weight (after drying) of < 1.5 g / m<sup>2</sup> per side is applied.



**Figure B.2-6: Aluminium coating process**  
[EUROFER CC]

## B.2.4 Lead-Tin Coating of Sheet

Pure lead is never used as coating material for steel due to the fact that it is not possible to produce a lead-steel alloy and obtain an adhesive coating. However, steel coils are coated with a lead-tin alloy containing 8 - 25 % tin, called 'terne' metal. The terne metal can also contain up to 3 % antimony. Tin and antimony first form alloys with the steel substrate, which provides the adhesion for the lead/tin surface coating.

Terne coating provides a high degree of external corrosion resistance. The coating keeps its integrity during deep drawing and forming, and it also acts as lubricant during same operations. Terne coatings have excellent solderability and are usually welded. It is widely used in the automotive industry for the manufacture of petrol tanks and for different applications such as gas meters.

A flow sheet for lead-tin coating (ternex process) is shown in Figure B.2-7. First, the cold reduced substrate is cleaned by (electrolytical) degreasing and pickled, usually in warm, diluted hydrochloric or nitric acid. Then, in cases of nickel flashterne coating, a thin nickel coating is applied electrolytically. This improves wetting of the substrate by the alloy in the following hot dip stage and yields continuous and uniform coatings. [ERM95]

The continuous film of nickel on both surfaces of the steel strip will readily alloy with tin to form the basis for a discontinuity free layer of ternemetal. The strip is passed through plating cells, containing titanium baskets filled with nickel pellets. An electrolyte consisting of Watts solution (nickel sulphate/ chloride) is heated and recirculated through the plating cell and is maintained at 65 °C with a pH of 2.5 - 5.0. [Com-CC-2]

In the following step, the steel enters the molten ternemetal bath at a temperature of 310 °C through a zinc ammonium chloride flux. To control coating thickness air knives are used nowadays. These provide a wiping action to remove surplus lead from the strips surface. Oil baths, which have been used before in coating thickness control, have been replaced due to bad environmental performance. After cooling, the coil can be post-treated for protection either by oiling or passivation.

#### **Passivation**

To seal the surface of the strip and passivate any pores or exposed areas of substrate against oxidation, the strip is led through a dip tank with the passivation agent, usually chromic acid based. A squeegee roll system on the exit of the tank stops any carry over from the tank and controls the film thickness. If required a drier can be used to raise the temperature of the strip and cure the chromate film on the surface of the strip.

#### **Oiling**

To apply a wet film of oil on the surface of the strip roller coater systems, spray systems or electrostatic oiling machines can be used

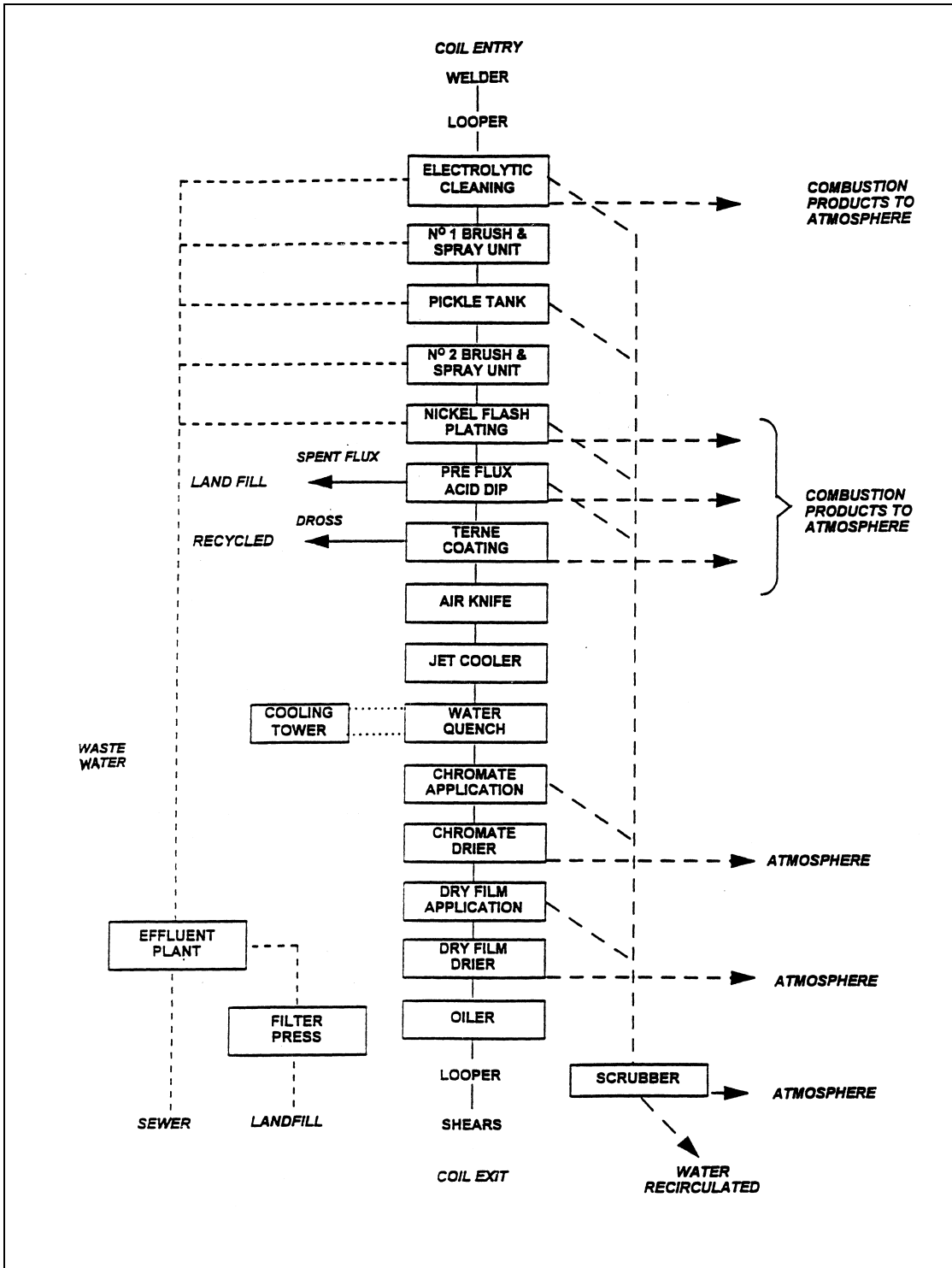


Figure B.2-7: Ternex process [EUROFER CC]



## B.2.5 Wire Hot Dip Coating

Wire is hot dip coated mainly with zinc and zinc alloys (e.g. Galvan 95 % Zn, 5 % Al); the main function of these types of coating is corrosion protection. Other coatings that are applied by hot dipping are tin and aluminium. Aluminium is used for some corrosion protection on niche products. Tin gives a shiny appearance and also provides a solder adhesive layer. The application processes for these hot dip coatings are basically the same.

A continuous hot-dip coating line for wire consists of following production steps: the wire is pickled, rinsed, dipped in a flux-bath, dried, passed through the molten metal bath and cooled again. Eventually a water based protective coating (so-called wax) can be applied after the hot dip coating step. [Com BG]

### B.2.5.1 Continuous Pickling of Wire

Following heat treatment (see also Chapter A.2.3.5) or as a starting step for hot dip coating, the wire is pickled to remove surface debris to improve its appearance or to prepare the surface for the application of coatings. This is usually done in-line either by immersing the wire in an acid bath or by subjecting it to a neutral salt bipolar electrolysis cell.

In acid pickling the wire is cleaned by passing it continuously through one or more hydrochloric acid baths; sometimes  $H_2SO_4$  is used. Due to the short residence times, the HCl acid is often heated (up to 60 °C) or is used in concentrated form.. The type of impurities that are removed in this bath depend on the previous process step:

- For heat treated wire: metal oxides, residues of soap carrier, possibly traces of lead.
  - For drawn wire: residues of soap, oil or other lubricant and traces of rust. Sometimes a degreasing agent is added to the HCl-bath to enhance removal of these substances.
- [Com BG].

Faster pickling and higher wire speeds are realised by increasing the length of the bath, by increasing temperature of HCl, by increasing the concentration of the bath or by applying electrolytic assisted pickling. HCl-fumes from the pickling baths are collected and removed by scrubbing.

After pickling, the wire is passed through a rinsing cascade. [Com BG]

### B.2.5.2 Fluxing

For good adhesion of the zinc coating, the wire is passed through a flux bath, a heated watery solution of  $ZnCl_2$  and  $NH_4Cl$ . (pure  $ZnCl_2$  is used for tin coating). Excess flux is removed from the wire by wiping. Prior to coating, the wire is dried; this can be done in a furnace or with the internal heat of the wire. With high wire diameters and/or efficient wipers, the internal heat of the wire (due to the heating in the flux bath) is sufficient to secure a dry wire. The wire must be dry before entering the flux bath to prevent squirting at the inlet of the zinc bath.

The same flux media are used as for batch galvanizing, however the concentration is generally much lower. For zinc coatings usually a  $ZnCl_2/NH_4Cl$  mixture is used (pure  $ZnCl_2$  is used for tin coating). [Com BG]

### **B.2.5.3 Hot Dipping (Galvanizing)**

The wire is passed through a molten zinc bath (430 - 470 °C). In the zinc bath, an iron - zinc diffusion layer is formed, consisting of sublayers of several Fe-Zn alloys. A zinc layer is formed on top of this, at the moment the wire leaves the zinc bath. Galvanizing can be divided in heavy (vertical) galvanizing (high coating thickness; coating mainly consists of the withdrawn zinc) and regular (horizontal) galvanizing (low coating thickness; the coating is mainly iron-zinc alloy layer). [Com2 BG]

Most zinc baths are heated through the bottom and the side walls with natural gas or other fuel. Exceptionally electric heating is used and/or heating is done from above the zinc bath.

A protective layer of particulate material or a bath cover can be applied on (a part of) the zinc bath, in order to minimize formation of zinc oxides and energy losses.

After the zinc bath, the wire is cooled to near ambient temperature using air and cooling water.

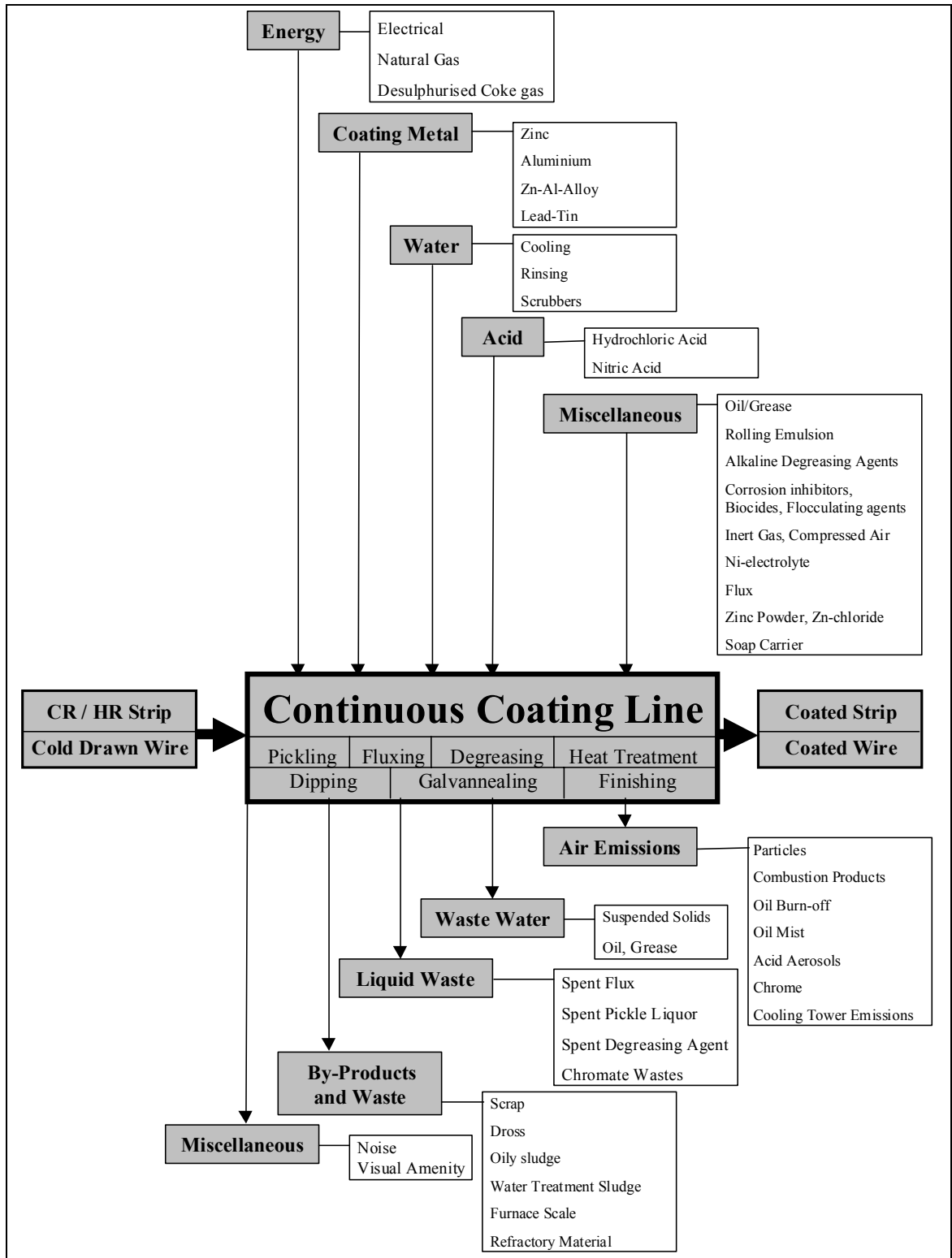
Hot dipping in other metals or alloys is done in the same way. [Com BG]

### **B.2.5.4 Finishing**

Eventually, a wax layer is applied for protection against formation of so-called white rust (superficial corrosion of the zinc layer).

### B.3 PRESENT CONSUMPTION AND EMISSION LEVELS FOR CONTINUOUS COATING LINES

#### B.3.1 Continuous Coating Mass Stream Overview



Note: Pickling only for HR band and wire coating; Fluxing for wire coating

Figure B.3-1: Input/Output balance for continuous hot dip (sheet)coating lines

Input / Consumption Level		
<b>Zinc</b> (coating metal) <sup>1</sup>	25 – 48	kg/t
<b>Energy:</b>		
natural gas	800 - 1300	MJ/t
electrical	44 - 140	MJ/t
hot water	20 - 44	MJ/t
<b>Hydrogen</b>	0.75 – 2.5	Nm <sup>3</sup> /t
<b>Nitrogen</b>	13 - 80	Nm <sup>3</sup> /t
<b>Water</b> <sup>2</sup>		
entry section:	8 -10	m <sup>3</sup> /h
coating section:	0.5 - 10.5	m <sup>3</sup> /h
exit section:	0.5 - 6	m <sup>3</sup> /h
<b>Water total</b> (added to the system)	0.167 – 0.4	Nm <sup>3</sup> /t
Output / Emission Level		
	Specific Emission	Concentration
<b>Waste air from combustion heating</b>		
SO <sub>2</sub> <sup>4</sup>	0 - 100 g/t	0 - 80 mg/m <sup>3</sup>
NO <sub>x</sub> <sup>4</sup>	0 - 100 g/t	0.5 - 700 mg/m <sup>3</sup>
<b>Chromium</b> <sup>4</sup> (from chemical treatment zone)	0.001 - 0.360 g/t	< 0.08 - 1.7 mg/m <sup>3</sup>
<b>Acid aerosols</b>		
<b>Waste water</b> <sup>4</sup>	(-0.002) - (-5) m <sup>3</sup> /t	
<b>Total Suspended Solids</b>	0.04 - 11 g/t	0.2 - 25 mg/l <sup>5</sup>
<b>COD</b>	5 - 150 g/t	23 - 750 mg/l
<b>Waste</b> <sup>3</sup> :		
<b>Oily sludge</b>	0.004 –0.3 <sup>6</sup> kg/t	
<b>Sludge from waste water treatment</b>	0.1 - 1.5 kg/t	
<b>Plate scrap</b> <sup>1</sup>	1.5 - 36 kg/t	
<b>Zn containing material</b> <sup>4</sup> (scum, surfaces mattes, slags, dust )	0 - 4.5 kg/t	
<b>Dross</b>		
<sup>1</sup> Source of data [Com-CC-2]		
<sup>2</sup> Source [EUROFER CC]		
<sup>3</sup> Single plant data, [EUROFER CC]		
<sup>4</sup> Source of [EC Study], including untreated discharge, lower end of scattering range from [Com-CC-2]		
<sup>5</sup> Unit changed from mg/m <sup>3</sup> to mg/l		
<sup>6</sup> data from 3 plants, included are spills of lubricants and hydraulic, for disposal or internal recycling		

Table B.3-1: Consumption and emission levels for the total coating line

## B.3.2 Galvanizing of Steel

### B.3.2.1 Pickling of Steel Sheet

Data from pickling in cold rolling mills also apply for this sector.

Input / Consumption Level		
HCl		kg/t
Output / Emission Level		
	Specific Emission	Concentration
Waste gas <sup>1</sup> : HCl	0.12 g/t	
Note: Source of data [EUROFER CC] <sup>1</sup> Single plant data		

Table B.3-2: Consumption and emission levels for pickling

### B.3.2.2 Degreasing

Fumes generated in degreasing and brushing are collected and scrubbed, using water or caustic soda solution or led via a demister without scrubbing.

Spent degreasing agent and waste water from the rinsing and brushing operations are sent to waste water treatment before release. Degreasing solution is generally regenerated and re-circulated to the degreasing baths. Oils are separated from the baths and the composition of the alkali solution is re-adjusted.

Sometimes the solution is treated in an emulsion separation centre and then biologically treated. [Com-CC-2]

Oil separated from the alkali solution is used as fuel for the production of heat.

Input / Consumption Level		
Water	0.063 – 0.25	m <sup>3</sup> /t
Detergents	< 0.45	kg/t
Output / Emission Level		
	Specific Emission	Concentration
Air:	NaOH, (PO <sub>4</sub> ) <sup>2-</sup>	0.05 g/t
Waste water:	NaOH, (PO <sub>4</sub> ) <sup>2-</sup>	0.45 kg/t
Oil		
Waste:	Oily sludge Fe <sub>2</sub> O <sub>3</sub> , Fe SO <sub>4</sub>	0.18 kg/t
Source of data [Com-CC-2], single plant data		

Table B.3-3: Consumption and emission levels for degreasing

### B.3.2.3 Heat Treatment

#### Non-oxidizing type (D.F.F.):

Natural gas and coke gas, previously in some cases desulphurised, are used for firing. The naked flame in this type of furnace is directly heating the strip surface. No degreasing of the strip is necessary, as the oil is burnt in the furnace. However, additional air emissions, apart from the fuel combustion products, are generated by the combustion of the oil. The pollutants released are: CO<sub>2</sub>, CO and NO<sub>x</sub>. As the furnace is operated under reducing conditions by use of inert gases the waste gas also contains H<sub>2</sub>, and N<sub>2</sub>.

If coke gas is used as fuel, SO<sub>2</sub> will also be generated, with a concentration depending on the sulphur content in the fuel.

#### Radiant type (R.T.F.):

Since there is no contact between the flame and the surface of the strip, air emissions are only generated by gas combustion, consisting mainly of CO<sub>2</sub>/CO, NO<sub>x</sub> and SO<sub>2</sub>, if coke gas is used as fuel.

Input / Consumption Level		
Hydrogen	0.75 – 2.5	Nm <sup>3</sup> /t
Nitrogen	13 - 80	Nm <sup>3</sup> /t
NH <sub>3</sub> (dissociated) <sup>1</sup>	0.7	Nm <sup>3</sup> /t
Energy		
Output / Emission Level		
	Specific Emission	Concentration
<b>Waste gas:</b>		
Heat Treatment Furnace(R.T.F) <sup>1</sup>		
Carbon monoxide (CO)	1.21 – 23.3	g/t
Nitrogen oxides (NO <sub>x</sub> )	55.4 - 105	g/t
Note: Source of data [EUROFER CC], [Com-CC-2]		
<sup>1</sup> Data from 3 plants		

Table B.3-4: Consumption and emission levels for heat treatment

### B.3.2.4 Hot Dipping (Galvanizing)

In modern facilities, the molten bath is heated by means of an electric induction systems. Older facilities using fuel-oil or gas produce the typical emissions (fumes corresponding to each different type of fuel). CO<sub>2</sub>, CO, NO<sub>x</sub>; if fuel-oil or coke gas is burnt, also SO<sub>2</sub> are emitted. Waste generated by galvanizing are bath splashes and dross formed in the bath.

Input / Consumption Level			
Zinc (coating metal) <sup>a</sup>	25 – 48	kg/t	
Energy:			
Output / Emission Level			
	Specific Emission		Concentration
Waste gas from heating the zinc bath <sup>1</sup> :			
CO	5 - 10	g/t	
NO <sub>x</sub> <sup>2</sup>	20 - 40	g/t	
SO <sub>2</sub> <sup>2</sup>	0.2 - 0.5	g/t	
Hydrocarbons	0.1 - 0.2	g/t	
Soot	0.1 – 0.2	g/t	
Plate scrap <sup>a</sup>	1.5 - 36	kg/t	
Zn containing material <sup>a</sup>	0 - 4.5	kg/t	
Note: source of data [ERM95]; a: Source of data [Com-CC-2]			
<sup>1</sup> Does not apply when electrically heated.			
<sup>2</sup> when using 0.3 % sulphur fuel oil: 110 g NO <sub>x</sub> /t and 36 gSO <sub>2</sub> /t [ERM95]			

Table B.3-5: Consumption and emission levels for galvanizing

### B.3.2.5 Galvannealing

In modern facilities, the strip is reheated in an induction furnace. When reheating is done in conventional gas-fired furnaces, waste gas with a composition that depends on the type of gas used is generated.

Input / Consumption Level			
Energy			
Output / Emission Level			
	Specific Emission		Concentration
Waste gas <sup>1</sup> :			
Carbon monoxide (CO)	0.84	g/t	
Nitrogen oxides (NO <sub>x</sub> )	0.93	g/t	
Note: Source of data [Com-CC-2]			
<sup>1</sup> when oil-fired, single plant data			

Table B.3-6: Consumption and emission levels for galvannealing

### B.3.2.6 Post Treatments

#### Oiling

Nowadays, the oily protection is mainly applied by electrostatic oily machines, which produce negligible emission levels.

#### Passivation

Cr emission data are already enclosed in the table B.3-1 on the page 254.

#### Phosphating

→ No information submitted.

### B.3.2.7 Finishing

The water + detergent method produces a temper mill emulsion that, when spent, must be collected and sent to the waste water treatment plant. Not all installations use emulsions, some use solution or nothing. [Com-CC-2]

Input / Consumption Level		
<b>Emulsion</b>		
<b>Energy</b>		
Output / Emission Level		
	Specific Emission	Concentration
<b>Effluent from skin pass mill<sup>1</sup>:</b> (previous to the treatment)		
<b>SS (filterable)</b>	30 mg/l	
<b>COD</b>	60 mg/l	
<b>Sum of hydrocarbons</b> (oil + grease)	8.0 mg/l	
<b>Zn total</b>	1 mg/l	
Note: Source of data [Com-CC-2] <sup>1</sup> single plant data		

**Table B.3-7: Consumption and emission levels for finishing**



### B.3.2.8 Waste Water Treatment

The following concentrations for selected waste water pollutants after treatment were reported:

Input / Consumption Level		
Corrosion inhibitors, partly Zn-based		
Biocides: sodium hypochlorite, sodium bromide		
Flocculating agents: Aluminium sulphate, polymers		
Output / Emission Level		
	Specific Emission	Concentration
Waste water discharge	0.43 <sup>c</sup> m <sup>3</sup> /t	
Waste water <sup>1,2</sup> :		
suspended solids <sup>3</sup>	0.04 <sup>c</sup> – 2.91 <sup>b</sup> g/t	0.2 – 25 <sup>c</sup> mg/l
Iron	0.09 – 0.54 <sup>b</sup> g/t	0.01 – 6 <sup>c</sup> mg/l
Nickel	0.04 - 0.004 <sup>b</sup> g/t	0.02 <sup>c</sup> mg/l
Zinc	0.05 - 0.005 <sup>b</sup> g/t	0.02 <sup>a</sup> – 1.23 <sup>c</sup> mg/l
Lead	0.0084 <sup>a</sup> g/t	0.03 <sup>a</sup> mg/l
Chromium Cr <sup>6+</sup>		<0.01–0.43 <sup>c</sup> mg/l 0 – 0.02 <sup>c</sup> mg/l
COD	5 – 150 <sup>c</sup> g/t	23 – 750 <sup>c</sup> mg/l
TOC	0.19 - 8.5 <sup>b</sup> g/t	
Hydrocarbons	0.074 <sup>a</sup> g/t	0.28 <sup>a</sup> – 5 <sup>c</sup> mg/l
Oil and fat	0.073 – 2.7 <sup>b</sup> g/t	
Phosphorus	0.0008 - 0.07 <sup>b</sup> g/t	0.08 <sup>a</sup> – 10 <sup>c</sup> mg/l
Water Treatment Sludge (dry material)	0.1 – 1.5 kg/t	
Chemical Treatment sludges (aqueous solutions and sludges from chromatizing process, dry material)	0.12 <sup>c</sup> kg/t	high concentrations of Cr and Cr <sup>6+</sup>
Note: source of data a: [Com D], b: [Com-CC-2], c: [EC Study]		
<sup>1</sup> some figures are single plant data, data base for ranges are figures from up to 6 plants		
<sup>2</sup> figures for specific emissions and concentration do not necessarily refer to the same plant		
<sup>3</sup> [EC Study] reported as high as 11 g/t TSS.		

Table B.3-8: Consumption and emission levels for waste water treatment

### B.3.3 Aluminizing of Sheet

The aluminium coating process gives rise to emissions to air, namely combustion products from firing fuels in the furnaces and to by-products, such as dross. The process is very similar to hot dip galvanising with similar emissions in the main products of combustion, cooling waters and by products such as dross.

Typical emissions of water are: pH 6.0 - 8.5, Temperature < 21 °C, flow 500 m<sup>3</sup>/day

Energy Consumption:

Electricity	67 kWh/t
Gas	273 kWh/t
Water	0.11 m <sup>3</sup> /t [Com-CC-2]

### B.3.4 Lead-Tin Coating of Sheet

There are no emissions of lead from the terne bath (380 - 450 °C working temperature) as it has been proved by extensive surveys on the environment in working places. [EUROFER CC]

From heating the terne metal and maybe the treatment baths, emissions to air (combustion products) arise.

Emissions from the oil bath and extractors on the exit of the terne pot are extracted and passed through a catalytic oxidizer. This oxidizes a range of hydrocarbons with molecular weights varying from 50 to over 250 and also removes odour from the fume. Fumes from cleaners, pickling, nickel plating and fluxing sections are passed through a water scrubber prior to emission. [ERM95]

There has been some information that oil baths (and also catalytic oxidizers) are no longer used and that nowadays air knives are used to control coating thickness. [Com-CC-2]

Other outputs to be expected from the process are solid wastes and by-products, like spent flux or dross, and waste water. [EUROFER CC]

Input / Consumption Level		
<b>Energy:</b>	<b>Electricity</b>	2.43 kWh/t
	<b>Gas</b>	1490 MJ/t
<b>Water</b>		3.0 m <sup>3</sup> /t
Output / Emission Level		
	Specific Emission	Concentration
<b>Waste water discharge:</b> (after effluent treatment)		
Suspended solids	30.0 g/t	mg/l
COD	90.0 g/t	mg/l
Chromium	0.028 g/t	mg/l
Cr <sup>6+</sup>	n.a.	mg/l
Copper	0.014	
Lead	0.155 g/t	mg/l
Nickel	0.565 g/t	mg/l
Zinc	0.266 g/t	mg/l
Iron	9.86 g/t	
<b>Emissions to Air:</b>		
NO <sub>2</sub>	27.58 g/t	
HCl	10.38 g/t	
SO <sub>x</sub>	negligible when gas fired	
Particulate	negligible when gas fired	
CO <sub>2</sub>	42.0 kg/t	
<b>Waste:</b>		
<b>Filter Cake</b> (effluent treatment)	7.52 kg/t	
<b>Caustic Waste</b>	1.47 kg/t	
<b>Zinc Chloride</b>	1.96 kg/t	
<b>Chromate</b>	0.73 kgt	
<b>Oil</b>	0.49 kg/t	
<b>Waste Sludge</b>	10.5 kg/t	

Note: source of data [Com-CC-2], single plant data

Figure B.3-2: Consumption and emission levels for lead-tin coating

Data available for one plant [UK-5/98]:

	With air knife / wet scrubber (after revamp)	Cooling and gauge control using oil / catalytic oxidizer ('Old system')
<b>Emissions to air:</b> particulates VOC all metals acid gases	< 1 mg/m <sup>3</sup> < 1 mg/m <sup>3</sup> < 1 mg/m <sup>3</sup> 30 mg/m <sup>3</sup>	150 mg/m <sup>3</sup> 100 mg/m <sup>3</sup>
<b>Waste water:</b> SS COD Fe Cr Cu Ni Pb Zn pH	400 mg/l 600 mg/l 250 mg/l 5 mg/l 2 mg/l 5 mg/l 2 mg/l 5 mg/l 6 - 11	
<b>Waste:</b>	iron-rich filter cake from effluent treatment, with high chlorine content	



## B.3.5 Wire Hot Dip Coating (Galvanizing)

### B.3.5.1 Continuous Pickling of Wire

Pickling is done in partially diluted HCl. The HCl bath is heated with a steam- or hot-water coil. Water is consumed in the form of rinsing water and scrubbing water and leaves the installation ultimately as waste water. [Com BG]

Input / Consumption Level		
HCl (expressed as 32 % HCl)	10 - 100 kg/t	
Energy for heating the HCl-bath <sup>1</sup>	no figure available	
Scrubber / rinsing water	0.5 - 5 m <sup>3</sup> /t	
Output / Emission Level		
	Specific Emission	Concentration
Spent HCl containing <sup>2</sup> :	5 - 100 l/t	150 - 275 g/l
		60 - 125 g/l
Waste water from scrubber / rinsing	0.5 - 5 m <sup>3</sup> /t	no representative figure available <sup>3</sup>
Emissions from scrubber:		
HCl		0 - 30 mg/m <sup>3</sup>
Note: source of data [Com BG], reference is tonnage of pickled wire <sup>1</sup> often the bath is heated by residual heat in the wire <sup>2</sup> other contaminants depending on previous steps, e.g. soap residues, pickled soap carrier, Pb... <sup>3</sup> huge variations		

Table B.3-9: Consumption and emission levels for pickling of wire

### B.3.5.2 Fluxing

The flux bath is heated with a steam- or hot water coil. Drying of the wire after the flux bath can be done in an oven or through the residual heat in the wire. Often, the oven is heated with the residual heat of the exhaust gas of the zinc bath heating. [Com BG]

Input / Consumption Level	
Flux salt	0.2 - 2.5 kg/t
Energy for heating the flux-bath	n.a.
Water (make-up/replace evaporation losses) <sup>1</sup>	
Output / Emission Level	
	Specific Emission
Spent flux	negligible
Note: source of data [Com BG], reference is tonnage of fluxed wire <sup>1</sup> negligible to rinsing and cooling water consumption	

Table B.3-10: Consumption and emission levels for fluxing of wire

### B.3.5.3 Hot Dipping (Galvanizing)

The zinc bath is heated through the walls and bottom using natural gas or other fuel. Tiles of zinc are added to the zinc bath. Through drag-in of traces of Fe, and through oxidation, dross is formed, which has to be removed.

Following the zinc bath, the wire is cooled with water. [Com BG]

Input / Consumption Level		
Zinc	15 - 150	kg/t
Energy for heating of the zinc-bath	n.a.	
Cooling water	0.2 - 1	m <sup>3</sup> /t
Bath cover material	n.a.	
Output / Emission Level		
	Specific Emission	Concentration
Zinc-containing residues (top-dross, bottom dross, waste bath cover material)	5 - 25	kg/t
Exhaust gas of zinc bath heating <sup>1</sup>		
Emissions of zinc bath:		
Zn <sup>2</sup>		0 - 1 mg/m <sup>3</sup>
Dust <sup>2</sup>		0 - 15 mg/m <sup>3</sup>
Note: source of data [Com BG]		
<sup>1</sup> typical emissions of natural gas fired furnace (unless other energy carrier is used)		
<sup>2</sup> small sources can have higher concentrations, as in most countries, small sources only have to comply with a limit for mass flow		

Table B.3-11: Consumption and emission levels for hot dipping of wire

#### B.3.5.4 Noise Issues in a Wire Plant

Excessive noise is primarily an internal occupational health issue, with precautions normally taken to protect employees where it is not practical to prevent or reduce noise at the source. In some instances, depending on the location of the process and noise characteristics, depending on local off-site aspects (other noise sources, nearby residential area,...), and depending on local plant aspects (noise reduction by the building structure), there can be a concern for noise off-site.

The main sources of noise in wire processes are:

- Rotating equipment, e.g. wet drawing machines; dry drawing machines; take-up units and pull-through units on coating lines.
- Air-wipes or air-brushes which clean the wire using compressed air can have a high frequency noise.
- Pay-off units of wire rod have a particular repetitive noise.
- Burners of ovens.

These operations are typically continuous operations and are operated inside a building. In this way, the impact outside the building is minimized to such an extent, that noise generated by these operations rarely is an issue when concerning noise off-site.

Case studies show that non-process sources outside the building, such as ventilation or plant utilities, are the main concern in wire plants located close to e.g. a residential area. Measures such as relocation, insulation or local enclosure can be considered for this last category of sources.

## **B.4 TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BAT FOR CONTINUOUS COATING LINES**

### **B.4.1 Galvanizing of Sheet**

#### **B.4.1.1 General Advice /Whole Plant**

##### **B.4.1.1.1 Oil-tight Trays or Cellars**

**Description:**

Several hydraulic stations and oil- or grease-lubricated equipment are required for galvanising lines. These units are usually situated in oil-tight trays or cellars to avoid penetration of oil into ground in case of leakage. [Com-CC-2]

**Main environmental benefits:**

- The risk to contaminate the soil is minimized. [Com-CC-2].

**Applicability:**

- New and existing plants [Com-CC-2].

**Cross media effects:** No [Com-CC-2]

**Operational data:**

**Economics:** IC and OC are both lows. [Com-CC-2]

**Driving force for implementation:** environment requirements [Com-CC-2]

**Reference literature:**

##### **B.4.1.1.2 Recycling of Oil Containing Waste**

**Description:**

Oil containing waste, such as the waste oil collected in the trays and sumps and the sludge from the oil separator of the water treatment plants, should be collected and stored separately from other waste. The collected oily waste can be used as fuel for blast furnace (in an integrated process) instead of landfilling. [Com-CC-2]

**Main environmental benefits:**

- Reduction in waste [Com-CC-2].
- Increase of the waste recycling rate [Com-CC-2].

**Applicability:** New and existing plants [Com-CC-2]

**Reference plant:** Many plants [Com-CC-2]

**Cross media effects:** No [Com-CC-2]

**Operational data:**

**Economics:** IC and OC are both medium [Com-CC-2]

**Driving force for implementation:** Environments requirements [Com-CC-2]

**Reference literature:**

### **B.4.1.2 Pickling of Steel Sheet**

The techniques to consider in the determination of BAT for pickling in sheet galvanizing plants are same as for pickling operations in cold rolling. For descriptions and comments on these techniques refer to Part A, chapters A.4.2.1.1, A.4.2.1.4, A.4.2.1.5 to A.4.2.1.10, A.4.2.1.16, A.4.2.1.17, A.4.2.1.22 to A.4.2.1.25.

### **B.4.1.3 Degreasing**

#### **B.4.1.3.1 Cascade (multiple) Use of Degreasing Solutions**

**Description:**

The solution from the electrolytic degreasing section is reused in the spray section, once a certain oil level is reached. The spent degreasing solution of the spray section is sent away to be regenerated. The oil residues out of the regeneration devices are incinerated out of the site, and the rinse waters are treated in the main water treatment plant. Leakages and splashes are collected and treated.

**Main achieved environmental benefits:**

- Reduced degreasing solution consumption (fresh water consumption).
- Reduction of waste water and sludge in the water treatment plant [Com-CC-2].

**Applicability:**

- New and existing lines, provided space is available. [Com-CC-2].

**Cross-media effects:**

- Increased energy consumption [Com-CC-2].

**Reference plants:** - several plants [Com-CC-2].

**Operational data:**

15 m<sup>3</sup>/h of demineralized water is needed. (For the material that need this quality with a production yield of 68 t/h) [Com-CC-2]

**Economics:** Investments costs are medium and operative costs are low. [Com-CC-2]

**Driving force for implementation:**

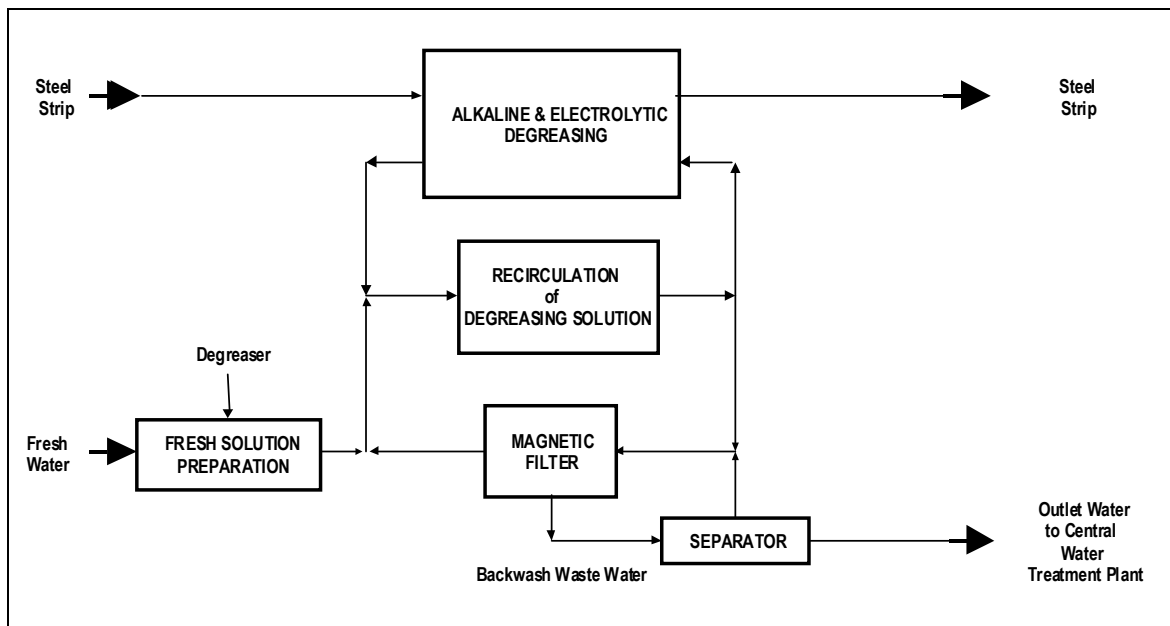
**Reference literature:**

#### **B.4.1.3.2 Cleaning and Recirculation of Degreasing Baths**

**Description:** More detailed information see Chapter D.4.3

Spent degreasing solution is cleaned, e.g. in an ultrafiltration device or a magnetic filter. The oily sludge may be used as reductor in the blast furnace; the treated degreasing bath is recycled. Fig shows an example of a degreasing solution circuit.





**Figure B.4-1: Example of a degreasing solution recycling system**  
[CC 11/99]

**Main achieved environmental benefits:**

- Reduction of alkaline chemical consumption, [Com-CC-2].
- Reduction of water volume and sludge volume in the water treatment plant. [Com-CC-2].

**Applicability:**

- New and existing plants with no space problems for pumps, pipes tanks etc. [Com-CC-2].

**Cross-media effects:**

- Increased energy consumption [Com-CC-2].
- 

**Reference plants:** Voest-Alpine line 1 and 2, Aceralia line 2, Galtec 1 and others [Com-CC-2]

**Operational data:** Water consumption of 5 m<sup>3</sup>/h with the same consideration than before. [Com-CC-2]

**Economics:** high investment and high operational costs. [Com-CC-2]

**Driving force for implementation:** Environmental requirements [Com-CC-2]

**Reference literature:**

### B.4.1.3.3 Degreasing by Burning Oil in the Heat Treatment Furnace

**Description:**

Oil on the steel surface is burnt in the heat treatment furnaces. Alkaline degreasing is omitted.

**Main achieved environmental benefits:**

- No emissions to water [Com-CC-2].
- No generation of waste [Com-CC-2].
- Emissions to the atmosphere are lower than those generated in alkaline liquid degreasing. [EUROFER CC].

**Applicability:**

- New and existing installations.
- When requirements for surface cleanliness and zinc adhesion are not very high. [Com-CC-2]

**Cross-media effects:** Air emission through burning of oil rest [Com-CC-2].

**Reference plants:** Galtec 1 [Com-CC-2]

**Operational data:**

In some cases it might still be necessary to have a degreasing section before the furnace for some high quality appliances. The furnace is not so easy to control as a radiant tubes furnace. Fumes from the furnace. [Com-CC-2]

**Economics:**

Investment and operative costs are reduced because no need for preceding sections. [Com E]  
It is cheap on operation and installation. [Com-CC-2]

**Driving force for implementation:**

**Reference literature:**

#### **B.4.1.3.4 Treatment of Spent Degreasing Baths**

**Description:** see Chapter D.4.4

**Main achieved environmental benefits:**

- Reduction of waste.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **B.4.1.3.5 Treatment of Alkaline Waste water**

**Description:** see Chapter D.4.5

**Main achieved environmental benefits:**

- Reduced emissions to water.
- 

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### B.4.1.3.6 Degreasing Vapour Collection and Treatment

**Description:**

Vapours generated by degreasing are collected by means of an exhaust device and subject to a scrubber or demister for abatement. Waste water originating from scrubbing are subject to water treatment.

**Main achieved environmental benefits:**

- Reduction of fugitive emission.
- Reduction in degreasing fume emission.

**Applicability:**

- New and existing plants with degreasing devices [Com-CC-2].
- Existing plants with no space problems [Com-CC-2].

**Cross-media effects:**

- Scrubber: water consumption (evaporation) and sludge generation in water treatment plant [Com-CC-2].
- Demister: depending on the cleaning technique used, treatment of spraying water or solvents [Com-CC-2].

**Reference plants:** - Several [Com-CC-2], Jenn An, Taiwan [Danieli]

**Operational data:** 5 m<sup>3</sup>/h of recirculate water (evaporate) for a production yield of 66 t/h [Com-CC-2]

**Economics:** medium [Com-CC-2]

**Driving force for implementation:** Local conditions or requirements from local authorities that lead to implementation. [Com-CC-2]

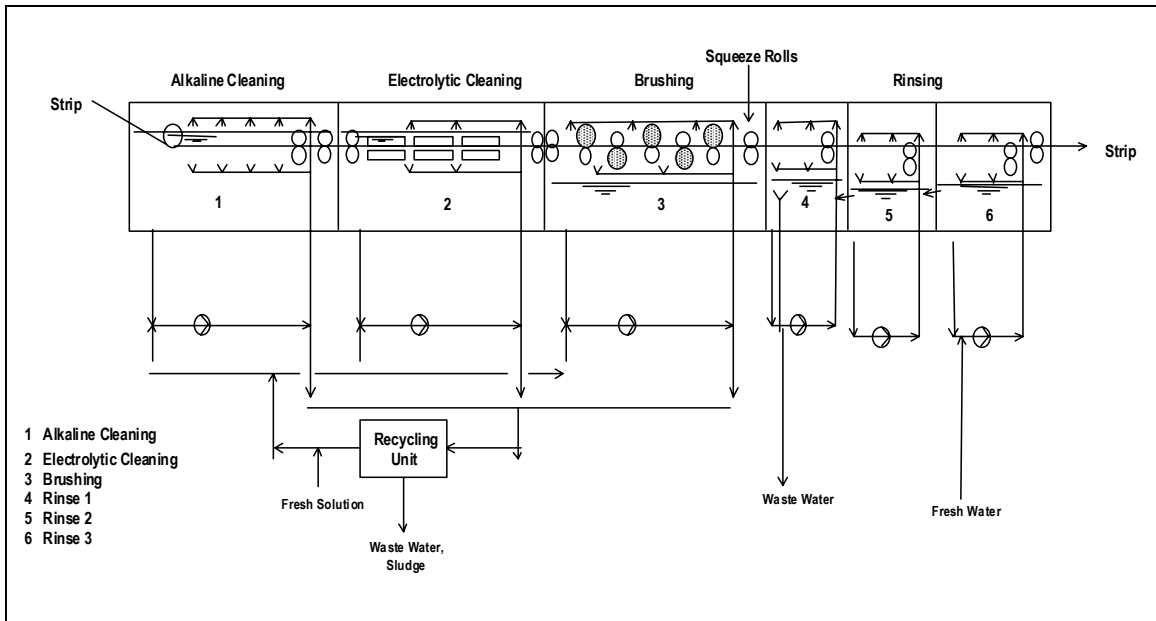
**Reference literature:**

### B.4.1.3.7 Using Squeeze Rolls

**Description:**

The remaining degreasing solution or rinse water on the steel strip is removed from the strip by squeeze rolls before leaving each treating section. This will assure that dragout of solution into next section is minimized and loss of chemicals and contamination of rinse water is also minimized. [Com-CC-2]

Fig shows an example of a chemical pre-treatment section of a hot dip galvanizing line for sheet using squeeze rolls and cascade rinsing (for efficient rinse water use).



**Figure B.4-2: Chemical pre-treatment section for a sheet hot dip coating line (example)**  
[CC 11/99]

**Main environmental benefits:**

- Reduction of raw materials consumption, [Com-CC-2].
- Reduction of waste water volume and of sludge in the waste water treatment plant [Com-CC-2].

**Applicability:**

- New and existing plants with degreasing and rinsing sections. [Com-CC-2].

**Cross media effects:** No [Com-CC-2]

**Reference plants:** many plants. [Com-CC-2]

**Operational data:**

**Economics:** The initial investment is not so high and the operating cost is cheap. [Com-CC-2]

**Driving force for implementation:**

**Reference literature:**

### B.4.1.4 Heat Treatment

#### B.4.1.4.1 Low-NOx Burner

**Description:** see Chapter D.2.1

**Main achieved environmental benefits:**

- Lower CO and NOx emissions [Com-CC-2].

**Applicability:**

- New and existing plants, sometimes when the gas is preheated with gas is not possible. [Com-CC-2].

**Cross-media effects:**

- Higher energy consumption.

**Reference plants:** Voest- Alpine HDG lines 1- 2, Aceralia line 2, Galtec 1 and many others. [Com-CC-2]

**Operational data:**

Concentration of NO<sub>x</sub> between 300 - 500 mg/Nm<sup>3</sup> and CO between 10 - 20 mg/m<sup>3</sup> [Com-CC-2]; other sources reported 250 – 400 mg/Nm<sup>3</sup> [Com2 A].

**Economics:** Expensive technique on operation (through higher consumption) and investment [Com-CC-2]

**Driving force for implementation:**

**Reference literature:**

#### B.4.1.4.2 Preheating of Combustion Air with Recovery Heat

**Description:** see Chapters D.1.1 and D.1.2

The heat of the exhaust gases is recovery by a heat exchanger (regenerative burner, recuperative burners or external recuperators, (see Part D) and transferred partially to the combustion air. [Com-CC-2]

**Main environmental benefits:**

- Reduction of energy consumption [Com-CC-2].

**Applicability:**

- New plants and existing plants in case of major modernisation [Com-CC-2].

**Cross-media effects:**

- Increase in NO<sub>x</sub> emissions [Com-CC-2]

**Reference plants:**

**Operational data:**

**Economics:** IC=medium, OC is cheap [Com-CC-2]

**Driving force for implementation:**

**Reference literature:**

#### B.4.1.4.3 Preheating the Strip with Recovery Heat

**Description:**

Downstream of the entry looper, bridging the period of strip welding, the strip passes through a preheating zone where the residual heat of the waste gas is utilized. [Com-CC-2]

**Main achieved environmental benefits:**

- Reduction of energy consumption [Com-CC-2].

**Applicability:**

- New and existing plants on major modernisation. Depending on the available heat on the fumes. [Com-CC-2]

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:** IC=medium, OC is cheap [Com-CC-2]

**Driving force for implementation:**

**Reference literature:**

#### **B.4.1.4.4 Steam Production with Recovery Heat**

**Description:** No description and technical information submitted.

**Main achieved environmental benefits:**

- Reduction of energy consumption.

**Applicability:**

- New and existing plants on major modernisation. Depending of the available heat on the fumes [Com-CC-2].

**Cross-media effects:**

**Reference plants:**

**Operational data:** Increase of the risk of corrosion by a possible condensation of water. It is important for this technique the existence near this installation of a steam consumer.

**Economics:** IC: high, OC: medium [Com-CC-2]

**Driving force for implementation:**

**Reference literature:**

#### **B.4.1.4.5 Inductive Heating System**

**Description:** No description and technical information submitted.

**Main achieved environmental benefits:**

**Applicability:**

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **B.4.1.5 Hot Dipping (Galvanizing)**

##### **B.4.1.5.1 Dross Treatment**

**Description:**

On hot dip galvanising lines, more than 10 % of the metallic zinc consumed appears as dross, mainly Zn and ZnO, on top of the molten zinc bath. Because of likely adverse effect on the galvanised steel sheet, it is manually removed. The arising residual product can be sold to zinc smelters or being treated directly on-site to receive a zinc ash, which has only 20 % of the former volume and can then be sold to the zinc producing industry for a higher price. Figure B.4-3 shows a diagrammatic view of a zinc recovery plant. [DFIU]

**Main achieved environmental benefits:**

- Reduction of waste.

**Applicability:**

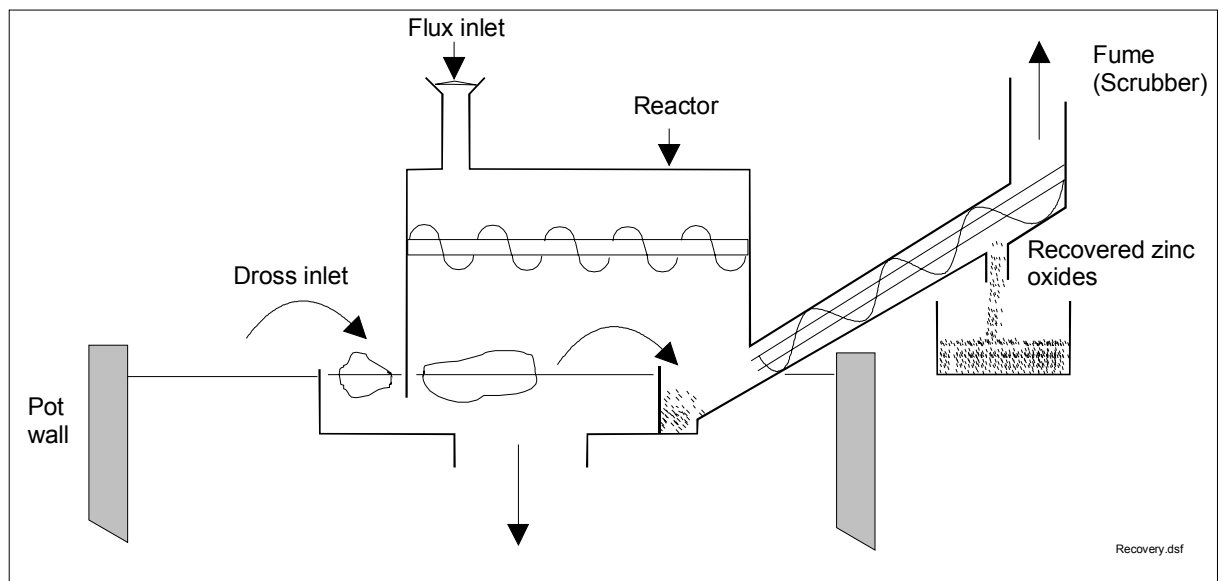
**Cross-media effects:**

**Reference plants:**

**Operational data: Economics:**

**Driving force for implementation:**

**Reference literature:**



**Figure B.4-3: Diagrammatic view of a recovery system for zinc from dross [DFIU-99]**

**Main achieved environmental benefits:**

- Reduction of waste.

**Applicability:**

**Cross-media effects:**

**Reference plants:**

**Operational data: Economics:**

**Driving force for implementation:**

**Reference literature:**

### B.4.1.5.2 External Recycling of Coating Material Slag

**Description:**

Zinc slag is collected and returned to the zinc supplier for recycling of zinc. [Com-CC-2]

**Main environmental benefits:**

- Reduction of waste [Com-CC-2].
- Saving natural sources.

**Applicability:**

- New and existing plants. [Com-CC-2].

**Cross media effects:** No [Com-CC-2]

**Operational data:**

**Economics:** IC and OC are both low [Com-CC-2]

**Driving force for implementation:** Environmental and economics [Com-CC-2]

**Reference literature:**

## **B.4.1.6 Galvannealing**

### **B.4.1.6.1 Induction Electrical Furnace**

**Description:**

An induction electrical furnace is a relatively new technique, which is applied in the Hot Dip Coating process. It is possible to use it to galvanneal the coated strip, as well as in the drier stage of the organic coating (if there were any) in the final finishing phase. Strictly speaking, this technique is not new (it appeared about five years ago). However, it undergoes a continuous innovation, such as frequency variations and others.

This application could improve the environmental performance of the conventional furnaces when dealing with a hot dip process context, since there is not gas emissions from this stage. The price of the electrical power is not necessary acceptable. [Com-CC-2]

**Main achieved environmental benefits:**

- Reduced air emissions.

**Applicability:**

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

.

## **B.4.1.7 Post Treatments**

### **B.4.1.7.1 Covering the Strip Oiling Machine**

**Description:** No description and technical information submitted.

**Main environmental benefits:**

- Reduction of oil fumes emissions in the atmosphere. [Com-CC-2].

**Applicability:**

- New and existing plants with this strip oiling device. [Com-CC-2].

**Cross media effects:**

**Operational data:**

**Economics:** IC is medium and OC is low. [Com-CC-2]

**Driving force for implementation:**

**Reference literature:**

### **B.4.1.7.2 Electrostatic Oiling**

**Description:**

Light heated oil (anticorrosion or deepdrawing oil) is electrostatically settled on the zinc surface. The machine is covered and the splashed oil is collected and reinjected. [Com-CC-2]



**Main achieved environmental benefits:**

- Reduced oil consumption.
- Reduced oil emissions [Com-CC-2].

**Applicability:**

- New and existing plants [Com-CC-2].

**Cross-media effects:** No [Com-CC-2]

**Reference plants:** all the SIDMAR lines. [Com-CC-2]

**Operational data:** It is not able to make the dry lubricant protection. [Com-CC-2]

**Economics:** Invest costs are high, operational costs are medium. [Com-CC-2]

**Driving force for implementation:**

**Reference literature:**

### B.4.1.7.3 Cleaning and Reuse of Phosphating Solution

**Description:**

The phosphate solution is filtered through filters while recirculated. Only a small amount of exhausted solution is discharged from time to time and treated externally. The waste water from the rinsing section is also treated externally in the water treatment plant. This treatment may also be carried out off site. [Com-CC-2]

**Main achieved environmental benefits:**

- Reduction of phosphating chemical consumption, [Com-CC-2].
- Reduction of water outlets and volume of sludge in the water treatment plant. [Com-CC-2].

**Applicability:**

- New installations and existing if space is not a problem in revamping [Com-CC-2].

**Cross-media effects:**

- Energy consumption [Com-CC-2].

**Reference plants:** Voest-Alpine [Com-CC-2]

**Operational data:**

**Economics:** IC=medium, OC=medium [Com-CC-2]

**Driving force for implementation:**

**Reference literature:** Voest Alpine, internal document. [Com-CC-2]

### B.4.1.7.4 Cleaning and Reuse of Chromating Solution

**Description:**

The chromium solution is filtered through filters while recirculated. Exhausted solution is discharged from time to time and treated externally in the water treatment plant. This treatment may also be carried out off site. [Com-CC-2]

**Main achieved environmental benefits:**

- Reduction of chromium chemical consumption, [Com-CC-2].
- Reduction of water outlets and volume of sludge in the water treatment plant. [Com-CC-2].

**Applicability:**

- New and revamped lines if no space problems [Com-CC-2].

**Cross-media effects:**

- Energy consumption [Com-CC-2].

**Reference plants:** Voest Alpine [Com-CC-2]

**Operational data:**

**Economics:** IC=medium, OC=medium [Com-CC-2]

**Driving force for implementation:**

**Reference literature:** Voest Alpine, internal document. [Com-CC-2]

### **B.4.1.7.5 Covered Process Baths and Storage Tanks**

**Description:**

Storage tanks and chemical treating bathes are covered (extraction system) to collect emissions of fumes and aggressive waste air. Com-CC-2]

**Main environmental benefits:**

- Prevention of fugitive releases of chemical fumes. Com-CC-2].
- Reduction in exhaust air volumes. Com-CC-2].

**Applicability:**

- New and existing plants Com-CC-2].

**Cross media effects:**

**Reference plants:** Voest-Alpine line 1 and 2, Aceralia line 2 Com-CC-2]

**Operational data:**

**Economics:** IC= medium, and OC are low. Com-CC-2]

**Driving force for implementation:**

**Reference literature:**

### **B.4.1.7.6 Using Squeeze Rolls**

**Description:**

The remaining solution on the steel strip is removed from the strip by squeeze rolls before leaving each treating section. This will assure that dragout of solution into next section is minimized and loss of chemicals. [Com-CC-2]

**Main environmental benefits:**

- Reduction of raw materials consumption, [Com-CC-2].

**Applicability:**

- New and existing plants with passivation process. [Com-CC-2].

**Cross media effects:** No [Com-CC-2]

**Reference plants:** many plants. [Com-CC-2]

**Operational data:**

**Economics:** The initial investment is not so high and the operating cost is cheap. [Com-CC-2]

**Driving force for implementation:**

**Reference literature:**

### B.4.1.7.7 Using Reverse Osmosis to Produce Deionized Water

**Description:**

For preparation of chemical treating solutions and for rinsing water deionised water is required. This was produced in former times by desalination through ion exchange filters. As these filters need chemicals and water for regeneration as well as they produce regeneration brine,...

**Main environmental benefits:**

- Reduction of chemicals consumption and avoidance of higher emissions in the natural waters.

**Applicability:**

- New and existing installations if is needed to change the deionised unit.

**Reference plant:** Voest- Alpine line 1 and 2

**Cross media effects:** No

**Operational data:**

**Economics:** Investments cost are high but operational costs are medium

**Driving force for implementation:** Environment and savings.

**Reference literature:**

### B.4.1.8 Finishing

#### B.4.1.8.1 Collection and Treatment of Skin Pass/Temper Solution

**Description:**

Used solution, containing zinc particles and anticorrosion compounds, is send to the water treatment section. The water could be recycled for the same or other purposes. Spent emulsion generated from tempering should be collected and send for water treatment. [EUROFER CC]

**Main achieved environmental benefits:**

- Reduced water pollutant load (95 %) [Com-CC-2].

**Applicability:**

- New and existing plants that use skin pass. [Com-CC-2].

**Cross-media effects:** - no

**Reference plants:** Galtec, Aceralia line 2, Voest-Alpine HDG 1 and 2 [Com-CC-2]

**Operational data:**

**Economics:** - High investment costs and medium operation costs. [Com-CC-2]

**Driving force for implementation:**

Environmental requirements, cost requirements, Yield increase and Quality requirements [Com-CC-2]

**Reference literature:**

### B.4.1.9 Waste Water Treatment

Generally, the waste water treatment plants treat not only the water from coating plants but also all the effluents generated in the rolling facilities. Normally, these plants consist of three different circuits: **chromic water** line, **oily water** line and the **general waste water line**.

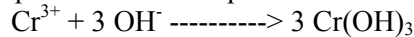
### B.4.1.9.1 Chromic Water Line

**Description:**

The function of this circuit is to remove the chrome ions existing in the water, mainly, the Cr(VI), due to its higher toxicity, and the Cr(III). In the treatment plant the Cr(VI) is reduced to Cr(III) with sodium bisulphite or ferric chloride; the latter is preferable due to the much smoother reaction conditions obtained regarding pH, as the bisulphite reaction requires a much lower pH, thus entailing a higher acid consumption. [EUROFER CC]

The following reaction takes place:  $Cr^6 + 3 Fe^{2+} \text{ -----} > Cr^3 + 3 Fe^{3+}$

In the following stage the  $Cr^{3+}$  precipitates due to a pH increase obtained by addition of hydrated lime.



The ferric hydroxide precipitates simultaneously with the chromic hydroxide. The slurry obtained is treated in a decanter, inerted with milk of lime and subsequently passed through a press filter. Treatment with a polymer to achieve flocculation is also possible. [EUROFER CC], [Com-CC-2]

**Main achieved environmental benefits:**

- Reduction of chromium emission with effluent.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### B.4.1.9.2 Oily Water Circuit

**Description:**

The aqueous effluents from those facilities where the strip is degreased prior to the coating processes are transferred to a neutralisation tank; neutralisation is achieved through the addition of hydrochloric acid. In case that acidic waste water from other processing steps (e.g. acidic rinse water) that cannot be recirculated is available, this may be used for neutralisation. [Weigel] After this step, the effluents enter a homogenisation tank and, subsequently, a coagulation and flocculation section. [EUROFER CC]

Coagulation is achieved through the addition of ferric chloride and hydrochloric acid and flocculation by means of a treatment with polymers such as aluminium polychlorid and other types of polyelectrolyte. [EUROFER CC]

From the flocculation tank, the effluent goes to a flotation tank where three phases are separated:

- a) Flocculated oily slurries
- b) Sediment slurries
- c) Water, to recycle

The flocculated oily slurries float as foam, by the injection of pressurised water through the bottom of the aero-floater. The air absorbed by the water is released with depressurisation, forming small bubbles that adhere to the flocculated oily slurries making them float as a foam, subsequently removed by means of a suitable mechanism. [EUROFER CC]

**Other Option/Treatment of Spent Degreasing Solution**

The basic emulsion could also be treated in a central plant. First, there is a separation in three phases by means of gravity. The upper phase is treated in an oil centre. The middle phase is treated in an emulsion centre. The bottom phase consists of sludge and is treated separately. By means of ultrafiltration, emulsions are separated in water and oil. The water part is treated in a conventional biological plant to reduce COD. [Com-CC-2]

**Main achieved environmental benefits:**

- Reduction of oil emission with effluent.

**Applicability:**

- New and existing plants.

**Cross-media effects:****Reference plants:****Operational data:**

**Economics:** Investment cost is very high, operatives ones are high, but its environmental performance are also very high. [Com-CC-2]

**Driving force for implementation:** environmental requirements. [Com-CC-2]

**Reference literature:****B.4.1.9.3 General Waste Water Circuit****Description:**

The treatment process of the waste water consists in a flocculation with subsequent filtering and cooling. In order to improve the removal of oil and solid particles, a small amount of coagulating agent and polyelectrolyte is added to produce a microfloculation.

The water and the flocculi are sent to a battery of two-layer sand and anthracite filters that retain the particles formed. The filtrated water is transferred to cooling towers and the slurries retained in the filters are removed and passed through a press filter for subsequent recycling. [EUROFER CC]

**Main achieved environmental benefits:**

- Reduction of pollutants in effluent.

**Applicability:**

- New and existing plants.

**Cross-media effects:****Reference plants:**

**Operational data:**

Substance	Concentration in mg/l <sup>1)</sup>	Type of sampling	Measurements in 1998 Operator/Comp. authority
Fe	1.5	Qualified random sample	28/5
Oil	0.2	Qualified random sample	28/5
Suspended solids	10	Qualified random sample	28/5
Cr	< 0.006	Qualified random sample	28/5
Ni	0.01	Qualified random sample	28/5
Zn	0.04	Qualified random sample	28/5

Note: Source of data: Senator für Bau und Umwelt, Bremen. Plant: BREGAL, in Bremen.  
<sup>1)</sup> Mean values of the qualified random samples from 1998. Waste water volume: 135549 m<sup>3</sup>

**Table B.4-1: Pollutant concentrations in water discharge from treatment of waste water from galvanization [Com2 D]**

**Economics:****Driving force for implementation:****Reference literature:****B.4.1.10 Cooling Water Systems****B.4.1.10.1 Closed Cooling Water Loop****Description:** see Chapters D.9.2

Separate and closed cooling water systems with recooling of the water by evaporative towers or plate heat exchangers.

**Main achieved environmental benefits:**

- Saving natural resources [Com-CC-2].
- Reduction of energy consumption. [Com-CC-2].

**Applicability:**

- New Installations and existing installation in case of major modernisation [Com-CC-2].

**Cross-media effects:****Reference plants:****Operational data:**

**Economics:** IC=high, OC=low [Com-CC-2]

**Driving force for implementation:** Site specific issues will govern the choice of cooling system and applicability on existing plants. [Com-CC-2]

**Reference literature:****B.4.1.10.2 Reuse of Cooling Water****Description:**

Design a water circuit to reintroduce the cooling waters to this process or for another purpose. [Com-CC-2]

**Main environmental benefits:**

- Saving natural resources, [Com-CC-2].
- Reduction of energy consumption [Com-CC-2].

**Applicability:**

- New and existing plants. [Com-CC-2].

**Cross media effects:**

**Reference plants:** Many plants. [Com-CC-2]

**Operational data:**

The recycling ratio of the cooling water can surpass easily 90 %. [Com-CC-2]

**Economics:** IC=high, OC=medium [Com-CC-2]

**Driving force for implementation:****Reference literature:**

## B.4.2 Aluminizing and Lead-Tin (Terne) Coating

Techniques to be considered in the determination of BAT, are basically the same as for Galvanizing, when the same processing steps are applied (e.g. pickling, passivation, etc.). Some additional measures for Lead-Tin (Terne) Coating are listed below:

### B.4.2.1 Nickel Plating

**Description:**

The electrolytic nickel plating facility is in enclosed and the exhaust air is ventilated to a wet scrubber. [Com-CC-2]

**Main achieved environmental benefits:**

- Reduction of emissions to air, especially of fugitive emissions.

**Applicability:****Cross-media effects:****Reference plants:****Operational data:****Economics:****Driving force for implementation:****Reference literature:**

### B.4.2.2 Hot Dipping

#### B.4.2.2.1 Air Knives for Thickness Control

**Description:**

To control coating thickness air knives are used which provide a wiping action to remove surplus lead from the strips surface. [Com-CC-2]

**Main achieved environmental benefits:**

- No emission of VOC and hydrocarbons to air (as with oil bath) [Com-CC-2].
- No generation of waste oil [Com-CC-2].

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:** British Steel, Brierley Hill, UK

**Operational data:**

Reduction of VOC from 150 mg/m<sup>3</sup> to < 1 mg/m<sup>3</sup> [UK 5/98]

No requirement for an incinerator to destroy emissions. [Com-CC-2]

**Economics:**

**Driving force for implementation:**

**Reference literature:**



## B.4.3 Wire Hot Dip Coating (Galvanizing)

### B.4.3.1 Continuous Pickling of Wire

#### B.4.3.1.1 Enclosing Pickling Baths / Treatment of Extracted Air

**Description:**

The acid-bath must be equipped with a hood or cover, kept under slight underpressure, or comparable enclosing. The extracted air can be treated by scrubbing with water using packed or plate scrubbers. [CET-BAT]

**Main achieved environmental benefits:**

- Reduction of fugitive emissions from pickling (acid vapour and aerosols).
- Reduction of acid vapour and aerosols by scrubbing.

**Applicability:**

- New and existing plants, especially as heated and concentrated HCl is used.
- Also applicable at continuous annealing and patenting lines with HCl in-line cleaning.

**Cross-media effects:**

**Reference plants:**

Most installations with continuous pickling that operate either at high HCl or increased temperature, are equipped with a scrubber. [CET-BAT]

**Operational data:**

Typical emission limits (concentration) are: < 20 to < 30 mg HCl per Nm<sup>3</sup>. This can be reached with a scrubber operated with water (no addition of NaOH needed). [CET-BAT]

**Plate scrubbers** achieve < 30 mg HCl/Nm<sup>3</sup>. They have a low water consumption and therefore limited amount of waste water. In some applications (e.g. high acid consumption, high acid temperature) complete reuse of scrubber waste water for dilution of fresh acid is possible. [Com BG2]

**Packed media scrubber** achieve < 20 mg/Nm<sup>3</sup> but with a higher water consumption as plate scrubbers, resulting in a higher amount of waste water. [Com BG2]

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### B.4.3.1.2 Cascade Pickling

**Description:**

Cascade pickling is performed in two or more baths in series. The acid flows (continuously or discontinuously) in counter flow from one bath to the next. This allows to achieve a very efficient use of the acid while still reaching good pickling quality. In this way, a higher conversion of the acid to metal salts can be reached, leading to a lower acid consumption. [CET-BAT]

**Main achieved environmental benefits:**

- Reduced consumption of fresh acid.
- Reduced spent acid (waste).

**Applicability:**

- New and existing plants.
- For existing plants available space might be a limiting factor.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

For cascade pickling an extra pickling tank is necessary, it is not sufficient to split an existing pickling tank into 2 sections. It requires a big enough building (extra building), with acid proof floor surface, secondary containment and an extra pump system. Depending on the application also additional cover, exhaust system and scrubber for the extra cascade are necessary. [Com BG2]

Extra cost is highly dependent on the capacity of the line. Estimate: euro 0.2 - 0.5 million. [Com BG2]

**Driving force for implementation:**

**Reference literature:**

### **B.4.3.1.3 Evaporative Recovery of Hydrochloric Acid**

**Description:** see Chapter D.5.9.2

**Main achieved environmental benefits:**

- Reduction in fresh acid consumption, reduction in fresh acid production (resources, energy).

**Applicability:**

- New and existing plants.

**Cross-media effects:**

For HCl, **evaporation** of HCl is a technically available but rarely used because of the important investment and energy costs.

**Reference plants:**

**Operational data:**

### **B.4.3.1.4 Recovery of Free Acid Fraction**

**Description:** see Chapter D.5.9.1

**Main achieved environmental benefits:**

- Reduced consumption of fresh acid.
- Reduced spent acid (waste).

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### B.4.3.1.5 (External) Regeneration of Spent Acid

**Description:** see Chapter D.5.10

**Main achieved environmental benefits:**

- Reduction of acidic waste.

**Applicability:**

- Regeneration plants require a minimum capacity, a minimum amount of spent acid to be treated which is far beyond the spent acid generated at a single wire plant.
- Wire industry depends on outside contractors for the recycling of spent acid.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### B.4.3.1.6 Reuse of Spent Acid as Secondary Raw Material

**Description:**

The chemical industry uses spent acid as a secondary raw material for the production of  $\text{FeCl}_3$  and, to a minor extent, for pigments. The possibility to recycle spent acid for the production of valuable chemicals is available in many regions in Europe. Some contractors impose or have to impose strict limits for some metal impurities in the spent acids. A few contractors have recently developed and patented special processes to remove e.g. Zn or Pb from some types of spent acid. [CET-BAT]

**Main achieved environmental benefits:**

- Reduction of acidic waste.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### B.4.3.1.7 Optimized Rinsing Procedure and Cascade Rinsing

**Description:**

Counter-current cascade rinsing in combination with measures like to minimize dragout by installing suited wiping device (air-knife, pad, drip-bar etc.), continuously monitor rinsing water quality, use of recuperated water / reuse rinsing water in other application.

**Main achieved environmental benefits:**

- Reduced water consumption, lower water treatment costs [Com BG2].
- Reduces carry-over of Fe-ions into the flux bath (increases life span of flux baths, reduces carry-over of Fe into zinc bath).

**Applicability:**

- New and existing plants.
- For existing plants available space might be a limiting factor.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### **B.4.3.2 Fluxing**

#### **B.4.3.2.1 Good Housekeeping and Bath Maintenance**

**Description:**

An excessive Fe-concentration in the flux bath causes drag-in of Fe into the zinc bath. Each kg of Fe entering the zinc bath causes the loss of 25 - 30 kg Zn by formation of dross. Therefore iron content should be kept at a low level (e.g. by sufficient rinsing and wiping in the rinsing step) and be controlled carefully. [CET-BAT]

A flux-bath should not have an over-flow; waste water from flux-baths should be limited to once or a few times per year for reasons of maintenance and cleaning. This can be reached easily by minimizing drag-in of rinsing water. In this way, overflow of ammonia to the waste water treatment is avoided. (Note: ammonia is not removed by the typical physicochemical waste water treatment at a wire plant.) [CET-BAT]

The flux consumption can be optimized by correct wire preparation, by frequent control of flux-salt concentration in the flux bath, etc. As it is much easier to put continuously just the right amount of flux on a wire than on a complex piece, flux concentration and consumption are much lower in wire galvanizing than it is in batch galvanizing. As a result, excessive formation of dust and flux fumes can be avoided on a well maintained wire galvanising line and it is possible to achieve low dust and metal emissions without the use of a filter. [CET-BAT]

**Main achieved environmental benefits:**

- Increased lifespan of flux bath.
- Reduced waste (dross) and emissions in the following galvanizing step.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### B.4.3.2.2 Regeneration of Flux Baths (on-site)

**Description:**

Through drag-in of rinsing water into the flux bath and through corrosion of the wire, Fe(II) is brought into the flux bath. Fe(II) is converted to Fe(III) through oxidation by oxygen absorbed from the ambient air. Fe(III) precipitates as Fe(OH)<sub>3</sub>. After several weeks or months, the line is stopped and Fe(OH)<sub>3</sub> is allowed to settle. The resulting sludge is disposed off; the liquid phase is returned to the flux bath.

If oxidation by ambient air is insufficient, then either the drag-in of Fe(II) can be reduced (see B.4.3.1.7) or other oxidation methods can be used (H<sub>2</sub>O<sub>2</sub> see D.7.1.1 or electrolytic oxidation see D.7.1.2).

If build-up of Fe(OH)<sub>3</sub> is too fast to be handled by occasionally stopping of the line, the sludge can be separated continuously in a settler.

**Main achieved environmental benefits:**

- Reduced amount of spent flux bath.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data and Economics:**

The goal is bringing the amount of spent flux to a very low level or possibly eliminating any production of spent flux. Many wire plants achieve this by prevention (minimizing drag-in of Fe(II)) rather than by investing in regeneration technology. A comparison between flux baths in a typical batch galvanizing plant and in a wire galvanizing plant learns that drag-in of Fe(II) per m<sup>2</sup> surface to be galvanized in a wire plant is roughly 2 - 5 % of the value in a batch galvanizing plant. In cases where the amount of spent flux can be kept very low by minimizing drag-in, investment in a regeneration unit may not be justified.

**Driving force for implementation:**

**Reference literature:**

### B.4.3.2.3 Re-utilization of Spent Flux Baths (off-site)

**Description:**

Spent flux baths are sent off-site, usually to flux agent producers, for re-cycling. The salts in the spent flux solution can be re-used for flux agent production.

**Main achieved environmental benefits:**

**Applicability:**

**Cross-media effects:**

**Reference plants:** Th. Goldschmidt, Germany

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **B.4.3.2.4 Enclose Flux Bath**

A flux solution (a heated watery solution of a mixture of  $ZnCl_2$ ,  $NH_4Cl$  and possibly other salts) emits only water vapour.

The flux bath could be covered with a hood or bath cover - This can have an advantage in terms of minimization of heat losses, when the flux bath is heated. [CET-BAT]

Enclosed flux baths were not considered BAT because the vapour escaping from the baths is not really dangerous and the advantage for the environment is too small compared to the costs. [Com2 B]

#### **B.4.3.3 Hot Dipping (Galvanizing)**

##### **B.4.3.3.1 Zinc Bath: Good Housekeeping**

**Description:**

The most important house-keeping methods are:

- Maintain a protective layer (particulate material) or a cover on the zinc bath. This minimizes loss of zinc by oxidation, minimizes the formation of flux fumes and drastically reduces energy losses of the zinc bath.
- Any moisture dragged into the zinc bath evaporates explosively. This cause of zinc dust can be eliminated by having a dry wire at the inlet of the zinc bath. [CET-BAT].

**Main achieved environmental benefits:**

**Applicability:**

**Cross-media effects:**

**Reference plants:**

**Operational data:**

By good house-keeping methods, it is perfectly possible to run a hot dip galvanising bath at very low emissions of Zn and dust (below  $5 \text{ mg/Nm}^3$  Zn, below  $10 \text{ mg/Nm}^3$  dust). [CET-BAT]

**Economics:**

**Driving force for implementation:**

**Reference literature:**

##### **B.4.3.3.2 Emission Capture and Treatment of Extracted Air**

**Description:**

When for one reason or another, good house-keeping would is not sufficient to reach low Zn and dust emissions, a hood or cover above the Zn-bath, extraction of air and installation of a filter can be installed. [CET-BAT]

**Main achieved environmental benefits:**

**Applicability:**

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### B.4.3.3.3 Smoke-reduced Flux Agent

**Description:**

In smoke-reduced flux agents ammonia chloride is partly substituted by other alkali chlorides (e.g. potassium chloride).

**Main achieved environmental benefits:**

- Reduced air emissions.
- Reduced hard zinc.

**Applicability:**

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### B.4.3.3.4 Storage of Zinc-containing Residues

**Description:**

Zn-residues originate from the Zn-bath (top-dross, bottom dross, waste bath cover). These residues should be stored separately and protected from rain and wind. The wire industry depends on subcontractors for the final disposal and recycling of these residues. Normally Zn-containing waste is recycled by the non-ferro industry (Zn-smelters). [CET-BAT]

**Main achieved environmental benefits:**

**Applicability:**

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### B.4.3.3.5 Cooling Water after Zn-bath

**Description:**

The cooling water can be operated in closed circuit, using a wet cooling tower, air cooler or similar device. As the quality of this water is quite high, one could consider to give a second function to any stream leaving this circuit.

Any waste water of this cooling water circuit should be treated in such a way that contamination (mainly dissolved Zn) is removed in a satisfactory way prior to discharge. [CET-BAT]

**Main achieved environmental benefits:**

**Applicability:**

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**





## B.5 BEST AVAILABLE TECHNIQUES FOR CONTINUOUS COATING LINES

In understanding this chapter and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- Identification of the key environmental issues of continuous coating lines. Among the important issues are: acidic air emissions, wastes and waste water; air emissions from furnaces; energy consumption of furnaces; Zn-containing residues and oil- and chrome-containing waste waters.
- Examination of the techniques most relevant to address those key issues.
- Identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide.
- Examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques.
- Selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this chapter that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous chapter. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical

characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this chapter are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

This chapter discusses the best available techniques for reducing the environmental impacts from continuous coating lines. Where possible, the structure follows the logic of the production line and identifies BAT for individual processing stages. However, some measures, especially primary or preventive measures, cannot be assigned to one single process step and have to be allocated to the plant as a whole. As far as possible and wherever the data available allowed, emission levels, efficiencies or recirculation rates are given as an indication of the improvement that can be expected by implementation of the techniques. For a number of techniques the obvious positive effect cannot be described by an exact number, but some of these techniques are nevertheless considered as BAT.

Unless stated otherwise the emission figures presented in the following BAT chapters are daily mean values. For emissions to air they are based on standard conditions of 273 K, 101.3 kPa and dry gas.

Discharges to water are indicated as daily mean value of a flow-rate-related 24-hour composite sample or a flow-rate-related composite sample over the actual operating time (for plants not operated in three shifts).

## B.5.1 Galvanizing of Sheet

For the best available techniques in pickling, refer to the BAT chapter of Part A/Cold Rolling Mills.

For **degreasing** operations in continuous galvanising plants, the following techniques are considered to be BAT:

- Cascade degreasing.
- Cleaning and recirculation of degreasing solution; appropriate measures for cleaning are mechanical methods and membrane filtration as described in Chapter A.4.
- Treatment of spent degreasing solution by electrolytic emulsion splitting or ultrafiltration to reduce the oil content; separated oil fraction should be reutilized, e.g. thermally; the separated water fraction requires treatment (neutralisation etc.).
- Covered tanks with extraction and cleaning of extracted air by scrubber or demister.
- Use of squeeze rolls to minimize drag-out.

The best available techniques for the reduction of emissions and energy consumption of **heat treatment furnaces** are considered to be:

- Low-NO<sub>x</sub> burners with associated emission levels of 250 - 400 mg/Nm<sup>3</sup> for NO<sub>x</sub> (3 % O<sub>2</sub>) without air preheating and 100 - 200 mg/Nm<sup>3</sup> for CO.
- Combustion air preheating by regenerative or recuperative burners.  
No data were submitted on NO<sub>x</sub> concentrations in connection with air preheating, but the figures given for reheating furnaces may serve as an indication. Limiting the preheating temperature may be seen as a NO<sub>x</sub> reduction measure. However, the advantages of reduced energy consumption and reductions in SO<sub>2</sub>, CO<sub>2</sub> and CO have to be weighed against the disadvantage of possible increased emissions of NO<sub>x</sub>.

or

- Preheating of strip.
- Steam production to recover heat from waste gas.

The **hot dipping** zinc bath is a source of zinc-containing residues, dross or hard zinc. BAT for these residues is separate collection and external recycling in the non-ferrous metals industry.

In installations where **galvannealing** is done, BAT to reduce emissions and energy consumption are:

- Low-NO<sub>x</sub> burners with associated emission levels of 250 - 400 mg/Nm<sup>3</sup> for NO<sub>x</sub> (3 % O<sub>2</sub>) without air preheating.
- Regenerative or recuperative burner systems.
- No data were submitted on NO<sub>x</sub> concentrations in connection with air preheating, but the figures given for reheating furnaces may serve as an indication. Limiting the preheating temperature may be seen as a NO<sub>x</sub> reduction measure. However, the advantages of reduced energy consumption and reductions in SO<sub>2</sub>, CO<sub>2</sub> and CO have to be weighed against the disadvantage of possible increased emissions of NO<sub>x</sub>.

Post-treatments of steel, such as oiling, phosphating and chromating, are done for protection. In **oiling**, oil fumes are generated, which are best reduced by:

- Covering the strip oiling machine.

or

- Electrostatic oiling.

The environmental impact from **phosphating** and **passivation/chromating** can be reduced by the following BAT:

- Covered process baths.
- Cleaning and reuse of phosphating solution.
- Cleaning and reuse of passivation solution.
- Use of squeeze rolls.
- Collection of skinpass/temper solution and treatment in waste water treatment plant.

For **cooling** (machines etc.), separate cooling water systems operating in closed loops are considered BAT.

**Waste water** arises in sheet galvanising from the chemical treatment sections and from rinsing operations. Waste water also arises from strip cooling, contaminated by abrasion dust, and from

the water sprays which are used to keep working rolls in the skin pass mill clean and which is contaminated by Zn-containing abrasion dust and lubricating oil. These waste water streams require treatment by a combination of sedimentation, filtration and/or flotation/precipitation/flocculation. The techniques described in Chapter 4 or equally efficient combinations of individual treatment measures (also described in part D) are considered BAT. The associated pollutant concentrations in the effluent are:

SS:	< 20	mg/l
Fe:	< 10	mg/l
Zn:	< 2	mg/l
Ni:	< 0.2	mg/l
Cr <sub>tot</sub> :	< 0.2	mg/l
Pb:	< 0.5	mg/l
Sn:	< 2	mg/l

With some of the existing continuous water treatment plants, a zinc level of < 4 mg/l is all that can be achieved. In these cases the best option is to switch to batch treatment.

## B.5.2 Aluminizing of Sheet

Most BAT are the same as for hot dip galvanising. However, there is no need for a waste water treatment plant as only cooling water is discharged.

BAT for heating:

Gas firing. Combustion control system

## B.5.3 Lead-Tin Coating of Sheet

Best available techniques for lead-tin coating are:

- **Pickling tanks** are to be enclosed and vented to a wet scrubber packed tower, with pH control. Achieved HCl emission levels are well below 30 mg/Nm<sup>3</sup>. Waste water from the tower and tank must then pass through a waste water treatment plant.
- Enclosed **nickel plating** process, ventilated to a wet scrubber.
- For **hot dipping**, air knives to control coating thickness are considered to be BAT; they result in no emissions
- For **passivation**, BAT is a no rinse system and hence no rinse waters from the system require treatment. If a drier is required, this should be a gas-fired oven. No effluent produced.
- **Oiling** by an electrostatic oiling machine.
- To treat process effluents e.g. acids from pickling or waste waters from scrubber, a waste water treatment plant is required.. BAT for this type of process is sodium hydroxide solution, added in a two stage neutralising process with automatic pH control of the dosing rate. A flocculent is then added to assist settlement of the precipitated solids in a settlement tank. Clean liquor then flows from the tank to sewer, river etc. The filter cake is then passed through a filter press and disposed to landfill. Establishing a route for recycling would be a BAT but, to date, no route has been found for this material.

## B.5.4 Coating of Wire

For the reduction of air emissions from **in-line pickling**, enclosed equipment or equipment fitted with hoods and scrubbing of extracted air is considered BAT. The BAT-associated emission level is 2 - 30 mg/Nm<sup>3</sup>.

For the reduction of acid consumption in pickling lines, the following techniques are considered to be BAT:

- Cascade pickling for new installations above a certain capacity. For small lines, the extra investment in a second tank, piping and process control equipment is not justified. A threshold-capacity of 15 000 tonnes/year per line is proposed. Conversion of existing one-bath lines to cascade pickling is expensive. The cost is probably too high, when compared to the advantages.
- Recovery of free-acid fraction.
- External regeneration of spent acid for all installations.
- Reuse of spent acid as secondary raw material.

To reduce water consumption the following techniques are considered BAT:

- Cascaded rinsing, in combination with other methods to minimize water consumption, for all new and for all large installations (> 15 000 tonnes/y).

For smaller lines, most new installations include cascade rinsing, possibly in combination with other methods to minimize rinsing water consumption. At smaller existing lines, the choices are often limited, e.g. adding extra rinsing cascades could be impossible because of space constraints.

For the remaining waste water, waste water treatment is required. The BAT for waste water treatment of a wire plant consisting of a hot dip coating line and associated processes, is physico-chemical treatment (neutralisation, flocculation, etc.). Associated pollutant concentrations in the effluent are:

SS: < 20 mg/l  
 Fe: < 10 mg/l  
 Zn: < 2 mg/l  
 Ni: < 0.2 mg/l  
 Cr<sub>tot</sub>: < 0.2 mg/l  
 Pb: < 0.5 mg/l  
 Sn: < 2 mg/l [Com BG3]

To reduce waste and waste flux solution, the following techniques are considered BAT for **fluxing operations**:

- Good housekeeping with special focus on reducing iron carry-over and bath maintenance.
- Regeneration of flux baths on site (side-stream iron removal).
- External reutilization of spent flux solution.

Basically, good housekeeping measures as described in Chapter B.4 are also considered BAT for **hot dipping**. Emission levels that are associated with these BAT are dust < 10 mg/Nm<sup>3</sup> and Zn < 5 mg/Nm<sup>3</sup>. Additionally, collection of all Zn-containing wastes, separate storage and

protection from rain and wind, and reuse in the non-ferrous metals industry are considered BAT.

If **cooling water** is needed after the zinc bath, closed loop or reuse of this quite pure water as make-up water for other applications is considered to be BAT.

## **B.6 EMERGING TECHNIQUES FOR CONTINUOUS COATING LINES**

### **B.6.1 Coating of Sheet**

#### **B.6.1.1 Roll Coaters**

These are rolls for applying organic coatings or paintings that are nowadays replacing to the chromating surface treatment. If compatible with the high speed in galvanising, this application improves notably the environmental performance in the finish stage, because there are not effluents with chromic products. [Com-CC-2]

#### **B.6.1.2 Vacuum Vapour Deposition**

This coating method is a physical process to deposit evaporated metal on base metal in a vacuum ( $< 50$  Pa). Metallic vapour is produced, mainly, by one of two processes: resistant heating and electron-beam bombardment.

A production line with zinc vapour deposition was developed by Nisshing Steel Company and Mitsubishi Heavey Industry Company in Japan, and commercial products have been produced since 1987. This production line works with a resistance heating system.

The production process is as follows: pre-treatment furnace, seal roll, coating chamber and evaporation bath. In the production line, the reducing furnace system of the galvanising line is adopted as a pretreatment process. [Com-CC-2]

##### **Physical Vapour Deposition (PVD)**

Strictly speaking the above process belong to this one. But nowadays several different processes coming from PVD are being investigated.

The PVD process can be used for the deposition of pure ceramic coatings (as well as metals and alloys). At least one of the constituents is physically evaporated from solid within the vacuum chamber. In the most advanced processes the sample to be coated is made the cathode in a glow discharge of the evaporated metal and gas atomic species. Thus, for example, titanium can be evaporated in nitrogen to produce titanium nitride. The benefit of the ionisation which results in the glow discharge is that the positively charged depositing species are accelerated to the sample surface and arrive with high energy, producing a dense, well adhered deposit. Also, since the energy is imparted at the surface, where it is needed, the process can be carried out at comparatively low bulk substrate temperatures ( $< 500$  °C). Thus, materials such as hardened high speed steel and hot working tool steels can be coated with pure ceramic films without being softened. There are various ways of producing the metal evaporant, such as electron beam guns, 'sputter' sources, and arc sources. The PVD process is highly flexible, permitting the deposition of virtually any material onto any other.

This method has become a lot of another evolution depending on the process to produce the vapour, but almost of them are only in experimentation field. [Com-CC-2]

#### **B.6.1.3 Passivation with Cr-free Products**

Cr-free passivation products are been studied in order to change the composition of those. The results of these studies have opened the possibility to a future change in the composition of

passivating solutions. The behaviour of alternatives has been good as primer (previous to an organic coating), but not so good as definitive protection. [Com-CC-2]

#### **B.6.1.4 Air-knives with Variable Profile**

This technique consists on a device with several metallic lamellas with an independent heating system. These can change the gap of the air-knives by means of a differential temperature in each part of the air-knives thus the coating profile is better controlled. This technique would produce a reduction of the consumption of the coating material, and improving of the quality in the thickness of the metallic layer and, then, and increase of the yield. [Com-CC-2]

#### **B.6.1.5 Application of the Fuzzy-logic for the Controlling of the Air-knives**

With an Artificial Neural Networks (ANN) software, the thickness gage would feedback the gap of the air-knives to optimize the coating. The system is designed as knowledge based system to learn from its previous experience. This technique would produce a reduction of the consumption of the coating material, and improving of the quality in the thickness of the metallic layer and, then, and increase of the yield. This is equivalent to a better energy efficiency. [Com-CC-2]

#### **B.6.1.6 Removing the Pot-roll (Catenary)**

When the strip leaves the snout, if it would be possible a strict control of the catenary traced by the strip, the pot-roll could be avoided.

##### **Removing the top-roll (air-cushion)**

After the bath, the strip go up to the cooling zone. In the first stage is advisable to avoid the contact of the strip anywhere whit other devices, because the coating temperature is still too high and could be marked the surface easily. This system consists on an air cushion on the top at the beginning of the cooling zone for this purpose. Thus, there are an increase of the quality and yield of the line. [Com-CC-2]

#### **B.6.1.7 Core-less Pot**

This pot is an induction system itself.

#### **B.6.1.8 Cooling by Micro Water Sprayed at the Cooling Tower**

With this device we can reduce the size of the cooling tower. This implies a reduction of the mechanical parts, rolls, etc. In the same way, there are a reduction of the probabilities of marks, oil-leaks, etc.



## **B.6.2 Coating of Wire**

### **B.6.2.1.1 Ultrasound Cleaning**

For removing smut from over-etched high carbon steel wire, smut = fine particle carbon compounds layer on surface, leading to rejection of the wire --- waste

### **B.6.2.1.2 Combined Electrolytic and Ultrasound Cleaning for Scale Removal**

Emerging:

as alternative to acid pickling

using neutral aqueous solutions of sodium sulphate, sodium chloride and sodium tripolyphosphate, with Anodic or cathodic D.C. electrolysis or P.R. (periodic current reversal)



## B.7 CONCLUDING REMARKS

The following conclusions and recommendations concern timing of the work, sources of information, availability and quality of data, consensus amongst experts of the TWG and recommendations for future work.

### Timing of work

The drawing up of this BREF took about 2 ½ years. The major steps have been:

- First TWG meeting (kick-off meeting) 11 – 12.12.97
- Submission of relevant information and data by TWG:
  - for Chapters 2 February – October '98
  - for Chapters 3 April – October '98
  - for Chapters 4 July – October '98
- First draft December 1998
- First consultation round 16.12.98 – 12.2.99
- Evaluation of comments and redrafting:
  - (*response to comments, clarification and request for additional information*) May – July '99
- Submission of missing information/data: September – November '99
- Second draft December 1999
- Second consultation 17.12.99 - 17.02.00
- Second TWG meeting 22 – 24.03.00
- Submissions on controversial issues that came up during the 2<sup>nd</sup> TWG meeting: 28.03.00 – 19.07.00
- Consultation on 'new' chapters (*revised Chapters 5, Chapter 7 Conclusions & Recommendations, Executive Summary, Chapter 4: SCR and SNCR*) 21.07.00 – 18.08.00
- Final draft

### Sources of information

65 reports dealing with the various aspects of the ferrous metals processing sector were submitted. These reports contain very different kinds of information (statistical data, description of production technologies, information on certain environmental measures including case studies and emission/consumption data). They have been prepared from different points of view; most of them only focusing on single aspects or media, only very few covering all environmental aspects.

During the period of work on the Ferrous Metals Processing BREF, industry shadow groups on hot rolling, cold rolling and continuous coating and the European General Galvanizers Association (EGGA) provided reports and papers on their sectors regarding the applied production techniques and some environmental measures. Germany submitted a report on 'BAT in the German Ferrous Metals Processing Industry'.

The availability of such documents is essential for the quality of the document, but their usefulness is potentially compromised if they are not sent in early in the process. Delays in submitting crucial information, especially on the techniques to be considered in the determination of BAT, have led to delays in issuing drafts of this BREF.

### Best available techniques

BAT have been identified for all three sub-sectors of ferrous metals processing and for the individual production steps. They are described in detail in the three Chapters 5 providing background and, where necessary, justification for selection as BAT and for the reported BAT-associated emission levels. The executive summary includes all these BAT conclusions.

### Level of consensus

Part A of this BREF contains several split views. There were three areas in which the TWG could not reach an agreement:

- BAT-associated dust levels for application of fabric filters/electrostatic precipitators
- SCR and SNCR NO<sub>x</sub> reduction measures for reheating furnaces
- S-content in fuel oil

On dust emissions, the TWG agreed that capturing and fabric filters are BAT, but there were two general points of view on what is achievable with fabric filters. Industry proposed, based on their experience and knowledge of achieved dust levels, the higher level of 20 mg/Nm<sup>3</sup>. Some Member States and environmental NGOs considered below 5 mg/Nm<sup>3</sup> to be the appropriate associated level for fabric filters, but there were only very few figures and for most applications no data presented to support this view (see also recommendations for future work).

Information and data on SCR and SNCR in reheating furnaces was received at a very late stage of the work; during and after the second TWG meeting. Some TWG members considered these techniques to be BAT, while others thought the available information on technical details and on economics was not sufficient to allow a final decision to be made on whether or not SCR and SNCR are BAT. As this controversy was raised almost at the end of this exercise, there was no time to resolve the outstanding issues (see also recommendations for future work).

Another point of dissent was the issue of limiting S-content in fuel oil. Although a level of S < 1% can lead to emissions as high as 1700 mg SO<sub>2</sub>/Nm<sup>3</sup>, some TWG members thought that this should be BAT. Others regarded a lower S-limit in the fuel oil or additional SO<sub>2</sub> reduction measures as BAT.

Parts B and C of this BREF enjoy a high level of consensus. No split views had to be noted. All parties in the information exchange process consider them an acceptable result.

### Recommendations for future work

A lack of data and information on the performance of techniques to be considered in the determination of BAT, especially on achieved emission and consumption levels and on economics, was noted as a flaw of this BREF document. For future BREF reviews, all TWG members and interested parties should continue to collect these data and information and should make them available earlier rather than later in the process.

For quite a number of the techniques to be considered in the determination of BAT, no information or only a technical description is available. Information on reference plants and actual performance data are scarce. For the revision of this document the missing information should be provided. Some of the techniques concerned are the following:

Part A:

- Optimized water pumps for laminar flows
- Implementation of degreasing bath cascades
- Hot water pre-degreasing
- Heat utilisation for heating degreasing bath
- Electrostatic oiling
- Optimization of oil spray
- Optimized finishing operation
- Cleaning and reuse of grinding emulsion
- Exhaust system (PRETEX/SBT)
- External use of spent acid pickle liquor

## Part C:

- Storage and handling of raw materials and auxiliaries
- Capture/treatment of emissions from tube finishing operations

## Part D:

- Implementation of degreasing bath cascades
- Hot water pre-degreasing
- Adsorption of surfactants and oil (precipitation followed by filtration)
- Electrolytic pickling
- Treatment of rinsing water using ion exchange, electrolytic iron removal, reverse osmosis, oxidizing iron removal

Several techniques are presented in the Chapters 6 ‘Emerging Techniques’. The progress in development and the suitability for application in the FMP sector should be checked for a potential move of these techniques to Chapter 4 ‘Techniques to be considered in the determination of BAT’ and/or to Chapter 5 ‘Best Available Techniques’.

The criticism was made that the presentation of some techniques was too positive, having been derived mainly from suppliers’ information, and that only the advantages were presented. This mainly concerns reclamation and regeneration processes for spent treatment baths, e.g. for spent pickling liquors or spent degreasing or flux baths. Here industry is requested to provide the information and results they have achieved with certain techniques, together with descriptions of any problems they have experienced.

There is a need for more emission and consumption data generally, but of particular interest are figures on NO<sub>x</sub> emissions (concentrations and specific emissions) both for furnaces that use air preheating and those that do not. Such data would make possible both a more thorough evaluation of the efficiency of reduction measures and a comparison of the advantages and disadvantages of energy savings vs. NO<sub>x</sub> emissions.

More data are required on achieved dust emission levels for the various production steps of hot and cold rolling (Part A), where a split view on the BAT-associated dust level had to be stated in the BREF. Especially, those parties advocating the lower level of 5 mg/Nm<sup>3</sup> should seek to provide data to substantiate their view.

It was reported that the number of installations applying SCR (pusher type furnaces) is likely to increase. When this BREF is reviewed, there should be more information available on the performance and applicability of SCR and SNCR for reheating furnaces. Existing SCR and SNCR installations will have a longer operating history to draw on, which should help to answer the criticism that the information available was based on too short an operating period. Possibly the disagreement on whether these techniques constitute BAT can be resolved then.

During the 2<sup>nd</sup> TWG meeting the point was raised that inductive heating was BAT for several applications in furnaces. In this BREF, inductive heating is included as a technique to be considered, but it was stated that the information available was not sufficient to decide whether the technique is BAT. More information and data should be collected to enable this decision to be made.

Another issue raised was the dioxin content of dust from batch galvanizing and potential risks of dioxin build-up when these dusts are recycled. Efforts should continue to compile information and data of actual dioxin contents in dusts for normal plant operation. Available data should be provided to the IPPCB and the TWG to allow a judgement on this problem and enable an evaluation of the potential risk.

A revision of this BREF document is recommended for the year 2005.



## **PART C**

### **Batch Galvanizing**





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## Best Available Technique Reference Document on Ferrous Metals Processing

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## C.1. GENERAL INFORMATION ON BATCH GALVANIZING

General galvanizing is a service industry, offering the application of zinc coating corrosion protection to steel fabricators or the users of fabricated steel products. The sector operates with short lead times and short order books to give enhanced service to customers. Distribution issues are important, and so plants are located close to market concentrations. Consequently, the industry consists of a relatively large number of plants, servicing regional markets in order to minimize distribution costs and increase economic efficiency. Only a few 'niche' operators are prepared to transport certain classes of fabrication for longer distances in order to exploit their special expertise or plant capability. Opportunities for these specialist operators are limited.

About 600 galvanizing plants with more than 30000 employees are distributed throughout the EU, as shown in Table C.1-1.

Member State	Number of plants in 1997	Steel Galvanized [t/a]
<b>Austria</b>	17	132916
<b>Belgium</b>	22	263268
<b>Denmark</b>	17	122500
<b>Finland</b>	19	73360
<b>France</b>	69	690105
<b>Germany</b>	185	1428610
<b>Greece</b>	4	n.a
<b>Italy</b>	74	810716
<b>Luxembourg</b>	1	n.a.
<b>Netherlands</b>	21	242717
<b>Portugal</b>	9	42368
<b>Spain</b>	35	314509
<b>Sweden</b>	34	120000
<b>United Kingdom (+ Ireland)</b>	88	738928
<b>Total:</b>	<b>595</b>	<b>4979997</b>
Note: Source of data [EGGA5/98], [EGGA/99]		

**Table C.1-1: Distribution of galvanizing plants in the EU**

The zinc consumption of the EU galvanizing industry (excluding Greece and Luxembourg) in 1997 was 381188 t. The main galvanizing countries are Germany with of 27.5 % of the production, Italy with 15.6 %, UK/Ireland with 14.2 % and France with 13.3 %. [EGGA/99]

In recent years the markets for galvanized steel have grown more rapidly than previously. The share of total market accounted for by various market sectors is shown in Table C.1-2.

Market	Tonnage [t]	Percentage [%]
<b>Construction</b>	2022886	39.0
<b>Infrastructure and highways</b>	832634	16.1
<b>Power transmission</b>	531042	10.2
<b>Agriculture</b>	524586	10.1
<b>Transport</b>	308786	6.0
<b>Fasteners</b>	254056	4.9
<b>Other</b>	712264	13.7
<b>Total</b>	<b>5186254</b>	<b>100.0</b>
Note: Source of data [EGGA/99];		

**Table C.1-2: Market segmentation for Galvanized Steel**

Industry turnover is estimated at EUR 1800 million per year. The capacities of the most economic operating units are related to the size of the steel fabrications to be treated and to the demand in the accessible market. Most companies in the sector are small or medium sized enterprises financed by private capital. Integration into the zinc production or steel fabrication industry is very unlikely. About half of the European capacity is in the hands of businesses that own one or two plants. Larger companies, owing up to 20 plants, have emerged in some Member States. Even so, the assets of these groups are widely distributed in order to service regional markets and the opportunity for concentration of productive capacity is limited. [EGGA5/98]

In recent years the cost of entry has risen, reflecting greater capital intensity arising from use of improved technology and increased environmental control. This has discouraged the entry of poor quality, short life operators. On the other hand, the sector is highly competitive as to price and quality of service. [EGGA5/98]

In general, the sector enjoys reasonable economic success but it is occasionally subject to price pressures because of over-capacities in some markets and variations in the price of zinc.

A significant part of recent investment has been spent on emission control measures. The hot dip galvanizing process gives rise to zinc-containing waste/by-products such as zinc skimmings and dross. These are recycled as raw material to the secondary zinc industry for the recovery of the valuable zinc. Aqueous process streams which contain zinc are either treated on-site for the extraction of metals before the aqueous stream is discarded, or aqueous blow down is removed from site by specialist contractors for further recovery treatment. [EGGA5/98]

## C.2. APPLIED PROCESSES AND TECHNIQUES IN BATCH GALVANIZING

### C.2.1 Batch Hot Dip Coating Overview

Hot dip galvanizing is a corrosion protection process in which iron and steel fabrications are protected from corrosion by coating them with zinc. Prevalent in batch hot dip galvanizing is job galvanizing - also referred to as general galvanizing - in which a great variety of input materials is treated for different customers. Size, amount and nature of the inputs can differ significantly. The galvanizing of pipes or tubes, which is carried out in semi- or fully-automatic special galvanizing plants, is usually not covered by the term job galvanizing.

The items to be coated in batch galvanizing plants are steel fabrications, such as nails, screws and other very small items; lattice grates, construction parts, structural components, light poles and many more. Tubes are sometimes also galvanized in conventional batch coating plants. Galvanized steel is used in construction, transport, agriculture, power transmission and everywhere that good corrosion protection and long life are essential. [EGGA5/98]

Figure C.2-1 shows the sequence of operations in a batch galvanizing, which usually comprises the following process steps:

- Degreasing.
- Pickling.
- Fluxing.
- Galvanizing (melt metal coating).
- Finishing.

A galvanizing plant essentially consists of a series of treatment or process baths. The steel is moved between tanks and dipped into the baths by overhead cranes.

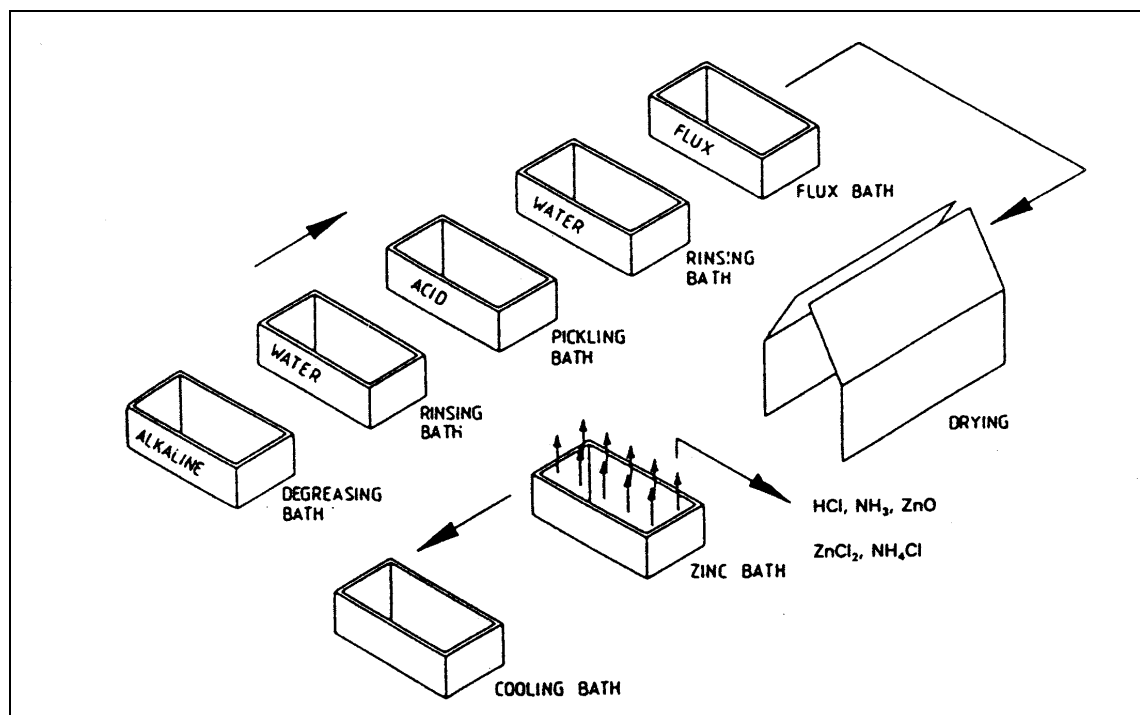


Figure C.2-1: Typical process flow for a general galvanizing plant [Galva94-1]

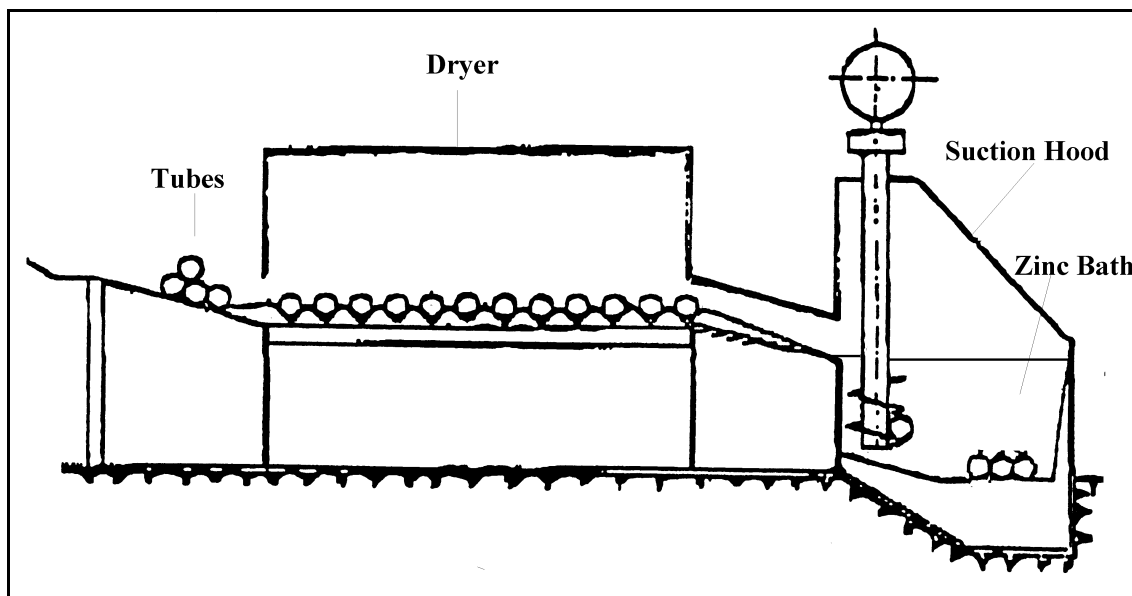
There are two basic plant layouts, distinguished by the design of the pre-treatment section: open- and closed pre-treatment.

Galvanizing plants with open pre-treatment locate pre-treatment vats and the other process operations in one bay. In these cases pickling baths are operated at room temperature to avoid air emissions (acid fume) and the associated corrosion of installations.

Galvanizing plants with dedicated, tightly enclosed pre-treatment sections are designed to operate pickling baths at elevated temperatures and thus reduce the number of pickling vats and the pickling time. Fume generated from the acid vats is collected and, in some cases, cleaned by suitable abatement devices.

For some special applications the galvanizing bath can be operated at elevated temperature using ceramic lined kettles instead of steel kettles; this process variation is referred to as 'high temperature galvanizing'.

Installations for tube galvanizing represent a special type of galvanizing plant, in which tubes are quasi-continuously coated. The handling of tubes in these plants is partly or fully automated. Figure C.2-2 shows the dipping principle of such plants.



**Figure C.2-2: Principle of tube galvanizing**  
[Welzel]

The principal pre-treatment steps are the same as for general galvanizing, but following the coating the excess zinc is removed from the outside of the tubes by blowing with compressed air. The excess zinc on the inside is removed by watersteam pressure pulse.

Although the basic technological principles have remained unchanged over the past 150 years, some developments have taken place mainly to improve the coating quality of reactive steels or small parts. Research has been done on adding V and Ti to the molten zinc bath and on developing a zinc-tin coating. Technigalva, with the addition of approximately 0.03 to 0.08 % Ni to the zinc bath, has been applied for some time now at full industrial scale. Zinkopal, in which a zinc-aluminium coating for small parts is used, was developed in Germany, where one plant is in operation. [Galva-97-1], [Com EGGA]



## C.2.2 Raw Material Handling

Zinc is received in bulk form and stored close to the galvanizing process. Chemicals, principally 28 % HCl, an input to the pickling process, are received in plastic or glass containers or by road tanker, and are stored according to manufacturers' directions. Other agents, such as mist suppressants and degreasing fluids, are similarly received in drums and stored according to manufacturers' directions. Materials for processing, consisting of a wide variety of steel fabrications, are received on site, usually by road haulage, and are unloaded by forklift truck or crane. [EGGA5/98]

## C.2.3 Preparation of the Input

Steel fabrications are inspected to ensure they are suitable for galvanizing. Iron and steel castings and some threaded components are abrasive blast cleaned before pickling. To handle fabrications throughout the galvanizing process they are attached to jigs or strongbacks by means of hooks or steel wire. Fasteners and other small components are loaded into perforated baskets, which are attached to the jigs. [EGGA5/98]

## C.2.4 Degreasing

To guarantee satisfactory galvanizing and to enhance the performance of filtering separators, a degreasing step is used to remove traces of coolants and lubricants from the fabricated steel. This is commonly done using **alkaline degreasing** baths. These baths contain surfactants, which remove oil and grease from the metal surface by emulsifying. The resulting unstable emulsions float on the surface of the bath and can be removed by gravitational separators, skimmers, micro- or ultrafiltration etc.

Concentration, bath temperature and immersion time of the work-pieces determine the efficiency of the degreasing baths. The normal temperature range for indirectly heated degreasing baths is 30 - 70 °C, although in some cases hot degreasing is applied at a temperature of about 85 °C. The baths consists of a sodium-hydroxide solution (1 - 10 %) plus other alkaline reagents, such as soda, sodium silicate, condensed alkaline phosphates and borax, and specific surfactants, emulsifying agents and dispersion agents.

An alternative method is **acidic degreasing**. Degreasing baths consist of diluted, strong inorganic acids, like hydrochloric acid and/or phosphoric acid with additives. Acidic degreasing agents usually form stable oil emulsions which obstruct bath maintenance measures such as skimming, separating, centrifuging or ultrafiltration. [ABAG]

When degreasing is skipped or when insufficiently degreased work-pieces enter the process flow, there is a risk of organic pollutants being carried over to subsequent process steps, possibly leading to organic pollution in the flux fume arising from the galvanizing kettle during dipping. Organic pollutants in the waste gas lead to operational problems with filtering precipitators (clogging etc.) and make the recycling of precipitated dusts difficult or even impossible. [EGGA5/98], [ABAG]

Degreasing may only be omitted if the input material is oil-free, which is the exception rather than the rule in batch galvanizing.

After degreasing, rinsing is necessary to prevent carry-over of degreasing agents which would shorten the life of pickling baths and reduce the re-usability of the bath.

## C.2.5 Pickling

To remove casting skin, roll skin, grid or scale the items are pickled in diluted hydrochloric acid. Therefore a galvanizing plant usually comprises a series of pickling baths with different acid concentrations ranging from 2 - 16 %, normally 12 – 16 % when freshly prepared. To prevent excessive pickling of steel items, especially in pickling high tensile steels, and to protect the steel pickling vats, pickling inhibitors (e.g. hexamethylenetetramine) are added to the bath. [EGGA5/98], [ABAG], [Com EGGA]

During operation the iron content of the pickling bath increases, while the amount of free acid decreases, making it necessary to top up the bath occasionally by adding fresh acid. Iron-(II)-chloride has a limited solubility in HCl. When this maximum is reached, pickling becomes impossible, but usually the pickling bath has to be replaced even sooner at lower  $\text{FeCl}_2$  concentrations. Discarding concentrations of 170 g  $\text{FeCl}_2/\text{l}$  (=75 g  $\text{Fe}^{2+}/\text{l}$ ) and 100 to 120 g  $\text{Fe}/\text{l}$  have been reported. [EGGA5/98], [ABAG], [Com EGGA], [Com DK]

Raising the temperature of the pickling bath can enable its use at relatively high concentrations of  $\text{FeCl}_2$ , e.g. 175 to 200 g/l with the bath at 35° C, with some increase in emissions. [Com2 EGGA]

Operators sometimes degrease articles with less heavy deposits of oil in the pickle tank. This practice may lead to an increased pickling time, greater volumes in discarded pickling bath per tonne of product and increased consumption of zinc. This practice cannot be considered as environmentally friendly.

Pickling in plants with open pre-treatment is usually done at ambient air temperature; plants with an enclosed pre-treatment sometimes operate with higher acid temperatures. Gaseous emissions of the pickling agent can arise from the pickling baths, depending on concentration and temperature of the bath, and from the pickled items. Hydrogen vesicles formed during the pickling process can also contain acid droplets. [EGGA5/98], [VDI-RL 2579]

## C.2.6 Stripping

Sometimes it is necessary to clean the suspension devices of zinc coatings, to remove faulty coatings from steel fabrications or to de-zinc fabrications whose coatings have to be renewed. This is commonly done by dipping in diluted pickle acid.

When pickling and stripping are carried out in the same treatment vat, pickle liquors are created which contain iron- and zinc chloride. Some galvanizers operate separate pickling and stripping baths because in their technical and economic environment, this favours recycling of the zinc contained in them. Spent stripping liquor can be either treated on site for zinc recovery or sent off-site to a contractor for zinc recovery.

In some cases spent stripping liquor is sent for neutralisation and disposal by external contractors. [Com2 Wedge]

## C.2.7 Rinsing

Rinsing is a very important step in the galvanizing process as it prolongs the life of subsequent treatment baths, reduces the generation of waste and increases the re-usability of by-products. After degreasing and pickling the fabricated steel is therefore rinsed/dipped in water baths, which are sometimes heated.

Carry-over of solution between baths depends on the type of work (i.e. its capacity for fluid retention) and the way in which it is handled, especially the drainage time permitted above a bath before the work is moved. The quantity of liquid carried-over can vary between 5 and 20 l/t black steel. Carry-over of degreasing solution into the pickling baths eventually leads to neutralisation of the bath; carry-over of acids and iron salts from pickling into the flux baths and further to the galvanizing pot would increase both the generation of hard zinc (dross) and the consumption of zinc. A carry-over of 1 g of iron results in about 25 g of hard zinc. [Com EGGA], [ABAG], [Com2 EGGA]

Water from rinsing can be used to prepare fresh pickling or degreasing baths as a way of recycling water and minimising aqueous blowdown.

## C.2.8 Fluxing

The purpose of fluxing is to enable liquid zinc to wet the surface of the steel, a necessary prerequisite for the galvanizing reaction, and with ammonium chloride-containing fluxes, to provide additional pickling (cleaning of the surface) during hot dipping. At temperatures of above 200 °C the ammonium chloride in the flux decomposes into  $\text{NH}_3$  and  $\text{HCl}$ , which results in an additional pickling effect. [EGGA5/98], [ABAG]

Fluxing is carried out in two different ways: dry and wet.

In **dry fluxing**, the steel is immersed in a fluxing bath, usually an aqueous solution of zinc chloride and ammonium chloride, typically maintained at 40 - 80 °C. Cold fluxing is possible but reduces the potential for air-drying of the work after removal from the flux bath. Typical bath characteristics are:

ZnCl <sub>2</sub>	150 - 300 g/l
NH <sub>4</sub> Cl	150 - 300 g/l
Density:	1.15 – 1.30 g/ml
Dissolved iron:	< 2 g/l

The pH-value of flux baths is normally adjusted to approximately 4.5 to secure precipitation of iron ions as iron(III)-hydroxide; but the pH of flux baths may be in the range of 1 to 5.0.

The total concentration of flux salt (sum of zinc chloride and ammonium chloride) and the ratio of the zinc chloride to ammonium chloride are both very important. Ammonium chloride in a typical good flux often accounts for 40 – 60 % of the total flux salt. [Com DK]

Ammonium chloride provides quick drying and better removal of iron oxides from the surfaces of the items, but also causes more fume, ash and dross formation during the coating process. When the pre-treatment of the workpieces is insufficient, more ammonium chloride is required. Zinc chloride prevents oxidation of the work-piece surfaces. This is particularly important when the drying time is long. Altogether, the optimum flux concentration and composition must be adjusted to the particular circumstances. [Com DK]

The iron content of the flux bath is extremely important for process control, economy and environment. A high concentration of iron in the flux (originating from drag-out from the pickling bath) will also influence the quality of the zinc coating. Iron carry-over from the flux bath to the zinc kettle will generate dross and may also increase the final thickness of the zinc layer for many steel grades. [Com DK]

To reduce the environmental impact of ammonium chloride during dipping, some galvanizers have changed to 'smoke-reduced' fluxes in which ammonium chloride has partly or completely been substituted by potassium chloride. [ABAG]

After withdrawing the work-pieces from the flux bath, some of the water from the adhering fluxing fluid evaporates. The extent of evaporation depends on the temperature of the flux bath and, if the bath is hot, the rate of removal of work from the bath (slower removal gives more evaporation). Further drying is sometimes achieved in dedicated drying. Exhaust gases from the galvanizing kettle can sometimes be a useful indirect source of heat to such a drying unit, although ancillary burners are often also used. Drying of the work helps reduce splashing and ejection of metal from the zinc bath as the work is dipped, a benefit which is increased if the work retains heat after leaving the dryer, i.e. if preheat is applied. [Com2 EGGA]

A small number of galvanizing works, especially those with exceptionally demanding fluxing requirements for intricate parts, operate an alternative process, called **wet fluxing**. In this process the fluxing agents flow as a layer of molten salt on the surface of the galvanizing bath. Steel parts to be galvanized are passed through the flux layer into the zinc bath. Then the molten salt layer is drawn back from the surface by means of a rake to allow the steel parts to be withdrawn from the galvanizing bath without further contact with the flux. [EGGA5/98]

### C.2.9 Hot Dipping

The fluxed steel fabrications are slowly lowered into a bath of molten zinc. With very long items, which do not fit in the kettle, double dipping has to be applied to cover the whole surface. The steel reacts with the zinc to form a coating consisting of a series of zinc-iron alloy layers topped by a layer of pure zinc when the parts are withdrawn from the bath. The period of immersion varies from several minutes for relatively light steelwork up to 30 minutes for the heaviest structural parts. [EGGA5/98]

The molten zinc has a temperature of 440 - 475 °C. Kettle dimensions vary greatly, depending on the market served and the type of fabrication treated. Typical dimensions are 7 m long by 1.4 m wide by 2.6 m deep, but kettles as long as 20m and as deep as 4 m are in use. The kettle, enclosed by the furnace casing, is installed in a pit or at floor level with access platforms. The kettle is normally heated externally, commonly by gas or oil-fired burners. Heating by immersion burners or by canopy heaters is used when the zinc temperature is above about 460°C (and a steel kettle cannot be used) or where there is insufficient kettle wall surface to transfer heat into the melt. Where economically viable, electrical heating is used, usually via radiation from the sides or top, occasionally also by induction or resistance. [EGGA5/98], [Com2 EGGA], [Com2 Fin]

The zinc bath usually also contains very small amounts of other metals, which either are impurities of the zinc input or are added as alloying elements. A typical bath composition is:

- Zinc                    98.9    wt-%
- Lead                    1.0    wt-%
- Iron                    0.03   wt-%
- Aluminium            0.002 wt-%
- Cadmium              0.02   wt-%
- Traces of other metals (e.g. tin, copper)

Aluminium and lead are added because of their influence on the thickness and the appearance of the coating. The addition of lead (from 0.1 to 0.15 per cent) has an influence on the physical properties of zinc, especially viscosity and surface tension. It helps to wet the steel before galvanizing and the zinc to flow from the surface after galvanizing. Lead can also be used to protect the kettle. In this case the molten zinc floats on a layer of molten lead on the bottom of the kettle. The thickness of the kettle's steel walls is measured on a regular basis to prevent breaking. [ABAG], [Com2 EGGA]

Where steel kettles are used, it is important that the kettle material (typically low-carbon steel with minimal additions of reactive elements such as silicon) is correctly chosen so as to reduce the effect of zinc attack, and that it is manufactured to withstand the high hydrostatic loads and thermal stresses generated during heat-up to operating temperature. Steel kettles internally clad to resist zinc attack can be obtained, but are significantly more expensive. [Com2 EGGA]

A small number of plants carry out 'high temperature galvanizing' using refractory lined vessels, which allow the zinc bath to be operated at higher temperatures, usually about 530 °C. This process is required to treat certain classes of steel (steel grades) and specific types of components. [EGGA5/98]

Ammonium chloride, a component of the flux agent, has a sublimation temperature below the zinc bath temperature, and this, together with the other reactions taking place, cause fumes to be generated during hot dipping. Galvanizing kettles are generally contained in a vented enclosure or ventilated by a lip extraction system. Commonly, the ventilation air is cleaned in bag filters and the precipitated dust is shipped off-site for recovery of valuable substances, namely flux agent. In some cases the precipitated dust is sent for landfill [Com2 Wedge] Some operators apply venturi scrubbers and use the scrubber blowdown for flux solution make-up. [EGGA5/98], [Com2 EGGA]

Reactions of zinc with steel, either from the fabrications that are being galvanized or from the kettle itself, lead to a build-up of zinc-iron alloy in the bath, which is known as hard zinc or dross. Dross can adhere to the walls of the bath, but mostly accumulates at the bottom where it is periodically removed using a submerged scoop or grab. Excess dross may interfere with galvanizing and may cause over-heating of an externally-heated kettle. The material removed is returned to the secondary zinc industry for recovery of the zinc content or to the zinc chemicals industry for the manufacture of zinc oxide. [EGGA5/98], [Com EGGA], [Com2 EGGA]

Zinc ash is formed at the surface of the zinc bath due to the reaction of zinc with oxygen in the air and with the flux. The oxidized material is removed and is reused directly in the plant or returned to the secondary zinc industry for recovery. [EGGA5/98], [GE6], [Com2 FIN]

## C.2.10 Finishing

Steel fabrications are withdrawn from the zinc bath; excessive zinc is removed by wiping or, in some cases, by rattling. The fabrications are then cooled and inspected. Small surface imperfections are repaired and the fabrications are removed from the jigs and made ready for dispatch. After hot dip coating some steel products are quenched in water to give them special properties. As protection against white rust, the products may be covered with oil emulsions or may be chromated.

In galvanizing fasteners and small components, a perforated steel basket containing the components is immersed in liquid zinc in the usual way. When the basket is withdrawn from the liquid zinc it is placed into a centrifuge system. Excess zinc coating is removed by centrifugal force. The galvanized components are ejected from the basket and cooled, while the basket is returned to the process. Proprietary and custom built systems are known. [Com2 EGGA]

When galvanizing tubes and pipes, the outside is blown-off with compressed air, the inside with steam to remove excess zinc after withdrawal from the zinc bath. During removal of excess zinc with steam, zinc dust is emitted, but the zinc particles can be collected and returned to the zinc baths or be utilized in the secondary zinc industry for zinc recovery. [EGGA5/98], [GE6]



### C.3. PRESENT EMISSION AND CONSUMPTION LEVELS IN BATCH GALVANIZING

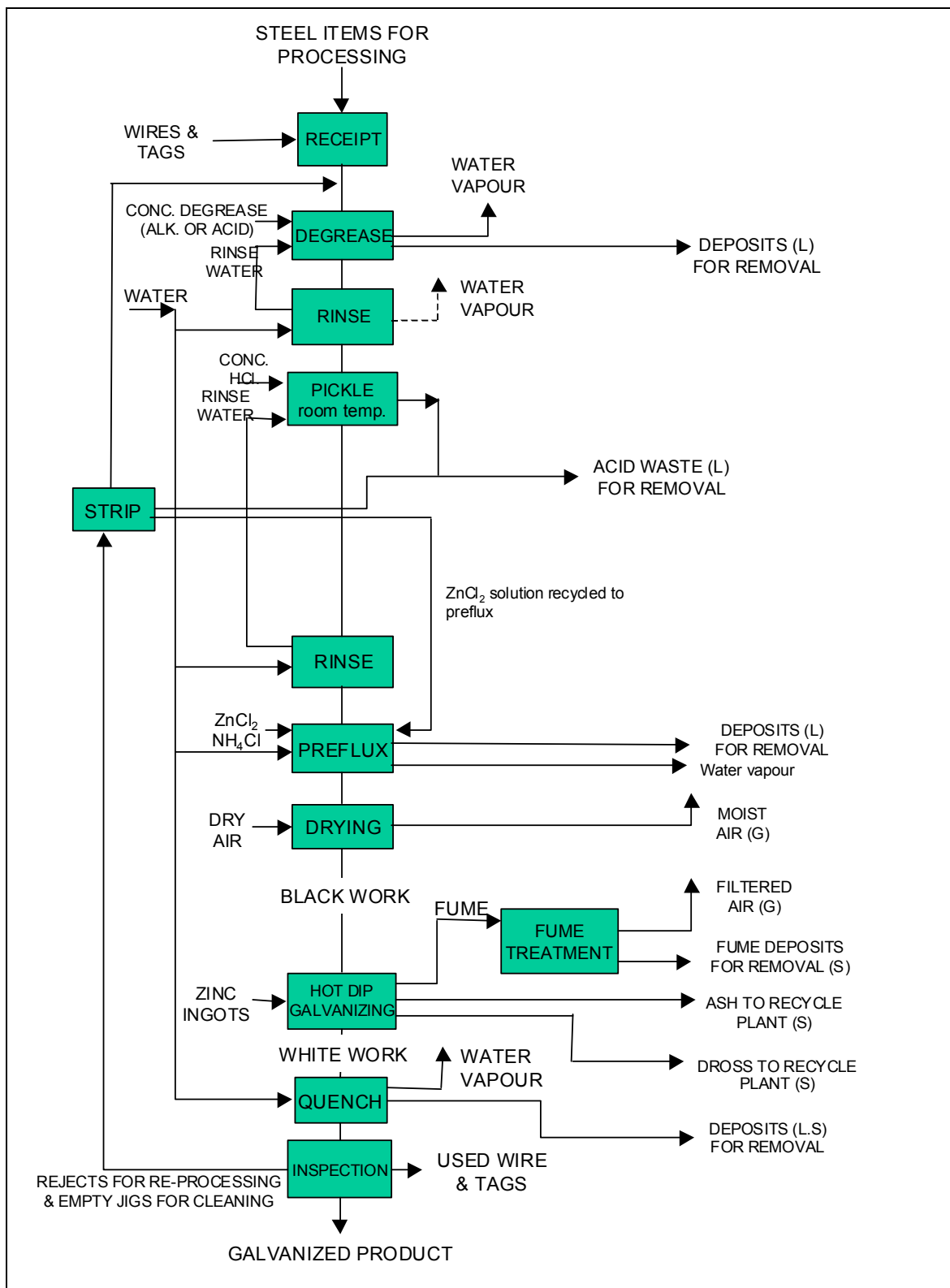


Figure C.3-1: Material flow sheet for general galvanizing plants

Many different factors influence the consumption of resources and the emission of pollutants and wastes for general galvanizing plants. Variations between plants are caused by: variations in the nature of the steel inputs such as size, shape and most of all, cleanness; the type of kettle used; the heating devices; the process flow and the degree of regeneration and reuse of materials in the process.

Environmental impacts to be expected from general galvanizing are emissions to air and the generation of waste, in most cases classified as hazardous. Waste water and emissions to water are a declining problem, as it is possible nowadays to run general galvanizing plants almost waste water free. [DK-EPA-93] Finland reported waste water discharge from water baths and floor washing with zinc contents of 5 – 25 mg/l and pH-value of 6 – 10. [Com FIN] Although waste water discharge is only a minor issue, zinc in surface water run off might have to be considered.

Sources of emissions to air are: the pre-treatment section, mainly from pickling operations; the molten zinc surface, especially during the dipping process, and the firing/combustion systems for heating of the zinc kettle or other treatment vats.

Wastes and by-products arising from batch galvanizing are zinc-containing dross and ash as well as spent treatment liquors and sludges from the maintenance of the baths. [DK-EPA-93] During transportation of the fabrications from one treatment bath to the other, fluids (acid, flux etc.) may drop from the work-pieces. This spillage is usually caught by drip pans and can either be recycled or collected as chemical waste.

The overall energy consumption for galvanizing fabricated steel is 300 - 900 kWh per tonne of product with the major part being spent on heating the zinc melt. [DK-EPA-93] The following chapters give more detailed information on consumption of resources and emissions from the characteristic processing steps of general galvanizing.

### C.3.1 Degreasing

Degreasing baths are made up of degreasing agents and water. The energy needed for heating the baths to operating temperature is supplied by oil or gas or as electrical energy, depending on local conditions for each individual plant. In many cases the degreasing systems are heated by waste heat recovery and heat exchange.

Degreasing results in chemical waste in the form of discarded baths and sludge. The amount of spent degreasing liquor to be discarded depends on the quantity of steel degreased and the degree of pollution. It correlates with the maximum working lifetime of the degreasing solution, which is usually 1 - 2 years. [ABAG] Other sources report a maximum lifetime of degreasing baths of up to 7 years. [Com EGGA], [Com2 EGGA]

Used alkaline degreasing baths contain sodium hydroxide, carbonates, phosphates, silicates, surfactants and free and emulsified oil and grease. Used acidic degreasing baths contain, apart from free and emulsified oil and grease, diluted hydrochloric and/or phosphoric acid, emulsifiers and corrosion protection inhibitors.

Spent degreasing baths are usually chemically and physically treated by special contractors (disposal companies). The emulsion is split into an oil-rich and an oil-poor phase. The aqueous, low-oil part is further treated, while the oil-rich part has to be disposed according to waste regulations. [ABAG]



Input / Consumption Level		
Degreasing agent	0 - 4	kg/t
Water	0 - 20	l/t
Energy	0 - 44.6	kWh/t
Output / Emission Level		
	Specific Emission	Concentration
Liquor and sludge <sup>1,2</sup>	0 - 5.4	kg/t
Oily sludge <sup>3</sup>	0.16	kg/t
Discarded degreasing bath	1 - 2	kg/t
Note: Source of data [EGGA5/98], [DK-EPA-93]		
<sup>1</sup> Contains discarded degreasing bath.		
<sup>2</sup> Typically 30 - 40 % solids.		
<sup>3</sup> Sludge periodically withdrawn from degreasing bath, single plant data [ABAG]		

Table C.3-1: Consumption and emissions from degreasing activities

### C.3.2 Pickling

Pickling baths are set up by diluting HCl, which is usually delivered at a concentration of 28 - 32 % w/w (or approx. 320 – 425 g/l HCl) to working concentration, typically 15 % w/w (or approx. 160 g/l HCl). In some cases pickling inhibitors are added. Average consumption of acid is about 20 kg per tonne product, but it is affected by the quality of the steel input: very low consumption rates (e.g. less than 10 kg/t) can be achieved for clean fabrications as against high consumption rates (up to 40 kg/t) for rusty parts. Pickling baths are usually operated at ambient air temperatures, so no energy is needed for heating. In the case of enclosed pre-treatment pickling, the solution temperature may be up to approximately 40° C. In this case the baths must be heated. Other energy consumptions in the pickling process result from the operation of auxiliary equipment such as pumps and cranes, although this may be considered negligible. [EGGA5/98], [Com2 EGGA]

Hydrogen chloride emissions arise from the pickling baths in different quantities, depending on the temperature and the concentration of the bath. These acid fumes are usually diffuse emissions. Extraction measures (e.g. lip extraction) or flue scrubbing are generally not applied, as general plant ventilation keeps the concentration of HCl in the workplace air below permitted limits [ABAG]. Special cases are plants operating enclosed pre-treatment sections, which sometimes operate with higher acid temperatures. Here the enclosure is extracted and the waste gas is usually scrubbed.

Wastes generated in pickling are spent pickle liquor and sludge. Spent pickle liquor consists of free acid, iron chloride (up to 140 - 170 g Fe/t), zinc chloride, alloying elements of the pickled steel and, sometimes, pickling inhibitors. Where stripping and pickling are done in the same bath, mixed pickle liquor is generated, with high zinc and iron contents. If degreasing is done in the pickling bath, free and emulsified oil and grease are present as well. The average composition of spent pickling baths are given in Table C.3-2.

	Pickling	Pickling (including stripping)
<b>Iron</b> (as FeCl <sub>2</sub> ) <sup>1</sup>	< 140 g/l	< 140 g/l
<b>Zinc</b>	5 - 10 g/l <sup>2</sup>	20 - 40 g/l
<b>HCl</b> (free acid)	30 - 50 g/l	30 - 50 g/l
<b>Pickle inhibitor</b>	approx. 50 ppm (1 l inhibitor per 20 m <sup>3</sup> pickle liquor)	
<b>Oil, grease, surfactants</b>	n.a. (carry-over from degreasing baths)	

Note: Source of data [ABAG]  
<sup>1</sup> Ratio of FeCl<sub>3</sub>: FeCl<sub>2</sub> is about 1:50 according to [ABAG], while [Com DK] reports the ratio of FeCl<sub>3</sub>: FeCl<sub>2</sub> is < 1:1000.  
<sup>2</sup> Requirements set by recycling companies are usually more stringent.

Table C.3-2: Composition ranges of spent pickle baths

Input / Consumption Level		
<b>Hydrochloric acid</b> <sup>1</sup>	9.2 – 40 <sup>2</sup>	kg/t
<b>Inhibitor</b>	0 - 0.2	kg/t
<b>Water</b> <sup>3</sup>	0 - 35	l/t
<b>Energy</b> <sup>4</sup>	0 - 25	kWh/t
Output / Emission Level		
	Specific Emission	Concentration
<b>Emissions to air:</b> <sup>a</sup>		
<b>Hydrogen chloride Dust</b>		0.1 – 5 mg/m <sup>3</sup> 1 mg/m <sup>3</sup>
<b>Waste acid and sludge</b> <sup>5,6,7</sup>	10 - 40	l/t
<b>Discarded pickle liquor</b>		

Note: Source of data [EGGA5/98], except a: [DK-EPA-93]  
<sup>1</sup> Consumption refers to 30 % HCl  
<sup>2</sup> [Flem BAT] reports up to 70 kg/t without reference to acid concentration  
<sup>3</sup> Lower end of the range represents cases in which the acid is delivered in lower concentrations or in end concentration (~ 16 %)  
<sup>4</sup> Energy needed for acid heating in enclosed pre-treatment plants.  
<sup>5</sup> Includes discarded spent pickle bath  
<sup>6</sup> Containing about 140 g Fe/l-spent bath as FeCl<sub>2</sub>  
<sup>7</sup> Acid waste reported by DK: 15 – 50 kg/t.[DK-EPA-93]

Table C.3-3: Consumption and emissions from pickling

### C.3.3 Stripping

The amount of items to be stripped, rejected galvanized items, suspension devices and fabrications whose coatings need to be renewed, ranges 1 -15 kg/t.

Stripping of workpieces is done using hydrochloric acid baths usually with lower concentrations and reactivity similar to those required for pickling. Some operators use partly spent pickle liquors or use the pickling bath for stripping but, as described later on, this leads to a number of environmental disadvantages.

Stripping operation using hydrochloric acid also generates waste acids, but with a different composition from those originating from pickling. If stripping is carried out in an acidic bath separate from the pickling baths then zinc chloride relatively uncontaminated by iron chloride is generated in the stripping bath. This solution can be recycled to the preflux (zinc ammonium chloride) bath. [Com FIN], [Com2 EGGA]

Iron chloride- and zinc chloride-containing solutions from combined pickling and stripping can be used in the fertilizer industry. Although attention has to be paid to zinc addition to

agricultural soils and the fact that statutory limits are not exceeded. [Com FIN], [Com2 UK Galv]

<b>Stripping</b>	
Iron (as FeCl <sub>2</sub> )	< 10 % of zinc content <sup>1</sup>
Zinc (as ZnCl <sub>2</sub> )	160 - 200 g/l
HCl (free acid)	< 10 g/l
Pickle inhibitor	approx. 50 ppm (1 l inhibitor per 20 m <sup>3</sup> pickle liquor)
Oil, grease, surfactants	n.a. (carry-over from degreasing baths)
Note: Source of data [ABAG]	
<sup>1</sup> Required by recycling company, can only be achieved by use of pickle inhibitors.	

**Table C.3-4: Composition range of spent stripping baths**

<b>Input / Consumption Level</b>		
<b>Hydrochloric acid</b>	0 - 6	kg/t
<b>Water<sup>1</sup></b>	0 - 7	l/t
<b>Output / Emission Level</b>		
	<b>Specific Emission</b>	<b>Concentration</b>
<b>Spent strip liquor<sup>2</sup></b>	1.2 -15	kg/t
Note: Source of data [EGGA5/98]		
<sup>1</sup> For adjusting pickle bath concentrations.		
<sup>2</sup> Example composition: zinc 200 g/l, iron 130 g/l, 10 g/l [DK-EPA-93]		

**Table C.3-5: Consumption and emissions from stripping**

### C.3.4 Fluxing

The flux bath is made up of the flux agent (usually ZnCl<sub>2</sub> x NH<sub>4</sub>Cl) and a certain amount of water to yield the right concentration. The flux agent is sometimes formed using KCl in place of some or all of the NH<sub>4</sub>Cl. In most cases, energy is needed to heat the flux baths, for which some operators use recovered heat.

Air emissions from fluxing baths are considered negligible, as the bath does not contain volatile compounds and the main emission is water vapour. Waste arising from fluxing operation includes discarded fluxing liquor and sludge. [DK-EPA-93]

Flux baths which are not continuously regenerated increase in acidity and iron content as they are used. They contain (depending on the flux agent) ammonia chloride, zinc chloride and /or potassium chloride. Batch recycling of preflux solution is common practice. In some cases used solution is returned to the preflux producer on a regular basis. [Com EGGA], [Com2 EGGA]

Input / Consumption Level	
Flux agent	0 - 3 kg/t
Water <sup>1</sup>	0 - 20 l/t
Energy	kWh/t
Output / Emission Level	
Spent flux	1 - 6 kg/t
Waste water and sludge <sup>1</sup>	0 - 20 l/t
Iron hydroxide sludge <sup>2</sup>	
Note: Source of data [EGGA5/98]	
<sup>1</sup> Lower end of the range refers to wet fluxing.	
<sup>2</sup> From continuous flux bath regeneration.	

**Table C.3-6: Consumption and emissions from fluxing**

Dryers located downstream of the preflux bath consume energy in heating the drying air. Some or all of this energy may be supplied from the flue of the galvanizing furnace. Moist air leaving the dryer to atmosphere (either inside or outside the factory) carries chlorides with it. Surplus preflux solution drips off the work into the dryer where it dries into crystalline form and is periodically removed. Where large fans are used to blow air through dryers they may require significant amounts of electrical energy and may cause noise. [Com2 EGGA]

### C.3.5 Rinsing I + II

General galvanizing plants consume 0 to 20 l/t of galvanized steel for rinsing operations, resulting in about the same amount of waste water and sludge. [EGGA5/98]

### C.3.6 Hot Dipping

The main raw material input for the dipping process is, of course, the coating metal zinc. The average consumption of zinc for 1 t of galvanized steel is 75 kg. Extreme figures in zinc consumption - high or low - can be attributed to the shape of the fabricated steel and the quality of the coating. Zinc consumption is, of course, proportional to the surface coated and the thickness of the coating. [EGGA5/98]

Gas, oil or electric energy provides the energy necessary for melting the zinc and maintaining the temperature of the zinc bath.

The galvanizing kettle is one of the major sources of emissions to air. During dipping, vapour, gas and particulate pollutants rise from the zinc bath and can be seen as a white cloud. Depending on the fluxes, the emissions comprise extremely fine sublimation and vaporisation products including ions of chlorine, ammonia and zinc, as well as the compounds zinc oxide, zinc chloride and ammonium chloride.

The kind and amount of emissions depend on the consumption of the flux, its composition and additional factors determined by the parts to be galvanized (kind, number, surface area/quality) and their pre-treatment (degreasing, pickling, rinsing, drying). Some sources reported the size of hygroscopic particles to be very small, mostly < 1 micron. While others reported that the average particle size was 30 microns and only about 5 % being < 1 micron [Com2 FIN].

According to some recently completed investigations on the distribution of particle sizes in airborne particulate emissions from the galvanizing bath following dipping of steel, there are no health concerns over particle size and mass of emissions to which galvanizing operators may be

exposed during the process of galvanizing. The investigation showed that the personal exposure monitoring data of the operators is both low in total mass, especially so in the case of 'low - fuming fluxes' or 'smoke reduced fluxes' and that the mass of small particles of less than 1 micron diameter is the same for both normal fluxes and 'low fuming fluxes'. Therefore there are no health concerns between the different flux types and no concerns over the size of the airborne particulate in any event. [Piat 19.9]

Less than 10% of the total mass ,itself less that 1.5 mg/m<sup>3</sup> in total, of the particulate is less than 1 micron.

In summary all health concerns are of not an issue.

The amount of dust emitted is closely related to the consumption of flux agent. Some investigations have shown that at a flux consumption of 2 kg/t the dust emission was between 0.2 and 0.3 kg/t, while the emission of dust with a flux consumption of 4 kg/t was approximately 1.2 kg/t of product. The dust concentration in the crude waste gas from dry galvanizing often reaches more than 100 mg/m<sup>3</sup>. With wet galvanizing the figures are even higher; a typical range is 80 to 180 mg/m<sup>3</sup>. If, as a result of process upset, the degreasing operation is inefficient, it is possible for oil or grease to enter the zinc bath and be subject to low temperature combustion. In this case the filter dust may contain up to 10 % grease and dioxins may be detected. [ABAG], [DK-EPA-93], [Galva94-1], [Com EGGA]

The waste gas is either treated in fabric filters, resulting in filter dust, or is scrubbed, giving rise to aqueous effluent which is normally treated. In addition to dust, small volumes of gaseous substances such as hydrogen chloride and ammonia are emitted, originating from the decomposition of the flux agent and recombination of ammonium chloride as airborne particulate [Com2 UK Galv]. Furthermore, the combustion of fuels to heat the galvanizing furnace results in emission of combustion products such as CO, CO<sub>2</sub>, and NO<sub>x</sub> (also, with oil combustion, SO<sub>x</sub>). Combustion air fans and burners may produce noise. [DK-EPA-93], [Com2 EGGA]

During dipping, zinc-containing solid by-products such as hard zinc, ash and squirts arise. **Hard zinc** (or **dross**) is enriched in the zinc bath during operation and originates from the galvanized work-pieces, from the vessel walls (reaction product of iron in the steel with the molten zinc) and from reaction of iron salts carried over from pickling and fluxing. Because of its higher density hard zinc collects at the bottom of the kettle from where it is periodically removed. Because of the high zinc content (95 to 98 %) the dross is sold to recycling companies for recovery.

**Zinc ash** with a lower density, floating on the surface of the galvanizing bath, consists mainly of zinc oxide and zinc chloride, with some aluminium oxide if alloyed to the metal bath. Ash is skimmed off before removing the dipped work-pieces, usually carrying large amounts of zinc out as well. Zinc content is 40 to 90 % and makes it valuable for recycling either directly in the plant by secondary zinc industry. [ABAG], [Com2 Wedge], [Com2 FIN]

From time to time small amounts of metallic zinc are ejected from the kettle, as a result of evaporation of moisture from the surface of the steel. They mostly adhere to the fume extraction equipment (if existing) from which they are removed for recovery of their metallic content. [Com EGGA] **Splashed zinc** can be remelted directly in the galvanizing bath or be sent for recovery off site. It may contain zinc oxide and/or be contaminated by hitting the floor if the kettle is not enclosed. [ABAG]

Input / Consumption Level		
Zinc	20 – 200 <sup>(1)</sup> kg/t	
Recovered Zinc (zinc ash)	0 - 15 kg/t	
Energy <sup>(2)</sup>	180 - 1000 kWh/t	
Output / Emission Level		
	Specific Emission	Concentration
Extracted gas from kettle <sup>(2)</sup> (suction hoods, encapsulation etc.)	1500 - -12000 <sup>(3)</sup> m <sup>3</sup> /t	
Emissions to air from zinc pot: <sup>a</sup>		
Dust	40 –600 g/t	10–100 <sup>(4)</sup> mg/m <sup>3</sup>
Zinc		2 – 20 <sup>(5)</sup> mg/m <sup>3</sup>
Hydrogen chloride		1 - 2 mg/m <sup>3</sup>
Lead	negligible	
Ash	4 - 25 kg/t	
Dross	5 - 30 kg/t	
Combustion gas: (NO <sub>x</sub> , CO/CO <sub>2</sub> , SO <sub>2</sub> )	500 - 3250 m <sup>3</sup> /t	
Filter dust <sup>(6)</sup>	0.1 - 0.6 kg/t	
Note: Source of data [EGGA5/98], except a: [DK-EPA-93] <sup>1</sup> extremely high Zn consumption maybe referred to galvanizing of very small parts, like bolts. Average: 73.4 kg/t <sup>2</sup> usually no abatement techniques applied, discharge via a stack <sup>3</sup> some data from DK state 20000 – 40000 m <sup>3</sup> /t <sup>4</sup> Other sources report 1- 3 mg/m <sup>3</sup> [Flatt/Knupp] <sup>5</sup> DK reports one example of a manual production line where 60 mg/m <sup>3</sup> of zinc where measured at a volume flow of 1500 m <sup>3</sup> /h. [DK-EPA-93] <sup>6</sup> Composition depends on flux agent, but basically it is ammonia chloride, zinc chloride and possibly Al, Fe, and organic compounds		

Table C.3-7: Consumption and emissions from the zinc kettle

### C.3.7 Finishing

#### Tube Galvanising

The removal of excess zinc from tube surfaces, by blowing compressed air or watersteam, leads to emissions of zinc and zinc containing dusts. The steam pressure pulse may also be a source of noise. Therefore the zinc blow-off is done into soundproofed collecting containers.

In those cases where quenching of galvanized work-pieces is inevitable, water consumption is up to 10 l/t of galvanized steel. The water is partly evaporated, partly re-used for making up process baths.

## C.4. TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BAT FOR BATCH GALVANIZING

### C.4.1 Storage and Handling of Raw Materials and Auxiliaries

→ No information submitted.

### C.4.2 Degreasing

#### C.4.2.1 Minimization of Oil and Grease Input

**Description:**

Customers of galvanizing plants should be persuaded to oil and grease their items as little as possible. Reducing the oil/grease input is a cheap, easy and effective measure to prolong the life of degreasing baths and thus reduce the amount of waste generated (spent bath and oily sludge).

**Main achieved environmental benefits:**

- Reduced spent degreasing baths.
- Reduced waste water and sludge.

**Applicability:**

- New and existing plants (the influence of the galvanizer on the state of the input material may be limited in job galvanizing).

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### C.4.2.2 Optimized Bath Operation

**Description:**

General measure to control degreasing bath operations by monitoring bath parameters such as temperature and concentration of degreasing agent, can be used for optimizing degreasing activities and thus make efficient use of the degreasing bath. Furthermore, degreasing efficiency can be improved by enhancing the contact of liquor and workpiece: e.g. by moving the workpiece, by moving the bath (agitation) or by using ultrasound. Cascade degreasing can also improve operation and reduce environmental impact.

**Main achieved environmental benefits:**

- Reduced spent degreasing baths.
- Reduced waste water and sludge.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### C.4.2.3 Maintenance and Cleaning of Degreasing Baths

**Description:** see also Chapter D.4.3

In alkaline degreasing the emulsions formed are unstable. Oil and grease readily conglomerate again and form a layer floating on the surface in still areas of the bath (i.e. where there is no degreasing bath current). Here the conglomerate can be separated and withdrawn by means of **skimmers, discharge launders, weirs** etc. With these measures, simply using natural gravity (separating time: a couple of hours), the life of degreasing baths can be prolonged by 2 to 4 times. Sludge withdrawn contains oils, grease, degreasing agent, scale, rust, dust etc. and is usually disposed of. [ABAG]

Separation is more effective using **centrifuge separators**, which split the oil and water phases within seconds. Very small oil and grease drops are separated more easily; the oil-rich part contains only 5 - 10 % water and unwanted carryout of degreasing chemicals is prevented. The life of the baths can be prolonged by up to 16 times. [ABAG]

In **micro- and ultra-filtration** the degreasing bath is pumped through membranes (3 - 8 bar) in which oil, grease and spent surfactants are held back due to the size of the molecules. To protect the membranes, the degreasing liquid is usually cleaned from particles in a settling tank. Micro- and ultra-filtration increase the lifetime of the bath by 10 to 20 times. The investment costs for micro-/ultra-filtration with the appropriate capacity for galvanizing plants are estimated at 80000 to 100000 DM. The membranes (pore size) have to be adjusted to the characteristic of the degreasing bath and have to match the cleaning requirements for each individual bath. With the ever changing conditions usually observed in job galvanizing (variation in contents, surfactants, oils, grease etc.), operational problems occur, like clogging, fouling and damage to the membrane. [ABAG] Appropriate membranes and specific bath chemistry have yet to be developed to allow application in batch hot dip galvanizing. [Com2 D]

All measures described above to prolong the life span of degreasing baths are also applicable to acidic degreasing baths, but due to the more stable emulsions formed, efficiency is reduced. [ABAG]

**Main achieved environmental benefits:**

- Reduced spent degreasing baths.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

- Generates oily sludge/concentrate (refer to C.4.2.5).

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**



### C.4.2.4 Continuous Biological Degreasing of the Degreasing Bath ('Biological Degreasing')

#### Description:

Oil and grease, accumulated in the degreasing bath, are decomposed by micro-organisms. The waste product is biological sludge which is drained off the system daily. The degreasing bath will get an unlimited service life, and the bath will provide optimum degreasing at any one time. [DK-EPA-93]

The degreaser liquid is based on alkali, phosphates, silicates and nonion- and kation-active tensides. A concentrate of these chemicals and micro-organisms is mixed continuously. In the degreasing tank itself, air is admitted to keep the biological processes going. Water is also added to compensate for the evaporation loss, as the bath is kept at the optimum operating temperature of 37 °C. The liquid from the degreaser tank is circulated across a lamellar separator at a rate of approx. 1 m<sup>3</sup>/h. In the lamellar separator the accumulated sludge consisting of a mixture of live and dead microorganisms (biosludge) is separated off. The sludge (approx. 10 l/d) is drained off manually via a bottom valve. The dosing of chemicals is performed by dosing pumps in the outlet box downstream of the lamellar separator. It may be difficult to be totally accurate, and excess consumption will probably be common. Dosing of required chemicals, is automatically controlled to maintain a pH value of 9.13. [DK-EPA-93]

#### Main achieved environmental benefits:

- Reduction of waste (spent degreasing bath) and thus of treatment sludge.

#### Applicability:

- New and existing galvanizing plants.

#### Cross-media effects:

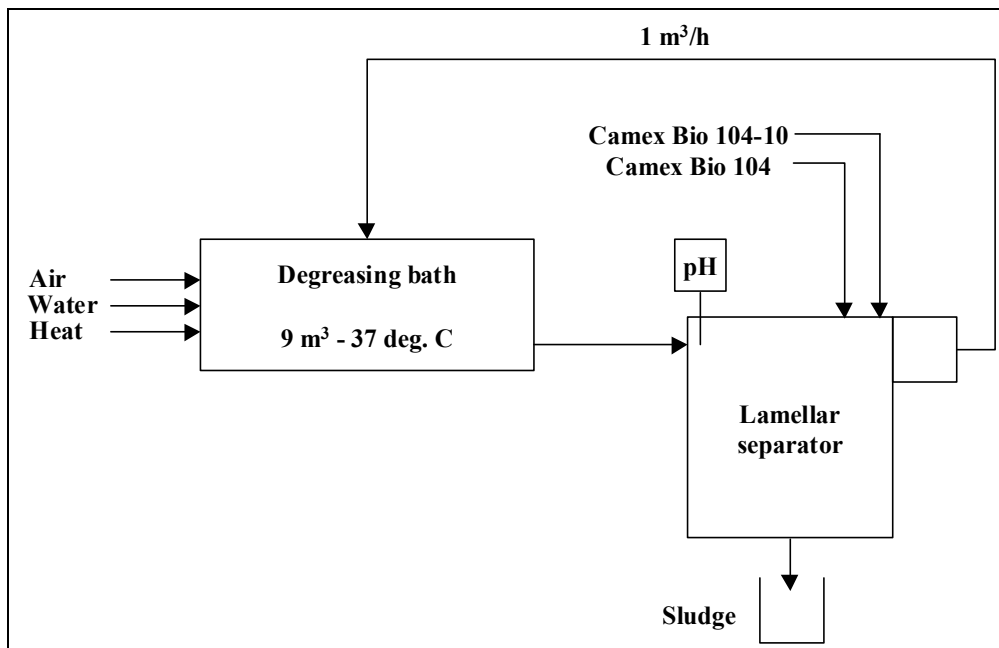
#### Reference plants:

Næstved Varmforzinkning ApS (period of experience: 6 years) [DK-EPA-93]; France; Verzinkerei Dieren, NL; 1 or 2 plants in Germany

#### Operational data and economics:

##### Example Næstved Varmforzinkning

Næstved Varmforzinkning introduced the process in 1987 and the operational experience is very positive (see Figure C.4-1). Today the degreasing is much more efficient and consistent than when they degreased in warm caustic soda lye and this results in quicker pickling with less acid attack on the base material. Both the consumption of pickling acid and discarded waste have dropped. When pickling has been completed the surface is more even and uniform than before. This has in turn resulted in lower consumption of zinc in the hot-dip galvanizing process itself. The new degreasing process has meant that the plant has been able to reduce the zinc content of the pickling bath from 10 – 15 % to 4 – 8 %. This has greatly improved the occupational environment in the production hall in that the conventional "acid smell" has disappeared, by and large. In practice, the consumption of Camex Bio 104 has been about 6 times higher than expected (per tonne of products per year). This is probably due to both overdosing and a necessary additional consumption of chemicals for the heavily oiled items processed at the plant. Furthermore, the items have a very large surface per unit weight which requires more chemicals per tonne of products. The system is probably 3 - 6 times bigger than necessary for Næstved Varmgalvanisering. The company simply bought the smallest system for biological degreasing sold by the Swedish firm, Camex. [DK-EPA-93]



**Figure C.4-1: Flow sheet for biological degreasing (example CAMEX)**  
[DK-EPA-93]

#### Economics:

Capital costs (as of 1987) incl. installation, but excl. degreaser tank:	DKK	325000
Operational costs:		
Camex Bio 104: 1550 kg at DKK 26	DKK	40300
Camex Bio 104 - 10: 100 kg at DKK 26	DKK	2600
2.5 tonnes of sludge at DKK 2440	<u>DKK</u>	<u>6100</u>
Total per year excl. hours and electricity	DKK	49000

It is difficult to quantify the financial advantages to the plant as compared with the earlier process where they degreased in warm caustic soda lye. The consumption of acid and zinc have dropped considerably and fewer products are scrapped since they introduced biological degreasing. However, the savings are also caused by other changes in products and production during the period in question. It is therefore difficult to decide exactly what financial advantages the new degreasing process is offering. [DK-EPA-93]

#### Example Galvanizing plant, Germany [ABAG-Bio]

The galvanizing plant switched operation from acidic degreasing to biological degreasing in the period December 1994 to April 1995. The initial production line included an acidic degreasing bath, consisting of diluted phosphoric acid and HCl, tensides and corrosion inhibitors, followed by a rinse. The bath quality was maintained by removing the oil from the surface and refreshing the acidic bath liquor. The acidic degreasing was changed to alkaline degreasing followed by a biological rinse bath treatment. Reported advantages of switch of operation were:

- Reduced pickling time (20 – 25 %).
- Increased pickling quality.
- Reduced fresh acid consumption.
- Reduced rejects.
- Reduced oily sludge.

The investment cost (excluding investment cost for treatment vats) for change of operation were reported to be 181000 DM for a galvanising plant with a capacity of 10000 tonnes per year. The energy consumption was increased (higher temperature of degreasing and biological rinse bath, pumps) and also the man hours to run the system was increased. Nevertheless, for this case

study annual saving potential of 250000 DM were reported and the time of amortisation was calculated to be 0.8 years. [ABAG-Bio]

**Driving force for implementation:**

**Reference literature:** [DK-EPA-93], [ABAG-Bio]

### C.4.2.5 Utilization of Oily Sludge and Concentrates

**Description:**

A variety of methods is used to remove oily sludge from the degreasing bath. This sludge contains solids together with a range of grease and oils. Depending on contaminant loading and calorific value, it can be used for energy recovery by incineration. The oily sludge is removed from site by a specialised contractor either for controlled disposal or for recovery of the oil contained in it. In some cases, if the water content is low, the sludge can be used as part of the fuel requirement for steam raising or heating plant. [Com EGGA]

**Main achieved environmental benefits:**

- Reduction of oil containing waste.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### C.4.2.6 Reduction of Carry-over to the Pickling Baths

**Description:**

The amount of solution carried out of degreasing baths and into the following pickling process can be minimized by allowing enough time for the solution to drip off, but especially by implementing a rinse step (more detailed information on rinsing see Chapter C.4.4).

**Main achieved environmental benefits:**

- Reduced consumption of degreasing solution.
- Prolonged lifespan of pickling baths, thus reduced acid consumption.

**Applicability:**

- New plants and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

## C.4.3 Pickling and Stripping

### C.4.3.1 Optimized Bath Operation and Control

**Description:**

Pickling efficiency, and thereby the necessary pickling time, changes during the lifetime of the bath. As the bath gets older, the iron concentration increases quite a lot, and less free acid is needed to keep the same pickling velocity as initially. Drastic changes in the pickle liquor, e.g. by replacing large volumes of the bath, may lead to unknown pickle conditions which may result in overpickling.

Careful monitoring of bath parameters (acid concentration, iron content etc), can help in optimizing the operation by raising the awareness of changes in the bath and allowing for changed operating procedures, such as shortening pickling time to avoid overpickling. Discharge of spent pickle liquor and addition of fresh acid in more frequent but small doses avoids drastic changes in bath characteristics and allows for smooth operation.

**Main achieved environmental benefits:**

- Reduced acid consumption.
- Less overpickling (associated with less waste).

**Applicability:**

- New and existing installations.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### C.4.3.2 Minimising Spent Pickle Liquor by use of Pickling Inhibitors

**Description:**

To protect parts of the workpieces, which are already metallically clean, from over-pickling, pickling inhibitors are added to the pickling solution. Pickling inhibitors can reduce the material loss of the work-pieces by up to 98 % and can reduce acid consumption. However, these organic inhibitors could have a negative influence on subsequent acid recycling processes and reducing acid consumption by use of pickling inhibitors should be considered carefully. [ABAG]

**Main achieved environmental benefits:**

- Reduced acid consumption.
- Less waste acid.

**Applicability:**

- New and existing installations.

**Cross-media effects:**

- Some pickling inhibitors may reduce the recycling options for waste acid.

**Reference plants:**

Vast majority (> 90 %) of all galvanizers use pickling inhibitors. [EGGA8/99]

**Operational data:**

Estimated reduction in acid consumption 10 – 20 % [EGGA8/99]

**Economics:**

Positive, cost savings [EGGA7/99]

**Driving force for implementation:**

- Enhanced quality of product.
- Reduced operational costs.

**Reference literature:****C.4.3.3 Activated Pickling****Description:**

Pickling in hydrochloric acid with a low acid percentage and a high iron content is referred to as activated pickling. When pickling steel in hydrochloric acid, the acid content is normally 10 - 12 % in order to get a reasonably quick pickling. However, at this acid percentage, the development of hydrogen chloride is rather high. When using activated pickling, the acid percentage may be halved without affecting the pickling rate negatively, provided the iron concentration is kept at 120 - 180 g/l. The temperature of the pickling bath needs to be kept at 20 – 25 °C.

**Main achieved environmental benefits:**

- Reduced acid consumption.

**Applicability:**

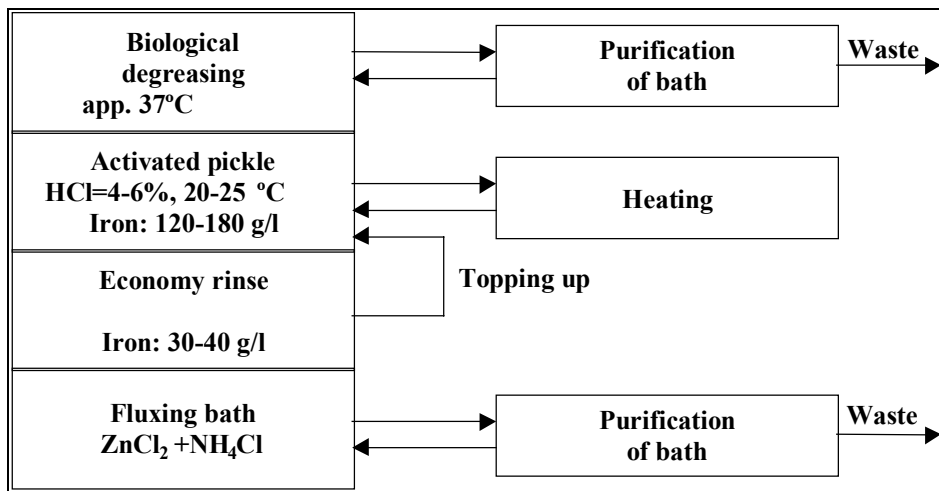
- New and existing plants.

**Cross-media effects:****Reference plants:**

FJ Varmforzinkning A/S, (period of experience: 5 years) [DK-EPA-93]

**Operational data and economics:****Example Ferritslev Jernvarefabrik (FJ )**

This system is used at Ferritslev Jernvarefabrik (FJ) where they also keep the pickling bath almost free of zinc. The discarded baths can be utilized as precipitation agent at the municipal sewage treatment plant. - FJ Varmforzinkning only has to pay the transport costs. [DK-EPA-93]



**Figure C.4-2: Flowsheet for activated pickling [DK-EPA-93]**

After biological degreasing the items are immersed directly into an activated pickling bath with 4 - 6 % hydrochloric acid and an iron content of 120 - 180 g/l. The items are suspended in black steel wires which are used only once. By doing so they prevent zinc coated suspension devices from entering the pickling bath. Furthermore, in a special stripping acid (4 - 7 % hydrochloric acid) zinc is stripped off items to be re-galvanized. Thus, the zinc concentration in the pickling bath may be kept at a very low level. [DK-EPA-93]

They have 4 pickling tanks of 100 m<sup>3</sup> each. From each tank 10 m<sup>3</sup>/h are circulated by means of a pump. The circulated volumes of water are mixed and pass through a heat exchanger before the water is returned to the individual tanks via a distribution system. In this manner they take care of both heating and circulation in the pickling baths. [DK-EPA-93]

It is important not to rinse between the biological degreaser and the pickler, since carry-over chemicals from the degreaser act as an inhibitor in the pickler, thereby preventing acid attack on the base material. [DK-EPA-93]

After the pickling bath, rinsing is carried out in a so-called economy rinse which is used to dilute the pickling bath when part of it is to be discarded. Typically, the economy rinse has an iron content of 30 - 40 g/l and, consequently, it reduces significantly the carry-over of iron into the flux bath. [DK-EPA-93]

Discarded stripping acid is delivered to Kommunekemi in the usual way. Discarded pickling acid is delivered to a firm which utilizes it as precipitation agent in municipal sewage treatment plants. When they change the bath they typically drain off 20 m<sup>3</sup> of bath which is replaced by 10 m<sup>3</sup> of hydrochloric acid and 10 m<sup>3</sup> of water from the economy rinse. [DK-EPA-93]

The production of hydrogen chloride in the acid hall is so low that even without extraction the hydrogen chloride content is 11 - 20 times below the occupational health and safety threshold value. Occupational environment measurements in the acid hall show hydrogen chloride concentrations in the air of 0.32 - 0.65 mg/m<sup>3</sup>. This is only 5 - 9 % of the threshold value for hydrogen chloride of the Danish Working Environment Service which is 7 mg/m<sup>3</sup>.

As activated pickling was introduced at the same time as biological degreasing and fluxing bath regeneration, it is difficult to quantify the financial advantages. In principle, extraction in the acid hall may be dispensed with. If they had extraction, air purification might be required. Their solution means that they can do without such equipment.

The service life of the pickling baths increases by about 50 % when using activated pickling, because the bath is not discarded until it has an iron content of 180 g/l compared with the usual 120 g/l. It is cheap to get rid of the discarded pickling bath when it does not contain substantial quantities of zinc. The plant only has to pay for the transport to Kemira Miljø in Esbjerg where the discarded bath is reprocessed into precipitation agent. [DK-EPA-93]

A heating system for the pickling baths is necessary when activated pickling is used, which means additional expense as compared with conventional pickling baths.

**Driving force for implementation:**

**Reference literature:**

### **C.4.3.4 HCl Recovery from Spent Pickle Bath**

#### **C.4.3.4.1 Evaporative Recovery (HCl)**

**Description:** see Chapter D.5.9.2

**Main achieved environmental benefits:**

- Reduction in fresh acid consumption, reduction in fresh acid production (resources, energy)

**Applicability:**

- New and existing plants

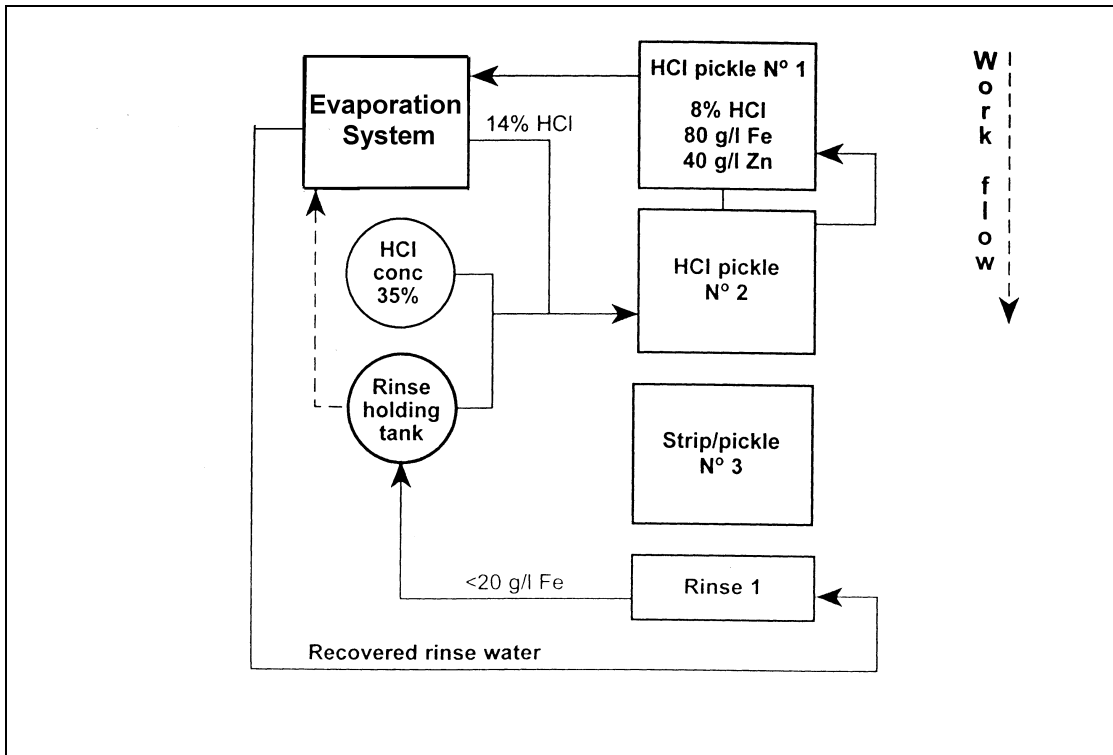
**Cross-media effects:**

- High energy consumption [Com2 D].
- Generation of iron chloride solution (concentrate), suitable for recycling?

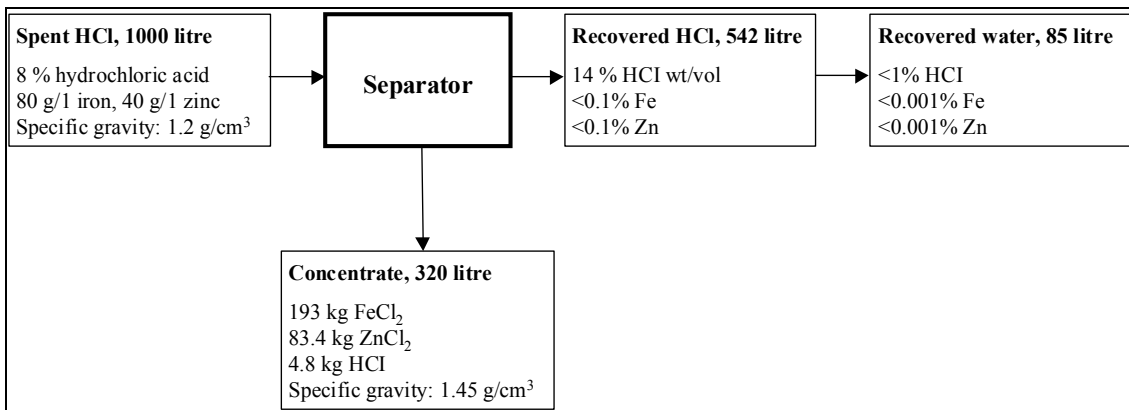
**Reference plants:**

**Operational data:**

Figure C.4-3 and Figure C.4-4 show the flow sheet and the mass balance for an example galvanizing plant.



**Figure C.4-3: Example flowsheet for evaporative HCl recovery in a galvanising plant based on [Cullivan-IG-97]**



**Figure C.4-4: Mass balance for evaporation recovery (example) [Cullivan-IG-97]**

The recovered acid can be returned to the pickling tank. Additional fresh acid blended into the pickling tank will make up for volume losses generated by the removal of the iron chloride solution and water. The recovered water can proceed either to the rinse tank, to the pickle tanks or to the flux bath. [Cullivan-IG-97]

The energy consumption for the plant as a whole is 230kWh/1000 l treated, net of energy recovery of 150kW by use of a special heat exchanger. [Com2 EGGA]

**Economics:**

**Driving force for implementation:**

**Reference literature:**



### C.4.3.5 External Regeneration of Spent HCl Pickle Bath

#### C.4.3.5.1 Fluidised Bed Process and Spray Roasting

**Description:** see Chapter D.5.10.1

**Main achieved environmental benefits:**

- Reduced consumption of fresh acid.
- Reduced waste water volume and sludge.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

The fluidised bed and spray roasting processes for HCl recovery are useful only for liquors which contain iron but no zinc. If zinc enters the feedstock there is a strong possibility of process upset. Although some sources quote a maximum level of 2 - 3g/l zinc in feedstock, it appears that the problem of zinc in feedstock has not been solved. In case of operational problems due to zinc content in the spent acid, pre-treatment measures to remove zinc might be necessary to allow regeneration. So far spray roasting is not applied for regeneration in batch hot dip coating.

**Economics:**

The processes are not practical at small scale, and so are not found in the general galvanizing industry. [Com EGGGA]

**Driving force for implementation:**

**Reference literature:**

### C.4.3.6 Separated Pickling and Stripping

**Description:**

In general, mixed spent acids, containing large amounts of iron and zinc, are very difficult to re-use or recycle. By pickling and stripping in separate tanks, zinc content in iron pickle baths can be kept as low as possible. Additionally, either single-use suspensions should be used where possible (wire) or multiple-use suspensions should be stripped before using. [ABAG]

**Main achieved environmental benefits:**

- Reduction of waste.
- Keeping waste streams separate allows for regeneration.

**Applicability:**

- New plants and existing plants.
- For existing plants, application may be limited due to space restrictions (for additional tanks).

**Cross-media effects:**

**Reference plants:** Otto, Kreuztal, Germany [Com2 D]

**Operational data:**

To reduce waste water generation, quenching water is often used to prepare and refresh pickle solutions. However, quenching water can add large amounts of zinc to pickling baths. Careful acid management can achieve zinc contents of 5 to 10 g/l in iron pickling baths. [ABAG]

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### C.4.3.7 Reduction of Zinc to Iron Ratio

**Description:**

Spent pickling baths can contain up to 5 % of free HCl. By adding iron swarf, the remaining acid can be converted to iron chloride. In low zinc-content mixed pickle baths this can lead to zinc - iron ratios that allow a regeneration of the mixed acid, e.g. by spray roasting. Contaminant traces in the pickle liquor of cadmium, lead, silicon and other alloying metals are precipitated and can be removed. 'Down-graded' pickle liquors, when thermally regenerated, usually result in higher quality iron oxides, which are more easily saleable. [ABAG]

**Main achieved environmental benefits:**

**Applicability:**

**Cross-media effects:**

**Reference plants:** *not used in practice [EGGA]*

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### C.4.3.7.1 Pre-treatment for Increased Reuse Options

**Description:** see Chapter D.5.9.3 and Chapter D.5.9.4

Pre-treatment by **diffusion dialysis** or **retardation**

**Main achieved environmental benefits:**

- Reduction of waste.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

- Both techniques (diffusion dialysis and retardation) require water, thus introducing additional water into the process, which in turn may conflict with the goal of effluent-free operation of batch hot dip galvanizing plants. [Com2 D].

**Reference plants:**

Diffusion dialysis was subjected to trials in a German galvanizing works. It was not successful in this application. [Com EGGA]

**Operational data:**

**Economics:**

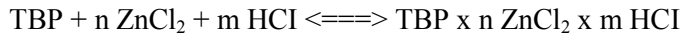
**Driving force for implementation:**

**Reference literature:**

### C.4.3.8 Recovery of Spent Mixed Pickle Liquor by Solvent-extraction

#### Description:

The solvent extraction process for selective zinc removal from spent HCl pickling acids uses the extractant Tributylphosphate (TBP) and is based on the following simplified reaction:



$\text{ZnCl}_2$  from the aqueous feed is bound as a chloride complex together with HCl to the organic, which is less dense than aqueous phase. Thus, it can be separated by decantation. When the loaded organic is intensively contacted with a new aqueous solution phase, the complexing reaction is reversed (re-extraction) so the stripped organic extractant can be recycled and a dilute aqueous  $\text{ZnCl}_2$  solution is produced. The  $\text{ZnCl}_2$  solution is evaporated to increase the zinc concentration. The condensate is recycled to re-extraction and the concentrate is sold. Figure C.4-5 illustrates the whole process schematically.

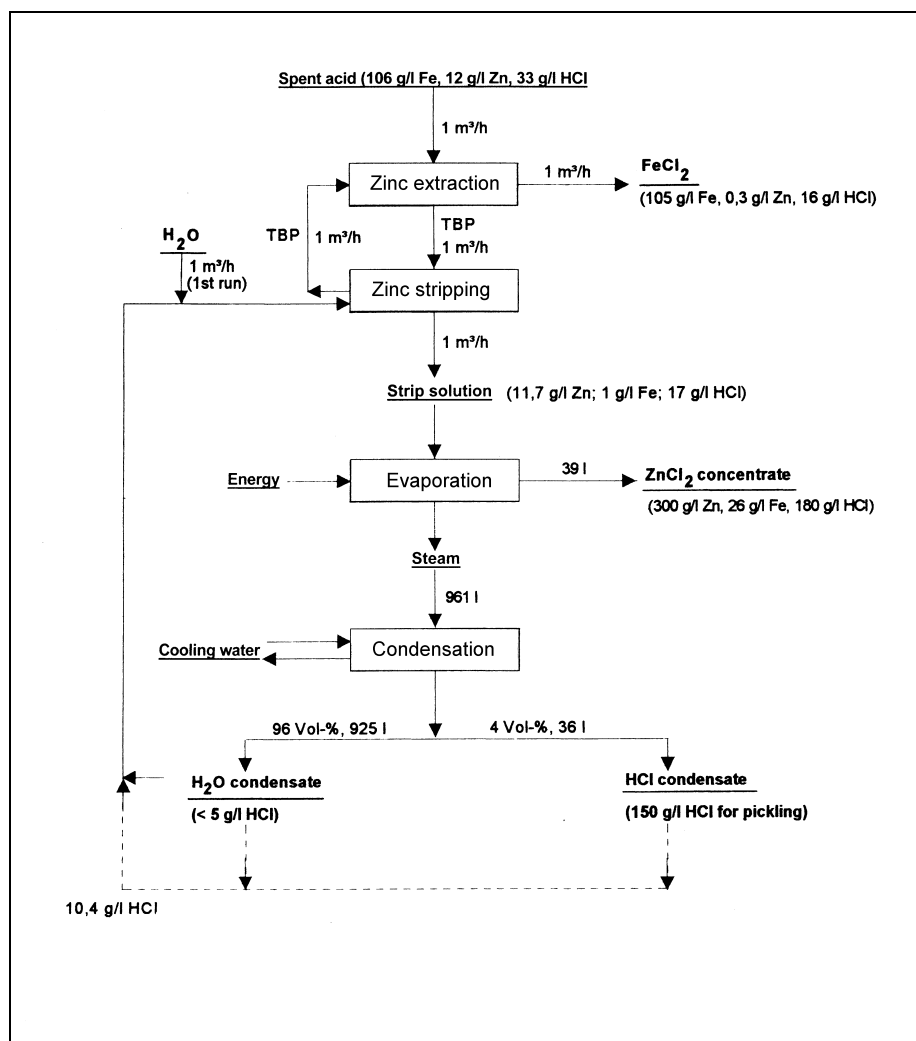


Figure C.4-5: Schematic of the solvent extraction process

Spent acid, stored in a special tank or in the pickling vessel, passes through a filter in which solid particles such as metal swarf, oxide scale, insoluble oils, dirt and cigarette ends etc are captured. The filtrate passes a buffering device and enters the first of three conventional mixer-settlers for zinc extraction by TBP. Zinc is extracted together with some free HCl and  $\text{FeCl}_3$ .

The zinc-loaded organic phase leaves the extraction section after three counter-current contacts with the spent acid. More or fewer stages are possible and depend on zinc concentration. The organic, which is less dense in comparison to the aqueous, leaves the settler over a weir which adjusts the phase boundary and organic to aqueous volume ratio.

The zinc-free FeCl<sub>2</sub> raffinate leaves the last mixer-settler (3rd extraction stage) from the bottom and is captured by a coalescer to remove residual organic. Raffinate is pumped to the storage vessel of the plant, which may be a fixed tank or a tank truck. The zinc loaded organic phase enters the re-extraction section (same container) consisting of three further mixer-settlers. Here it comes into contact with normal tap water and condensate from the evaporation unit. ZnCl<sub>2</sub>, FeCl<sub>3</sub> traces and HCl are washed from the extractant, which is recycled to the extraction vessel. The aqueous solution (strip solution) again passes a coalescer and is pumped to the evaporation container.

The strip solution is very low in zinc and normally has no further use. For that reason, it is concentrated to about 300 g zinc per litre. Any other suitable concentration can be achieved.

Evaporation is carried out by a steam heated evaporator constructed of PVDF.

The zinc concentration in the pregnant liquor is of minor interest for the extraction process. Ideally, the strip solution will contain about 30 g/l zinc. The lower the zinc concentrations in the spent acid, the higher will be the nominal throughput of acid due to a higher aqueous/organic ratio. However, higher zinc feed leads to higher treatment costs.

Heat for evaporation is delivered by steam produced in two small steam generators. The steam generators can be fired with natural gas or propane and have a high conversion efficiency. Steam is fed under pressure to the PVDF tubes of the evaporator. Heat is thus transferred to the strip solution.

The vapour passes a condenser cooled by salt-free tap water in circuit. In this way it is possible to completely recover the evaporated water and HCl with a cooling tower.

Vapour condensation can be arranged in two steps. At first the water with low free HCl (<5 g/l in total volume) will be captured. This fraction is about 85 to 95 per cent of total condensate. Then the tank is changed and filled with the remaining condensate, rich in acid. A final concentration of 15 - 18 per cent, suitable for pickling, should be achievable. The acid can be re-used in-house. Due to technical problems this selective HCl recovery was not possible within the project period.

Evaporation can be carried out more or less continuously. It is complete when the zinc concentration in the evaporator feed reaches 300 g/l. The final concentration can vary depending on the customer's requirement.

**Main achieved environmental benefits:**

- Reuse of mixed (zinc-containing) acid.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

- Chemicals used/solvents.

**Reference plants:**

A liquid-liquid extraction plant for the recovery of acids containing zinc and iron is operated by Norsk Hydro at Oberhausen, Germany.

Trials and investigations were done with a mobile plant at the Berliner Grossverzinkerer/Metaleurop. Meanwhile the mobile unit has been turned into a stationary plant. [Com2 D]

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### **C.4.3.9 Reuse of Spent Mixed Pickle Liquors**

#### **C.4.3.9.1 Iron Removal and Reuse as Flux**

**Description:**

Spent hydrochloric acid from combined pickling and stripping with high concentrations of iron and zinc can be processed and recovered like a flux bath (see Chapter D.7.1.1). After oxidation with hydrogen peroxide and neutralisation with ammonia the iron hydroxide sludge is separated. The remaining liquid contains high concentrations of zinc chloride and ammonium chloride and can be reused as a flux solution. [Com DK]

**Main achieved environmental benefits:**

- Reduced waste.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

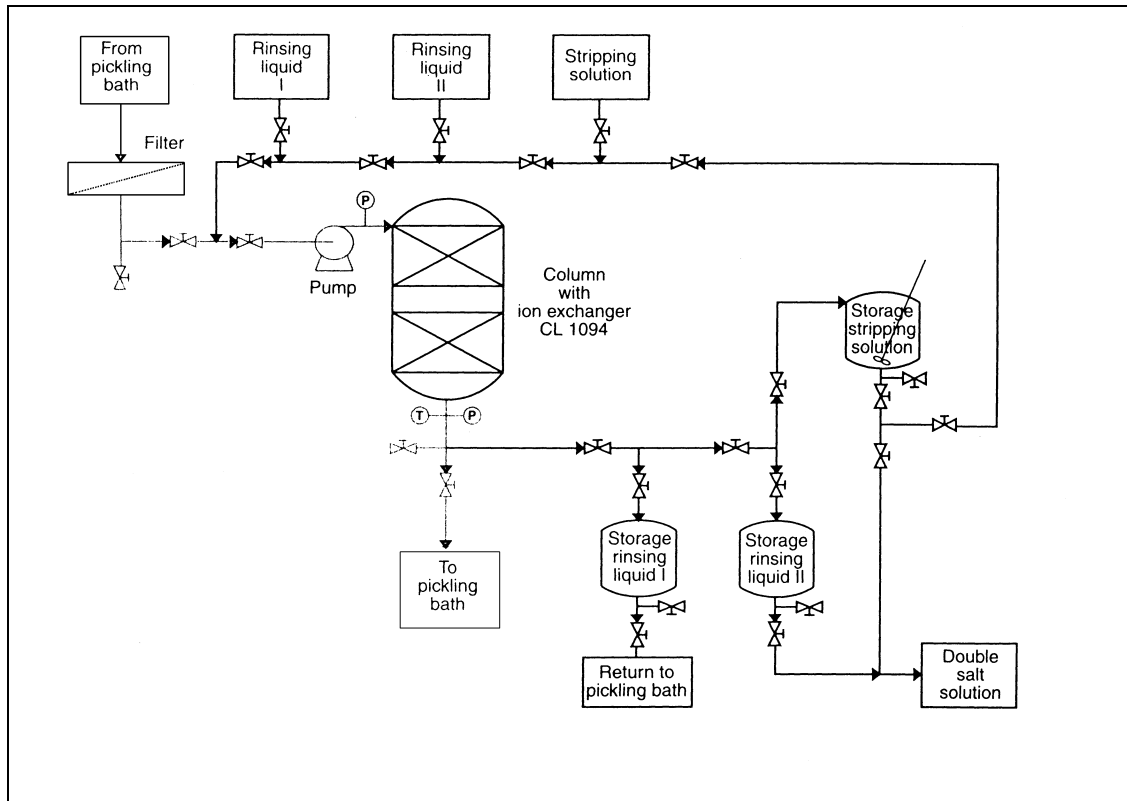
#### **C.4.3.9.2 Zinc Removal from Hydrochloric Acid Pickling Baths**

**Description:**

The process (see Figure C.4-6) is divided into 4 stages, namely:

- Zinc removal.
- Rinsing I (Elution 1).
- Stripping and regenerating.
- Rinsing II.

Pickling acid is pumped out of the bath through a plate-filter to remove any solid particles. The clear liquid then flows through the column. In the column, zinc is removed from the pickling acid and absorbed by the ion-exchange material. After leaving the column, the zinc-free liquid is pumped back into the pickling bath. Thus the system recycles the acid. However, the acid does not necessarily have to be recirculated and can be processed and then stored in a vessel (once-through process) or pumped out into another vessel, run through the column and stored in a third tank (batch process). In the second stage, after the ion-exchange material becomes saturated with zinc, the column has to be rinsed to remove the pickling acid.



**Figure C.4-6: Flow chart for removal of zinc from pickling baths [Sprang-IG-97]**

In the second stage, after the ion-exchange material becomes saturated with zinc, the column has to be washed to remove the pickling acid. The wash is then pumped out of the stock vessel, through the column, and into a separate storage vessel. The solution thus obtained is an HCl solution that can be used to modify the strength of the pickling bath. In the third stage, the ion-exchange material is stripped with an alkaline solution in order to remove the zinc. If second stage rinsing does not take place, iron hydroxide is precipitated, interfering with the process. The stripping solution is used several times before it becomes concentrated. When the stripping solution has reached saturation it can be used to modify the composition of the flux bath. The stripping solution contains only  $ZnCl_2$  and  $NH_4Cl$ . After the ion-exchange material has been stripped and regenerated, the last remains of the solution must be removed. This is done in the fourth stage by rinsing with tap water. If this were not done, the pickling acid would become polluted with  $NH_4^+$  and, although solving the initial problem of zinc contamination, would create a new one ( $NH_4^+$  pollution).

**Main achieved environmental benefits:**

- Reduced waste.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:** It was commented that this technique requires considerable capital costs and running costs and that scales of economy are a critical factor and may not be achievable with many typical size general galvanizing sites. [Com2 UK Galv]

**Driving force for implementation:**

**Reference literature:**

#### C.4.3.10 Treatment of Waste Acid by Neutralisation

**Description:** No information submitted.

**Main achieved environmental benefits:**

- Neutral sludge instead of acidic waste liquid.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

- Large amounts of non-recyclable mixed zinc and iron hydroxide sludges [Com2 D].
- No recovery or regeneration of acid, fresh acid requirement.

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### C.4.3.11 Acid Bath Operation Range

**Description:** see Chapter D56.1

**Main achieved environmental benefits:**

- Reduction of air emissions, especially acid fumes.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### C.4.3.12 Capture of Emissions from Pickling and Abatement

**Description:** see Chapter D.5.2 and D.5.3

Capturing the emissions by roof extraction, wall exhaust, lip extraction to lateral hoods in combination with plate or packed scrubbers. Scrubbing liquid can be recirculated to the pickling tank.

**Main achieved environmental benefits:**

- Reduction of air emissions, especially acid fumes

**Applicability:**

- New installations.
- Existing installations with some limitations due to space.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

Scrubbers can achieve HCl emission levels of below 10 mg/m<sup>3</sup>.

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### **C.4.3.13 Enclosed Pre-treatment Section (Degrease/Pickling)/Air Extraction and Abatement**

**Description:** see Chapter D.5.3

**Main achieved environmental benefits:**

- Reduction of air emissions, namely acid fumes and degreasing vapour.

**Applicability:**

- New installations.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

## **C.4.4 Rinsing**

### **C.4.4.1 Installation of Rinsing Bath/ Static Rinse Tank**

**Description:**

After pickling, the steel items are rinsed in a static rinse tank (they same procedure can be applied after degreasing). When the water becomes too contaminated to secure efficient rinsing, the water is reused in the preceding process bath as make-up water for evaporation losses and drag-out. With the proper design and operational practice all rinsing water can be used the galvanizing plant.

**Main achieved environmental benefits:**

- Waste water –free operation.



**Applicability:**

- New plants.
- Existing plants provided that space for rinsing tanks is available.

**Cross-media effects:****Reference plants:****Operational data:****Economics:****Driving force for implementation:****Reference literature:****C.4.4.2 Rinsing Cascade****Description:**

Counter-current rinsing (see below for description of example)

**Main achieved environmental benefits:**

- Reduces pollution of the fluxing bath [DK-EPA-93].
- Waste water-free operation.

**Applicability:**

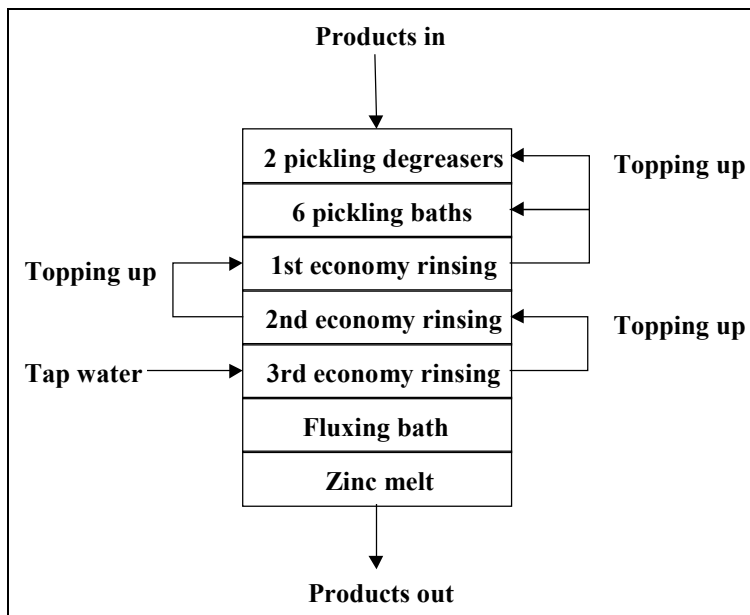
- New installations.
- Existing if space is available (due to requirement of more than 1 additional tank, very limited).

**Cross-media effects:****Reference plants:**

Herning Varmforzinkning A/S, (period of experience: 1.5 years) [DK-EPA-93]

**Operational data:****Example Herning Varmforzinkning:****3-step closed rinsing system after pickling**

At Herning Varmforzinkning they have started using 3 rinsing tanks without outlet after the pickling process. Here the pollution of the fluxing bath is reduced by 85 - 90 % resulting in longer life of the fluxing bath and less fluxing waste. The rinsing tanks are used for diluting new pickling baths by which procedure the 3 rinsing tanks are evenly diluted. The first tank is used for diluting the pickling bath, after which the first tank is then diluted with water from the second tank, which again is diluted with water from the third tank, which is diluted with tap water. [DK-EPA-93]



**Figure C.4-7: Cascade rinsing installed in galvanizing plant [DK-EPA-93]**

All items are pickled for a minimum of 10 minutes in a so-called pickle-degreaser acting as degreaser and pickler at the same time. It is a 10 % hydrochloric acid with degreasing chemicals admixed to it. After this they pickle for somewhat longer in a purer hydrochloric acid. After the final pickling they rinse in three consecutive economy rinses after which the items are immersed in the fluxing bath and finally the zinc melt. [DK-EPA-93]

There are 2 pickling degreasers of 23 m<sup>3</sup> in which the liquid is changed when iron content has reached 129 g/l, which takes about 6 months. Then a new pickling degreaser batch is mixed from 12 - 15 m<sup>3</sup> of water from the 1st economy rinse and 8 - 11 m<sup>3</sup> 30 % hydrochloric acid. [DK-EPA-93]

There are 6 tanks of 23 m<sup>3</sup> of pure hydrochloric acid pickling liquid with approx. 10 % free acid. These pickling baths are not changed until the iron content reaches more than 100 g/l, which has not happened yet (the system was introduced on December 1st, 1991). These pickling baths have a somewhat longer life than the pickling degreasers, because coarse pickling takes place in the pickling degreasers which are soon saturated with iron. The clean pickling baths are expected to have a service life of 1.5 - 2.0 years. New pickling baths are started with half economy rinse and half 30 % hydrochloric acid. [DK-EPA-93]

The following average iron values have been measured in pickling baths, rinsing tanks and fluxing baths: [DK-EPA-93]

- Pickling bath: Iron = 75 - 85 g/l
- 1st economy rinse: Iron = 40 - 50 g/l
- 2nd economy rinse: Iron = 25 - 35 g/l
- 3rd economy rinse: Iron = approx. 10 g/l
- Fluxing bath: Iron = approx. 5 g/l

When the iron concentration in the fluxing bath reaches 10 g/l the bath is discharged into a road tanker and brought to the Vildbjerg factory where they have a purification and regeneration system for fluxing baths. The road tanker returns with 23 m<sup>3</sup> of purified fluxing bath so that production can immediately be continued at the Herning factory. [DK-EPA-93]

From the beginning the company had hoped that the clean pickling baths could be kept free of zinc, but this has proved impossible in practice. The zinc content in the pickling degreaser is so high that the carry-over to the clean pickling baths results in considerable zinc pollution in these pickling baths. [DK-EPA-93]

**Economics:**

At the Herning plant the system requires 3 rinsing tanks of 23 m<sup>3</sup> as opposed to going direct from the pickling bath to the fluxing bath. The advantage is that the fluxing bath does not get polluted nearly as soon. The fluxing bath is purified in their own fluxing bath purification plant at the company's other factory at nearby Vildbjerg. It is difficult to quantify the savings achieved. [DK-EPA-93]

**Driving force for implementation:**

**Reference literature:**

## C.4.5 Fluxing

### C.4.5.1 Bath Maintenance

**Description:**

To make up for entrainment losses and to keep the concentration of flux baths constant, flux agents and water are added on a regular basis. To prevent carry-over of iron chlorides from pickling baths, the pickled workpieces should be rinsed thoroughly before fluxing. Close monitoring of the iron content is necessary. Nevertheless, a build-up of iron chloride cannot be prevented completely, so that the flux solution has to be exchanged or regenerated periodically.

**Main achieved environmental benefits:**

- Reduction of waste, avoids premature discarding of flux baths.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### C.4.5.2 Iron Removal from Flux Baths by Aerating and Precipitation of Iron

**Description:**

The flux solution is aerated to assist iron precipitation and then the solution is decanted in order to remove the resulting sludge from the bottom of the tank. This operation has the advantage of reducing iron levels, albeit not to very low levels. [Com2 Wedge]

**Main achieved environmental benefits:**

- Reduction of waste.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### C.4.5.3 Iron Removal from Flux Baths Using H<sub>2</sub>O<sub>2</sub> for Oxidation

**Description:** see Chapters D.7.1.1

**Main achieved environmental benefits:**

- Reduction of waste (spent flux).

**Applicability:**

- New plants.
- Existing provided space is available.

**Cross-media effects:**

- Generation of iron hydroxide sludge (60 % water, 6.5 % zinc, 20 % iron) requiring disposal.

**Reference plants:** CM Jernvarer A/S, (period of experience: 0.5 year) [DK-EPA-93]

**Operational data:**

**Example CM Jernvarer AIS:**

CM Jernvarer AIS has established a regeneration system for their fluxing bath enabling them continuously to remove iron pollution from their bath. In the purifying process the admixed hydrochloric acid is neutralised, thus generating ammonium chloride which is one of the two components of the bath. Optimum composition of the fluxing bath is maintained by dosing extra zinc chloride and ammonium chloride calculated on the basis of routine chemical analyses. [DK-EPA-93]

The system has been designed for continuous purification of the fluxing bath, and about 5000 litres are purified daily. With this capacity, the system is actually capable of purifying a fluxing bath being polluted by iron corresponding to a production of at least 10000 tonnes of products per year. The bath is pumped through a reactor to which hydrogen peroxide and ammonia water are dosed by a redox and pH controller. The iron is oxidized and precipitated as iron hydroxide sludge. The sludgy fluxing bath is collected in a sludge thickener where the sludge is separated. The sludge is then de-watered in a filter press, the filtrate and decanting water from the thickener being collected in a storage tank from where it is reused in the fluxing bath. Discarded fluxing bath with a high iron content may also be purified by the system. It is either fed slowly together with the lightly polluted fluxing liquid from the fluxing tank or it may be purified separately by several successive treatments. Discarded stripping acid may be treated too. In this case a reduced dose is required to avoid getting too high sludge concentrations in the liquid. The stripping acid contains great volumes of zinc chloride which are admixed to the fluxing bath in this process. However, since a certain ratio between ammonium chloride and zinc chloride has to be maintained in the fluxing bath, there is an upper limit to the volume of stripping acid that may be taken into the system if the zinc chloride concentration is to be kept at the optimum value. [DK-EPA-93]

In the purification of old fluxing baths no ammonium water was dosed because the pH value remained at the desired value of 4.5. Normally the consumption of ammonia is 2.4 g 25 % ammonium water per g of iron II (dissolved iron). This corresponds to an expected consumption of 1800 kg of ammonium water for the regeneration of fluxing baths of 50 m<sup>3</sup>.

There were no major problems during the running-in period, and after some minor adjustments the system is today running as planned with minimum time spent on operation and maintenance. After purification of the old fluxing baths the system is today linked to the fluxing bath used in the production so that they are continuously keeping the iron concentration as low as possible. They have not yet started on treating discarded stripping acid in the system. [DK-EPA-93]

#### Economics:

The system has cost DKK 310000 including equipment, installation, commissioning, and consulting, but exclusive of two storage tanks for purified and non-purified fluxing bath. The system is located in existing buildings. During the first 3 months 50 m<sup>3</sup> of old fluxing bath with a high content of iron (14 - 15 g/l) have been purified. The costs have been:

270 l of 35 % hydrogen peroxide at DKK 7.00	DKK 1890
4 tonnes of filter cake at DKK 1500	DKK 6000
Electricity	<u>DKK 1000</u>
Total	DKK 8890

Direct savings compared with shipping to Kommunekemi:

50 m <sup>3</sup> of old fluxing bath to Kommunekemi	DKK 75000
Fluxing chemicals: 20 tonnes at DKK 8800	<u>DKK 176000</u>
Total	DKK 251000

In practice, the savings amounted to about DKK 100000 only, because the plant would have cleaned the fluxing bath manually, if they had not had a regeneration system. When cleaning manually they only ship the bottom sludge to Kommunekemi. There will also be very great indirect savings which are difficult to quantify. The consumption of zinc will drop substantially (5 - 10 %) when a fluxing bath with a low iron content is used, and the production of hard zinc and zinc ash will be reduced too. The payback period is probably less than 1 year. [DK-EPA-93]

#### Example Galva 45:

Results (January-April 1993) of the flux regeneration process in operation at Galva 45, France are shown below:

		<b>First line (7m bath)</b>	<b>New automated line (3.5m bath)</b>
Total salt content	(g/l)	461	450
ZnCl <sub>2</sub> % - NH <sub>4</sub> Cl%		55 - 45	57 - 43
Temperature	(°C)	46	50
Fe	(g/l)	0.9	0.38
ZnCl <sub>2</sub> or NH <sub>4</sub> Cl addition		0	

#### Advantages in purifying fluxing baths

- Quality improvement: by maintaining acid and iron in the flux at very low levels (below 1 g/l), there would be a sharp reduction in dross formation and, consequently, fewer coating defects due to dross inclusion in the zinc. The zinc coating would have a more regular thickness and hence a shiny appearance. The reduction in the number of workpieces with surface defects would lead to a reduction in the workpieces having to be recycled.
- Reduction in zinc consumption: there would be reductions in zinc pick-up and of ash and dross formation, leading to valuable reductions in total zinc consumption.

- Increased internal profitability, thanks to the flux production and the reduction of effluent solution, which compensated for reagent costs and for iron solid residue disposal costs. Direct savings were approximately 1.7 ECU per tonne of galvanized workpieces.
- Ecological process: there was a marked reduction in residue production since the tonnage of effluent solutions used to produce the flux was higher than the production of the new iron solid residue.

### Economics:

Operating costs might change from one plant to another. They also depend on the production level of each galvanizing plant and especially on the chemical composition of the pickling and rinsing solutions, the temperature and required composition of the fluxing bath. Nevertheless, the estimated benefits which would be expected using flux regeneration in a conventional galvanizing plant are shown in Table C.4-1.

The savings due to production of flux salts, reduction of zinc consumption and of workpieces for recycling and to suppression of spoiled fluxing bath treatment cost is estimated at 13.79 ECU per tonne galvanized. With an estimated labour cost of 0.74 ECU/ton, the net profit would be about 13.0 ECU/tonne. For a galvanizing plant that produced 20000 tonnes a year, the estimated annual saving would be 261000 ECU.

	Unit	Specific consumption or production (unit/tonne Fe)	Specific saving (+) or cost (-) (ECU/unit)	Specific saving (+) or cost H (ECU/tonne Fe)
<i>Consumptions</i>				
NH <sub>4</sub> OH	l	0.920	-0.183	-0.168
H <sub>2</sub> O <sub>2</sub>	l	0.345	-0.731	-0.252
Dross	kg	0.310	-0.519	-0.161
Spent pickling solution	kg	8.330	+0.094	+0.783
<i>Productions</i>				
Flux	kg	1800	+0.926	+1.667
Fe filtration cake	kg	0.770	-0.192	-0.148
TOTAL				+1.721
Note: Source of data. These figures are based on January to April 1993 operation data for the Galva 45 galvanizing line. The specific consumption/production figures as reagent costs may change somewhat from plant to plant				

**Table C.4-1: Typical specific consumption/production and cost/saving for a flux regeneration**

The savings in spent pickle solution disposal cost used for this calculation take into account a temporary 30 % French authority subsidy. In normal conditions, without subsidy, the savings would be higher.

<b>Savings</b>	<b>ECU/tonne</b>
(1) Flux salts production including reagent cost and effluent reduction	1.72
(2) Zinc consumption reduction	9.11
(3) Reduction in reglvanizing of workpieces	2.28
(4) Suppression of spoiled fluxing bath treatment cost	0.68
<b>TOTAL:</b>	<b>13.79</b>
<b>Costs:</b>	
(5) Labour	0.74
<i>Net Profit</i>	13.05
Note: Source of data [PURIFLUX]. The savings are estimated values to be expected by the introduction of the regeneration process in a conventional 20000 tonnes/year galvanizing plant. They will vary from one plant to another.	

**Table C.4-2: Summary of savings and costs**

**Driving force for implementation:**

**Reference literature:**

#### **C.4.5.4 Iron Removal from Flux Baths Using Electrolytic Oxidation**

**Description:** see Chapter D.7.1.2

**Main achieved environmental benefits:**

- Reduction of waste (spent flux).

**Applicability:**

- New plants.
- Existing provided space is available.

**Cross-media effects:**

**Reference plants:**

**Operational data and economics:**

**Example Industrial Galvanizers Corporation:**

The galvanizing plant is processing 10000 - 12000 tonnes per year of general work which includes a reasonable proportion of tube and manufactured products. The average steel section thickness processed by this plant is approximately 3mm. [CEPT]

The three identifiable plant operating costs associated with iron contamination of flux are: effluent disposal, zinc usage cost and chemical usage cost. The costs will vary from plant to plant and vary within a plant depending on the method used to control the composition of the preflux solution. In the case studied, a rinse system was used to avoid carry-over of acid and iron into the preflux solution. [CEPT]

An examination of the operating costs of the plant before and after introduction of regeneration has shown the following cost savings:

Effluent disposal	20.2 %
Dross production	27.6 %
Chemicals	10.5 %
Ash production	39.0 %
Zinc	10.4 % [CEPT]

**Advantages:**

- Eliminating the need for rinse overflow or rinse treatment.
- Minimizing the sludge for disposal from conventional flux treatment.

Savings have far exceeded our expectations. These savings were in effluent disposal, zinc usage and chemicals usage and, in this case study, exceeded A\$12.50 per tonne of dipped steel. The original cost benefit analysis, on which the units were justified, predicted pay-back periods of 12 to 24 months. In operation, this prediction has been significantly bettered and recovery of capital expenditure was achieved in 6 to 9 months. [CEPT]

It is believed that the additional savings have been a result of improvements in plant management that were not included in the original estimation, but have been achieved through greater attention to detail in work practice. This greater attention to detail has been a direct result of the implementation of the technology. The regeneration system, together with monitoring of the condition of the preflux bath, has thus proven to be a very useful management tool for monitoring metal preparation line performance. [CEPT]

**Disadvantages:**

It was commented that the system requires considerable operator input, and that problems of sourcing spare parts (from Australia) have been reported. [Com2 EGGA]

**Driving force for implementation:**

**Reference literature:**

### **C.4.5.5 Iron Removal from Flux Baths Using Ion Exchange Columns**

**Description:** see Chapter D.7.1.3

**Main achieved environmental benefits:**

- Reduction of waste (spent flux).

**Applicability:**

- New plants.
- Existing, provided space is available.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Example Dutch plant**

**Advantages:**

- Decrease in zinc pick-up from 9.5 to < 7 %.
- Higher production rate - increase of over 10 %.
- Lower production of zinc ash.
- Lower production of fume.
- Lower dross production from 8 t/2 wks to 2 t/6 wks.
- Higher quality product [Sprang-IG-97].



### C.4.5.6 Reuse/Regeneration of Spent Flux Baths (off-site)

**Description:** see Chapter D.7.2

Spent flux baths are sent off-site, usually to flux agent producers, for re-cycling. The salts in the spent flux solution can be re-used for flux agent production.

**Main achieved environmental benefits:**

**Applicability:**

**Cross-media effects:**

**Reference plants:** Th. Goldschmidt, Germany

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

## C.4.6 Hot Dipping

### C.4.6.1 Enclosed Galvanizing Pot

**Description:**

Enclosures in combination with **scrubbers** or **fabric filters**.

Figure C.4-8 and Figure C.4-9 show some examples of enclosure designs.

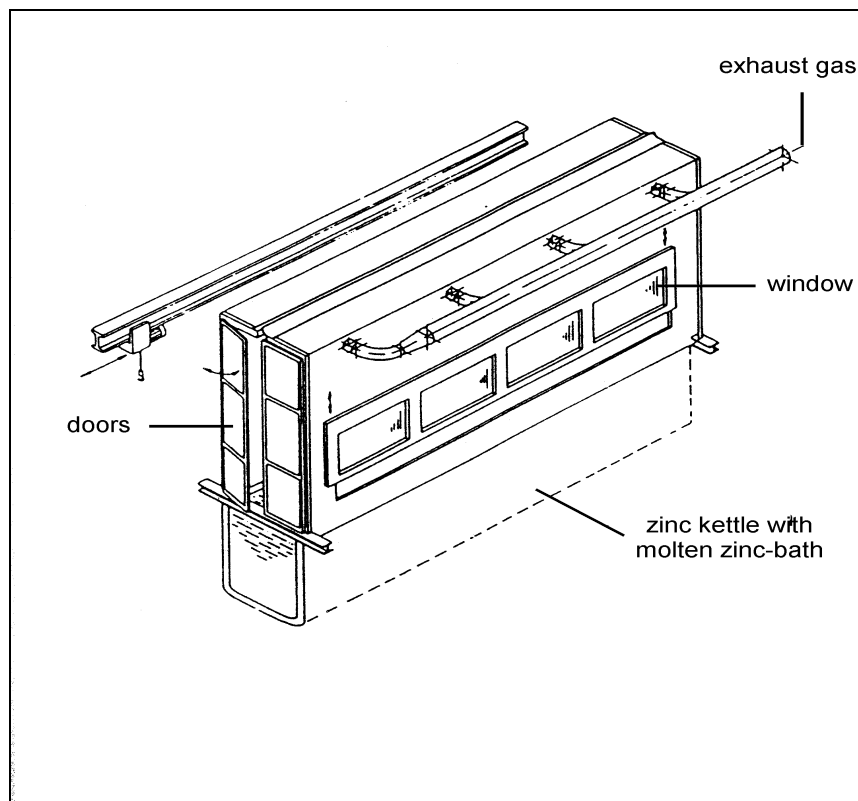
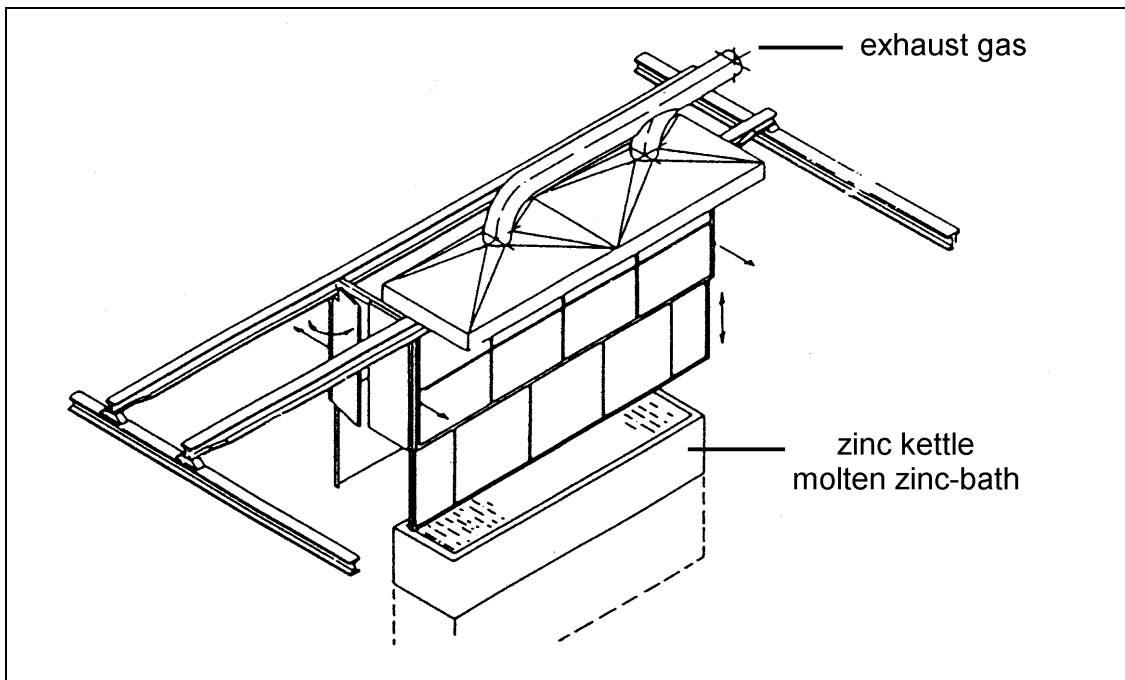


Figure C.4-8: Stationary enclosure  
[Galva-94-1]



**Figure C.4-9: Moveable enclosure with vertical moving side walls**  
[Galva-94-1]

**Main achieved environmental benefits:**

- Reduction of fugitive air emissions (reported 95 – 98 % capture of dust and other emissions [Com2 B]).
- Reduction of squirts.
- Energy savings due to reduced surface heat loss from the galvanizing bath. [Com2 EGGA].

**Applicability:**

- New and existing plants.
- Loading in longitudinal direction of bath.

**Cross-media effects:**

- Energy consumption (electrical energy is used for extraction fans, filter cleaning and possibly filter heating), but compared to other suction systems weaker suction is required (meaning less energy is needed). [Com2 B].
- Wet scrubbers: generate waste water, requiring treatment, less recycling potential than for dry filter dust.

**Reference plants:** Verzinkerei Rhein-Main GmbH, Groß-Rohrheim, Germany

**Operational data:**

Table C.4-3 compares examples of particulates and fume from galvanizing kettles for different abatement techniques.

Component	Emission [mg/m <sup>3</sup> ] No abatement	Emission [mg/m <sup>3</sup> ] Wet scrubber <sup>(1,2)</sup>	Emission [mg/m <sup>3</sup> ] Bag filter <sup>(3)</sup>
Dust	20	< 1.7	4.2 - 4.6
Zinc	2.3	0.11 - 0.38	0.49 - 0.52
ZnCl	n.a.	0.16 - 0.34	n.a.
NH <sub>4</sub> Cl	7.4	0.02 - 0.05	n.a.
NH <sub>3</sub>	2.6	n.a.	n.a.
HCl	23	n.a.	n.a.

Note: Source of data [Dan-EPA]  
<sup>1</sup> Volume flow = 39500 m<sup>3</sup>  
<sup>2</sup> Pb-content: 0.005 - 0.007 mg/m<sup>3</sup>  
<sup>3</sup> Cd-content: < 0.0002 mg/m<sup>3</sup>  
<sup>3</sup> Volume flow = 13400 m<sup>3</sup>

Table C.4-3: Concentrations in emissions from galvanizing kettles

### Example Verzinkerei Rhein-Main GmbH

#### Operational data:

Component	Emission <sup>1)</sup> in mg/m <sup>3</sup>
Dust	< 1
Zinc	0.03
ZnCl	0.1
NH <sub>4</sub> Cl	32
HCl	< 10

Note: Source of data [UBA-Hoesch-87]; volume flow = 23400 m<sup>3</sup>/h; removal system: fabric filter  
 1) Mean values from 8 individual measurements; average measuring period 32 minutes, calculated as absolute period of immersion with 5 to 8 dipping operations each

Table C.4-4: Concentrations in emissions from galvanizing kettles

#### Economics:

At Verzinkerei Rhein-Main, investment costs of DM 1634167 and operating costs of DM 309000 were incurred in 1985 for enclosure in combination with a fabric filter. The operating costs include DM 259000 for service of capital [UBA-Hoesch-87].

Other sources reported dust emissions from hot dipping of 1 – 3 mg/m<sup>3</sup> using fabric filters. [Flatt/Knupp]

#### Economics:

#### Driving force for implementation:

#### Reference literature:

### C.4.6.2 Lip-extraction at Galvanizing Pots

#### Description:

Lip-extraction in combination with **scrubbers** or **fabric filters**.

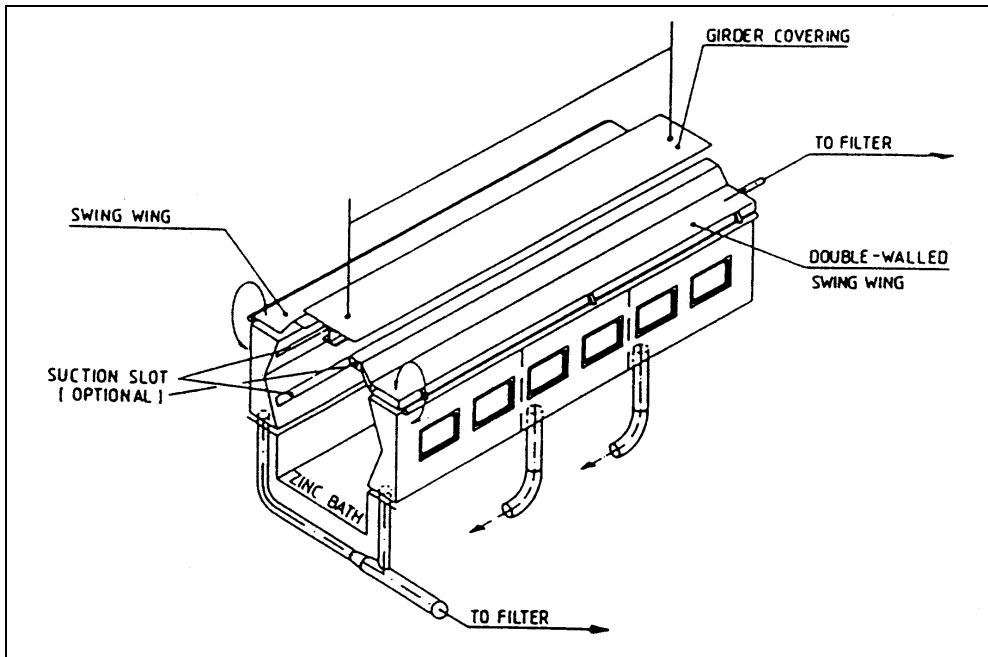


Figure C.4-10: Bilateral peripheral exhaust with auxiliaries  
[Galva-94-1]

#### Applicability:

- New and existing plants.

#### Cross-media effects:

- Energy consumption (electrical energy is used for extraction fans, filter cleaning, and possibly filter heating).
- Wet scrubbers: generate waste water, requiring treatment, less recycling potential as for dry filter dust.

**Reference plants:** Fa. Wilhelm Hähn, Kreuztal-Ferndorf, Germany

#### Operational data:

##### Example Wilhelm Hähn, Germany

Table C.4-5 gives some examples of emissions from a galvanizing kettle under different conditions.

Point of measurement	As <sup>3+</sup> [µg/m <sup>3</sup> ]	Cd <sup>3+</sup> [µg/m <sup>3</sup> ]	Pb <sup>2+</sup> [µg/m <sup>3</sup> ]	Zn <sup>2+</sup> [mg/m <sup>3</sup> ]	NH <sub>4</sub> <sup>+</sup> [mg/m <sup>3</sup> ]	Cl <sup>-</sup> [mg/m <sup>3</sup> ]	Dust [mg/m <sup>3</sup> ]
Above zinc surface without air extraction	106.9	117.2	125.3	44.5	197.9	14.3	384.6
Above zinc surface with air extraction	1.4	2.9	53.1	0.9	0.2	1.2	0.5
Crude gas	3.6	5.1	49.0	6.2	17.5	7.4	24.1
Cleaned gas	0.1	0.1	1.8	0.017	9.0	2.7	0.1

Note: Source of data [UBA-Hähn-83]  
Based on case study: lip extraction, 3380 m<sup>3</sup>/m<sup>2</sup>·h = 32958 m<sup>3</sup>/h, abatement: bag filter

Table C.4-5: Examples for emissions from a galvanizing kettle

The emissions data are mean values from six individual measurements with an average measuring period of 18 minutes, calculated as absolute immersion period with 2 – 4 dipping operations each. Repeat measurements conducted in 1996 confirm these data and showed the following results: dust <math>0.13 \text{ mg/m}^3</math> and HCl  $0.9 \text{ mg/m}^3</math>. These values are mean values from 4 individual measurements with an average measuring period of 28 minutes, calculated as absolute immersion period with 3 - 4 dipping operations each.$

Fabric filters show reduction efficiencies of 99.6 %.

**Economics:**

The burden on the product due strictly to pollution abatement measures, such as venting during degreasing, hot rinsing, flux bath and zinc bath as well as fabric filter for dust removal, averaged DM 32/t product in 1983. [UBA-Hähn-83]

**Driving force for implementation:**

**Reference literature:**

### C.4.6.3 Smoke-reduced Flux Agent

**Description:**

In smoke-reduced flux agents, ammonia chloride is partly substituted by other alkali chlorides (e.g. potassium chloride).

**Main achieved environmental benefits:**

- Reduced air emissions.
- Reduced hard zinc.

Table C.4-6 compares the shares of flux agents emitted, remaining on coated workpieces and contained in zinc ash for common ammonia chloride flux and potassium chloride flux.

Flux agent	Emission	Work piece	Zinc ash
ZnCl <sub>2</sub> : 89 % NH <sub>4</sub> Cl: 11 % Salt content: 170 g/l	33 %	2 %	65 %
ZnCl <sub>2</sub> : 32 % KCl: 68 % Salt content: 170 g/l	19 %	1 %	80 %
Note: Source of data [ABAG]			

**Table C.4-6: Emission comparison of normal and smoke-reduced flux agents**

**Applicability:**

- New and existing.

**Cross-media effects:**

- Zinc ash may be increased (reported by some sources).
- Smoke reduced fluxes produce less visible fume but fumes of visibility is a function of particle size there is a potential for smaller size therefore less visible airborne particulate therefore greater possibility for adverse health effect of respirable dust. [Com2 UK Galv]. Results from recent investigations, however state: no health concerns between the different flux types and no concerns over the size of the airborne particulate. [Piat 19.9]

**Reference plants:**

**Operational data:**

Flux agents based on zinc chloride/alkali chloride do not result in an additional pickling effect during hot dipping and therefore do not dissolve more iron. This reduces the generation of hard zinc on one hand, but also requires optimum pickling in the pre-treatment section to achieve high quality coatings. [ABAG]

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **C.4.6.4 Reuse of Filter Dust**

**Description:**

Precipitated dust from bag filters consist basically of ammonia chloride and zinc chloride (flux agent). The dust is collected, packed in bags and periodically sent for recycling to flux agent producers. Recycling might be limited by oil and grease content (less than 3 % is required) or by dioxin content.

**Main achieved environmental benefits:**

- Reduction of waste.

**Applicability:**

- New and existing plants with fabric filters.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:**

**Reference literature:**

#### **C.4.6.5 Reducing the Generation of Hard Zinc**

**Description:**

The following measures reduce the generation of hard zinc:

- Sufficient rinsing following pickling.
- Continuous regeneration of the flux bath.
- Use of fluxing agents low in ammonium chloride which have a low pickling effect (removal of iron).
- Avoiding local overheating in the externally heated galvanizing kettles (reaction with the boiler walls) [Com D], [Com2 EGGGA].

**Main achieved environmental benefits:**

- Less waste, more efficient use of raw material (no need to recycle hard zinc).

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:**

**Operational data:**

**Economics:**

**Driving force for implementation:****Reference literature:****C.4.6.6 Reducing the Generation of Splashes****Description:**

The following measures reduce the generation of splashes:

- Sufficient drying after the flux bath.
- Areas surrounding the galvanizing kettles must be kept clean to obtain recoverable zinc containing a minimum of impurities. [Com D].

**Main achieved environmental benefits:**

- Less waste, more efficient use of raw material (no need to recycle splashes for zinc recovery).

**Applicability:**

- New and existing plants.

**Cross-media effects:****Reference plants:****Operational data:****Economics:****Driving force for implementation:****Reference literature:****C.4.6.7 Reuse of Zinc Ash****Description:**

Zinc grains can be melted from the zinc ash and recycled back to the galvanizing pot. The reduction grade is 60 – 70 %. The remaining zinc oxide ash is refined further in specialised industry. [Com FIN]

- Special melting pots are used to collect the zinc ash.
- Melting pot is put to the Zinkof-furnace, in which zinc ash is melted at temperature of about 520 °C with a rotating movement. The molten zinc (60 - 65 wt-%) is returned to the molten zinc kettle. The remaining oxide zinc ash is ground and sold to the secondary zinc industry.

**Main achieved environmental benefits:**

- Reduced waste.

**Applicability:**

- New and existing plants.

**Cross-media effects:**

**Reference plants:** four galvanizing plants in Finland, for example KS-Sinkki Oy, Lievestuore, Finland [Com2 FIN]

**Operational data:**

With described technique recycled zinc amount is 11.5 kg/t of galvanized steel. Price of the equipment is about 200 000 FIM. In addition to that, grinding equipment for grinding zinc ash also has to be provided and it costs about 60 000 FIM. Net profit, when all the costs, except investment costs, are included, is about 2.20 – 2.80 FIM/kg recycled Zn depending upon the market price of zinc.

**Economics:**

**Driving force for implementation:**

**Reference literature:**

### **C.4.6.8 Heat Recovery from Galvanising Kettle Heating**

**Description:**

Galvanizing kettles may be fired either by gaseous or liquid fuels. The method most commonly used for heat recovery from combustion gas is transfer to air or water. Heat exchangers typically fabricated from banks of stainless steel tubes are used to recover heat from flue gas to air. The flue products are normally on the tube side. Flue products may be introduced at 500 to 700° C when the furnace is operating at full production rate. The heat exchanger may be placed directly in the furnace flue duct but, in the absence of forced extraction of flue gases, only a small flue gas pressure drop can be tolerated. This limits the rate of heat transfer.

Shell and tube heat exchangers can be used to transfer heat from flue products to water or steam, with flue gas on the shell side. Another common type of exchanger is a bank of finned tubes placed in the flue duct. In this case water is on the tube side.

Gases may be drawn through the heat exchanger using a fan downstream of the exchanger in order to increase the overall coefficient. This is a common arrangement for gas-to-water heat exchange. Both heat exchanger and fan are located in a branch parallel to the main flue duct, thus avoiding any back-pressure effect on the furnace. The fan consumes a small amount of power.

In a few cases flue gases are contacted directly with the outer surface of a pre-treatment tank, transferring heat by radiation and convection.

Heat exchangers for oil fuels and for surface heated baths require special design due to the presence of SO<sub>2</sub> and ash in the flue gases. [Com2 EGGA]

**Main achieved environmental benefits:**

- Reduced fuel consumption.

**Application:**

- New and existing plants
- In principle, can be applied to any installation subject to economic analysis, which depends on fuel price, thermal rating of furnace and demand for waste heat.
- not normally interesting on two burner systems (small kettles) because there is not enough heat available to be useful. Heat recovery systems are very frequently installed on four and six burner systems.

**Cross media effects:**

**Reference plants:**

**Operational data:**

**Economics:** Energy reductions in the range 15 – 45 kWh/t black steel.

**Driving force for implementation:** Fuel costs.

**Reference literature:** Trade literature.



### C.4.6.9 Efficiency of Furnace Heating/Control

**Description:**

Furnace heating efficiency should be considered in two parts. They are firstly the efficiency with which heat is transferred from the prime heat source to the galvanizing bath and, secondly, the efficiency with which the transferred heat is employed in maintaining the zinc temperature.

The efficiency of heat transfer to the kettle is governed by basic principles of heat transfer and combustion engineering. Combustion of gases and oils results in a flow of flue gas products which carries away sensible and latent heat. This amounts typically to 45 – 55 % of the gross calorific input of the fuel at maximum input. A small amount of electrical energy is used to drive the combustion air fan, and the pump or compressor used in oil heating. Use of electricity for heating involves energy loss owing to reactance effects and often also to cooling of temperature-sensitive parts of the heating system. Losses may be around 15 % of the metered power. For all energy sources, there is additional heat loss from the furnace case, although for a well-insulated furnace this is small, typically 2 % of the energy input. All losses in this category increase as the heat input increases.

Losses from the system are also due to radiation and convection from the molten metal surface and from exposed parts of the top of the bath, such as the top flange on a steel kettle. The extent of these losses depends on the surface areas, conditions and temperatures, but is typically 15 to 25 % of the heat originally transferred to the bath.

Flue gas heat losses may be reduced by optimizing the combustion process, by optimizing excess air for combustion and by reducing air ingress to the furnace casing. The low temperature operation of the galvanizing process implies that there are limited opportunities for energy saving by reduction of losses. The burner system must be capable of accommodating a turn down ratio of approximately 15:1.

Surface losses may be reduced during working (subject to adequate ventilation) by use of an enclosure over the bath, or limiting the open part of the surface to that required for the type of galvanizing in progress. When the kettle is on hot standby, reductions in heat loss can be obtained by the use of insulated covers which extend over the furnace top. Reducing the bath temperature during hot standby periods rarely saves significant amounts of energy and, with steel kettles, cycling of the bath temperature adversely affects the protective zinc-iron alloy, thus reducing the kettle's working life.

Furnace efficiency is also affected by the control system. Higher efficiencies are obtained with control systems which most closely match the heat input to the heat demand. Determination of heat input is based on the molten zinc temperature, measured by thermocouples either immersed in the zinc or – for steel kettles – possibly by contact with the external kettle wall. Depending on the flexibility of the heating system the controller often uses PID (Proportional, Integral, Derivative) or other control logic to keep the zinc temperature as constant as possible.

Combustion systems include High/Low (either maximum or minimum heat is delivered for a period), Modulating (the heat input varies constantly over a range between maximum and minimum), or Pulsing (a continual succession of maximum and minimum heat inputs is delivered equating to a net intermediate heat input).

**Main achieved environmental benefits:****Applicability:****Cross-media effects:****Reference plants:****Operational data:****Economics:**

**Driving force for implementation:**

**Reference literature:**

**C.4.6.10 Capture/Treatment of Emissions from Tube Finishing Operations**

→ No information submitted.

## C.5. BEST AVAILABLE TECHNIQUES FOR BATCH GALVANIZING

In understanding this chapter and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- Identification of the key environmental issues of batch galvanising. Among the important issues are: emissions to air (HCl from pickling and dust and gaseous compounds from the kettle); spent process solutions (degreasing solutions, pickling baths and flux baths); oily wastes (e.g. from cleaning of degreasing baths) and zinc-containing residues (filter dust, zinc ash, hard zinc).
- Examination of the techniques most relevant to address those key issues.
- Identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide.
- Examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques.
- Selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this chapter that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous chapter. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this chapter are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

This chapter discusses the best available techniques for reducing the environmental impacts from batch galvanising. Where possible, the structure follows the logic of the production line and identifies BAT for individual processing stages. However, some measures, especially primary or preventive measures, cannot be assigned to one single process step and have to be allocated to the plant as a whole. As far as possible and wherever the data available allowed, emission levels, efficiencies or recirculation rates are given an indication of the improvement that can be expected by implementation of the techniques. For a number of techniques, the obvious positive effect cannot be described by an exact number, but some of these techniques are nevertheless considered as BAT.

Unless stated otherwise the emission figures presented in the following BAT chapters are daily mean values. For emissions to air they are based on standard conditions of 273 K, 101.3 kPa and dry gas.

Discharges to water are indicated as daily mean value of a flow-rate-related 24-hour composite sample or a flow-rate-related composite sample over the actual operating time (for plants not operated in three shifts).

For **degreasing** operations in batch galvanising plants, the following techniques are considered BAT:

- Installation of a degreasing step, unless items are totally grease-free which is rarely the case in job galvanizing.
- Optimum bath operation to enhance efficiency, e.g. by agitation.
- Cleaning of degreasing solutions to extend lifetime (by skimming, centrifuge, etc.) and recirculation; reuse of oily sludge, e.g. thermally.

or

- 'Biological degreasing' with *in situ* cleaning (grease and oil removal from degreaser solution) by bacteria.

A primary measure to minimize environmental impact from **pickling** and **stripping** is to operate both in separate treatment vessels, since 'mixed acids' (with both high iron and zinc

contents) cause problems in regeneration or reuse. As long as there are no suitable treatment options for mixed acid, separate pickling and stripping and reuse of spent stripping liquor (external or internal e.g. to recover fluxing agent) are considered to be BAT for new and existing plants.

If separation of pickling and stripping is not possible, e.g. when there is insufficient space to install additional pickling/stripping tanks, external reuse of the mixed acids for flux production is considered BAT.

One central treatment plant for spent mixed pickle liquors using solvent-extraction and one galvanizing plant operating this process have been reported (see Chapter C.4.3.8). Where such (external) treatment plants are available, recovery of HCl from spent mixed pickle liquors using solvent-extraction may be considered a viable alternative to fluxing agent recovery (see above).

For **HCl pickling** the following techniques are considered to be BAT to reduce environmental impacts:

- Close monitoring of bath temperature and concentration parameters: and operating within the limits given in Part D/Chapter D.6.1 'Open Pickling Bath Operation'.
  - If operation outside the operational range given in D.6.1 is desired, e.g. if heated or higher concentrated HCl-baths are used, installation of an extraction unit and treatment of the extraction air (e.g. by scrubbing) are considered BAT. The associated HCl emission level is 2 – 30 mg/Nm<sup>3</sup>.
  - Special attention to the actual pickling effect of the bath and use of pickling inhibitors to avoid over-pickling.
  - Recovery of free-acid fraction from spent pickle liquor.
- or
- External regeneration of pickling liquor.
  - Zn removal from acid.
  - Use of spent pickle liquor for flux production.

Neutralisation of spent pickle liquor and the use of spent pickling liquor for emulsion splitting are not considered BAT.

Generally, good drainage between pre-treatment tanks is advocated. Furthermore, **rinsing** after degreasing and after pickling to avoid carry-over into subsequent process baths and thus to prolong the lifetime of these baths is essential. BAT is:

- Static rinsing or rinsing cascades.
- Reuse of rinse water to replenish preceding process baths.
- Waste water-free-operation (waste water may be generated in exceptional cases, in which waste water treatment is then required).

For **fluxing**, control of bath parameters and the optimized amount of flux used are important to reduce emission further down the process line as well. For the flux bath itself, side-stream regeneration of the solution (using e.g. H<sub>2</sub>O<sub>2</sub>, electrolytic oxidation or ion exchange) or, if installation of a regeneration unit is not possible, regeneration by externals is possible. Both internal and external flux bath regeneration are considered BAT.

The main problem arising from **hot dipping** is air emissions resulting from reaction of the flux agent during dipping. The following techniques are considered to be BAT:

- Capture of emissions from hot dipping by enclosure of the pot or by lip extraction followed by dust abatement (e.g by fabric filters or wet scrubbers). The dust level associated with these techniques is  $< 5 \text{ mg/Nm}^3$ .
- Internal or external reuse of collected dust for flux production. As this dust may occasionally contain dioxins at low concentration due to upset conditions in the plant (badly degreased items being galvanised), only recovery processes yielding fluxing agents free of dioxins are BAT.

Although the opportunities for energy saving by heat transfer from flue gases from the galvanizing kettles are limited due to low volumes and relatively low temperatures ( $450^\circ\text{C}$ ), it is good practice to recover heat from this source either to hot water used elsewhere in the plant or to air for drying.

For all **Zn-containing wastes** (dross, hard zinc, and splashes/squirts), separate storage and protection from rain and wind, and reuse in the non-ferrous metals industry or other sectors to recover the valuable substances they contain are considered to be BAT.

## C.6. EMERGING TECHNIQUES FOR BATCH GALVANIZING

The process of galvanizing requires steel articles to be exposed to liquid zinc for sufficient time for the zinc and steel to react to form the galvanized coating. The thickness and nature of the coating are controlled by European standard. In recent years the quality of assets in the industry has improved markedly, but the fundamental nature of the process has not changed due to the limitations imposed by the need to expose heavy steel items to liquid zinc. There is, therefore, no emerging technique which is based on fundamentally different principles.

However, substantial efforts have been made, and continue to be made, to improve performance in the control of emissions to water and air.

The separation of Zn and Fe from mixed content pickle liquors has been a subject of interest for some time. Several processes have been developed and reported in the open literature. These techniques meet the requirements of BAT insofar as they maximise the recovery and recycling of contained values while continuing to limit emissions. Overall, the water balance of the galvanizing process is such that substantial make-up is required. In all cases reviewed by EGGA aqueous blow-down is recycled internally as part of make-up water. Build-up of unwanted constituents does not appear to be a difficulty. A variety of BAT-compliant processes is likely to emerge in the near to medium term future.

Similarly, investigations into the reduction of fume emissions at source, either by the use of low fume fluxes based on current fluxes or by the use of novel fluxing systems, are under way. The promised benefit of fume reduction at source is the possible substitution of the fabric filter by a simpler device such as a drop-out box with significant reduction in pressure drop and thus power requirement. These investigations are recent and reported in the open literature only to a limited extent. Early indications are that the technique produces a low but, nevertheless, slightly higher particulate emission than the standard flux / fabric filter system, but requires significantly less power. It is possible that judgement about the balance of on-site particulate emissions and power plant greenhouse gas emissions will be such that the technique could be regarded as BAT compliant. [EGGA 7/00]

Developments on a novel flux formulation (thermaflux, US patent) which calim a reduction of lead content in the galvanizing bath and reduction of metal spitting during dipping, were reported. Technical feasibility has still to be proofed; no application of this technique in batch galvanizing is known.





## C.7. CONCLUDING REMARKS

The following conclusions and recommendations concern timing of the work, sources of information, availability and quality of data, consensus amongst experts of the TWG and recommendations for future work.

### Timing of work

The drawing up of this BREF took about 2 ½ years. The major steps have been:

- First TWG meeting (kick-off meeting) 11 – 12.12.97
- Submission of relevant information and data by TWG:
  - for Chapters 2 February – October '98
  - for Chapters 3 April – October '98
  - for Chapters 4 July – October '98
- First draft December 1998
- First consultation round 16.12.98 – 12.2.99
- Evaluation of comments and redrafting:
  - (*response to comments, clarification and request for additional information*) May – July '99
- Submission of missing information/data: September – November '99
- Second draft December 1999
- Second consultation 17.12.99 - 17.02.00
- Second TWG meeting 22 – 24.03.00
- Submissions on controversial issues that came up during the 2<sup>nd</sup> TWG meeting: 28.03.00 – 19.07.00
- Consultation on 'new' chapters (*revised Chapters 5, Chapter 7 Conclusions & Recommendations, Executive Summary, Chapter 4: SCR and SNCR*) 21.07.00 – 18.08.00
- Final draft

### Sources of information

65 reports dealing with the various aspects of the ferrous metals processing sector were submitted. These reports contain very different kinds of information (statistical data, description of production technologies, information on certain environmental measures including case studies and emission/consumption data). They have been prepared from different points of view; most of them only focusing on single aspects or media, only very few covering all environmental aspects.

During the period of work on the Ferrous Metals Processing BREF, industry shadow groups on hot rolling, cold rolling and continuous coating and the European General Galvanizers Association (EGGA) provided reports and papers on their sectors regarding the applied production techniques and some environmental measures. Germany submitted a report on 'BAT in the German Ferrous Metals Processing Industry'.

The availability of such documents is essential for the quality of the document, but their usefulness is potentially compromised if they are not sent in early in the process. Delays in submitting crucial information, especially on the techniques to be considered in the determination of BAT, have led to delays in issuing drafts of this BREF.

### Best available techniques

BAT have been identified for all three sub-sectors of ferrous metals processing and for the individual production steps. They are described in detail in the three Chapters 5 providing

background and, where necessary, justification for selection as BAT and for the reported BAT-associated emission levels. The executive summary includes all these BAT conclusions.

### Level of consensus

Part A of this BREF contains several split views. There were three areas in which the TWG could not reach an agreement:

- BAT-associated dust levels for application of fabric filters/electrostatic precipitators
- SCR and SNCR NO<sub>x</sub> reduction measures for reheating furnaces
- S-content in fuel oil

On dust emissions, the TWG agreed that capturing and fabric filters are BAT, but there were two general points of view on what is achievable with fabric filters. Industry proposed, based on their experience and knowledge of achieved dust levels, the higher level of 20 mg/Nm<sup>3</sup>. Some Member States and environmental NGOs considered below 5 mg/Nm<sup>3</sup> to be the appropriate associated level for fabric filters, but there were only very few figures and for most applications no data presented to support this view (see also recommendations for future work).

Information and data on SCR and SNCR in reheating furnaces was received at a very late stage of the work; during and after the second TWG meeting. Some TWG members considered these techniques to be BAT, while others thought the available information on technical details and on economics was not sufficient to allow a final decision to be made on whether or not SCR and SNCR are BAT. As this controversy was raised almost at the end of this exercise, there was no time to resolve the outstanding issues (see also recommendations for future work).

Another point of dissent was the issue of limiting S-content in fuel oil. Although a level of S < 1% can lead to emissions as high as 1700 mg SO<sub>2</sub>/Nm<sup>3</sup>, some TWG members thought that this should be BAT. Others regarded a lower S-limit in the fuel oil or additional SO<sub>2</sub> reduction measures as BAT.

Parts B and C of this BREF enjoy a high level of consensus. No split views had to be noted. All parties in the information exchange process consider them an acceptable result.

### Recommendations for future work

A lack of data and information on the performance of techniques to be considered in the determination of BAT, especially on achieved emission and consumption levels and on economics, was noted as a flaw of this BREF document. For future BREF reviews, all TWG members and interested parties should continue to collect these data and information and should make them available earlier rather than later in the process.

For quite a number of the techniques to be considered in the determination of BAT, no information or only a technical description is available. Information on reference plants and actual performance data are scarce. For the revision of this document the missing information should be provided. Some of the techniques concerned are the following:

Part A:

- Optimized water pumps for laminar flows
- Implementation of degreasing bath cascades
- Hot water pre-degreasing
- Heat utilisation for heating degreasing bath
- Electrostatic oiling
- Optimization of oil spray
- Optimized finishing operation
- Cleaning and reuse of grinding emulsion
- Exhaust system (PRETEX/SBT)
- External use of spent acid pickle liquor

## Part C:

- Storage and handling of raw materials and auxiliaries
- Capture/treatment of emissions from tube finishing operations

## Part D:

- Implementation of degreasing bath cascades
- Hot water pre-degreasing
- Adsorption of surfactants and oil (precipitation followed by filtration)
- Electrolytic pickling
- Treatment of rinsing water using ion exchange, electrolytic iron removal, reverse osmosis, oxidizing iron removal

Several techniques are presented in the Chapters 6 ‘Emerging Techniques’. The progress in development and the suitability for application in the FMP sector should be checked for a potential move of these techniques to Chapter 4 ‘Techniques to be considered in the determination of BAT’ and/or to Chapter 5 ‘Best Available Techniques’.

The criticism was made that the presentation of some techniques was too positive, having been derived mainly from suppliers’ information, and that only the advantages were presented. This mainly concerns reclamation and regeneration processes for spent treatment baths, e.g. for spent pickling liquors or spent degreasing or flux baths. Here industry is requested to provide the information and results they have achieved with certain techniques, together with descriptions of any problems they have experienced.

There is a need for more emission and consumption data generally, but of particular interest are figures on NO<sub>x</sub> emissions (concentrations and specific emissions) both for furnaces that use air preheating and those that do not. Such data would make possible both a more thorough evaluation of the efficiency of reduction measures and a comparison of the advantages and disadvantages of energy savings vs. NO<sub>x</sub> emissions.

More data are required on achieved dust emission levels for the various production steps of hot and cold rolling (Part A), where a split view on the BAT-associated dust level had to be stated in the BREF. Especially, those parties advocating the lower level of 5 mg/Nm<sup>3</sup> should seek to provide data to substantiate their view.

It was reported that the number of installations applying SCR (pusher type furnaces) is likely to increase. When this BREF is reviewed, there should be more information available on the performance and applicability of SCR and SNCR for reheating furnaces. Existing SCR and SNCR installations will have a longer operating history to draw on, which should help to answer the criticism that the information available was based on too short an operating period. Possibly the disagreement on whether these techniques constitute BAT can be resolved then.

During the 2<sup>nd</sup> TWG meeting the point was raised that inductive heating was BAT for several applications in furnaces. In this BREF, inductive heating is included as a technique to be considered, but it was stated that the information available was not sufficient to decide whether the technique is BAT. More information and data should be collected to enable this decision to be made.

Another issue raised was the dioxin content of dust from batch galvanizing and potential risks of dioxin build-up when these dusts are recycled. Efforts should continue to compile information and data of actual dioxin contents in dusts for normal plant operation. Available data should be provided to the IPPCB and the TWG to allow a judgement on this problem and enable an evaluation of the potential risk.

A revision of this BREF document is recommended for the year 2005.



# **PART D**

## **Techniques Common to several Sub-sectors**

Techniques to be considered in more than one sub-sector in the  
determination of BAT

In order to avoid repetition in describing certain techniques to be considered in the determination of BAT, Part D contains detailed technical descriptions and information on techniques which might be applied to several sub sectors. Sector-specific aspects of the techniques (main achieved environmental benefits, applicability, cross-media effects, reference plants, operational data, economics, driving force for implementation and reference literature) are covered in the relevant part of this document (A, B or C), in which cross-references to Part D are included where relevant.



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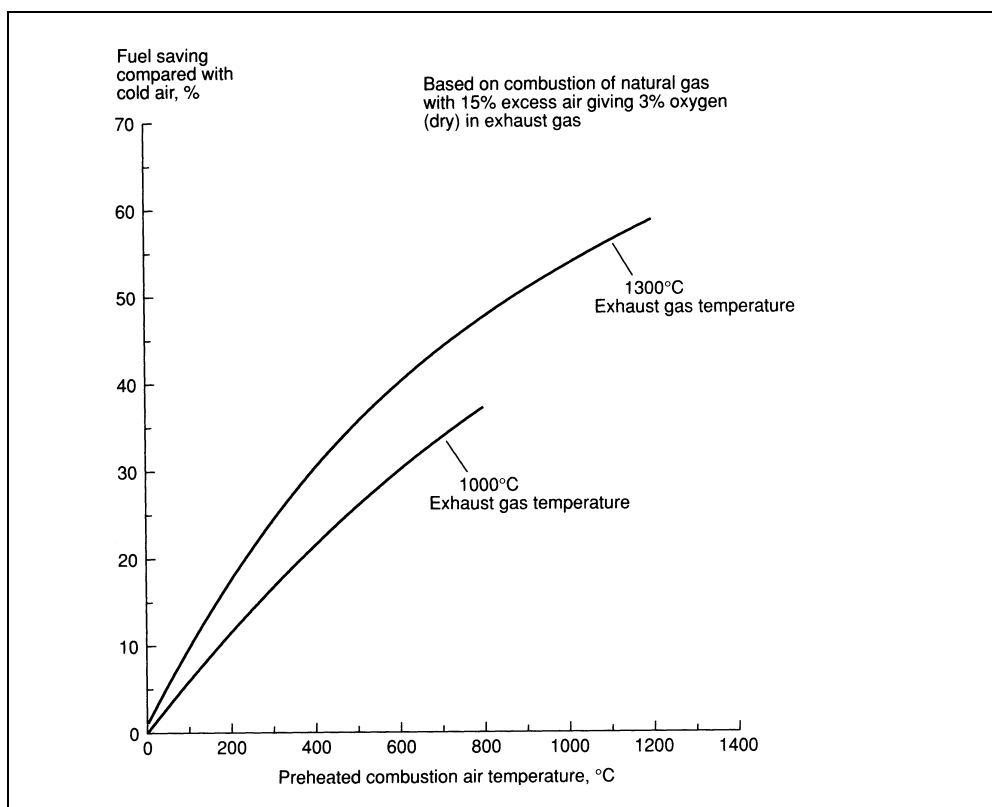
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## D.1 FURNACES: THERMAL EFFICIENCY

To improve thermal efficiency of furnaces, the exhaust gases from the furnace may be used to preheat the combustion air. Thermal efficiency increases with increasing preheated air temperature and decreasing waste gas temperature. The diagram in Figure D.1-1 shows potential fuel savings achieved by combustion air preheating. Actual values might differ from these theoretical figures as they are subject to a number of other influences.



**Figure D.1-1: Potential fuel savings with preheated combustion air [ETSU-G76]**

In general, two systems exist: the regenerative and the recuperative system/burner.

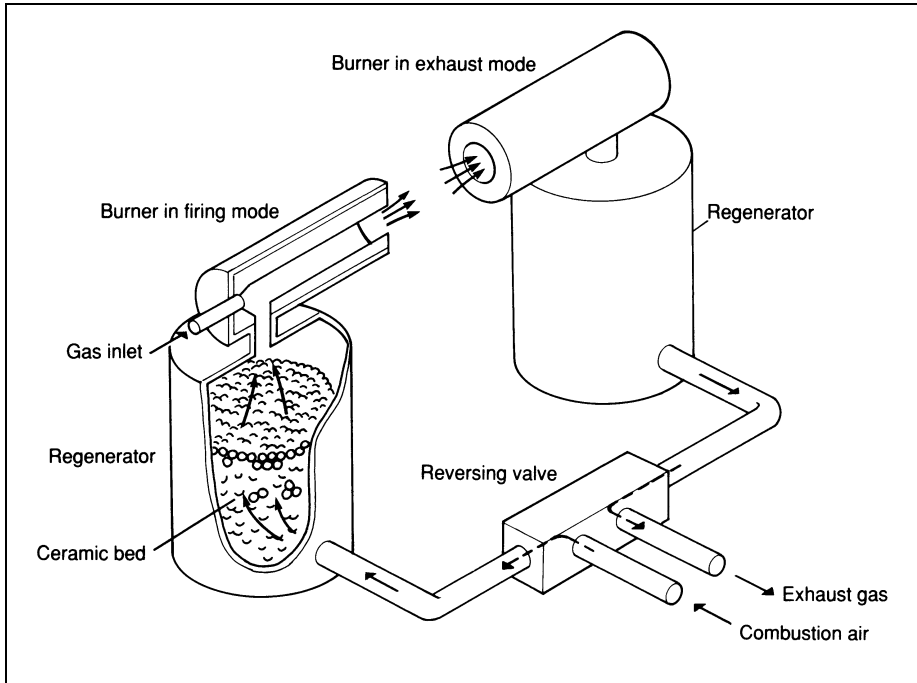
### D.1.1 Regenerative Burners

Regenerative systems use two sets of heat exchangers, containing for example brick chequer material or ceramic balls. Figure D.1-2 shows an example for such a regenerative burner system. While one burner is in firing mode, the regenerator of the other burner is heated by direct contact with the exhaust gas., the other heats the incoming combustion air. After a period of time the flows are switched to reverse the process. Such systems can achieve air preheating temperatures of up to 1100 °C (and 1300 °C), but actual temperatures are dependent on the waste gas inlet temperature. Based on the air preheat temperatures NO<sub>x</sub> emissions can be as high as 3000 mg/m<sup>3</sup>. [CITEPA]

A special type of regenerative burner is the integral bed burner which has a more compact design as the regenerative bed is incorporated in the body of the burner. These kind of burners

are especially suitable for retrofitting furnaces where space constraints may be a problem and for small furnaces.

Regenerative systems are preferred for high waste gas temperatures to achieve air preheat temperatures above 600 °C. The air preheat temperature is limited by the process temperature and is generally 150 to 200 °C below the process temperature. Thermal efficiency of the furnace of 80 % and fuel savings of up to 60 % can be achieved. [EUROFER HR], [EUROFER CR]

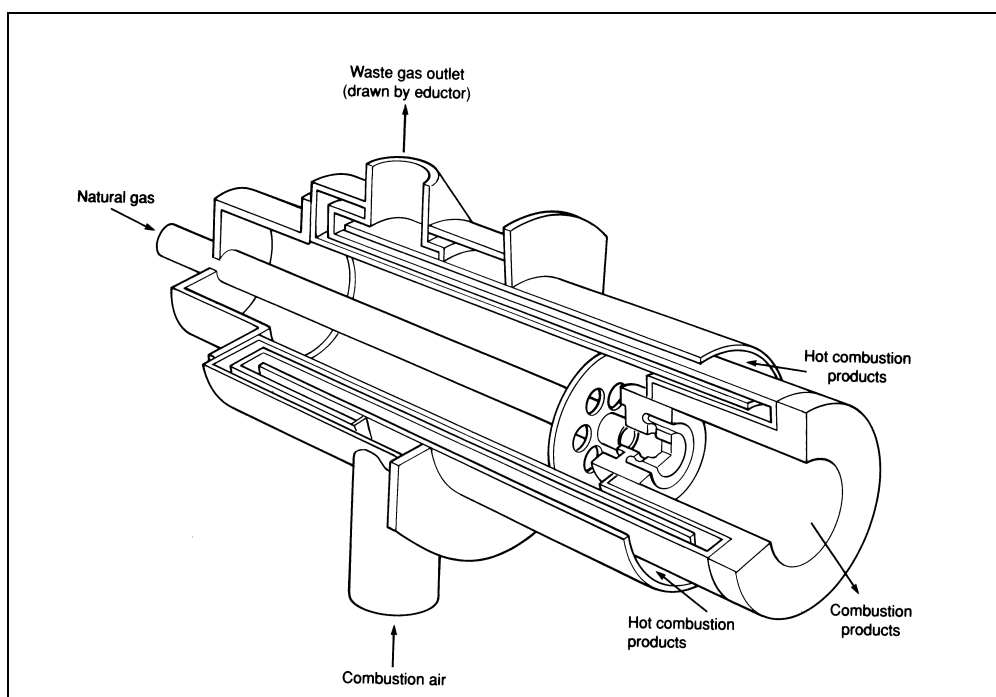


**Figure D.1-2: Schematic of a regenerative burner system**  
[ETSU-G76]

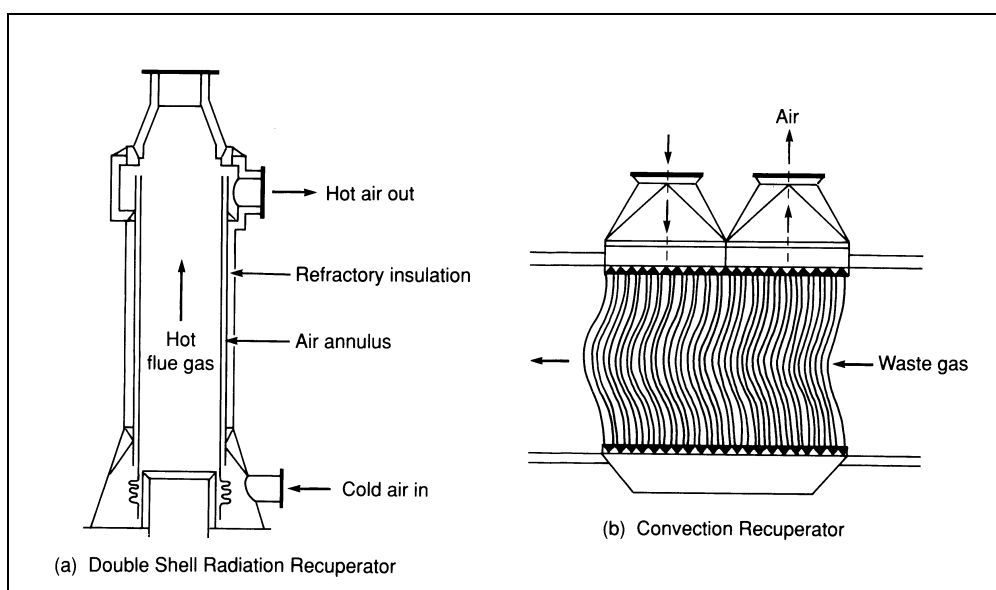
A regenerative system is particularly attractive for batch processes because batch processes generally do not contain a preheat zone. In continuous furnaces equipped with a central recuperator system, a similar thermal efficiency is reached by means of a long unheated (preheat) zone, where the heat of the flue gases is transmitted by convection to the cold stock. [EUROFER HR]

## D.1.2 Recuperators and Recuperative Burners

A recuperator is a heat exchanger fitted in the exhaust gas outlet, which allows heat to be transferred continuously through the heating surfaces to the incoming combustion air. Various equipment designs are available. (Self-) recuperative burners have integral heat exchangers for preheating combustion air.



**Figure D.1-3: Schematic of a self-recuperative burner**  
[ETSU-G76]



**Figure D.1-4: Typical exhaust gas recuperators**  
[ETSU-G76]

Recuperating the heat of flue gases allows air preheat temperature up to 550 or 620 °C depending on the process temperature. Higher air preheat temperatures are technically possible, but entail excessive cost due to the heat resistant construction-materials that would be required. A thermal efficiency of approximately 65 % can be reached. [EUROFER HR]

## D.2 FURNACES: NO<sub>x</sub> REDUCTION MEASURES

The simplest method of reducing NO<sub>x</sub> emissions is to switch from a 'dirty' fuel to a 'clean' one, which in fact means switching to gas. This may not however be feasible for existing plants and, in practice, available plant gases determine the type of fuel used in furnaces. Also, for liquid and solid fuels the sulphur content is usually of more concern than the nitrogen. [HMIP-95-003]

Another simple method is to limit the preheat temperature of combustion air, which lowers the NO<sub>x</sub> emissions in the flue gas, but at the same time will result in higher fuel consumption and cause higher CO<sub>2</sub> emissions. In this case a balanced compromise between energy efficiency and emission reduction needs to be found.

NO<sub>x</sub> reduction methods may be classified as primary and secondary. The *primary methods* modify the combustion process itself to limit the NO<sub>x</sub> formed in the combustion chamber. This is usually done by controlling the oxygen available to the fuel and/or the peak flame temperature. Such control can be achieved most easily by retrofitting conventional burners with 'low-NO<sub>x</sub> burners', in which the mixing of fuel and air is carefully controlled to produce staged combustion. Other methods, including so-called flameless burners, external flue gas recirculation or water injection, are only under development and are described in Chapter 6. [HMIP-95-003]

Secondary measures 'clean-up' the flue or exhaust gas by destroying the NO<sub>x</sub> that has been formed during the combustion process. Methods for removing NO<sub>x</sub> (NO and NO<sub>2</sub>) from exhaust gases fall into two categories. Dry processes involve the conversion of NO<sub>x</sub> to N<sub>2</sub> by injection of a reducing agent and may or may not involve a catalyst. The most widely used dry processes are selective in their operation, that is they are designed to remove NO<sub>x</sub> only, but a few techniques also remove SO<sub>2</sub>. Wet processes involve passing the flue gas through an aqueous solution which usually removes NO<sub>x</sub> and SO<sub>2</sub> simultaneously. [HMIP-95-003]

The problem of wet methods is the accumulation of large amounts of waste water which must be treated before being disposed of. In contrast, dry processes do not generate any by-products for disposal other than spent catalyst and are generally simpler and more economic to apply than wet processes. However, some dry methods are sensitive to SO<sub>2</sub> and particulates in the gas stream. [HMIP-95-003]

### D.2.1 Low-NO<sub>x</sub> Burner

Low-NO<sub>x</sub> burner is a general term for a series of new burner types that combine several design features to reduce the NO<sub>x</sub> emission level. Main principles of these burners are the reduction in peak flame temperature, the reduction in residence time in the high temperature zone and the reduction in oxygen availability in the combustion zone. This is generally achieved by air staging, fuel staging and/or internal flue gas recirculation. [HMIP-95-003] As there is a multitude of different burner designs, also varying from supplier to supplier, Figure D.2-1 and Figure D.2-2 show only a selection of different low-NO<sub>x</sub> burners available.

The **recirculation of the flue gases** from the furnace into the flame can be favoured by burner design as shown in Figure D.2-1. This lowers the O<sub>2</sub>-concentration in the air/fuel mixture and creates a quiet flame with lower temperature. The recirculation also achieves a chemical reduction of the NO<sub>x</sub> in the flue gases by the hydrocarbons in the fuel. [EUROFER HR]

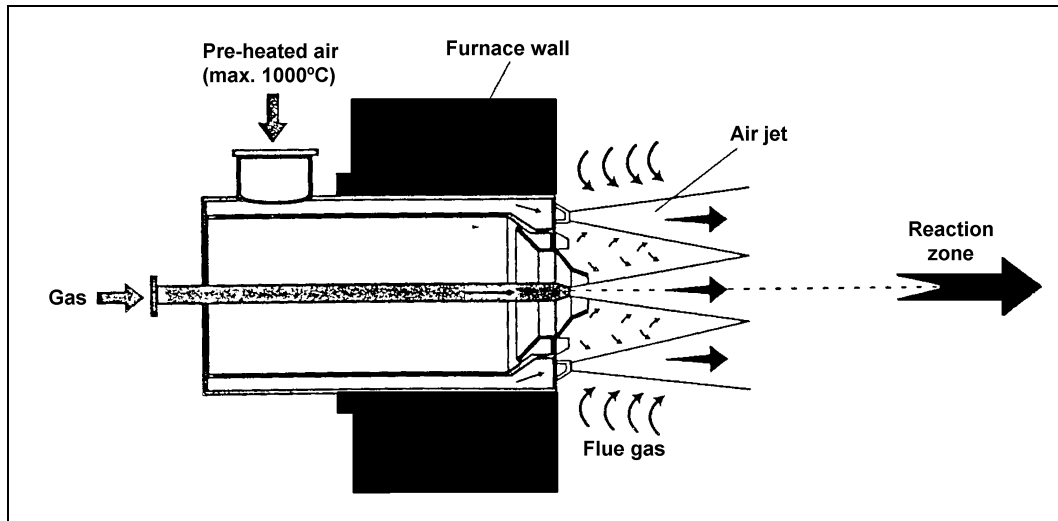


Figure D.2-1: Schematic of a Low-NO<sub>x</sub> Burner with internal Flue Gas Recirculation [ETSU-45]

A further reduction of the NO<sub>x</sub> level and of the dependency of the NO<sub>x</sub> level on the air preheat temperature can be achieved by burners with an increased jet flow, where the flame in some cases is not anchored to the tile of the burner or where the gas and combustion air inlets are separated. [EUROFER HR]

A common mode of operation of low-NO<sub>x</sub> burners lies in the creation of a fuel-rich zone within the flame. This favours the conversion of fixed nitrogen, that is chemically-bound fuel-nitrogen, to N<sub>2</sub>. It also has the effect of reducing the peak flame temperature. Both fuel and thermal NO<sub>x</sub> mechanisms are retarded and NO<sub>x</sub> is reduced. There are two main types of low-NO<sub>x</sub> burners which both involve the use of staged combustion to achieve the desired effect. These are air-staged and fuel-staged burners.

In **air-staged burners**, the first stage of combustion occurs in a slightly fuel-rich zone, at an optimum fuel/air ratio (1.1 - 1.3) for conversion of the fuel nitrogen to N<sub>2</sub>. A second stage of combustion is operated fuel-lean by addition of secondary air in a such way as to complete the fuel burnout, with careful temperature control to minimize the formation of thermal NO in this zone.

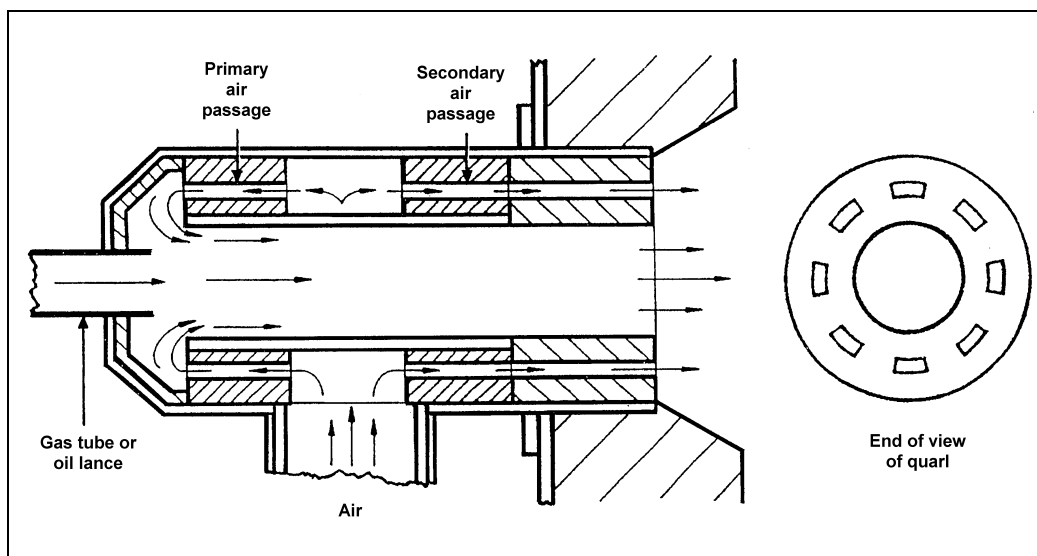


Figure D.2-2: Schematic example of an air staged low-NO<sub>x</sub> Burner [HMIP-95-003]

There are various designs of air-staged burners which differ in the way the two combustion zones are created. In aerodynamically air-staged burners, all the combustion air flows through the same burner opening, in such a way that aerodynamics is used to create the first, fuel-rich zone. External air-staged burners use a separate air stream to complete burnout. In air-staged pre-combustor burners, the fuel-rich zone is established in a separate pre-combustor section. Key design factors controlling the effectiveness of air-staged burners are the temperature and residence time in each stage. Manufacturers generally claim a reduction in uncontrolled NOx emissions on gas firing of 50 – 60 % by means of air staging. [HMIP-95-003]

In **fuel-staged burners**, NO is allowed to be formed in the primary combustion zone, but fuel is injected downstream to create a secondary fuel-rich, or 'reburn' zone where the NO is reduced to N<sub>2</sub>. Further air is added downstream to complete combustion of the excess fuel in a tertiary combustion zone, again with careful control of temperature to minimize thermal NO formation. Reburn fuels can be natural gas or coal.

The key reactions responsible for conversion of NO to N<sub>2</sub> in the fuel-rich zones of both types of low-NOx burners are those between NO and small hydrocarbon- and nitrogen-containing radicals (such as CH, CH<sub>2</sub>, NH, NH<sub>2</sub>, NCO) which are present under these conditions. The mechanisms of NOx chemistry are complex and effectiveness of the methods described here to reduce NOx formation depends on a number of factors including burner design, operation, fuel quality (particularly the volatile and fuel-nitrogen content), particle size (especially for liquid and solid fuels) and scale of operation.

Low-NOx staged combustors are the most applicable of control techniques for industrial furnaces and do not present many difficulties of installation. Some, but not all, designs of staged combustor result in lower burner exit velocities and this reduction in momentum may cause changes in furnace aerodynamics and hence problems with heat transfer distribution. Similarly, flames will tend to lengthen which may necessitate increases in excess air levels to avoid direct flame contact with the material being heated. [HMIP-95-003]

Low-NOx burners can be more complex and/or bulky than conventional burners and may give rise to problems in furnace design or in retrofitting existing furnaces. Investment cost for retrofit depends on the type and size of furnace and to what degree the new burners are compatible with the existing combustion equipment. No increase of operating costs is connected with low-NOx burners. [ETSU-45]

## D.2.2 Limiting Air Preheating Temperatures

Emission levels of NOx increase with increasing preheating temperatures of combustion air as is shown in Figure D.2-3 and Figure D.2-4. Thus limiting air preheating can be a measure to limit NOx emissions.

On the other hand, the preheating of combustion air is a commonly applied measure to increase the energy efficiency of furnaces and to decrease fuel consumption, as has been described in Chapter D.2. The increase of fuel consumption to be expected from reducing air preheat temperatures can be seen in Table D.2-1.

Generally, plant operators are interested in reducing the fuel consumption as this implies a monetary benefit, but the reduction of fuel consumption can additionally reduce other air pollutants, such as CO<sub>2</sub>, SO<sub>2</sub> and particulates. Thus a choice has to be made between energy efficiency and decrease of SO<sub>2</sub> and CO<sub>2</sub> emissions on one hand and increase of NOx emissions on the other hand. When keeping air preheating temperatures high, the application of secondary NOx reduction measures might be necessary.



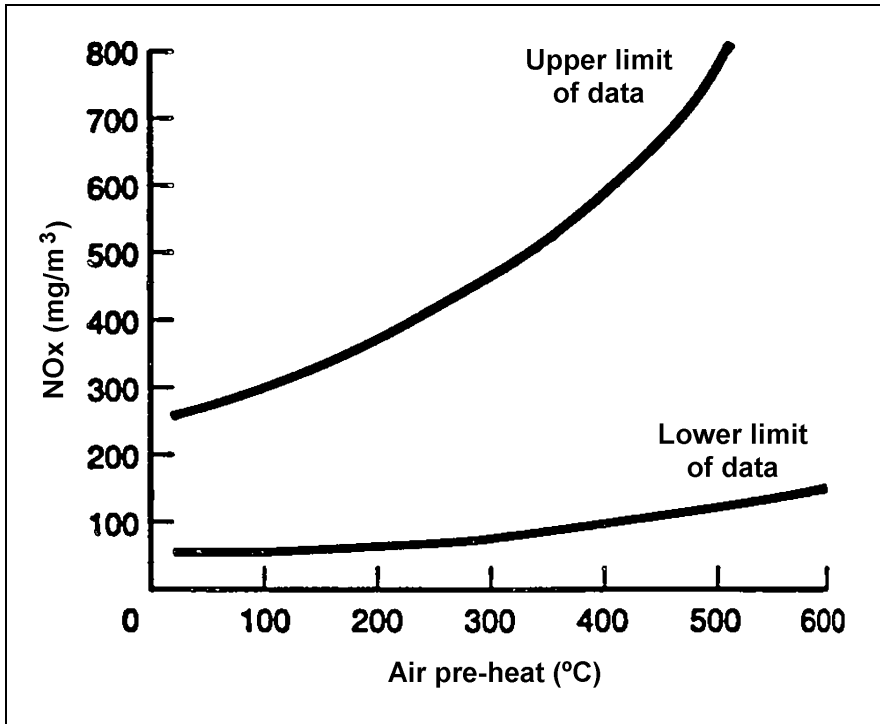


Figure D.2-3: Influence of air preheating temperatures (low range) on NO<sub>x</sub> emissions <sup>1</sup> [ETSU-45]

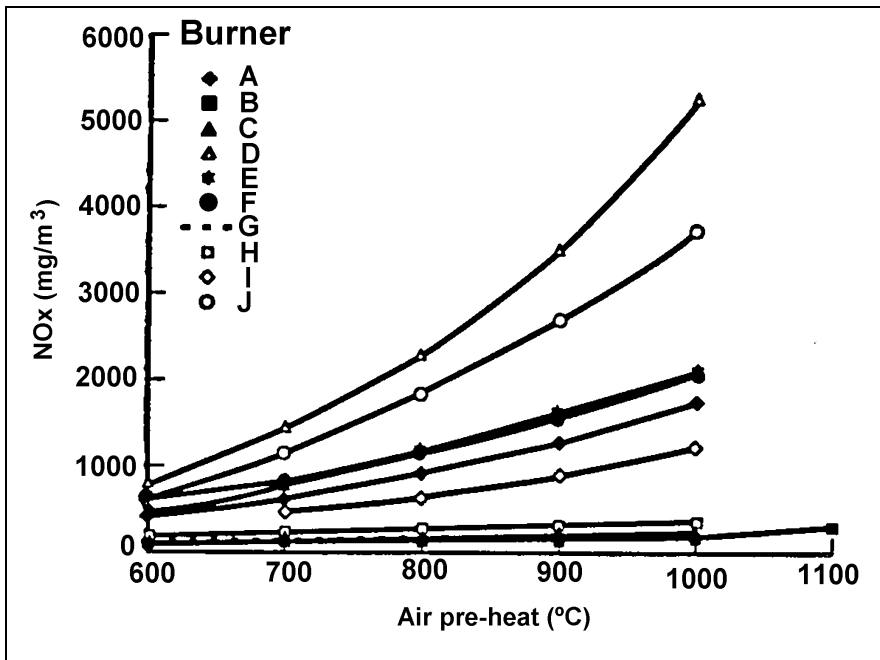


Figure D.2-4: Influence of air preheating temperatures (high range) on NO<sub>x</sub> emissions <sup>1</sup> [ETSU-45]

<sup>1</sup> NO<sub>x</sub> concentrations expressed as mg/m<sup>3</sup>, corrected to 3 % oxygen on a dry basis, at 0°C and 101.3 kPa

Initial air pre-heat [°C]	Final air pre-heat [°C]								
	1000	900	800	700	600	500	400	300	200
1000	0.0	6.0	12.6	19.9	28.3	37.7	48.6	60.4	74.5
900		0.0	6.3	13.1	21.1	30.0	40.3	51.4	64.7
800			0.0	6.4	13.9	22.2	31.9	42.3	54.9
700				0.0	7.0	14.9	24.0	33.8	45.6
600					0.0	7.4	15.9	25.0	36.0
500						0.0	7.9	16.4	26.7
400							0.0	8.4	17.4
300								0.0	8.8
200									0.0

Table D.2-1: Calculated percentage increase in fuel consumption from reduced air preheat [ETSU-45]

### D.2.3 External Flue Gas Recirculation (FGR)

Flue gas recirculation (FGR) is a technique for limiting peak flame temperatures. Recirculating flue gases into the combustion air will reduce the oxygen to 17 to 19 % and lower flame temperatures, hence limiting thermal NOx formation. [HMIP-95-003], [HR]

The NOx reductions achieved by FGR are shown in Figure D.2-5. The diagram is based on a range of test data.

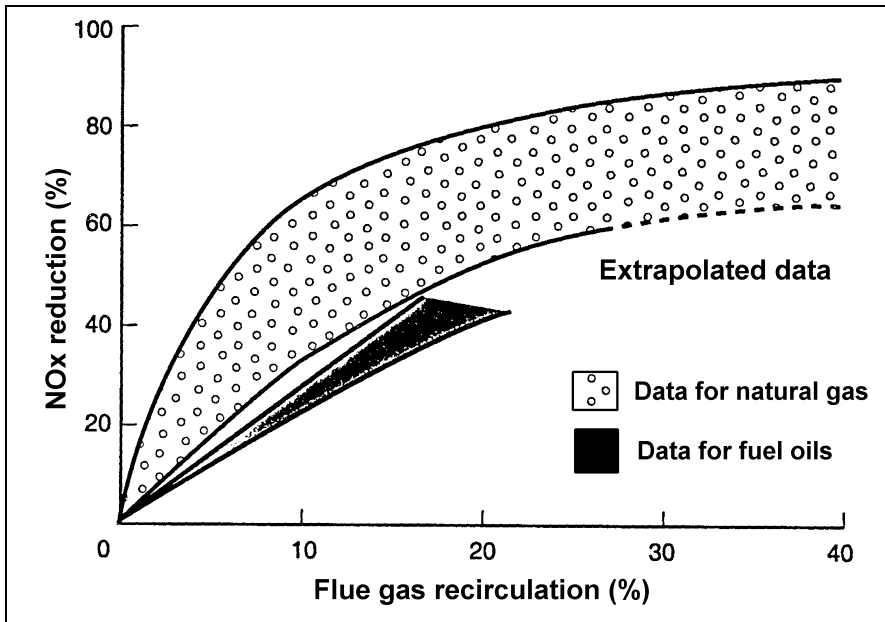


Figure D.2-5: Effect of flue gas recirculation on NOx emission [ETSU-45]

Some data from several different test rigs showed that FGR can achieve NOx reductions approaching 70 – 80 % depending on the fraction of the flue gas that is recirculated (FGR 20 to 30 %), the temperature of the recirculated gases and whether or not the FGR is to be applied to a low-NOx burner system. Fractional reductions compared directly to a staged combustion burner

should be somewhat less, but the overall reductions with respect to baseline should still be greater, although there are insufficient experimental results to quantify this for high temperature industrial burners. [HMIP-95-003]

In principle, FGR should be applicable to most reheating and heat treatment processes. However, in practice, for retrofitting, there may be physical difficulties in installing ductwork and problems of accessibility. [HMIP-95-003]

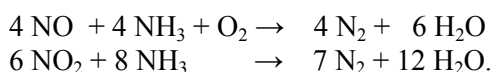
At least one manufacturer offers FGR in conjunction with its low-NO<sub>x</sub> burner range and there may well be others.

Regarding operational problems, there is some concern that there may be flame stability problems at 'turndown' and that increased water vapour contents in the combustion products can increase for example the scaling of the steel that is being heated. [HMIP-95-003]

Some doubts exist about how FGR is actually done in a multiburner combustion system. Variable composition fuels (and hence variable waste gas volumes) could also result in combustion control problems. [EUROFER HR]

## D.2.4 Selective Catalytic Reduction (SCR)

The SCR process is the most highly developed and widely used method for NO<sub>x</sub> removal from exhaust gases. The process involves the reduction of NO and NO<sub>2</sub> to N<sub>2</sub> of ammonia over a catalyst bed. The overall reactions are:



The optimum temperature window for these reactions is 300 – 400 °C. Usually, ammonia is added slightly sub-stoichiometrically (0.9 – 1.0 mole per mole of NO<sub>x</sub>) to suppress carry-over. [HMIP-95-003], [ETSU-45], [HMIP-95-003]

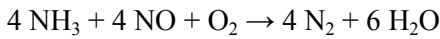
The most effective and widely used catalyst is vanadium pentoxide, V<sub>2</sub>O<sub>5</sub>, supported on TiO<sub>2</sub>. Other substances exhibiting catalytic activity are Fe<sub>2</sub>O<sub>3</sub> and CuO; the noble metals (Pt, Pd, Ru, Rh); oxides of the metals W, Mo, Cr, Co and Ni; certain zeolites and activated carbon. The catalyst may be employed in a variety of structures and configurations to alleviate the problem of blockage by particulates depending on the severity of the problem. A honeycomb shaped catalyst is suitable in a fixed bed configuration because it permits the particles to pass through without clogging. A moving bed configuration allows a deactivated or clogged catalyst to be constantly regenerated. A parallel-flow arrangement is also suitable. [HMIP-95-003]

Deactivation by poisoning (Na, K, As), erosion or solid contamination may limit the lifetime of the catalyst. [EUROFER HR]

The efficiency of NO<sub>x</sub> reduction by SCR depends on the catalyst used and the initial NO<sub>x</sub> concentration. Values of up to 95 % have been reported, with a typical range being 70 – 90 % [HMIP-95-003], [ETSU-gir-45]

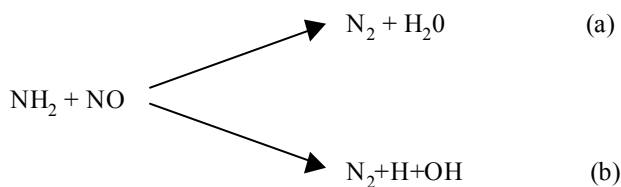
## D.2.5 Selective Non-Catalytic Reduction (SNCR)

In this process, also known as the thermal DeNO<sub>x</sub> process, ammonia is injected directly into the flue gas at higher temperatures to reduce NO to N<sub>2</sub>, without the aid of a catalyst. To ensure the maximum possible reduction of NO<sub>x</sub> it is necessary to inject the reagent at a point in the process where the exhaust gas temperature is within an optimum range. For ammonia the range is between 850 °C and 1000 °C and for urea the range is from 950 °C to 1100 °C. The overall reaction is:



The presence of excess O<sub>2</sub> in the exhaust gas is thus required, as well as a residence time of 0.1 to 0.4 seconds. A feature of this process is that it is only effective over a narrow temperature window. [HMIP-95-003]

The reaction mechanism is a homogeneous gas phase one, the key step being:



The chain-branching channel (b) producing radicals is crucial to sustaining the reaction: without it, the reaction would quickly terminate. This reaction is in competition with reactions of NH<sub>2</sub> with oxidizing radicals (O, OH) which lead to the formation of NO. This competition explains the existence of the temperature window. At temperatures below the low temperature limit, NO reduction is limited by radical chain termination steps in the mechanism competing effectively with chain-branching steps; at temperatures above the high temperature limit, NH<sub>3</sub> oxidation dominates over NO reduction leading to net NO formation. Additives influence this window by altering the balance between these processes. [HMIP-95-003]

Ammonia is potentially explosive and its safe storage would be a significant consideration with cost implications. [HMIP-95-003]

## D.2.6 Comparison of NOx Reduction Methods for Furnaces

Technique	Advantages	Disadvantages
<b>Low-NOx burners</b>	<ul style="list-style-type: none"> <li>- Moderate to high level of NOx reduction</li> <li>- Fuel consumption unchanged</li> <li>- Low or zero operating cost penalty</li> </ul>	<ul style="list-style-type: none"> <li>- High capital cost</li> <li>- Longer flame (?)</li> <li>- Poor flame shape (?)</li> <li>- Reduced flame velocity (?)</li> <li>- Poor furnace temperature uniformity (?)</li> <li>- Reduced flame stability (?)</li> <li>- Larger burners (?)</li> <li>- Poor turndown (?)</li> </ul>
<b>Limiting air preheat</b>	<ul style="list-style-type: none"> <li>- Can be simple, with low or zero capital cost</li> <li>- Moderate to high level of NOx reduction</li> </ul>	<ul style="list-style-type: none"> <li>- Increased fuel costs</li> <li>- Downrating of combustion equipment</li> <li>- Reduced flame stability</li> <li>- Reduced burner velocity therefore furnace temperature uniformity</li> </ul>
<b>Flue gas recirculation</b>	<ul style="list-style-type: none"> <li>- Moderate to high level of NOx reduction</li> <li>- Improved temperature uniformity(?)</li> <li>- Medium capital costs (if no uprating required)</li> </ul>	<ul style="list-style-type: none"> <li>- High capital cost (if uprating required)</li> <li>- Increased fuel and electricity costs</li> <li>- More space required (especially if uprating required)</li> <li>- Reduced flame stability</li> <li>- Downrating of existing combustion system</li> </ul>
<b>SCR</b>	<ul style="list-style-type: none"> <li>- High level of NOx removal</li> <li>- Combustion system not downrated</li> </ul>	<ul style="list-style-type: none"> <li>- Very high capital costs</li> <li>- Increased energy and operating costs</li> <li>- Ammonia slip</li> <li>- Ammonia storage problems</li> <li>- Sensitive to changes in temperature/flowrates</li> <li>- Requires specific waste gas temperature</li> </ul>
<b>SNCR</b>	<ul style="list-style-type: none"> <li>- Moderate to high level of NOx reduction</li> <li>- Combustion system not downrated</li> </ul>	<ul style="list-style-type: none"> <li>- High capital cost</li> <li>- Increased energy and operating costs</li> <li>- Ammonia slip</li> <li>- Ammonia storage problems (unless urea is used)</li> <li>- Sensitive to changes in temperature/flowrates/stoichiometry</li> <li>- Requires specific furnace temperature</li> </ul>
<p>Note Source [ETSU-gir-45]            (?) Indicates a possible or likely effect</p>		

**Table D.2-2: Comparison of NOx reduction methods (as reported by [ETSU-gir-45])**

Technique	Typical range of NOx reduction	Initial capital cost (GBP '000)	Operating cost (GBP/GJ)	Total cost of technique (GBP '000/year for 50 MW furnace)					
				2000 hours/year	3000 hours/year	4000 hours/year	5000 hours/year	6000 hours/year	8000 hours/year
Low-NOx burners	Up to 97	328	0.0	53.7	53.7	53.7	53.7	53.7	53.7
Limiting air preheat		NA	0.0257 for 50 % NOx reduction	92.5	139	185	231	278	370
Flue gas recirculation	Up to 93 (44.74 15 % FGR)	75.6 (631)*	0.098 (0.072)*	47.6 (129)*	65.2 (142)*	82.9 (154)*	101 (167)*	118 (180)*	153 (206)*
SCR	up to 95 (Typically 70 - 90)	1100 - 2530	0.0722	205 - 438	218 - 451	231 - 464	244 - 477	257 - 490	283 - 516
SNCR (with NH <sub>3</sub> )	up to 85 (Typically 50 - 60)	350 - 650	0.0361	69.9 - 119	76.4 - 125	82.9 - 132	89.4 - 138	95.9 - 145	109 - 158
<p>Note Source of data [ETSU-45]</p> <p>NA Not available and, for the purposes of calculation, assumed to be small compared with operating cost.</p> <p>* Figures in brackets refer to case where burners and regenerators would need to be uprated.</p> <p>NB1 Flue gas recirculation operating cost figures all based on 15 % FGR. Estimated fuel consumption penalty = 3.2 % Increased fan running costs (based on regenerative burners) = 1.6 % of fuel costs (0.32 % if burners and regeneratoars were uprated).</p> <p>NB2 Water injection cost figures all based on 15 kg (water)/Gj (fuel): Estimated fuel cost penalty = 11.8 % Cost of water not included.</p>									

**Table D.2-3: Estimated costs of NOx reduction techniques for a 50 MW furnace (as reported by [ETSU-gir-45])**

## D.3 OIL EMULSIONS

### D.3.1 Cleaning and Reuse of Emulsion

Rolling emulsions from the mill stands, wet wire drawing lubricants etc. pick up particulate matter, steel slivers, scale and dust during operation. As the degree of contamination rises, these impurities affect the quality of the product and lead to process failure. To enable emulsion systems to be run as circulation systems and to extend the lifetime of the emulsions, the cleanliness is controlled closely.

Solids can be removed from emulsions by gravity in **settling tanks, in separators, mesh filters, magnetic filter etc.**

To remove solids a **centrifuge** utilizes centrifugal forces. Dirty liquid is fed into the spinning rotor or bowl, whereby the liquid is accelerated and distributed onto the internal walls of the bowl. The solids separate and compact at the perimeter of the bowl. The solids remain in the bowl while the liquid exits, as it is displaced by the incoming liquid.

Once the bowl fills to maximum allowable capacity with waste solids, the automatic cleaning cycle is activated. At this point, the feed of dirty liquid is shut off and the rotor comes to a complete stop. The internal scraping blades then rotate back and forth against the rotor while removing the solids, which dump into a collection hopper. [El-Hindi]

Depending on the particle size of the solids, **mesh filters** or **media filtration** using disposable paper can be used. The liquid is forced through the filter media which extracts the fines, by gravity, pressure or vacuum.

However, a partial flow of the emulsion may need to be withdrawn from the system to maintain quality.

### D.3.2 Treatment of Spent Emulsion / Emulsion Splitting

The partial flow discarded from the emulsion circuit systems requires treatment prior to discharge. This treatment basically constitutes the separation of the water and the oil phase. The purified water is discharged. The separated oil or oil-containing sludge may be reused, e.g. thermally by incineration. There are many different emulsion splitting systems each comprising several processing steps. Treatments available comprise:

- Thermal: by evaporation and splitting with chemical additions.
- Chemical: acid splitting, salt splitting, combined dosage of coagulants and polyelectrolytes.
- Flotation.
- Adsorption.
- Electrolytical.
- Membrane filtration (ultra-filtration, reverse osmosis).

#### D.3.2.1 Thermal Breaking/Thermal Emulsion Splitting/Evaporation

Thermal breaking utilizes a heat source, e.g. an internal heating tube or immersion gas burner, to raise the emulsion temperature to accelerate the evaporation rate, driving away the water content. The water exits as vapour leaving the increasingly concentrated oil as a separate discharge. [El-Hindi]

The air saturated with water vapour is passed through coalescing elements to retain any possible droplets of coolant in the air stream prior to discharge. As an option, a condenser unit using a water-cooled coil can be installed in the discharge stack to retrieve the water as condensate. This water stream can then be used as make-up water to be reintroduced to the emulsion system. [El-Hindi]

The concentrated oil left in the chamber is subjected to a cookdown cycle to drive out more water content. By thermal breaking, an emulsion with initial concentrate of 5 to 7 percent oil can be ultimately reduced to 90 percent oil and 10 percent water. With the greater amount of water content removed, the disposal volume and cost are much less. With the greater concentration of oil, the reuse option of incineration is more feasible. [El-Hindi]

### D.3.2.2 Chemical Breaking of Emulsions

In splitting with acid/salt, the emulsified oil will mostly be adsorbed to sludge and will not be separated as an oil phase. The addition of acids, iron/aluminium salts or polyelectrolytes causes the oil emulsion to destabilise due to the neutralisation of the charged colloidal oil particles. Splitting of oil-containing emulsions with acids or salts is not a state-of-the-art technique, due to the generation of large amounts of oil-containing neutralisation sludges and the contamination of waste water by salt. Acids/salts can be used as aftertreatment in combined processes if only small amounts of residual oil need to be removed.

Polyelectrolytes soluble in the oil phase (so-called „organic splitters“, e.g. tertiary and quaternary polyamines) do not produce sludge during the splitting process itself, but generate a liquid oil phase which can be removed and utilized. This process can be used to treat emulsions with a high content of emulsified oil (a well-suited pre-treatment technique when a combination of processes is applied). Polyelectrolytes (often used in combination with absorbents) through which the proportion of emulsified oil is bound within flocs and which produce a removable sludge (flotation or sedimentation) should only be used when the oil content is low (less than 300 mg/l), in order to reduce flocculant consumption, sludge volume and, thereby, costs. When a combination of processes is applied, flocculation can be used as aftertreatment. [Com2 D]

### D.3.2.3 Flotation

Flotation is a gravity separation process using different density of two media. The lighter medium (e.g. oil) is collected at the surface of the heavier medium (e.g. water) in a tank with low turbulence. Even heavier media (e.g. flocs) can be collected at the water surface if flocs are made lighter by gas bubbles sticking to the flocs. Gas bubbles must be smaller than the flocs, otherwise they will not stick. Small bubbles are usually produced by pressurising water and gas together (dissolved air flotation), electrolytically (water split into hydrogen and oxygen gas bubbles) or by high shear forces (mechanical dispersing of gas into water). [Com2 A]

Flotation emulsion breaking usually means a two-step process consisting firstly of chemical emulsion breaking (by dosing acid, flocculents and polyelectrolyte or electrochemically by dissolving the anode) and secondly of flotation for separating the flocs from water. [Com2 A]

The layer of floating sludge forming at the water surface (flotate) is removed mechanically. In general, flotation techniques can be distinguished *inter alia* by the way the gas bubbles are produced:

- Pressure relief flotation (introduction of air-saturated pressurised water).
- Electroflotation (electrolytical decomposition of water with formation of hydrogen and oxygen bubbles).
- Dispersion flotation (generation of microbubbles through injection of air via a hollow shaft).



No additional solids arise in the flotage sludge when polyelectrolytes are used for emulsion splitting instead of acids/salts. [Com2 D]

#### **D.3.2.4 Adsorption**

Adsorption means adhering the oil particles to the surface of a solid or semisolid adsorbent. The adsorbent may either be a fixed bed of solids (e.g. activated carbon) through which the emulsion is flowing or may be a powdered solid (e.g. activated carbon) or semisolid flocs (e.g. iron hydroxide) distributed into the liquid. Powder or flocs have to be finally separated from liquid by settling, flotation or filtering. [Com2 A]

Oil-contaminated adsorbent has to be discharged when exhausted and treated as sludge or has to be burnt (or sometimes regenerated in case of fixed beds).

Fixed bed adsorbers and powder type adsorbers are only usable for very low oil concentrations, otherwise adsorbent is exhausted too fast and is therefore too expensive. It is not common as basic emulsion treatment but it is sometimes used as a final polishing step of other types of emulsion breaking. Adsorption to semisolid flocs is part of the chemical emulsion breaking. [Com2 A]

A special kind of adsorption are coalescing filters. These filters are filled with regular or irregular wire mesh, plastic or ceramic filling and will cause small oil droplets to collect and adhere to this filling. If collected oil volume increases, oil droplets (now bigger in size) will escape and rise up to the water surface from where they are skimmed off. Coalescing filters are sometimes used as emulsion pre-treatment to remove free oil droplets from an emulsion. [Com2 A]

Use of adsorbents for treating spent emulsions consumes large amounts of chemicals and generates considerable quantities of oil-containing waste sludge. [Com2 D]

#### **D.3.2.5 Electrolytical Emulsion Splitting**

In electrolytical emulsion splittings aluminium anodes are dissolved; the resulting sludge flakes bond the oil and float. To improve the separation effect polyelectrolyte can be added. In addition, control of the pH-value and the electrical conductivity is maintained.

All of the oil contained in the emulsion has to be removed as sludge. The process does not produce an oil phase fit for use. [Com2 D]

#### **D.3.2.6 Ultrafiltration**

A successful alternative for emulsion with low initial oil concentration (< 2 %) is the use of ultrafiltration (UF), see Figure D.3-1, to mechanically split out the oils or soaps. The oil is separated at the molecular level, as the emulsion is forced through membrane filters. The membranes block oil molecules, while the water molecules pass through. The water, which passes through, is called permeate, while the restrained oil is called concentrate. Typically, the concentration of the concentrate (oil) does not exceed 25 percent and is limited by the plugging of the membranes. As membranes are plugged, the ultrafilter cartridges must be periodically backwashed. [El-Hindi]

The average separation efficiency of UF, related to normal industrial water, is approx. 40 l/h per m<sup>2</sup> filter surface. [EUROFER HR]

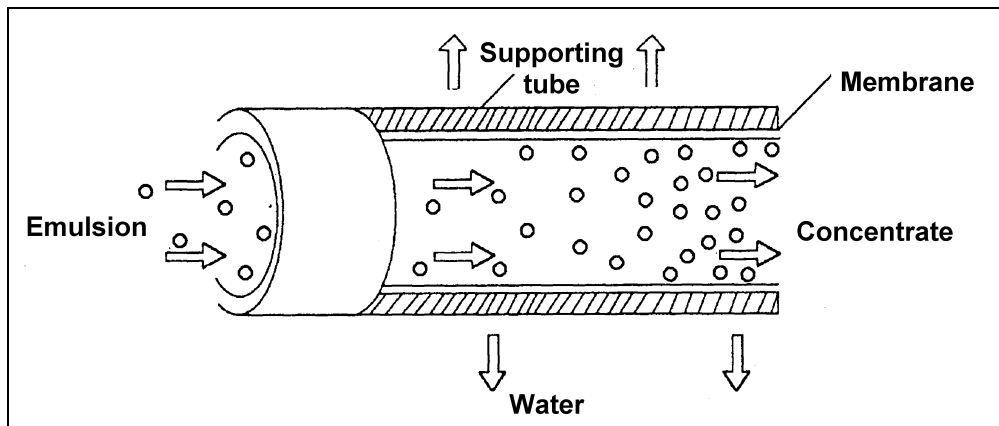


Figure D.3-1: Principle of ultrafiltration  
[Fichtner]

### D.3.3 Extraction of Oil Mist /Emulsion Fumes and Oil Abatement

Emulsion fumes from the mill stands are extracted and passed through separators for cleaning. Eliminators containing baffle packing and impingement plates or mesh pads to separate the oil from the extracted airflow and in some cases electrostatic precipitators are used. Reduction efficiency is > 90 %.

## D.4 ALKALINE DEGREASING

### D.4.1 Implementation of Degreasing Bath Cascades

→ No information submitted.

### D.4.2 Hot water pre-degreasing

(degreasing with hot water, 60–80 °C, can remove 99 % of the oil)

→ No further information submitted.

### D.4.3 Maintenance and Cleaning of Degreasing Baths

High oil contents make degreasing solutions unusable and cleaning measures are applied to extend the life span of the bath. The following measures can be applied:

#### D.4.3.1 Mechanical Cleaning

Sludge, a mixture of oil, other impurities and spent degreaser, settling at the bottom of degreasing baths can be removed by **scratchers**. Suspended particles can also be removed by sedimentation in **gravity separators**.

As the emulsions of degreasing agents and oil/grease from the metal surface are usually unstable, they float on the surface in calm areas after a while. Calm areas can be achieved by special design features of the degreasing tank or if this is not possible, e.g. when the degreasing

solution is sprayed, by introducing a special calm tank where the solution can settle. The floating oil and grease can be removed by **skimmers**, **discharge launders**, etc.

With these measures, simply using natural gravity (separating time: a couple of hours), the life of degreasing baths can be prolonged by 2 or 4 times. Sludge withdrawn contains oils, grease, degreasing agent, scale, rust, dust etc. and is usually disposed. [ABAG], [Fichtner]

Separation is more effective using **centrifuge separators** or hydrocyclones, which split the oil and water phases within seconds. Very small oil and grease drops are separated more easily; the oil-rich part contains only 5 - 10 % water and unwanted carryout of degreasing chemicals is prevented. The life of the baths can be prolonged by up to 16 times. [ABAG]

### D.4.3.2 Magnetic Separators / Filters

Magnetic separators can be used to remove the mixture of iron fines and oil from degreasing baths.

→ No further information submitted.

### D.4.3.3 Adsorption of Surfactants and Oil (Precipitation followed by Filtration)

→ No information submitted.

### D.4.3.4 Membrane Filtration

In **micro- and ultrafiltration** (see also Figure D.3-1: Principle of ultrafiltration) the degreasing bath is pumped through membranes (3 - 8 bar) in which oil, grease and spent surfactants are held back due to the size of the molecules. To protect the membranes, the degreasing liquid is usually cleaned from particles in a settling tank or by other means first. Micro- and ultrafiltration increase the lifetime of the bath by 10 to 20 times. [ABAG]

Figure D.4-1 shows the flow sheet of such a filtration plant; in regular production the degreasing liquid is pumped out of the bath into a standard plate filter where all solid particles are removed. The filtrate then goes on to a storage vessel, also known as a circulation vessel. The vessel contains the concentrated degreasing solution. [Sprang-IG-97]

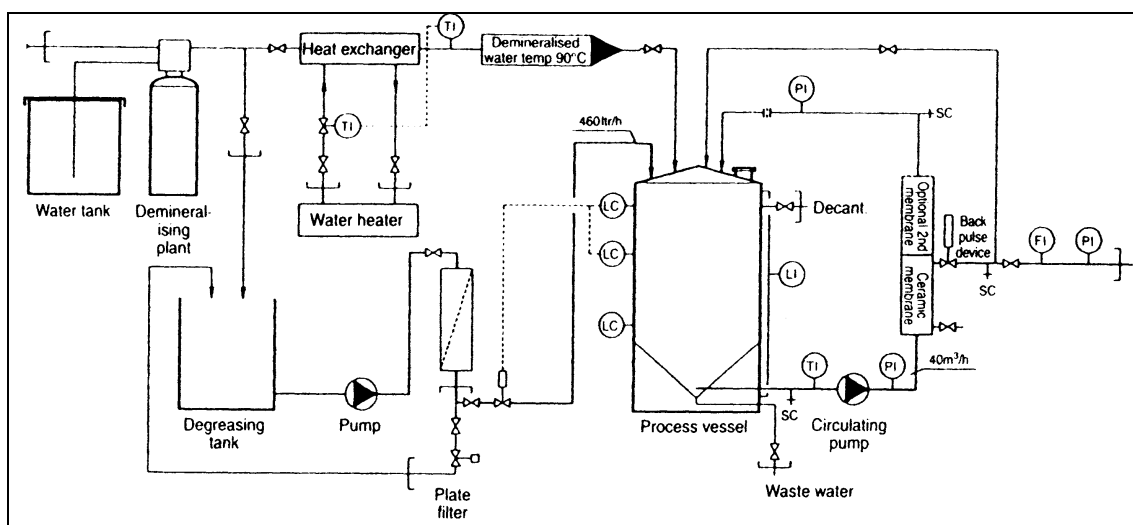


Figure D.4-1: Example flowsheet for ceramic filtration of degreasing solution [Sprang-IG-97]

A second pump forces degreasing solution through the membrane section at high speed and pressure (approximately 2.5 bar). The free oil and oil dissolved by the surfactant are filtered out by the membrane while the clear liquid and free surfactants flow through it and back into the degreasing bath. Thus, any oil that forms is removed during the course of normal production. Liquid circulates through the storage vessel and concentrates over time. When the oil concentration is high enough the unit is turned off and the liquid (oil and water) in the storage vessel allowed to settle. After a period of time a two stage process takes place; the oil is separated from the water phase and to recycle the active surfactants, a basic component of the degreasing solution, thermal shock is employed in the second stage. This shock causes the surfactant to release the oil trapped in it and to separate into two phases. Separation is highly effective and high-grade oil recovered. [Sprang-IG-97]

#### D.4.4 Treatment of Spent Degreasing Bath

Even though cleaning measures are applied to degreasing baths and the degreasing solution can be circulated/ used over some time, degreasing baths eventually have to be discarded or partial flows have to be discarded on a continuous basis to maintain the degreasing quality. To reduce the oil load, the same measures can be applied as described for emulsion breaking/splitting in oil emulsion systems (see previous chapter).

The generated oily waste may be reused, depending on the oil concentration, e.g. by incineration. The filtrate or the already de-oiled water phase is then further treated in a waste water treatment plant (see following Chapter D.4.5).

#### D.4.5 Treatment of Alkaline Waste Water

Partial flows from the degreasing solution cleaning circuit, rinsing water from the electrolytic degreasing and waste water from the skin pass mill stand, which can not be reused in the mills, have to be treated prior to discharge. They are usually neutralised with lime or HCl in a neutralisation plant, passed through filters and finally discharged. The sludge is dewatered in filter presses and discharged for landfill deposit.

#### D.4.6 Degreasing Fume Collection and Treatment

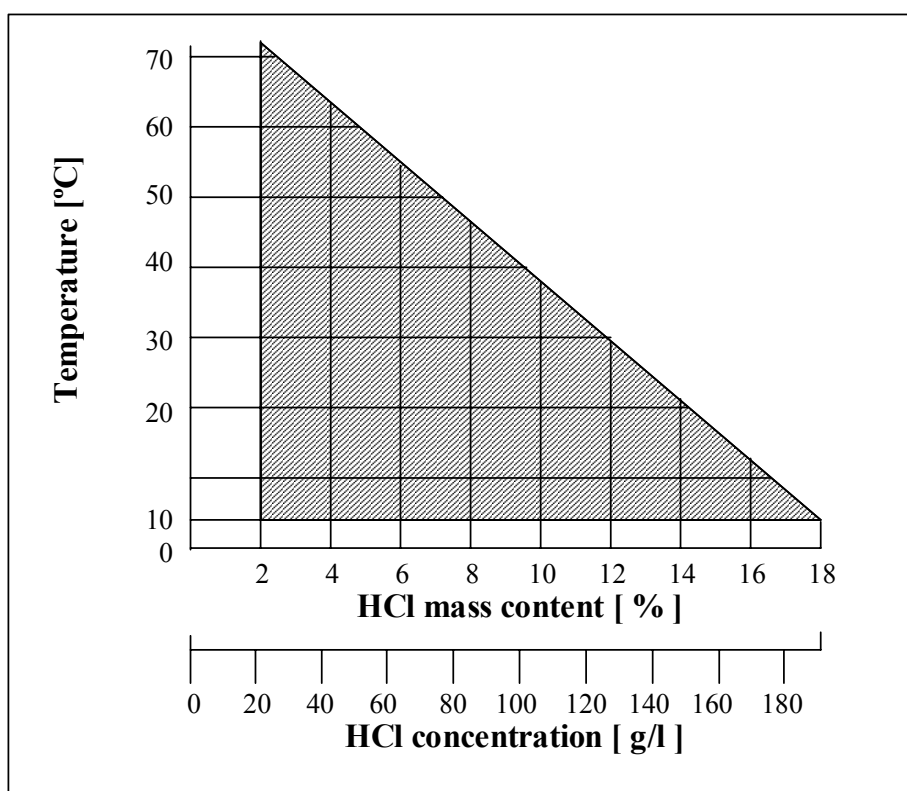
Fumes generated by degreasing operations can be collected and extracted by commonly known measures, such as closed degreasing tanks, enclosures extraction hoods, etc. The extracted air can then be cleaned by means of **demisters**. The separation is based on mass inertia. Particles (liquids or solids) with a certain mass and speed follow their original direction. When they collide with obstacles, because of their mass inertia they are separated from the carrier gas stream. Obstacles are created by means of simple walls, fillings (i.e. mesh wire), labyrinths etc. [Com-CC-2]

## D.5 PICKLING

### D.5.1 Open Pickling Bath Operation

The hydrogen chloride content in the gaseous phase above a hydrochloric acid pickling bath depends to a large degree on bath temperature and concentration and is determined by thermodynamic equilibrium and the vapour pressure of the acid.

Figure D.5-1 shows the limiting curve for the operation of open HCl pickling baths given in the [VDI-RL-2579]<sup>1</sup>



**Figure D.5-1: Limiting curve for the operation of open HCl pickling baths [VDI-RL-2579], [Galv-BAT-E]**

It is indicated that emissions from pickling baths are below  $10 \text{ mg/m}^3$  when the operating point (temperature and HCl concentration) of the baths is within the shaded area of this diagram. [VDI-RL-2579]

By close control of process parameters (temperature, concentration) and by ensuring that bath operating conditions are within these given limits, vapour extraction systems and subsequent abatement techniques may become redundant.

During operation the ferrous chloride concentration in the pickling baths rises. This results in an increased pickle effect. At the same time, ferrous chloride in hydrochloric acid affects the vapour pressure of the acid in the same way as if the acid concentration was increased: the vapour pressure is increased. Comparing a pickle liquor with 1 % HCl and 6 % iron at  $140 \text{ }^\circ\text{F}$

<sup>1</sup> Emission Control Guideline for Hot-dip Zinc Galvanizing Plants of the German Engineers Association, (Verein Deutscher Ingenieure)

(60 °C) with a straight 10 % acid solution, the vapour pressure is increased by five times. [Esco 3]

So, in determining the optimum operating range with respect to emission reduction, the ferrous chloride content should be taken into account.

Another aspect influencing the amount of acid vapour emitted is the air flow rate over the pickle bath. Assuming an absolutely still atmosphere over the bath, the evaporation of acid would come to a halt as the equilibrium, determined by the vapour pressure, is reached. A more or less strong and constant air flow over the pickling tank sweeps away the acid vapour and keeps the evaporation process going. The result is not only increased acid consumption, but also higher acid emissions. Air movement and, in the case of extraction systems, the extraction rate should be kept as low as possible.

## **D.5.2 Emission Control/Collection from Pickling**

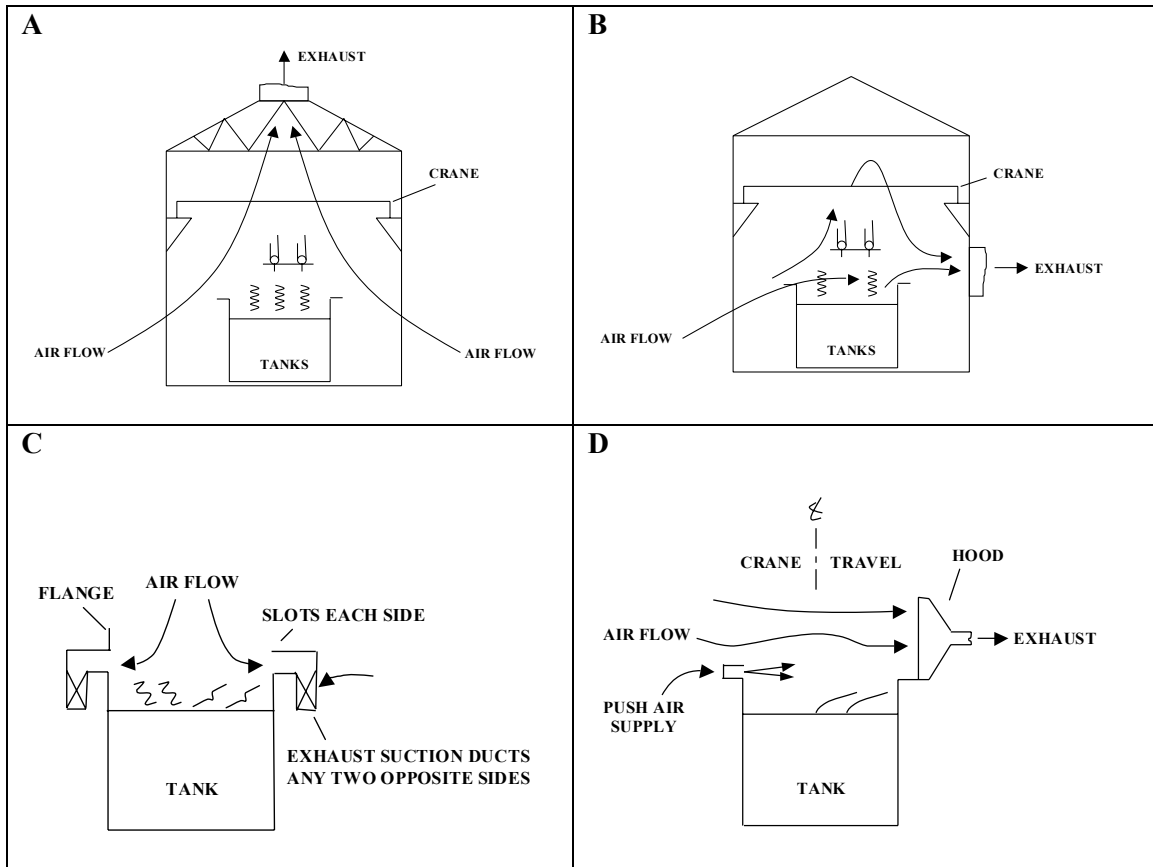
In order to extract air emissions from pickling and/or other process baths, a variety of different designs and techniques is available. Figure D.5-2 shows a collection of possible extraction designs applied in conventional open pickling tank operations.

The more open and the further away the extraction device is from the actual emission source the smaller is the capture efficiency and the larger the volumes that need to be extracted to achieve an acceptable emission capture efficiency. Roof and wall exhaust systems are usually easy to install and cheaper, but the resulting large air flows require large fans and emission abatement devices. Furthermore, the building itself and the roofs act as collection hoods for acidic emissions and deteriorate accordingly. Also any equipment, such as cranes and hoists, close to the pickling tanks or in the building will corrode rapidly.

Lip extraction and lateral hoods are designed to exhaust only from the area of the pickling tank, thus the resulting volume flows are much smaller.

Batch processes usually require open accessible tanks for loading and removing the items to be pickled, therefore only the former measures are applicable.

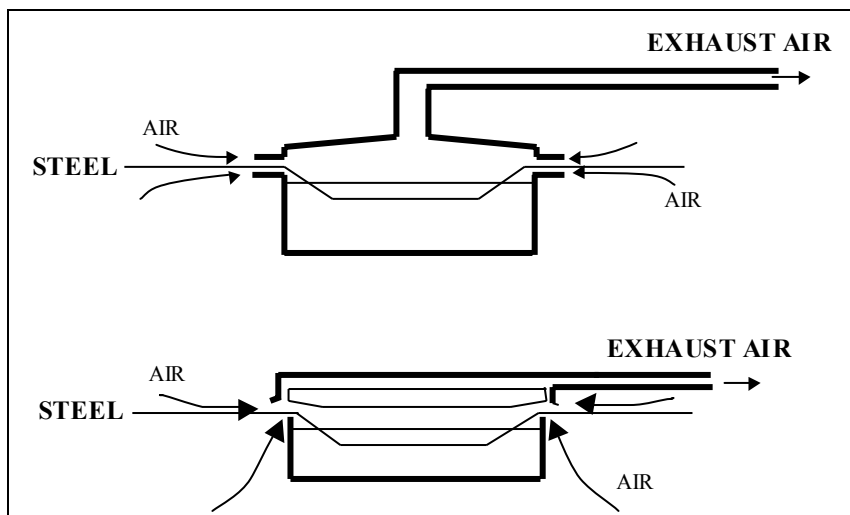
The most effective way to capture the emissions from pickling, however, is completely closed/sealed tanks as shown in Figure D.5-3. These types of tanks can be applied in continuous processes (e.g. for pickling sheet and wire) where the steel/wire enters the pickling tank through small openings. The tanks are kept under slight negative pressure to avoid escape of fumes.



A: roof extraction  
C: lip extraction

B: wall exhaust  
D: lateral hood

**Figure D.5-2: Different extraction systems based on [Stone]**



**Figure D.5-3: Design principles for closed pickling tanks [ESCO x]**

### D.5.3 Abatement Techniques for Acid Gases, Vapour and Aerosols from Pickling (and Acid Regeneration)

Wet scrubbing systems are used to remove acid gas, aerosols or vapour from waste gases. The principal of wet scrubbing is absorption of gas or liquid in the scrubbing medium by close gas-liquid contact. Absorption systems can have either aqueous or non-aqueous liquid phases. The selection of the appropriate reagents depends upon the properties of the pollutant to be removed from the gas stream.

Water is suitable for absorbing soluble acidic gases such as: hydrogen chloride and hydrogen fluoride and also for absorbing ammonia. Alkaline solutions are suitable for absorbing less soluble acidic gases such as sulphur dioxide, hydrogen sulphide and chlorine. [Martin]

The gas absorber needs a liquid/gas interface of high surface area across which mass transfer can occur. This is usually achieved using packing materials which are coated with liquid or by droplet/bubble formation. The absorber design also has to provide a means for renewing the liquid absorbent so that a high driving force for mass transfer is maintained.

Gas absorption is a rate process and consequently the concentration gradient (driving force for the reaction) and the surface area of contact between the liquid and gaseous phase are crucial design parameters. The surface area is determined by the packing material or droplet size. Gas and liquid flow rates and pressure drop across the absorber influence the driving force, the efficiency and in some cases the surface area (droplet formation). In the following sections the principal wet scrubbing systems used in connection with scrubbing of waste gas from acid pickling are described.

**Packed Scrubbers** (Figure D.5-4) consist of an outer shell containing a bed of packing material on support grids, liquid distributors, gas and liquid inlets and outlets, and a mist eliminator.

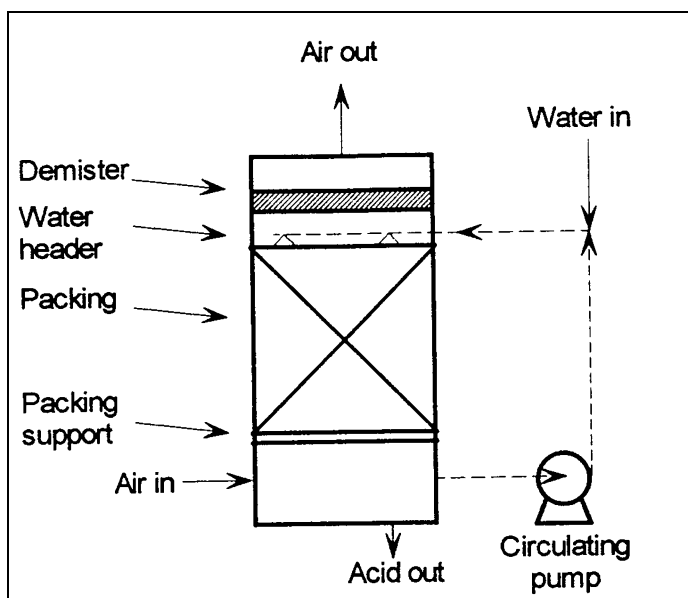


Figure D.5-4: Principle of packed scrubbers [ESCO 2]

The water is usually delivered to the top of the packing bed, and runs down, by gravity, splashing over the packing, while the waste gas enters the bottom of the scrubber, and is washed by the water as it passes upwards through the bed. With this *countercurrent flow* design, the most contaminated gas contacts the most contaminated water at the bottom of the scrubber, and



the cleanest gas contacts the cleanest water at the top of the scrubber. Other designs are possible in which the liquid and gas flows may be cocurrent or cross current. [ESCO 2]

To get even flow and good contacting of air and water, the water has to be distributed evenly over the top of the packing bed - this is usually done by a distribution header, equipped with spray nozzles. Also, to ensure that the gas can flow through the whole bed, the packing is held up by a packing support. This packing support has to be open enough to allow the water and air to pass through without creating too much pressure drop, while still being strong enough to hold the packing up, even when it is dirty, and flooded with water. [ESCO 2]

A disadvantage of packed scrubbers is that, in order to function properly, the packing needs quite a high water flow rate - about 200 gpm of water for 20000 cfm of air (equals 1.34 l/m<sup>3</sup>). So, instead of using fresh water, most packed scrubbers have recirculation pumps, which pump the water from the bottom of the scrubber to the top of the packing. A small, continuous flow of water has to be added to the scrubber to purge the acid removed from the gas stream, through the overflow. The disadvantages of this practice are: [ESCO 2]

- The pump requires maintenance.
- The water at the top of the packing is now contaminated, so the advantages of countercurrent flow are no longer obtained.
- Any dirt in the water is pumped back into the packing, where it may separate and block the distribution header or the packing. [ESCO 2].

Still, in comparison to plate scrubbers, packed scrubbers generate a large flow of low-concentration acid.

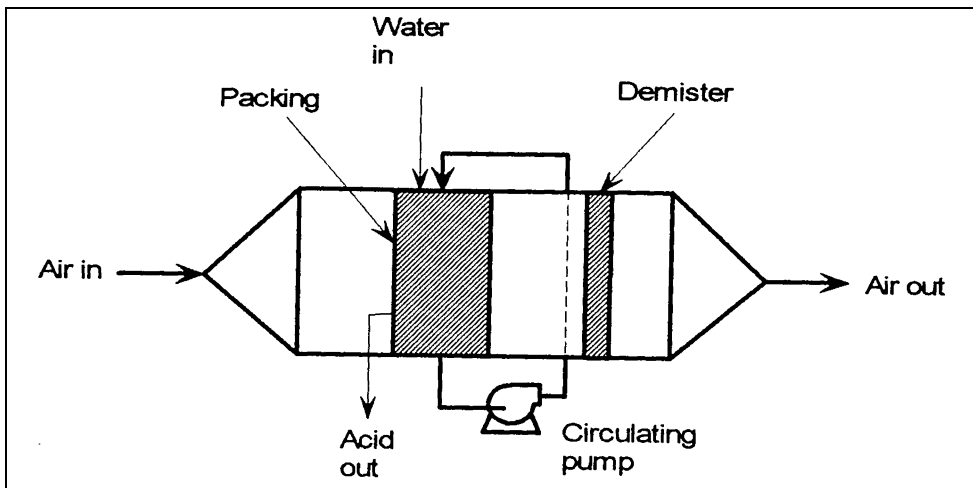
Higher scrubbing efficiency can be obtained in packed scrubbers by increasing the depth of the packing bed. [ESCO 2]

The packed scrubber's strengths are its simple construction, toleration of poor installation, and ability to operate over a wide range of gas flow rates. However, to keep a packed scrubber running at design efficiency (as opposed to just "running" i.e. having the air flow through it) requires a significant maintenance effort to keep the circulating pump going, ensuring that the water distribution on to the packing is even, and keeping the packing clean. [ESCO 2]

The conventional packed scrubber is a vertical tower, with the air flowing up, and the water running down. A variation on this is the **cross-flow scrubber** (Figure D.5-5). In the cross-flow scrubber, the waste gas flows horizontally through the packing, while the liquid still flows down, across the flow of the waste gas. The basic set-up is the same as for conventional packed scrubbers, and a circulating pump is still needed to keep the packing wet. [ESCO 2]

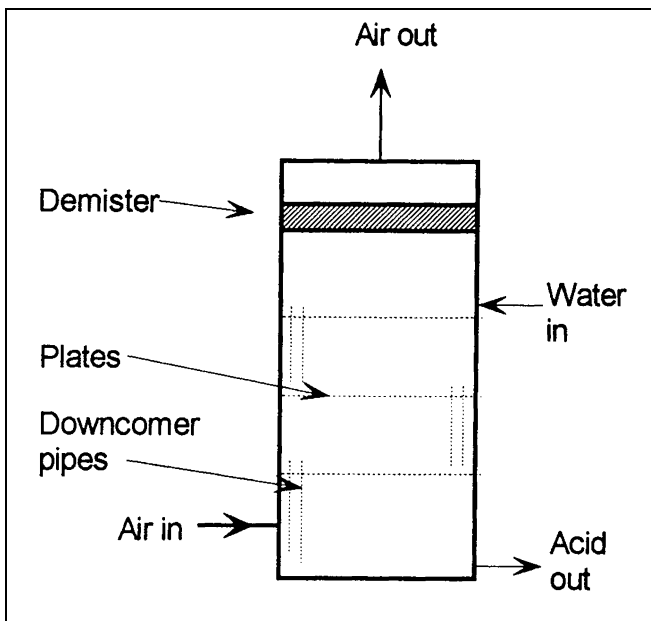
The advantage of the cross-flow scrubber is that it needs less head room, and the ducting is usually simpler and less expensive than for a vertical scrubber. However, cross-flow scrubbers are slightly less efficient than vertical counterflow at removing soluble gases. [ESCO 2]

An advanced type of cross-flow scrubber emulates the multi-stage scrubbing of a plate scrubber. In this version there are several packed beds in series. Each bed has a separate water supply, or circulation system, and may use a structured packing, rather than a random one. This advanced type of scrubber has quite a high pressure drop, and is not currently used in pickling applications. Random packed cross-flow units are widely used. [ESCO 2]



**Figure D.5-5: Principle of a cross-flow scrubber**  
[ESCO 2]

**Plate scrubbers** (Figure D.5-6) consist of a vertical tower with several horizontal perforated trays (sieve plates) stacked in it. Baffles are situated a short distance above the apertures in the plates. Scrubbing liquid enters the top of the tower and flows along each of the trays successively. Dirty gas enters the bottom of the tower and flows upwards, passing through the perforations in the plates. The velocity of the gas is sufficient to prevent liquid seeping through the perforations. [Martin]



**Figure D.5-6: Principle of plate scrubbers**  
[ESCO 2]

The absorption efficiency can be increased by adding more plates to the absorber (increasing the tower height) and by increasing the liquid flow rate. [Martin]

Because the water forms a pool on each plate, only a small flow of water is needed for efficient contact. The flow is also needed to flush out dissolved fumes, and also to offset a little weeping that occurs through the holes, due to surface tension effects. In general, recirculation pumps are

unnecessary on plate scrubbers, and these scrubbers operate in true countercurrent flow. [ESCO 2]

Plate scrubbers are simple and have no moving parts, but require careful installation, to ensure the plates are level, and steady air flow. [ESCO 2] They can be susceptible to plugging and scaling, and are not suitable for foaming liquids. [Martin]

The plate scrubber's advantages are its low maintenance requirements, and once-through flow of water, which is useful in making high strength solutions suitable for recycling into the pickling tank. However, a plate scrubber needs careful installation (to level the plates), and has a limited range of air flow variation. [ESCO 2]

All that is needed to keep a plate scrubber operating at design efficiency is the proper flow rate of water to the top tray, and an air flow rate within the designed range. Reported water consumptions ranged from 0.06 to 0.13 l/m<sup>3</sup>. [ESCO 2]

A key element of scrubbers – as shown above - is the **demister** (entrainment separator, mist eliminator). This is a device that ensures that the air leaving the scrubber is as free as possible of water droplets. [ESCO 2]

Demisters all work on the principle that air can change direction much more easily than water drops. By guiding the air through a channel or maze with several changes of direction, the water droplets are made to impact on a solid surface, where they build into larger drops, which are too heavy to be carried by the air. [ESCO 2]

There are two main types of demister: *knitted mesh* and *chevron baffles*.

The knitted mesh type is simple to handle and install, and separates the water by agglomerating it on fine plastic fibres. Its disadvantages are that it tends to remove dust, as well as water, and the fine plastic fibres deteriorate in time. Eventually (3 - 5 years), the accumulated dust and fibre debris plug up the demister, and it has to be replaced. [ESCO 2]

The chevron type of demister consists of a bank of parallel, S-shaped blades, through which the gas passes - the water is removed by impact on the blade surface. This type of demister is not susceptible to plugging, and has an almost unlimited life. [ESCO 2]

Both types of demister will remove over 99.99 % of the droplets created in wet scrubbers. [ESCO 2]

In a **fume filter** (see Figure D.5-7), the air passes at low velocity through a compacted fibrous bed. As it flows through, the droplets impact on the fibres, agglomerate, and eventually become large enough to drain away by gravity. As this kind of filter also removes dust from the air, it requires washing at regular intervals for cleaning. However, while packed and plate scrubbers usually use several gpm of water on a continuous basis, the filter only uses 30 - 50 gal/day (equals 114 – 190 l/d) for rinsing, and this water can be returned to the pickle tank ('no-effluent' scrubber). [ESCO 2]

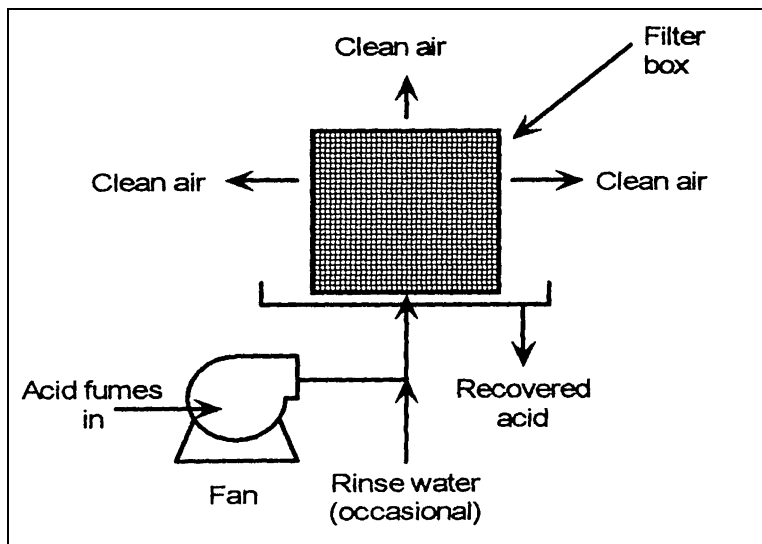


Figure D.5-7: Principle of fume filter  
[ESCO 2]

#### D.5.4 Hydrochloric Acid Pickling

For HCl scrubbing, plate and packed scrubbers are both widely used and suitable devices, but plate scrubbers have the advantage that they produce a small volume of fairly strong acid, which can be returned to the pickle tank as recovered acid. This recovers the acid, which would otherwise be wasted, and so reduces the cost of waste treatment. [ESCO 2]

One problem that can sometimes arise in HCl pickling is the formation of aerosols, very fine droplets of liquid, that flow like a gas, but are already liquid. The particles will go right through a conventional scrubber completely untouched. The reasons for formation of these aerosols are not well understood, but they seem to appear if the exhaust gas from the pickle line is very warm and is suddenly cooled, for example, by mixing with a colder stream of air. This will usually only happen in high temperature strip lines which have very tight fume covers, or in acid regeneration plants. [ESCO 2]

Process conditions should be design in such a way that the formation of HCl aerosols is avoided. If this is not possible, installation of spraying zones or the use of high energy scrubbers (such as a venturi), a cooling scrubber or an agglomerating filter is necessary. [ESCO 2], [Rituper-93]

Packed Scrubbers: achieve HCl emission levels of below  $10 \text{ mg/m}^3$  [Rituper-93]

#### D.5.5 Sulphuric Acid Pickling

Sulphuric acid tanks do not emit acid vapours, but they do generate very fine droplets - almost aerosol size. These droplets are produced by the bursting of very fine hydrogen bubbles, which are created in the pickling process by the action of the acid on the steel, at the surface of the tank. These droplets are the acid fume which can be smelled near sulphuric pickling tanks. [ESCO 2]

The droplets are not fine enough to be true aerosols, but are too fine to be removed in a conventional entrainment eliminator. Removal of the droplets is a purely mechanical process -

the acid droplets have to impact on a surface, and be made to agglomerate until they are large enough to separate from the air. Packed and plate scrubbers have been successfully used for this purpose, and, in this application, cross-flow scrubbers are just as efficient as vertical counterflow towers. Another device which has been used successfully for sulphuric acid removal is the fume filter. [ESCO 2]

A combination of intensive spraying zone and droplets separator (demister) achieves H<sub>2</sub>SO<sub>4</sub> emission levels of 5 – 10 mg/m<sup>3</sup>. [Rituper]

### D.5.6 Electrolytic Pickling

→ No information submitted.

### D.5.7 Mixed Acid Pickling

Stainless steel is pickled in a mixture of nitric and hydrofluoric acid. Nitric acid is a low-boiling liquid, and hydrogen fluoride (HF) is a gas, like HCl; therefore these tanks emit vapours. In addition, they discharge droplets, generated by the bursting of nitrogen oxide (NO<sub>x</sub>) bubbles - however, these droplets are not so fine as the sulphuric droplets made in steel pickling, and are less of a problem. [ESCO 2]

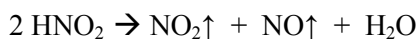
The nitric and HF vapours and droplets are easily removed in a packed or plate scrubber, using a small throughput of water. [ESCO 2] However, if aerosols are present, the operation of an intensive spraying zone may be required for an efficient aerosol precipitation. [DFIU]

The NO<sub>x</sub> gases are not easily removed, however, because they are not very soluble in water (refer to Chapter D.6.8.3 – D.6.8.5 for NO<sub>x</sub> abatement). [ESCO 2]

A problem that can occur in HF scrubbers is scaling, caused by the deposit of insoluble calcium fluoride. This is produced by the reaction of hard (calcium-bearing) water with the hydrofluoric acid, and can plug up the packing, the outlet pipes, downcomers or re-circulation piping. The best way to avoid this problem is to install a water softener to remove the calcium from the supply to the scrubber. [ESCO 2]

### D.5.8 NO<sub>x</sub> Reduction Measures for Mixed Acid Pickling

When stainless steel is pickled in mixed acid, the nitric acid reacts with the metal or metal oxides and is reduced to nitrous acid (HNO<sub>2</sub>), which is, in turn, in equilibrium with a mixture of nitrogen oxides.



In the case of batch pickling operations (e.g. for stainless steel tube), pickling is carried out at ambient temperature. Batch processes usually apply open tanks, where a lower temperature and longer pickling times (e.g. 60 - 90 minutes) reduce the rate of emission of NO<sub>x</sub> fumes.

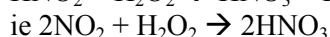
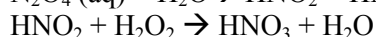
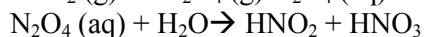
Coil, sheet or wire pickling, if carried out continuously, requires higher acid temperatures in order to maintain an effective pickling result in short pickling times (ie usually 2 - 4 minutes). As higher acid temperatures generates higher emissions of NO<sub>x</sub> fumes, closed tanks are installed. The following NO<sub>x</sub> suppression and reduction measures are available:

### D.5.8.1 NO<sub>x</sub> Suppression by Injection of Hydrogen Peroxide (or Urea)

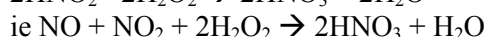
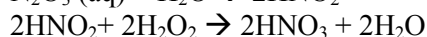
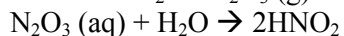
The reaction between hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and NO<sub>x</sub> occurs in the aqueous phase, in which NO<sub>x</sub> reacts with water to form nitrous acid (HNO<sub>2</sub>).

The HNO<sub>2</sub> is relatively unstable and will readily decompose back to NO<sub>2</sub>, NO and H<sub>2</sub>O. The NO<sub>x</sub> would ultimately be emitted from the process. However, the presence of H<sub>2</sub>O<sub>2</sub> rapidly oxidizes the HNO<sub>2</sub> to the more stable HNO<sub>3</sub>, thus preventing the re-formation and emission of NO<sub>x</sub>. This behaviour is detailed in the following chemical reaction equations:

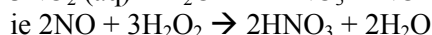
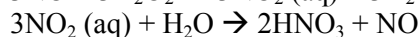
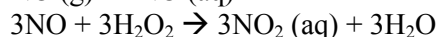
#### NO<sub>2</sub>



#### NO/NO<sub>2</sub>



#### NO



The key to the efficient usage of hydrogen peroxide in NO<sub>x</sub> suppression, by addition to the pickling bath, lies in effective mixing.

When hydrogen peroxide is added to the pickling liquor containing both oxides of nitrogen and transition metal ions, it will either oxidize the NO<sub>x</sub>, according to the chemistry outlined above, or will itself undergo catalytic decomposition by reaction with the metal ions.

#### NO<sub>x</sub> suppression by H<sub>2</sub>O<sub>2</sub> injection into a recirculation loop

Austenitic steels are generally endothermic in pickling character, while ferritic steels are exothermic due to the differences in chemical composition. Therefore, some form of temperature control is installed. The normal method is to incorporate a recirculation loop, whereby the bath liquor is recirculated through either a heater or a cooler.

One method of effective mixing of H<sub>2</sub>O<sub>2</sub> and the bath liquor is to inject the hydrogen peroxide into the recirculated pickle liquor. The bath contents are pumped around a recirculation loop at a rate of up to ten bath changes per hour. Hydrogen peroxide (35 %) is dosed into this loop at up to 1 litre per minute, dependent upon the process conditions pertaining. A schematic diagram of this operation is shown in Figure D.5-8.

Trials carried out have shown that NO<sub>x</sub> suppression efficiencies in excess of 90 % have been achieved by this technique.

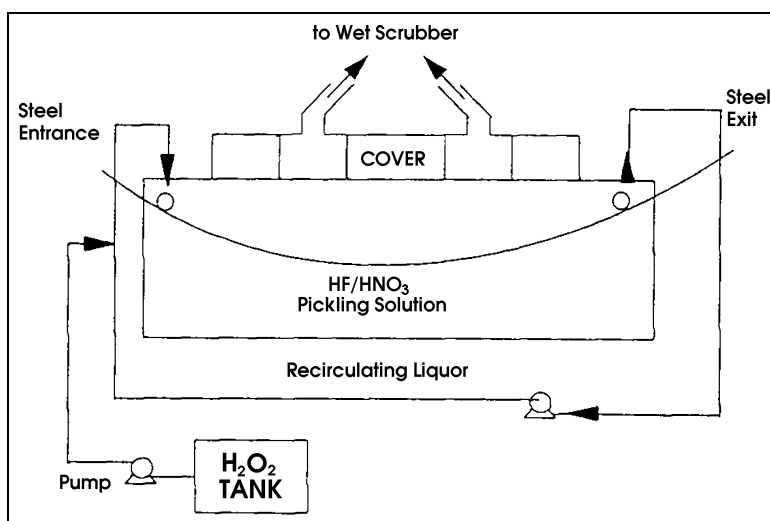


Figure D.5-8: Schematic for injecting  $H_2O_2$  into pickling acid recirculation loop [WireInd-10-97]

#### NO<sub>x</sub> suppression by $H_2O_2$ injection into the pickling bath via a sparge pipe

The capital cost of a new installation of a recirculation loop to a pickling bath can be high if a static pickling bath is in operation. Therefore, an alternative method of  $H_2O_2$  addition to the pickling bath is to directly inject  $H_2O_2$  into the pickling bath via a bifurcated sparge located in the pickling bath. A simple sparge pipe, made from 30 mm  $\varnothing$  polypropylene tubing, with 3 mm holes drilled at 150 mm intervals, is inserted into the bath. [WireInd-10-97]

Due to the large amount of insoluble scale which builds up in the pickling bath, the sparge pipe is arranged with the holes pointing at 45° downwards to the horizontal to minimize blockages. The sparge pipe is positioned at the steel entry end of the bath, just beneath the moving steel sheet, to prevent accidental collision with the sheet and also to use the constant movement of the steel sheet as a method of effectively mixing the  $H_2O_2$  into the pickling bath. A schematic diagram of the sparge pipe system is shown in Figure D.5-9.

Trials carried out have shown that NO<sub>x</sub> suppression efficiencies in excess of 90 % have been achieved using this technique. [WireInd-10-97]

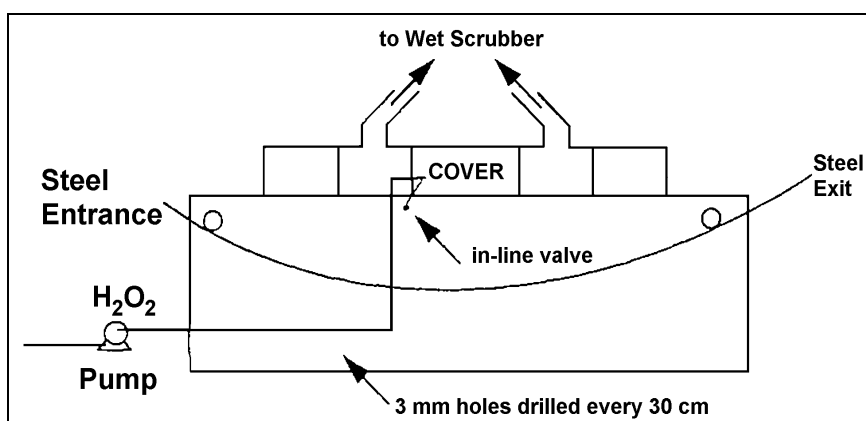


Figure D.5-9: Schematic for injecting  $H_2O_2$  into pickling baths via a sparge pipe [WireInd-10-97]

#### NO<sub>x</sub> suppression by $H_2O_2$ injection into a spray pickling facility

A further example of NO<sub>x</sub> suppression using hydrogen peroxide is the one used for pickling of stainless steel plate in a spray chamber. The nitric acid/hydrofluoric acid pickling liquor is

sprayed onto both sides of the stainless steel plate; the pickling liquor is then returned from the spray chamber to the pickling holding tank, from where it is recycled to the spray chamber. [WireInd-10-97]

A pilot trial was carried out at a facility by injecting hydrogen peroxide into the liquor recirculation line immediately before it splits into two branches. It was found that more than 90 % of NO<sub>x</sub> emissions were suppressed within ten minutes of hydrogen peroxide being introduced, indicating that the NO<sub>x</sub> suppression reaction took place at the site of NO<sub>x</sub> generation. [WireInd-10-97] Other sources report NO<sub>x</sub> reduction by up to 70 % [fmp012].

NO<sub>x</sub> suppression by hydrogen peroxide has no adverse affect on stainless steel product quality. [WireInd-10-97]

#### **Advantages of NO<sub>x</sub> suppression by hydrogen peroxide**

- Hydrogen peroxide converts NO<sub>x</sub> to nitric acid in-situ, and therefore reduces nitric acid consumption, in some cases by 20 – 30 %.
- No major plant change is required.
- Existing hydrofluoric acid scrubber can be used with no neutralisation of the scrubber liquor required, as the weak hydrofluoric acid solution formed can be returned to the process.

### **D.5.8.2 Nitric Acid-free Stainless Steel Pickling**

In mixed acid pickling of stainless steel, the nitric acid contributes an acid and an oxidant to the metal pickling process. Theoretically, therefore, the replacement of the acid contribution by another acid, for example sulphuric acid, and the oxidant contribution with hydrogen peroxide, will result in a nitric acid-free metal pickling solution.

Trials have been carried out at various steel mills in Europe, where this technology has been successfully used for stainless steel pickling techniques. [WireInd-10-97]

These processes rely on the oxidizing nature of the ferric ion; the ferric ion content of the pickling liquor is maintained at a minimum concentration of 15 g/l. This is achieved by the introduction of an oxidizing agent to oxidize the ferrous iron (Fe<sup>2+</sup>) formed during the pickling reaction to ferric iron (Fe<sup>3+</sup>).

The oxidizing agent chosen is normally hydrogen peroxide, as this does not introduce any foreign ions into the pickling bath and the method of addition is essentially the same as that used in NO<sub>x</sub> suppression techniques. This treatment can be used on all types of production facilities, i.e. continuous or batch pickling. [WireInd-10-97]

The actions of HF/H<sub>2</sub>O<sub>2</sub> mixtures on stainless steel are considerably less aggressive than that of HF/HNO<sub>3</sub> at high pickling temperatures (ca 50 – 60 °C), although the reverse of this has been shown when pickling has been carried out at ambient temperatures of approximately 20 – 25 °C. [WireInd-10-97]

Additives, such as nonionic surfactants and corrosion accelerators, are also added to the pickling bath, to maintain pickling efficiency. Stabilisers are added, to prolong the life of the hydrogen peroxide in the pickling bath. [WireInd-10-97]

Pilot trials which have been carried out have shown that the nitric acid-free pickling process has a number of advantages when compared with the conventional nitric acid/hydrofluoric acid process. [WireInd-10-97]



**Reported advantages of hydrogen peroxide-based nitric acid-free pickling**

- In certain cases, shorter pickling times.
- Reduced sludge formation.
- Longer bath life.
- Greatly reduced intergranular corrosion.
- Less aggressive pickling, which means reduced attack on the metal surface and reduced weight loss of the steel.
- Reduced NO<sub>x</sub> emissions and nitrate effluent discharges (in fact, there is an overall reduction in volume of effluent per tonne of product per bath).
- All effluents can be precipitated by lime treatment.
- Sometimes no major modifications are required to use the process in existing pickling plants; with no major equipment required except for a simple control system.
- There is a reduction in product dissolution and a potential for an improvement in product quality.

The hydrogen peroxide-based nitric acid-free pickling process can operate effectively at low temperatures, therefore saving on heating costs compared with the conventional nitric acid/hydrofluoric acid process, which is usually required to operate at approximately 60 °C to be effective. [WireInd-10-97]

**D.5.8.3 Absorptive Scrubbing**

Wet absorbers, as described in Chapter D.6.3, are used to abate NO<sub>x</sub> fumes from mixed acid pickling. As NO and NO<sub>2</sub> are insoluble or only partially soluble in water, other washing media, such as NaOH, H<sub>2</sub>O<sub>2</sub> or urea, are used.

The efficiency of NaOH absorbers depends on the NO<sub>x</sub> concentration and on the NO:NO<sub>2</sub> ratio in the waste gas. To achieve satisfactory reductions long oxidation times or multi-stage scrubbers are necessary.

To enhance the efficiency of NO<sub>x</sub> abatement, two or more packed columns may be installed; one part operated as a reduction column, the other as an oxidation column. The reduction columns are operated countercurrently with NaOH and a reductant: sodium hydrosulphide solution (NaHS). The reductant along with high pH reduces the NO<sub>2</sub> entering the column bottom to nitrogen and washes and neutralises any free acid that may be entrained in the gas stream. Fresh NaOH and NaHS are added to the washing liquid based on pH value and the oxidation reduction chemical potential (ORP). [LUDL]

The gas stream from the reduction column then enters the oxidation column where NO is oxidized to NO<sub>2</sub>. The gas enters the column at the top and flows cocurrently with the oxidizing solution (e.g. sodium chlorite - NaClO<sub>2</sub>) at low pH. The sodium chlorite forms chlorine dioxide (ClO<sub>2</sub>) that oxidizes the NO. Fresh acid and NaClO<sub>2</sub> are added based on pH and ORP. The cycle of reduction and oxidation may be repeated to achieve sufficient NO<sub>x</sub> abatement rates. [LUDL]

When H<sub>2</sub>O<sub>2</sub> is used for scrubbing, the scrubbing liquor usually consists of a mixture of HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> at typical concentrations of 20 wt.-% and 0.5 wt.-% respectively. A benefit of using H<sub>2</sub>O<sub>2</sub> is that the by-product of the scrubbing process is nitric acid, instead of sodium nitrate when using sodium hydroxide. This acid is recovered in usable concentrations and recycled back to the pickling process. Thus not only is the sodium nitrate waste disposal cost eliminated but the overall nitric acid consumption is reduced. [CITEPA]

**D.5.8.4 Selective Catalytic Reduction (SCR)**

→ For description refer to D.2.4.

**D.5.8.5 Selective Non-Catalytic Reduction (SNCR)**

→ For description refer to D.2.5.

**D.5.8.6 Comparison of NO<sub>x</sub> Reduction Methods for Mixed Acid Pickling**

Table D.5-1 compares the different NO<sub>x</sub> reduction measures and an gives an overview of cost.

	NOx Suppression by Injection		Nitric Acid-free Stainless Steel Pickling <sup>2</sup>	Absorptive Scrubbing		Selective Catalytic Reduction	Selective Non-Catalytic Reduction
	H <sub>2</sub> O <sub>2</sub>	Urea <sup>1</sup>		NaOH	H <sub>2</sub> O <sub>2</sub>		
<b>Capital Costs</b>	low	low		high	high	very high	
<b>Variable costs</b>	high	low		low	high	low	
<b>HNO<sub>3</sub> Consumption</b>	lower	higher		no influence	lower	no influence	
<b>NOx Reduction</b>	very high	very high		low	very high	very high	
<b>By-products</b>	recovered	no problem		difficult to discharge	recovered	no problem	
<b>Steel Surface Quality</b>	better <sup>3</sup>	better <sup>3</sup>		no influence	no influence	no influence	
1 Comment: urea injection can lead to ammonia compounds in the effluent [Com2 CR]							
2 Comment: only limited application [Com2 CR]							
3 Comment: neither urea nor hydrogen peroxide injection give rise to better surface finish [Com2 CR]							

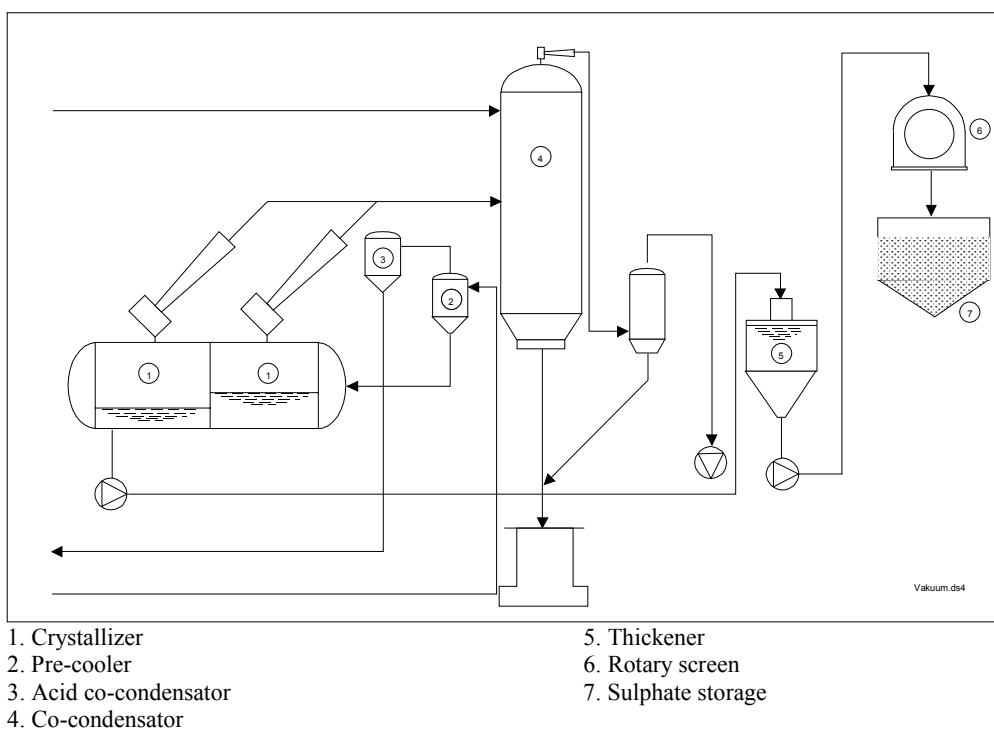
**Table D.5-1: Comparison of different NOx reduction measures for mixed acid pickling (as reported in [CITEPA])**



## D.5.9 Free Acid Reclamation

### D.5.9.1 Crystallization ( $H_2SO_4$ )

The sulphuric acid recovery process by crystallization is based on the solubility relations of water, sulphuric acid and iron sulphate. Iron sulphate is more soluble at increasing temperatures and crystallizes out of saturated solutions when being cooled. For the recovery of free sulphuric acid from spent pickle from  $H_2SO_4$  pickling lines, the heptahydrate crystallization process, yielding  $FeSO_4 \cdot 7H_2O$ , is usually applied in industry. With respect to the type of cooling, the following heptahydrate crystallization processes for regeneration are available: crystallization with indirect cooling, cyclone crystallization and vacuum cooling crystallization. The treatment of spent pickle solution by crystallization avoids the need to neutralise free acid; furthermore the iron is precipitated as heptahydrate and does not have to be neutralised either. With crystallization processes a significant enhancement of the waste water releases and a reduction of the salt load can be achieved. As an example, Figure D.5-10 shows the vacuum cooling crystallization process.



**Figure D.5-10: Vacuum cooling crystallization process for  $H_2SO_4$  [DFIU98]**

### D.5.9.2 Evaporative Recovery (HCl)

The evaporative hydrochloric acid recovery system is a forced circulation flash evaporator with controlled two-stage condensation/separation. The spent acid solution is aggressively heated to extract the acid and water from the spent waste. Only a concentrated ferrous chloride solution remains.

The spent acid solution is to the recovery unit via a filter and a preheat exchanger, utilizing the remaining heat of the acid and water vapours generated in the evaporative process. The preheated spent acid solution then enters the evaporation section where it quickly loops through the main heat exchanger and into the separator vessel where water and acid vaporise. Acid and

water vapour are continuously driven from the waste solution until the solution temperature reaches about 110 °C. At that temperature, the solution has reached saturation and is ready for removal from the evaporator. A PLC (programmable logic controller) automatically adjusts the rate of spent acid fed into the process and the volume of ferrous chloride concentrate removed from the loop and stored in a holding tank. [Cullivan-IG-97]

Forced by the expanding vapours in the separator, the acid and water vapours are driven through the feed exchanger and into the acid condenser. The condensing acid vapour combines with some of the condensing water vapour as it descends through the acid condenser. The concentration of the acid is controlled in this step to return the right quality to the pickling process. The remaining water vapour is led into the water condenser where it is cooled and scrubbed of any residual acid vapour. No vapours leave the system because the process cools any remaining vapour to a condensate. The final condensate can be re-used, e.g. as rinse water in the pickling process.

An optional heating loop added to the acid condensing section can provide a precise pickling acid concentration. Since the recovered acid concentration typically ranges from five per cent to 15 per cent, this additional cost is usually not warranted. The recovered acid is strong enough for pickling and is combined with a more concentrated mix of HCl when fresh make up acid is added. [Cullivan-IG-97]

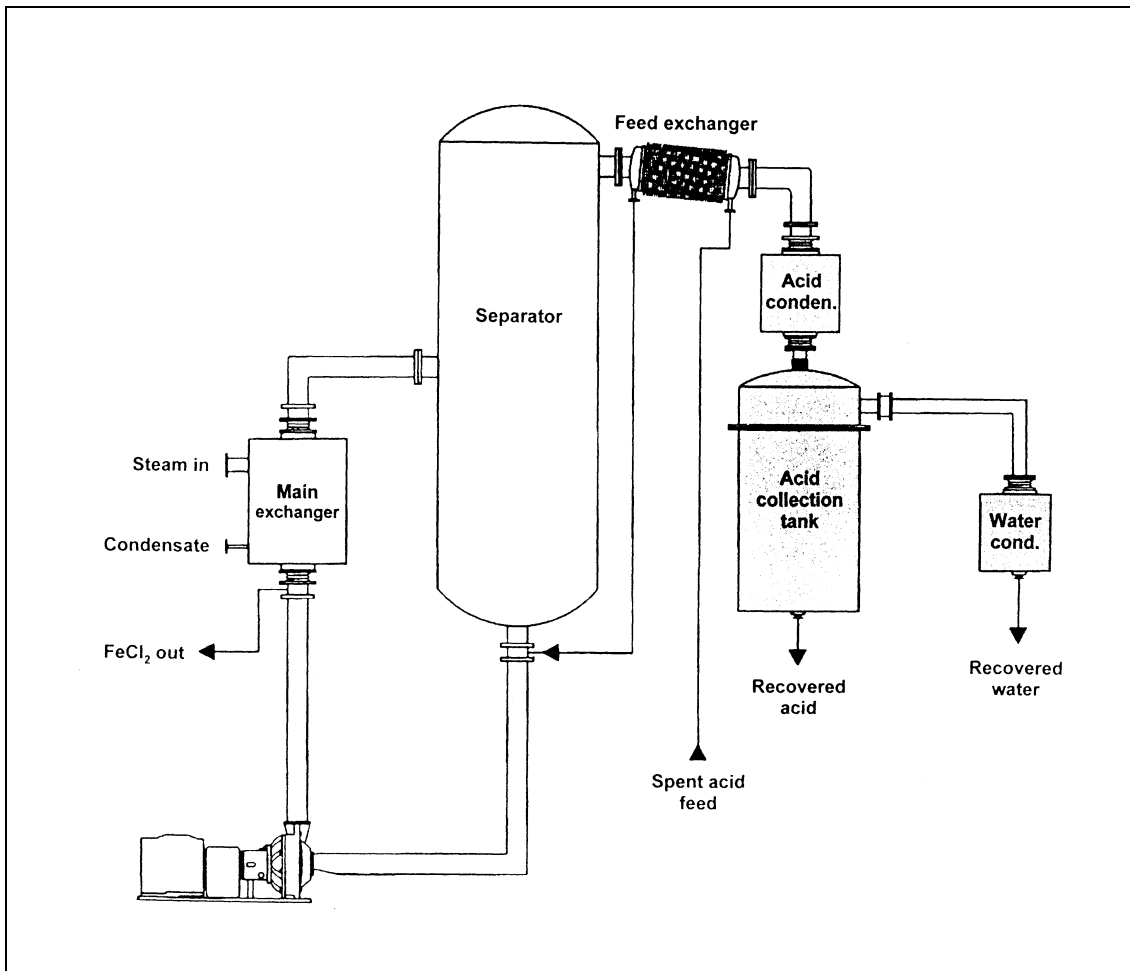


Figure D.5-11: Evaporative acid recovery  
[Cullivan-IG-97]

The process is easy to operate. Since it has only a few moving parts and the acid vapours essentially clean the system while it operates, downtime for maintenance of heat exchangers and

reactors has proven minimal. Normal maintenance includes changing filters, attending to pumps and checking the boiler and cooling tower loops to ensure optimum performance. [Cullivan-IG-97]

### D.5.9.3 Retardation (HCl, H<sub>2</sub>SO<sub>4</sub>, HF/HNO<sub>3</sub>)

The principle of the process is based on the adsorption of free, undissociated acid to ion-exchange resins as the dissolved metals pass through the resin bed. In backwashing with water, the adsorbed acid is re-released because of the difference in osmotic pressure. Free-acid recovery rates are about 80 – 90 % for hydrochloric acid and sulphuric acid. The advantages of the process are that it requires little apparatus and space. The energy requirement for the regeneration process is confined to electrical energy. Electricity consumption varies between approximately 0.25 and 0.40 kWh/kg of iron depending on throughput. The requirement for demineralised water is approximately 1 m<sup>3</sup>/m<sup>3</sup> of regenerated pickling solution. [Com D], [Fichtner]

The use of the retardation process is feasible when acid consumption is at least about 40 l/h. The average metal content in the pickling solution should not exceed 50 - 60 g/l. The resulting waste consists of a metallic salt solution which, depending upon composition, can be utilized. [Com D], [Fichtner]

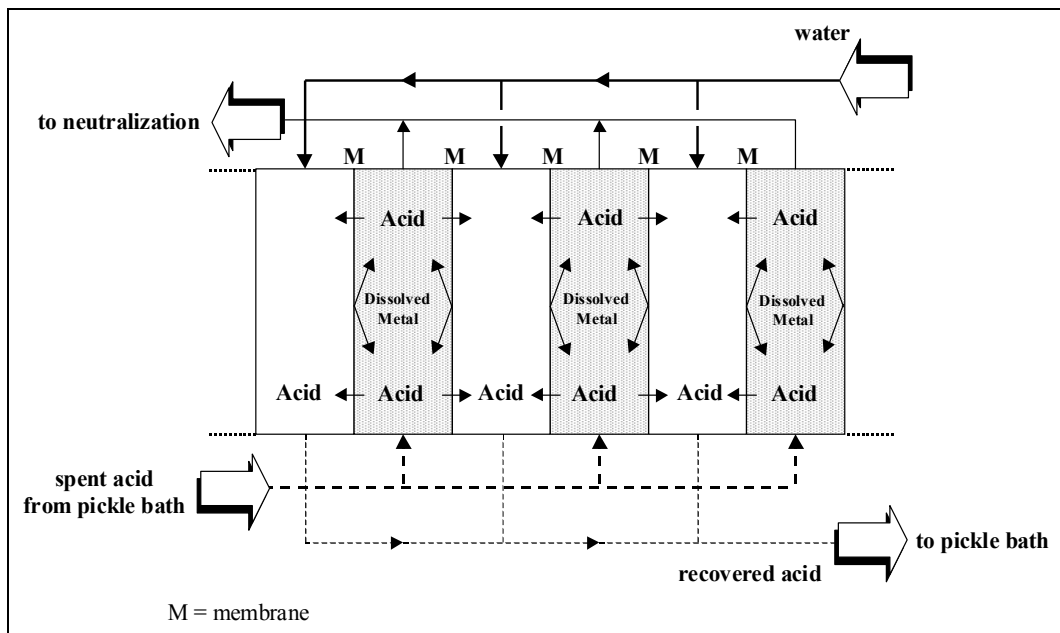
### D.5.9.4 Diffusion dialysis (HCl, H<sub>2</sub>SO<sub>4</sub>, HF/HNO<sub>3</sub>)

The diffusion dialysis process uses ion exchange membranes, which separate two different liquids: the used acid and demineralised water. The concentration difference between the two solutions is the motive power of this process. The special anion exchange membranes, having a positive surface charge in their polymer structure, make the diffusion of dissociated acid (anions) through the membrane possible, while the cations (metals) are held back by their positive charge. The hydrogen ion is an exception in this case. Owing to its small size, it diffuses- together with the anions - through the membrane. [OSMOTA]

The membranes are assembled in a membrane stack similar to a filter press with a usual specific capacity of 0.5 - 2 l/hm<sup>2</sup>. The demineralised water and the used acid are led in countercurrent through the cells in an alternating manner. The demineralised water adopts the free acid and the resulting diffusate is recycled to the pickling process. The other part-stream - dialysate - is mostly led to the neutralisation. In certain cases this part stream can also be recycled or retreated. [OSMOTA]

For years, the process of diffusion dialysis has been used successfully for recovery of H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub> and HF. It is possible to extract 80 - 85 percent of free acids from used pickling solutions and to recycle it in a purified form with about 5 percent metal pollution. [OSMOTA]

The membrane lifetime is normally 3 - 5 years, but it can be reduced by oxidizing substances such as hydrogen peroxide, chromic acid, nitric acid with concentrations of over 20 % as well as temperatures over 45 °C and organic substances such as tensides, oils, grease, solvents or cleaners. In most cases in which organic substances cause membrane fouling, a pre-treatment of the raw solution with activated carbon does help. [OSMOTA]



**Figure D.5-12: Principle of Diffusion Dialysis [Fichtner]**

The advantages of the process are that it requires little apparatus and space and has low operating costs. The energy requirement for diffusion dialysis is confined to electricity to run the pumps. Electricity consumption per kg of removed iron varies between 0.1 and 0.23 kWh. The requirement for demineralised rinse water is approx. 1 m<sup>3</sup>/m<sup>3</sup> regenerated pickling solution. Diffusion dialysis can be used when acid consumption is at least about 60 l/h. The average metal content in the pickling solution should not exceed 50 - 60 g/l. [Com D], [Fichtner]

**Further reported advantages of the process:**

- Small energy requirement.
- Considerable reduction of fresh acid requirement, of neutralisation and deposition costs.
- Very low maintenance costs.
- Long membrane life.
- Short amortisation time [OSMOTA].



## D.5.10 Acid Regeneration

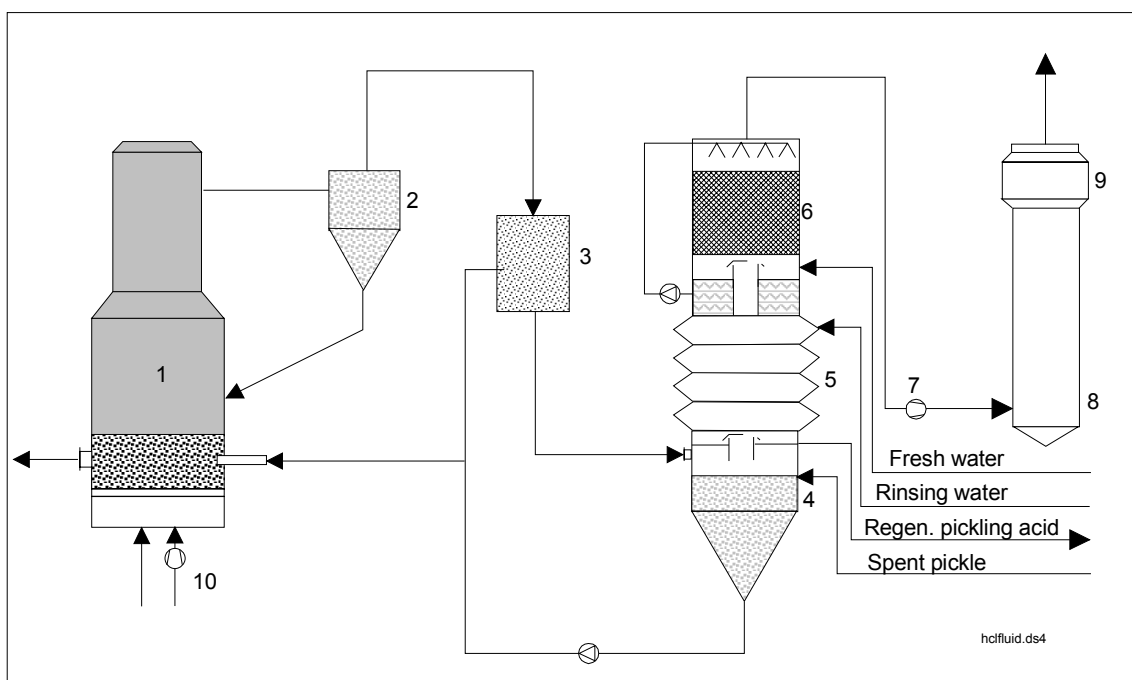
### D.5.10.1 Pyrohydrolyse

#### D.5.10.1.1 Fluidised Bed Process (HCl)

The basis of the process is the thermal decomposition of spent pickle liquor, which is converted at high temperature in the presence of water vapour and oxygen into hydrochloric acid and iron oxide:



Figure D.5-13 shows the main sub-processes of the fluidised bed acid regeneration process. The spent pickle liquor is pumped into a separating vessel and then concentrated in a Venturi loop by hot gases from the reactor. A share of the concentrated pickle from this loop is continuously fed into the fluidised bed of the reactor. Within the fluidised bed, which consists of iron oxide granulate, acid and water are evaporated at a temperature of about 850°C and iron chloride is converted into iron oxide and hydrochloric gas according to equation (1).



- |                          |                       |
|--------------------------|-----------------------|
| 1. Fluidised bed reactor | 6. Wet scrubber       |
| 2. Cyclone               | 7. Off-gas ventilator |
| 3. Venturi-scrubber      | 8. Stack              |
| 4. Separating vessel     | 9. Mist eliminator    |
| 5. Absorber              | 10. Fan               |

**Figure D.5-13: Fluidised bed HCl acid regeneration process [DFIU98]**

Growth and new formation of iron oxide grains in the fluidized bed are controlled so that a dust-free granulated product is obtained with a grain size of 1 to 2 mm and a bulk density of about 3.5 t/m<sup>3</sup>. The granular product is discharged continuously from the bottom of the reactor, and transported by a vibrating cooling chute and vibrating spiral conveyor to the oxide storage bin.

The hot off-gas from the reactor contains hydrochloric gas, overheated steam, combustion products and small amounts of iron oxide dust, which is separated from the gas in a cyclone and recycled to the fluidised bed. The off-gas is then cooled to a temperature of about 100°C in the Venturi scrubber. The thermal energy of the hot off-gases is used to concentrate the spent pickling liquor by evaporation before it is fed to the reactor. Very fine dust particles in the gas stream are removed by scrubbing.

From the venturi scrubber, the cooled gas stream goes to the absorber, where hydrogen chloride is absorbed adiabatically with rinse liquor from the pickling line and fresh water. The hydrochloric acid thus produced has a concentration of approximately 18 wt-%. It is recycled to the pickling plant or held in a storage tank. After passing through a scrubbing stage and a mist collector, the off-gas is virtually free of hydrochloric acid and is released to the atmosphere.

The iron oxide granular product can be used as raw material in various industries. The most important options are the production of magnetic materials (eg, hard and soft ferrites), iron powder for the fabrication of sintered parts and welding electrodes, and as an additive for the production of magnetic tapes, abrasives, tiles, glass, cosmetics and pigments.

The described fluidized bed hydrochloric acid regeneration can process spent pickle liquor of any iron concentration. Even at the high iron concentration of pre-concentrated pickle liquor, up to 250 g/l, the pipes do not block. Furthermore, spent pickle liquor with a high content of sludge (eg, from the pickling of high silicon steel) can be utilized without difficulty because of a special design of injection equipment.

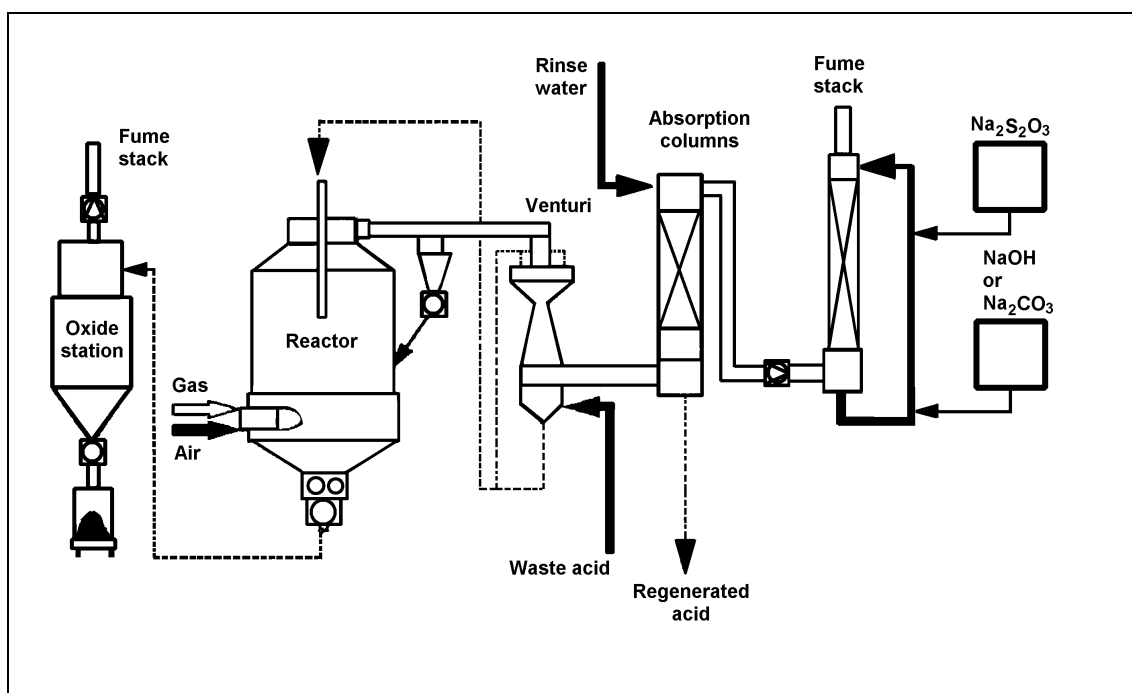
As the recovered acid is nearly Fe<sup>++</sup> free, the recovery efficiency is considerably higher than 99 %, contrary to other regeneration processes, where up to 10 g/litre Fe<sup>++</sup> can be expected.  
[Rituper-1]

#### D.5.10.1.2 Spray Roasting (HCl, HF/HNO<sub>3</sub>)

Another regeneration option for **hydrochloric acid** is the spray roasting process. The principle of operation is similar for all roasting processes, but with some variation in equipment used. An example is shown in Figure D.5-14. The pyrohydrolytic separation of iron chloride and water is carried out at a temperature of about 450°C (temp of reaction Sidmar: 600 °C) in the spray roasting reactor. The spent acid is fed to a venturi recuperator where the hot gases coming from the reactor are cooled and the acid is pre-concentrated. The concentrate is then sprayed into the directly fired reactor from above. Hot burn gases cause the fine droplets to evaporate as they descend. The ferrous chloride is separated into hydrochloric gas and iron oxide by means of steam and oxygen in the air according to the following reaction:



The iron oxide thus formed is collected at the bottom of the reactor and conveyed pneumatically to an oxide bin. The piled weight of the powder is about 0.3 - 0.4 t/m<sup>3</sup>. (0.48 – 0.6 Sidmar) This oxide is a valuable raw material for the production of magnetic materials, i.e. hard and soft ferrites.



**Figure D.5-14: Spray roasting HCl acid regeneration process [Karner-1]**

The hydrochloric gas, steam and combustion gases are ducted via the pre-vaporiser to an absorber. The resulting off-gas is subsequently cleaned by alkaline washing and is released via a stack into the atmosphere. The generated iron oxide can be used for different purposes according to its quality.

The gases containing HCl are absorbed in an adiabatic column where rinse water from the pickling line can be used as absorption water. The generated hydrochloric acid (about 18 %) can be returned to the pickling process. The off-gas from the absorption unit is subsequently cleaned in a caustic scrubber with the addition of sodium thiosulphate, which results in pollutant concentrations of less than  $2 \text{ mg/m}^3$  of HCl and free  $\text{Cl}_2$ .

Because of the application of the iron oxide by-product in the ferrite industry, higher quality demands on the oxide have arisen in recent years. Besides physical parameters such as specific surface area, primary particle size and tap density, which are important for the solid state reactions of the iron oxide with manganese, nickel and zinc oxide, the impurity level of the oxide is critical. Therefore a preprocessing process was developed to produce **ultra-pure iron oxide** with especially low contents of silicon, phosphorous and heavy metals such as chromium, nickel or copper. The process flow sheet is shown in Figure D.5-15, presenting the following process steps:

- Reduction of free acid and cementation of heavy metals by scrap.
- Increase of pH by ammonia addition.
- Partial oxidation of  $\text{Fe}_2^+$  to  $\text{Fe}_3^+$  leading to specific adsorption of Si and P to ferric and aluminium hydroxide.
- Filtration to remove hydroxide sludge.

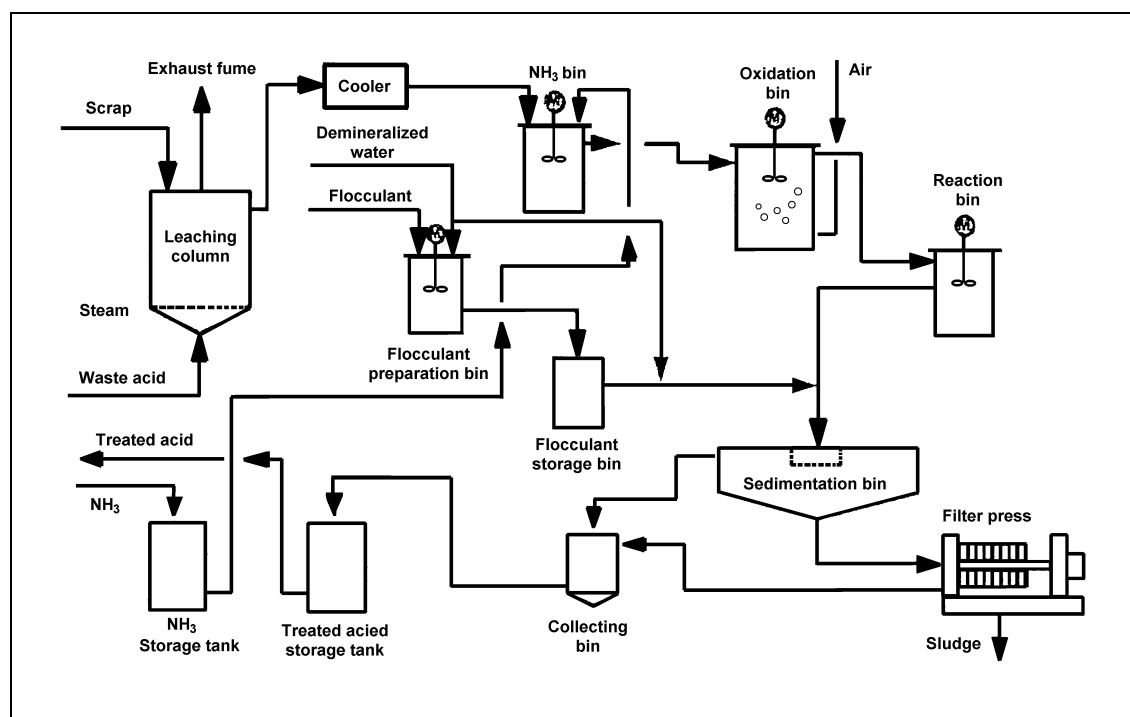
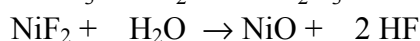
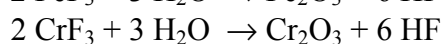
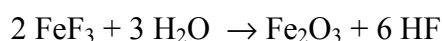
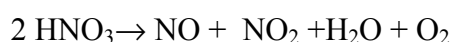


Figure D.5-15: Process flowsheet for the production of high purity oxides [Karner-1]

The spray roasting process for the regeneration of **mixed acids** from stainless steel pickling is quite similar to the one for hydrochloric acid, but it also includes an isothermal absorption step and a tail-gas cleaning system using a catalytic converter for NO<sub>x</sub>. The spent pickle liquor containing the fluoride complexes of iron, chromium, nickel and minor metals as well as free hydrofluoric and nitric acid is first led to a pre-evaporiser, where it is partly evaporated by the contact with hot gases from the reactor. The pre-concentrated pickle liquor is fed into the reactor via nozzles. Inside, the reactor decomposition reactions of the following type are taking place:



In addition nitric acid is partly decomposed into nitrogen oxides:



The reactor is directly heated with burners using natural or other gases. The mixed metal oxide is collected at the bottom of the reactor. The oxide is kept at 500 to 600 °C at the flat bottom of the reactor to reduce the fluoride content below 1.5 %. This oxide is usually pelletized and can be recycled to the EAF. [Karner-1], [Com-Karner]

The reactor off-gases, which contain water vapour, combustion gases, HF, HNO<sub>3</sub> and NO<sub>x</sub> are led to a two-stage absorption unit, where cooled recirculated acid is used for absorption. Hydrogen peroxide is added to the second column in order to oxidize NO to NO<sub>2</sub>, which can be absorbed more easily. Contrary to the hydrochloric acid regeneration, the absorption is carried out isothermally, i.e. the liquid in the 2 columns is recycled and cooled in external heat exchangers. In the columns, regenerated acid is produced which contains all of the free and bound hydrofluoric acid and up to 85 % of the nitric acid. The regenerated acid is reused in the pickling process. [Karner-1], [Com-Karner]

The off-gas after the absorption columns is first cleaned in an (alkaline) wet scrubber to remove traces of HF and the tail gases, which still contain NO<sub>x</sub> from nitric acid are cleaned by a selective catalytic reduction using NH<sub>3</sub> or urea or ammonium compounds as a reducing agent. The NO<sub>x</sub> is thus converted to harmless nitrogen and water. Figure D.5-16 shows the flowsheet of such a spray roasting process for mixed acids (Pyromars process). [Karner-1], [Com-Karner]

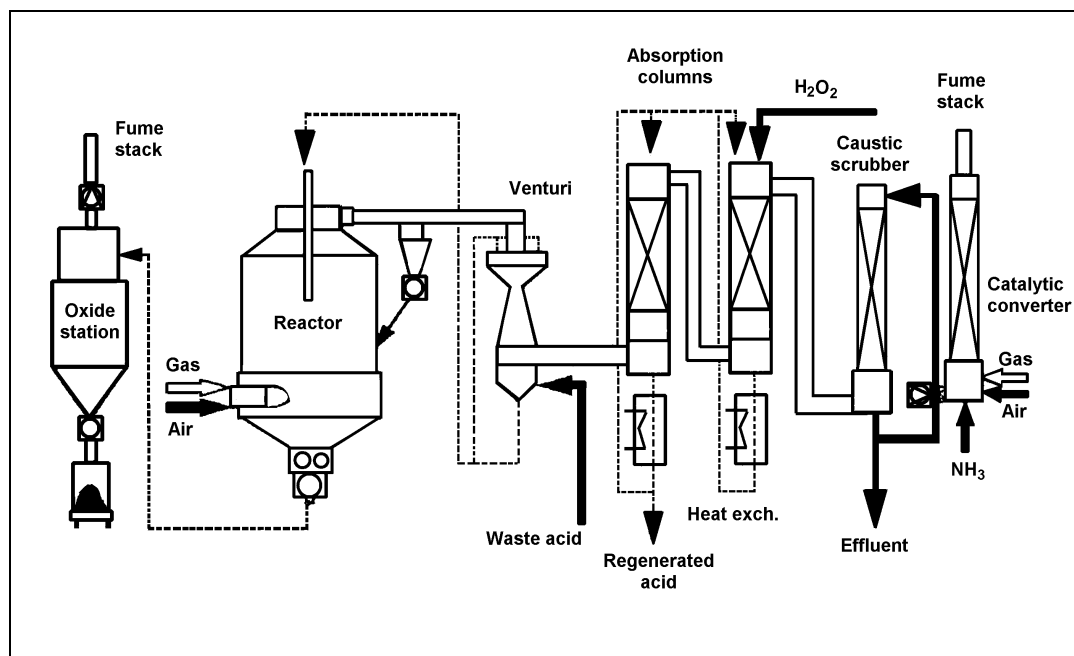


Figure D.5-16: Spray roasting mixed acid regeneration process [Karner-1]

### D.5.10.2 Electrolytic Regeneration (HCl, H<sub>2</sub>SO<sub>4</sub>)

The electrolytic regeneration of acid is based on iron precipitation at the cathode of the electrolytic cell and water splitting and acid reformation at the anode.

For HCl a recovery of free and iron-bond acid is possible but, simultaneously with the water splitting at the anode, chloride gas is formed. This requires a waste gas extraction and waste gas cleaning unit.

In regenerating H<sub>2</sub>SO<sub>4</sub> an additional electrolyte (ammonia sulphate) is used and cathode and anode are separated by an ion exchange membrane. Iron is precipitated on cathodic stainless steel plates while sulphate ions in the anodic part re-form H<sub>2</sub>SO<sub>4</sub> which can be recycled to the pickling operation.

### D.5.10.3 Bipolar Membrane (HF/HNO<sub>3</sub>)

Acid regeneration using bipolar membranes comprises a combination of processing steps. First, the free acid is recovered, e.g. by diffusion dialysis. Then the remaining spent acid solution is neutralised with potassium hydroxide (KOH), thus generating metal hydroxides and salts such as potassium chloride (KCl) or -with mixed acids- potassium fluoride (KF). The metal hydroxides are precipitated as sludge and further processed, e.g. dewatered. By thoroughly washing the metal hydroxide sludge, virtually all chloride and fluoride is transferred into

solution. The KCl/KF-containing salt solution is then further concentrated by electro dialysis. The generated water can be used for metal hydroxide sludge washing. [Fichtner]

The bipolar membrane process is an electrically driven membrane process similar to electro dialysis in that it employs ion exchange membranes to selectively separate charged ions in solution, but distinguished by the water splitting characteristics of a bipolar membrane. [EC Haskoning]

The membranes are composed of two distinct layers of oppositely charged ion exchange materials. Subjected to an electrical current, the cations in the salt solution (potassium) pass through the cation exchange membrane into a parallel water flow; the anions (chloride, fluoride) pass through the anion exchange membrane into another parallel water flow. Due to the bipolar membrane, the water is continuously dissociated (split) into  $H^+$  and  $OH^-$ . With the anions and cations of the salt solution, acid and base, in this case KOH, are generated. The acid is recycled to the pickling process; the KOH is recycled to the neutralisation step. [Fichtner]

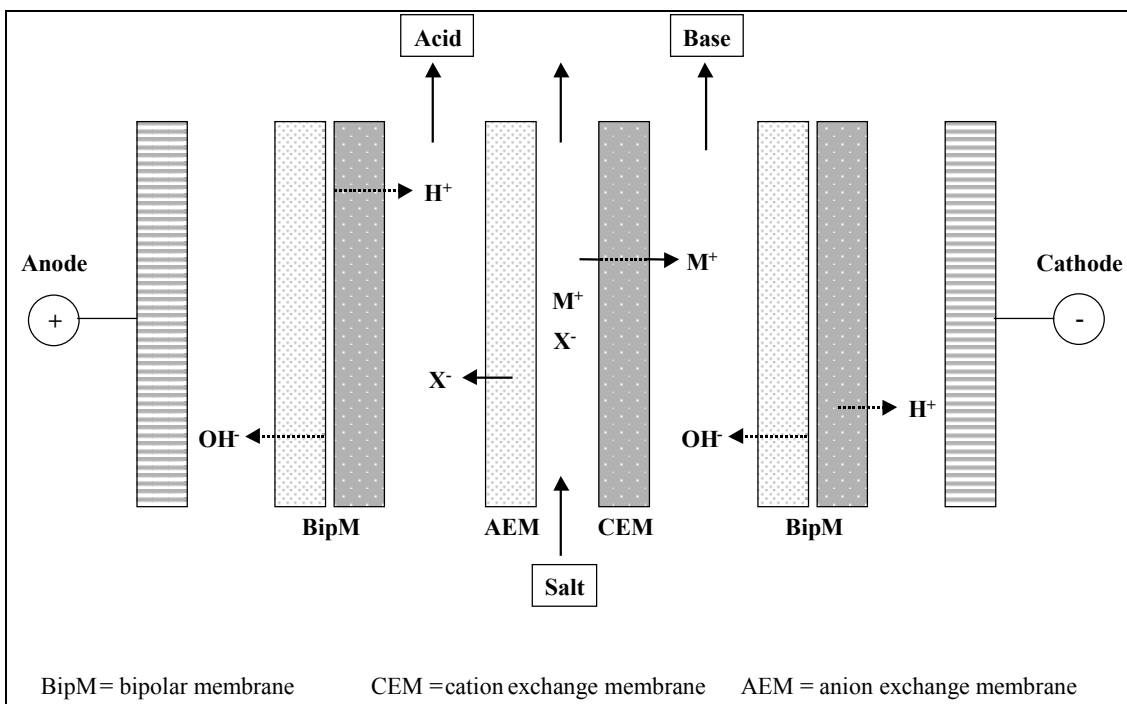
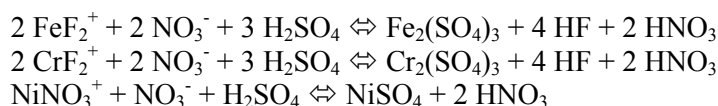


Figure D.5-17: Principle of Salt Splitting by Bipolar Membranes [Fichtner]

#### D.5.10.4 Evaporation Process (HF/HNO<sub>3</sub>)

In this evaporation process, the spent pickling acids are concentrated together with sulphuric acid at 80 °C under vacuum to drive off HNO<sub>3</sub> and HF which are condensed and recycled. The precipitated metal salt is neutralised with Ca(OH)<sub>2</sub>-slurry.

The spent pickling acids are fed to a vacuum evaporator together with circulating sulphuric acid. In the vacuum evaporator the mixed acid is heated to 80 °C. Make-up sulphur acid is added to such an extent that the concentration of at least 60 % is reached. This concentration ensures a high yield of recovered pickling acids. Metal fluorides and nitrates forms metal sulphates and liberated acid. These reaction products build up according to the following reactions:



The water, HF and HNO<sub>3</sub> are vaporized and condensed. The overflow of the condenser is led to the product tank.

The metals form sulphate chain complexes in the strong sulphur acid solution, which cause incomplete crystallization of the metal sulphates. These complexes are decomposed by raising both the temperature and the H<sub>2</sub>SO<sub>4</sub> concentration, which leads to the precipitation of the metals and to evaporation of acid (HF and HNO<sub>3</sub>) residues. This heat treatment occurs in a submerged combustion evaporator.

A long residence time in the evaporation-crystallization circuit also improves the filtering properties of the sulphate salt formed at a temperature of 80 °C. The sulphate slurry from the crystallizer tank is pumped to the cone thickener. The underflow of the thickener is led to the press filter to separate metal sulphate cake. The filtrate is returned to the crystallizer. The sulphate cake is fed into the neutralising reactor. In the reactor the cake is mixed with lime.

The heat treatment is done in a submerged combustion evaporator. The combustion gases are ducted down below the liquor surface through a dip tube. The sulphur acid concentration of 80 % is reached at 150 °C. The combustion gases are washed using a venturi scrubber to recover HF and HNO<sub>3</sub> acids. This solution is combined with the main pickling acid stream, which is condensed in the vacuum evaporator stage. The underflow of the submerged evaporator is led to the crystallizer tank.

A very positive fact is that the process barely changes the fluoride and nitrate concentration levels in the recovered acids. A slight increase of the concentrations is obtained, which ensures a proper water balance of pickling lines.

The process equipment has to be constructed using high quality materials. Special corrosion-resistant steel grades and fluorocarbon polymers have found extensive use as construction materials for the process equipment. The flowsheet of the Outokumpu Pickling Acid Recovery process is presented in Figure D.5-18.

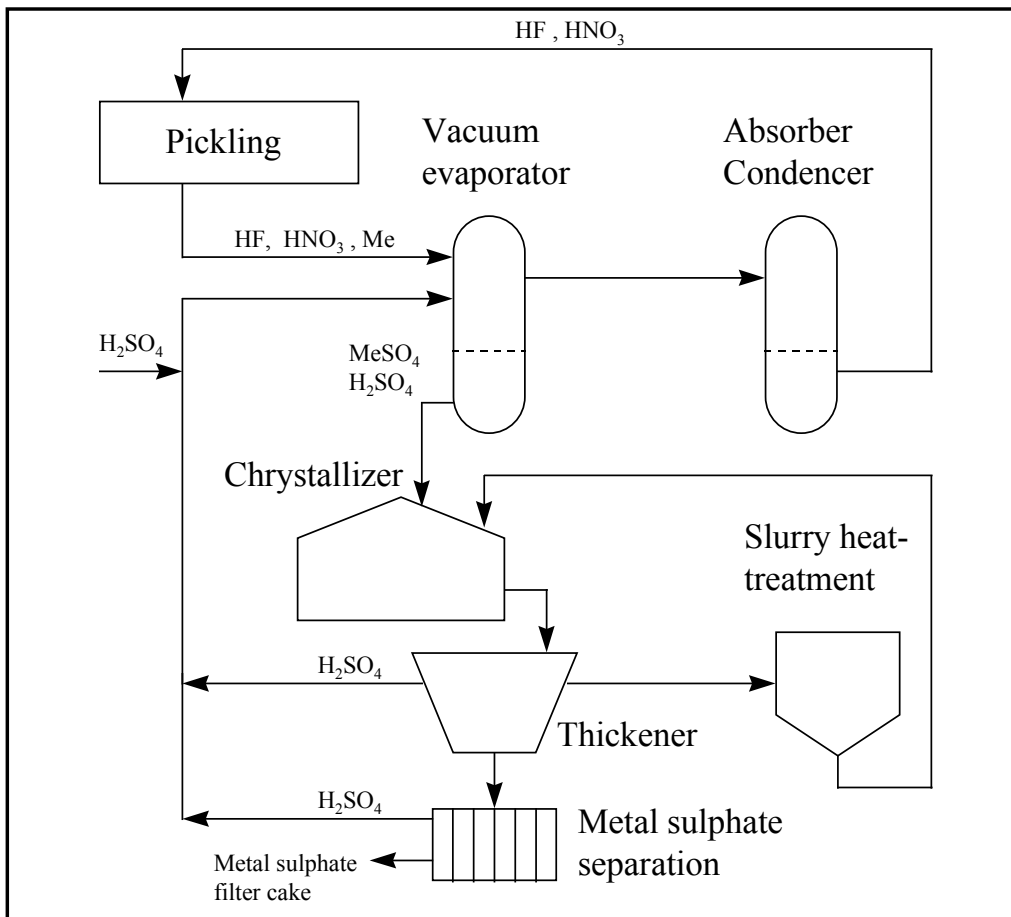


Figure D.5-18: Evaporation Process for Mixed acid Regeneration [Com2 Fin]

### D.5.10.5 Overview of Regeneration and Recovery Processes

The following Table D.5-2 gives an overview of the available acid regeneration and acid reclamation techniques.



Processes for recovery and regeneration of spent acids from HCl pickling plants							
	Pyrohydrolysis	Retardation	Dialysis	Electrolytic oxidation	Electrolytic Fe-precipitation	Chemical oxidation	Ion exchange
<b>1. Principle of process.</b>	Regeneration	Recovery of free HCl	Recovery of free HCl	Transformation of FeCl <sub>2</sub> to FeCl <sub>3</sub>	Regeneration of HCl Electrolysis	Transformation of FeCl <sub>2</sub> to FeCl <sub>3</sub>	Recovery of free HCl acid
<b>2. Other products</b>	Iron-oxides	-	-	FeCl <sub>3</sub>	Ferrous shots	FeCl <sub>3</sub>	FeCl <sub>3</sub>
<b>Waste for disposal</b>	-	Acidic FeCl <sub>2</sub> solution	Acidic FeCl <sub>2</sub> solution	-	-	-	-
<b>3. Regeneration rate total acid</b>	> 99 %	For neutralisation	For neutralisation	> 95 %	> 95 %	> 95 %	
<b>free acid</b>		75 - 90 %	75 - 90 %				50 - 70 %
<b>4. Input for regeneration</b>	- Electrical energy - Natural gas - Fresh- and waste-water	- Electrical energy - VE-water	- Electrical energy - VE-water	- Electrical energy - muriatic acid	- Electrical energy	- Electrical energy - HCl + air or Cl <sub>2</sub> or HCl + H <sub>2</sub> O <sub>2</sub>	- Electrical energy - VE-water - Oxidation agents as for chemical oxidation
<b>5. Field of application l/h</b>	> 300	> 40	> 60	> 20	> 20	> 20	> 40
<b>6. Complexity of installation</b>	High	Low	Medium	Low	Medium	Medium	High
<b>7. Required space</b>	Big	Small	Medium	Small	Small	Medium	Medium
<b>8. Benefit / cost ratio</b>	High	Medium	Medium	Medium	Medium	Low	Low
<b>9. # plants<sup>1</sup></b>	ca. 250	ca. 15	ca. 5	2	???	???	1
Processes for recovery and regeneration of spent acids from H <sub>2</sub> SO <sub>4</sub> pickling plants							
	Crystallization (indirect cyclone- or vacuum-cooling)	Retardation	Dialysis	Electrolytic oxidation	Process with HCl and pyrolysis	Crystallization and roasting	Precipitation with solvents
<b>1. Principle of process</b>	Recovery of free H <sub>2</sub> SO <sub>4</sub>	Recovery of free H <sub>2</sub> SO <sub>4</sub>	Recovery of free H <sub>2</sub> SO <sub>4</sub>	Regeneration	Regeneration	Regeneration	Recovery of free H <sub>2</sub> SO <sub>4</sub>
<b>2. Other products</b>	FeSO <sub>4</sub> ; 7H <sub>2</sub> O	-	-	Ferrous shots	Iron-oxide	Iron-oxide	Iron-oxide
<b>Waste for disposal</b>	(If Cr, Ni, Zn present)	Acidic FeSO <sub>4</sub> for neutralisation	Acidic FeSO <sub>4</sub> for neutralisation	-	-	-	(If Cr, Ni, Zn present)
<b>3. Regeneration rate total acid</b>				> 99 %	> 95 %	> 95 %	
<b>free acid</b>	> 99 %	80 - 90 %	75 - 85 %				> 99 %
<b>4. Input for regeneration</b>	- Electrical energy - Steam - Cooling water	- Electrical energy - VE-water	- Electrical energy - VE-water	- Electrical energy - Additional electrolyte in loop	- Electrical energy - Natural gas - Cooling water - HCl in loop by fresh- and rinsing water	- Electrical energy - Steam - Natural gas - Cooling water - Fresh and waste water	- Electrical energy - Steam - Cooling water - Solvent in loops
<b>5. Field of application l/h</b>	> 200	> 40	> 60	> 20	> 500	> 500	> 200
<b>6. Complexity of installation</b>	Medium/ high	Low	Medium	Medium	High	High	High
<b>7. Required space</b>	Medium/ big	Small	Medium	Medium	Big	Big	Medium
<b>8. Benefit / cost ratio</b>	Medium	Medium	Medium	Medium	Low	Low	Low
<b>9. # plants<sup>1</sup></b>	ca. 80	ca. 30	ca. 5	2	1	1	n.a.

Table D.5-2: Overview of regeneration and reclamation processes (as submitted by [DFIU99])

Processes for recovery and regeneration of spent acids from HNO <sub>3</sub> / HF pickling plants								
	Solvent extraction	Retardation	Dialysis	Crystallization	Pyrohydrolysis	Bipolar membranes	Outokumpu process <sup>2</sup>	Kawasaki process
<b>1. Principle of process</b>	Total regeneration	Regeneration of free acids	Regeneration of free acids	Regeneration of free acids	Total regeneration	Total regeneration	Total regeneration	Total regeneration
<b>2. Regenerate / reg. acid</b>	Total HNO <sub>3</sub> and HF	Free HNO <sub>3</sub> and HF	Free HNO <sub>3</sub> and HF	Free HNO <sub>3</sub> and HF	Total HNO <sub>3</sub> and HF	Total HNO <sub>3</sub> and HF	Total HNO <sub>3</sub> and HF	Total HNO <sub>3</sub> and HF
<b>3. Other products</b>	-			Metal fluorides	Metal oxide	Metal hydroxides	Ni(OH) <sub>2</sub>	Ironoxide
<b>Waste for disposal</b>	Metallic salt solution	Metallic salt solution	Metallic salt solution				Metal hydroxides	Metallic salt solution
<b>3. Regeneration rate total acid</b>	HNO <sub>3</sub> 80 - 95 % HF 50 - 65 %				HNO <sub>3</sub> 80 - 90 % HF 90 - 99 %	HNO <sub>3</sub> 90 - 95 % HF 90 - 97 %	HNO <sub>3</sub> > 97 % HF 99 %	HNO <sub>3</sub> 75 - 90 % HF 85 - 95 %
<b>free acids</b>		HNO <sub>3</sub> 80 - 95 % HF 80 - 90 %	HNO <sub>3</sub> 85 - 95 % HF 80 - 90 %	HNO <sub>3</sub> 80 - 95 % HF 50 - 55 %				
<b>4. Input for regeneration</b>	- Electrical energy - H <sub>2</sub> SO <sub>4</sub> - Cooling water - TBP in loop - Activated carbon	- Electrical energy - VE-water	- Electrical energy - VE-water	- Electrical energy - Cooling water	- Electrical energy - Natural gas - Cooling water - Fresh- and waste water - H <sub>2</sub> O <sub>2</sub> or similar	- Electrical energy - Caustic potash solution in loop - Diatom earth	- Electrical energy - H <sub>2</sub> SO <sub>4</sub> in loop- - Propane - Limestone - Steam - Cooling water	- Electrical energy - Extraction agents TBP und D2EHPA in loop - NH <sub>4</sub> HF <sub>2</sub> in loop - Natural gas, - Freshwater
<b>5. Field of application l/h</b>	>300	>40	>60	>300	>500	>100	4500	>1000
<b>6. Complexity of installation</b>	Medium	Low	Medium	Medium	High	High	Medium	Very high
<b>7. Required space</b>	Medium	Small	Medium	Medium	Large	Medium	Medium	Very large
<b>8. Benefit / cost ratio</b>	Medium	Medium	Medium	Low	Medium	Medium	Medium	Medium
<b>9. # plants <sup>1</sup></b>	2	ca. 30	ca. 5	1	2	2	2	1
<sup>1</sup> world-wide, as at 1990, production and pilot plants								
<sup>2</sup> Source of data [Com2 FIN]								

Table D.5-2 cont.: Overview of regeneration and reclamation processes (as submitted by [DFIU99])

## **D.5.11 Treatment of Acidic Waste / Waste Water**

### **D.5.11.1 Neutralisation of Acidic Waste Water**

Acidic waste water from rinsing, from fume absorbers of the pickling tank exhaust system or from flushing (plant cleaning) that can not be reused elsewhere in the plant, neutralised (e.g. with alkaline waste waters from other plant operations) and treated prior to discharge to reduce the emissions. Dissolved metal ions are transformed into hydroxides or sparingly soluble salts and subsequently eliminated by sedimentation, in many cases by adding flocculants. The precipitated metal sludge is de-watered in filter presses and disposed of.

Neutralisation (of spent pickling baths) generates a large quantity of sludge. The sludge, mainly consisting of iron hydroxide and water, can be recycled for iron production as long as it is not contaminated by unacceptable metals (e.g. zinc) or by other constituents. Care should be taken to avoid mixing of waste water streams or sludges which can make recycling difficult.

Neutralisation can also create large amounts of neutral salts (e.g. NaCl, CaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, CaSO<sub>4</sub>), most of which are very soluble in water and are discharged with the treated water. Removal is only possible by very special, and in most cases uneconomical, treatment (reverse osmosis, electrodialysis or evaporation followed by ion exchange and concentrate evaporation with salt drying). Even if these salts are removed, their mixed composition limits re-use and disposal to landfill may be restricted by their solubility. [EUROFER CR]

A distinction has to be made between neutralisation sludges from stainless steel pickling and from carbon steel pickling. The sludge resulting from neutralisation of mixed acid wastes is usually landfilled, as it cannot be recycled. [Com2 CR]

## D.6 HEATING OF PROCESS LIQUORS (ACID, EMULSIONS...)

Heating of process liquors may be necessary at several stages in ferrous metals processing, e.g. for heating acid baths, for emulsion splitting or for reducing/evaporating waste water. In principle two techniques are available: **heat exchangers** and **submerged combustion** (immersion gas burner). The formerly applied technique of steam injection (e.g. for heating acid baths), is not considered here as it leads to unnecessary dilution of process baths. The principles of both, heat exchanger and submerged combustion, are shown in Figure D.6-1 and Figure D.6-2.

In heat exchangers the heating media and the liquid to be heated are separated by a partition and no mixing (or contamination) takes place. With immersion gas burners the heating media, hot flue gas, is blown directly into the liquid to be heated and both are mixed. Either heating technique has advantages and disadvantages and application depends to some extent on the individual situation of a plant.

Where waste heat is available in the form of steam or in the form of another heating medium with a lower temperature, heat exchangers are commonly used. Several designs of heat exchangers exist, tube or plate, and depending on the chemical properties of the product to be heated and/or the heating media, high quality material has to be used. Heat exchangers need large surfaces to achieve the heat transfer.

If fuel gas is readily available or steam has to be produced first, it might be sensible to use a burner to heat the liquid directly and thus increase the thermal efficiency. Disadvantages are that the product may be contaminated with CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub> etc., which could cause problems, and that portions of the product (e.g. acid vapour, droplets) may be carried out with the flue gas, making a waste gas treatment necessary. [VOEST]

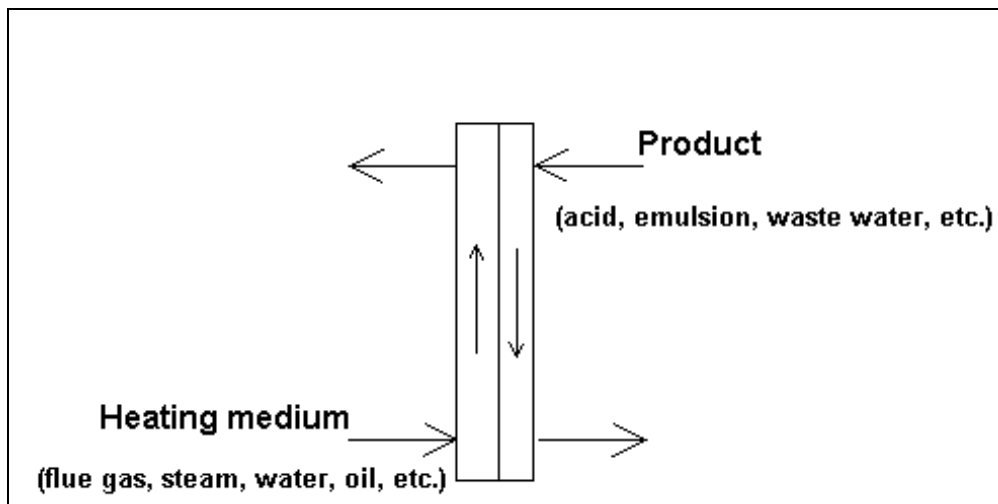
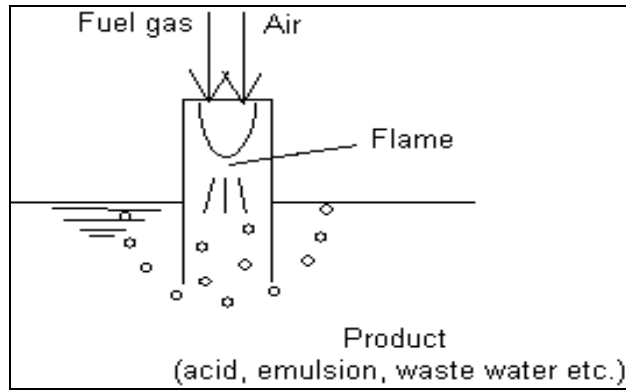


Figure D.6-1: Principle of heat exchangers  
[VOEST]



**Figure D.6-2: Principle of submerged combustion**  
[VOEST]

Some advantages of submerged combustion were reported, beside financial savings, reduced energy consumption and acid consumption were claimed.

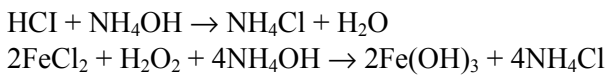
## D.7 FLUXING

### D.7.1 On-site Regeneration of Flux Baths (Iron Removal)

During operation the iron concentration in a flux solution is increased. At a certain level, the flux solution becomes unusable. In order to be able to recirculate the solution, the iron content needs to be removed. This can be done continuously or in batch operation.

#### D.7.1.1 Iron Removal Using Ammonia and H<sub>2</sub>O<sub>2</sub> Oxidation

By means of addition of ammonia (for pH adjustment) and H<sub>2</sub>O<sub>2</sub> (oxidant), iron is precipitated as Fe(OH)<sub>3</sub> and NH<sub>4</sub>Cl is produced according to the reactions:



The precipitated iron hydroxide sludge is withdrawn and disposed of.

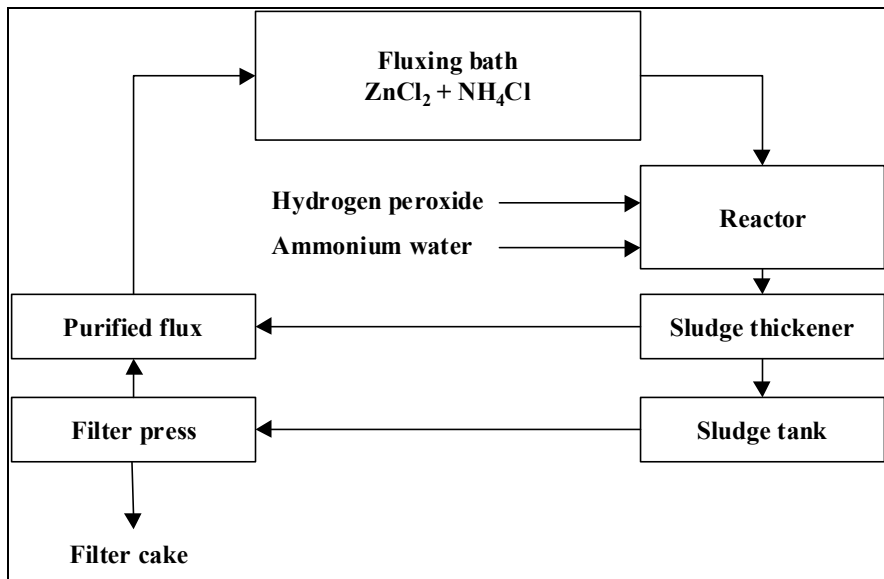
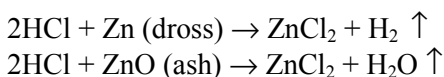


Figure D.7-1: Flow sheet for flux regeneration  
[DK-BAT-93]

Zinc, initially present in solution or introduced by the workpieces impregnated with solution from the rinsing or pickling baths, remains as ZnCl<sub>2</sub>.

Normally, the ratio of NH<sub>4</sub>Cl/ZnCl<sub>2</sub> produced is higher than the ratio required by most galvanizers and the amount of salt produced is not sufficient to compensate for the consumption of flux. This can be corrected by addition of depleted pickling or de-zincing solution, which increases the production of fluxing salts. Another option to influence the NH<sub>4</sub>Cl/ZnCl<sub>2</sub> ratio of salts produced, is to pre-react the depleted pickling or the de-zincing solution with dross or ash; thus producing ZnCl<sub>2</sub> instead of NH<sub>4</sub>Cl:

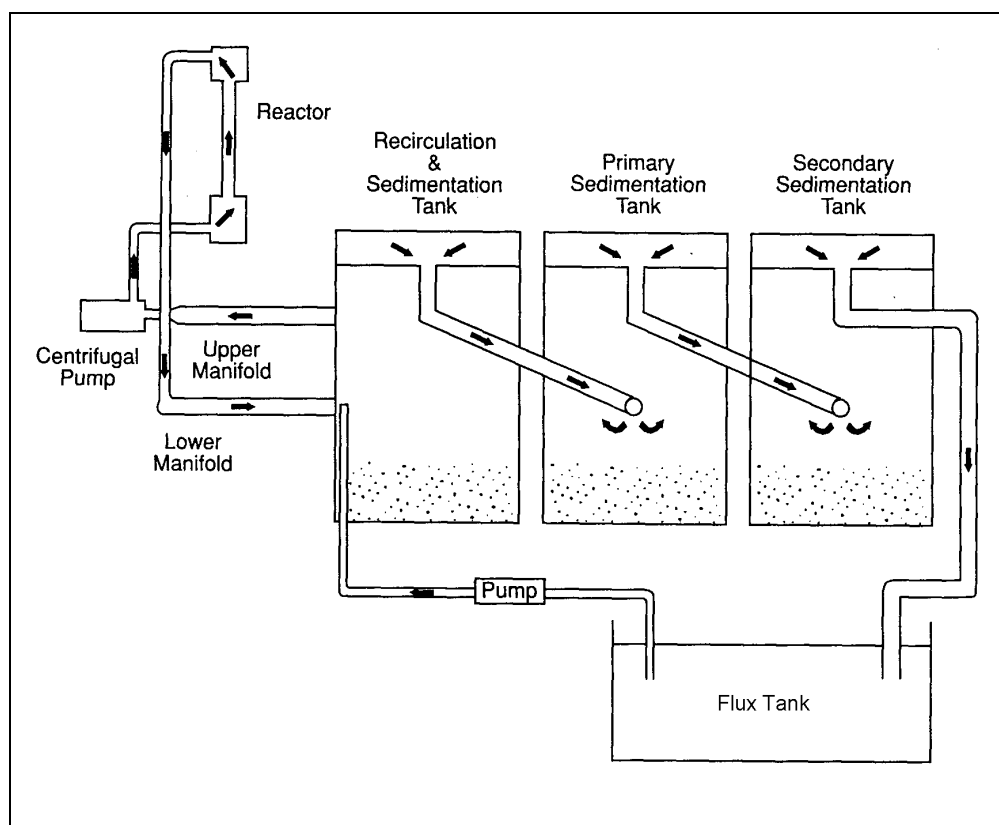


Automated pH and redox controls allow for a selective iron precipitation (about 50 % iron in the solids) and a low oxidizing potential, avoiding the destruction of any organic additive in the flux. To obtain maximum thickening and filtration efficiency, a selective flocculant is added to the pulp in the flocculator, resulting in a high settling rate of solids, excellent clarity of the overflow and improved filtration characteristics of the underflow. A solid content of the press-filter cake of around 50 % is achievable.

It is possible to generate flux solution with a composition required by the galvanizer. For an optimum composition of the flux, zinc chloride or ammonium chloride additions may be required. [DK-BAT-93]

### D.7.1.2 Iron Removal Using Electrolytic Oxidation

The electrolytic oxidation process consists of a reactor module or series of reactor modules for the electrolytic oxidation of dissolved iron and a set of sedimentation tanks for the removal of precipitate from the process stream. A schematic flow diagram is shown in



**Figure D.7-2: Schematic of the electrolytic oxidation process**  
[Choice/Barr-IG-94]

As flux solution passes through the reactor, ferrous iron (II) is oxidized to ferric iron (III). The ferric iron (III) is precipitated as hydroxide. This is accompanied by the generation of acid. As a result of these changes, the concentrations of dissolved iron and acid capacity in the stream leaving the reactor are lower than in the entering stream. Because of this, and because work continues to import rinse water or pickle solution to the main flux tank, the iron and acid capacity in the recirculation tank are lower than in the main flux tank. The relationship between the iron concentrations in the two tanks depends on a number of factors but, in practice, the concentration in the recirculation tank can be brought down to near zero grams per litre and steady concentrations in the main tank of less than 2 grams per litre can be achieved easily,

while concentrations of 1 gram per litre or lower can be achieved with careful operation. [Choice/Barr-IG-94]

- the system is based on a chloride balance and all the chloride carried over from the rinse tank to the flux tank is utilized in the generation of zinc ammonium chloride make-up
- iron is removed
- no waste water treatment is necessary,
- promotion of the rinse water to the acid tanks allows a significant saving in acid costs
- water input and costs are minimized [Choice/Barr-IG-94]

Sourcing spare parts for the equipment was reported as a potential problem as the supplier is based in Australia. [Com2 EGGA]

### **D.7.1.3 Iron Removal Using Ion Exchange Columns**

The ion-exchange process uses resin to absorb the iron. As this process is sensitive to solid particles, the flux solution is filtered first. This can be done with a standard plate-filter. By adding concentrated NaOH, the pH is set to the required pH value. The neutralisation unit is continuously stirred to create a homogeneous solution. The solution is then pumped through the ion-exchange column where iron is absorbed by the resin. After leaving the column, the liquid is returned to the rinse/flux bath. When the resin is saturated with iron, it must be stripped and regenerated. The stripping/regeneration solution is pumped from a storage vessel through the column into another vessel. An exchange of iron and acid takes place in the column. Iron is dissolved in the HCl, while the acid is absorbed by the resin. [Sprang-IG-97]

## **D.7.2 External Reutilization of Spent Flux Baths**

### **D.7.2.1 NH<sub>3</sub> Removal, Precipitation and Partial Reuse for New Flux Production**

→ No information submitted.

### **D.7.2.2 H<sub>2</sub>O<sub>2</sub> Oxidation, Total Reuse for New Flux Production**

→ No information submitted.



## D.8 RINSING

### D.8.1 Efficient (multiple) Use of Rinsing Water

Figure D.8-1 shows the variety of rinsing techniques available; ranging from out-dated flow rinsing to sophisticated combined rinsing systems. The associated water consumptions are listed in Table D.8-1. Due to the high water consumption of flow rinsing, this technique is no longer acceptable. Multiple (cascade) use of rinse water and static rinse tanks result in sufficiently high concentrations in the rinse water to allow for the **reuse in preceding process baths** or to allow for **regeneration or reclamation measures** applied to the process baths to be applied to the rinse water as well.

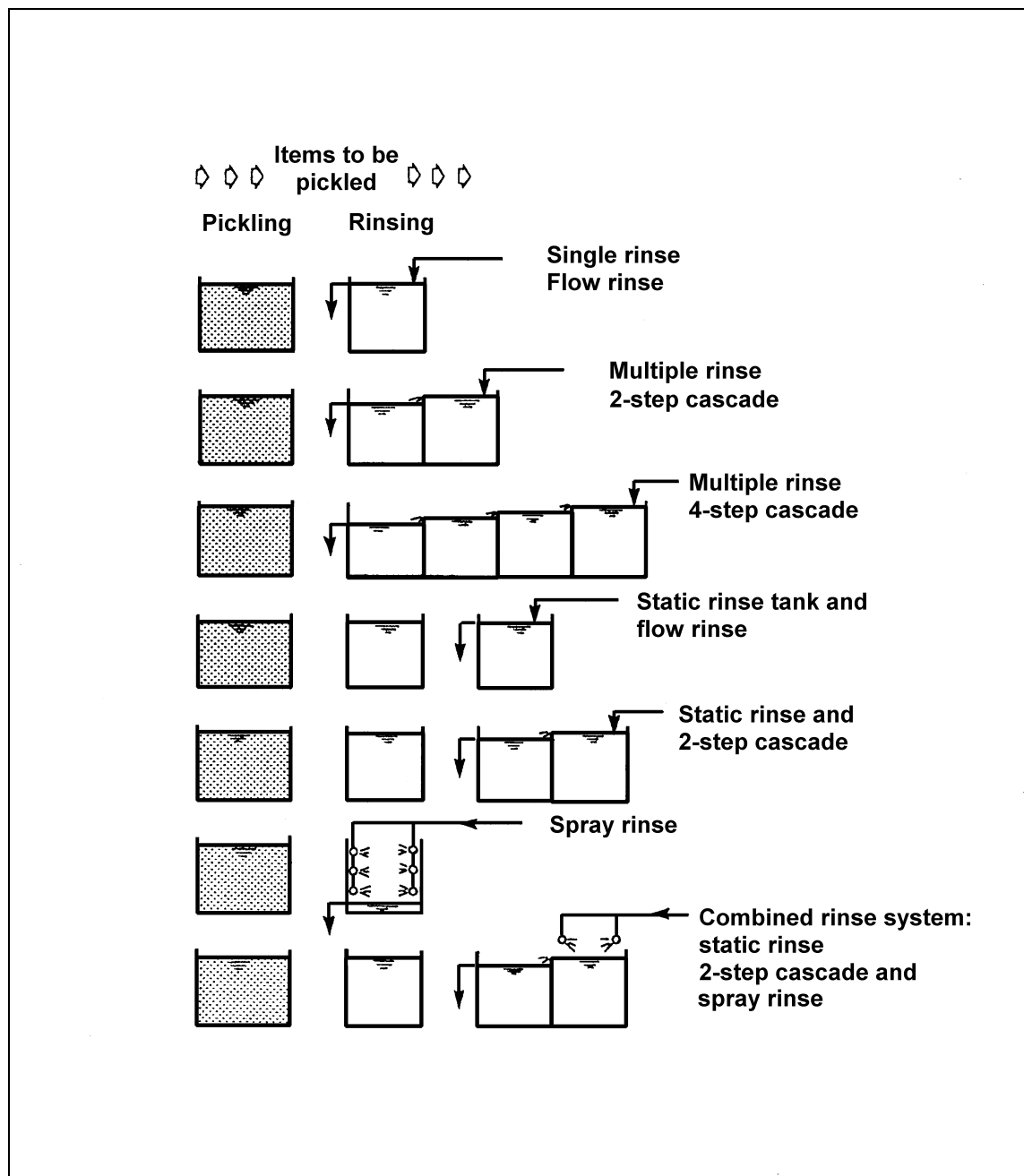


Figure D.8-1: Rinsing systems  
[Rituper93]

Concentration in pickle bath [g/l]		100				200				600			
Residual concentration in last rinse bath [mg/l]		5	10	20	50	5	10	20	50	5	10	20	50
Rinse criteria		$2 \cdot 10^4$	$10^4$	$5 \cdot 10^3$	$2 \cdot 10^3$	$4 \cdot 10^4$	$2 \cdot 10^4$	$10^4$	$4 \cdot 10^3$	$1.2 \cdot 10^5$	$6 \cdot 10^4$	$3 \cdot 10^4$	$1.2 \cdot 10^4$
Rinse system	Number of Baths	Rinse water consumption [m <sup>3</sup> /h]				Rinse water consumption [m <sup>3</sup> /h]				Rinse water consumption [m <sup>3</sup> /h]			
Flowrinse	1	2000	1000	500	200	4000	2000	1000	400	12000	6000	3000	1200
2-step cascade	2	14.1	10	7.1	4.5	20	14.1	10	6.3	34.6	24.5	17.3	11
3-step cascade	3	2.7	2.1	1.7	1.3	3.4	2.7	2.1	1.6	5.0	4.0	3.1	2.3
4-step cascade	4	1.2	1.0	0.9	0.7	1.4	1.2	1.0	0.8	1.9	1.6	1.3	1.0
Static and flow rinse	2	400	200	100	40	800	400	200	80	2400	1200	600	240
Static rinse 2-step cascade	3	6.3	4.5	3.2	2.0	9.0	6.3	4.5	2.9	15.5	11.0	7.7	4.9
Static rinse 3-step cascade	4	1.6	1.3	1.0	0.7	2.0	1.6	1.3	0.9	2.9	2.3	1.8	1.3
Spray rinse Efficiency 100 %	1	9.9	9.2	8.5	7.6	10.6	9.9	9.2	8.3	11.7	11.0	10.3	9.4
Spray rinse Efficiency 30 %	1	3.3	3.1	2.9	2.6	3.6	3.3	3.1	2.8	4.0	3.7	3.5	3.2

Note: carry-over 100 l/h

Table D.8-1: Comparison of water consumption for different rinsing systems [Rituper93]

## D.8.2 Treatment of Rinsing Water

Ion exchange, electrolytic iron removal, reverse osmosis, oxidizing iron removal

→ No information submitted.

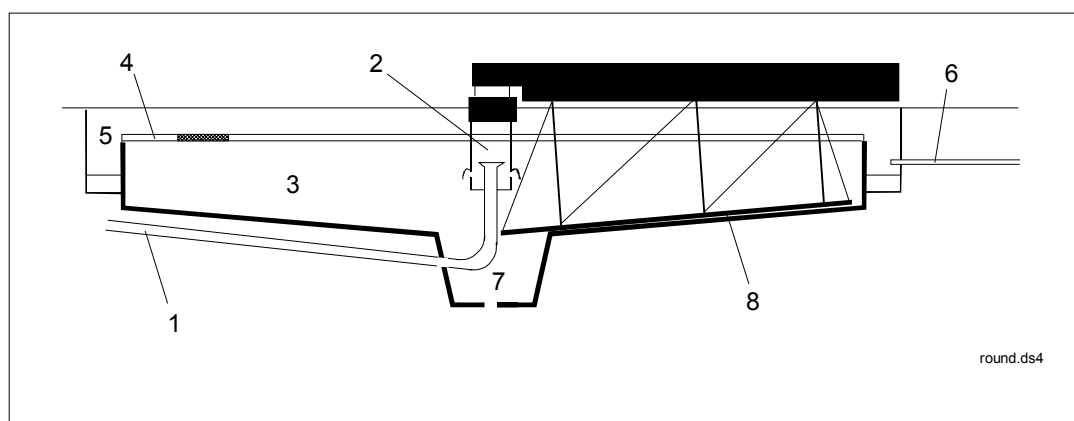
## D.9 PROCESS WATER AND WASTE WATER TREATMENT

### D.9.1 Treatment of Oil- and Scale-bearing Process Water

In most cases coarse scale is captured close to the spot where it arises by **scale pits**, small gravity separators, to prevent installations from damage, e.g. if it is necessary to transport the scale-loaded water by pumps. Scale pits can reduce the content of suspended solids in the waste water (load of 20 - 40 m<sup>3</sup>/(m<sup>2</sup>h)) from 200 - 800 mg/l to 60 - 100 mg/l. The advantage of decentralised scale arresting is that there is no sedimentation in the flume channels and less corrosion takes place.

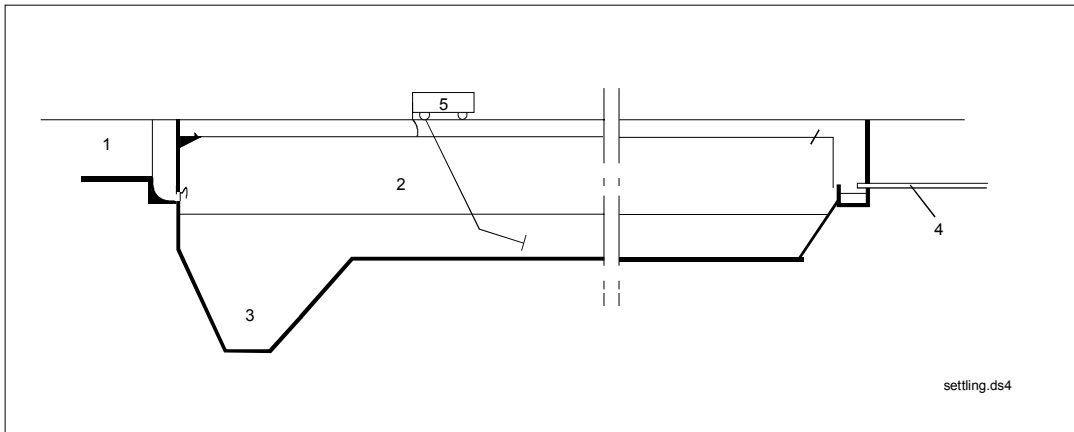
For further coarse cleaning (intermediate cleaning), the water is usually physically treated in settling tanks to separate coarse scale and hydrocarbons. Different designs are available, e.g. vertically and horizontally flown **settling tanks**. Figure D.9-1 and Figure D.9-2 depict examples of gravity separators.

The basic principle of these separators is that coarse particles settle on the bottom of the basin by gravity, while the major part of the oil dispersed in the water rises to the surface. The water is discharged via an outlet equipped with a submerged barrier in front to prevent the oil floating on the surface from being discharged with the purified water. The deposited sediments are usually conveyed to a sump by scrapers where they can be removed by excavators or pumps.



- |                          |  |
|--------------------------|--|
| 1 Waste water inlet      | 5 Clear water collecting pipe                        |
| 2 Distribution cylinder  | 6 Clear water outlet                                 |
| 3 Reservoir              | 7 Sludge reservoir                                   |
| 4 Clear water spill-over | 8 Ground scraper                                     |
|                          | (suction pipes for sludge removal are not indicated) |

**Figure D.9-1: Circular Settling Tank (vertical)**  
[DFIU98]



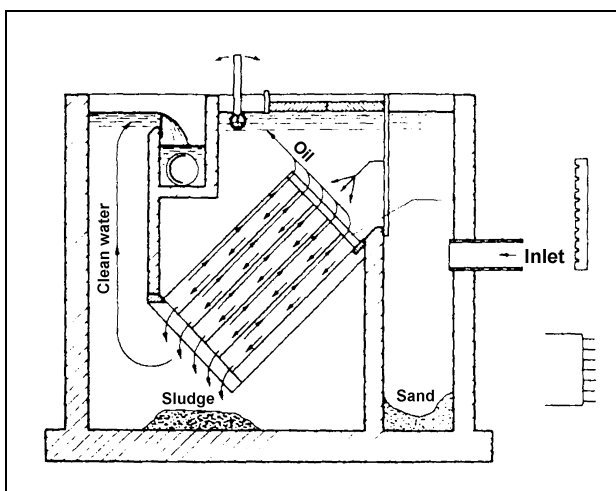
- |                                  |                      |
|----------------------------------|----------------------|
| 1 Waste water inlet              | 4 Clear water outlet |
| 2 Useful space for sedimentation | 5 Sludge scraper     |
| 3 Sludge reservoir               |                      |

**Figure D.9-2: Horizontal Flow Settling Tank**  
[DFIU98]

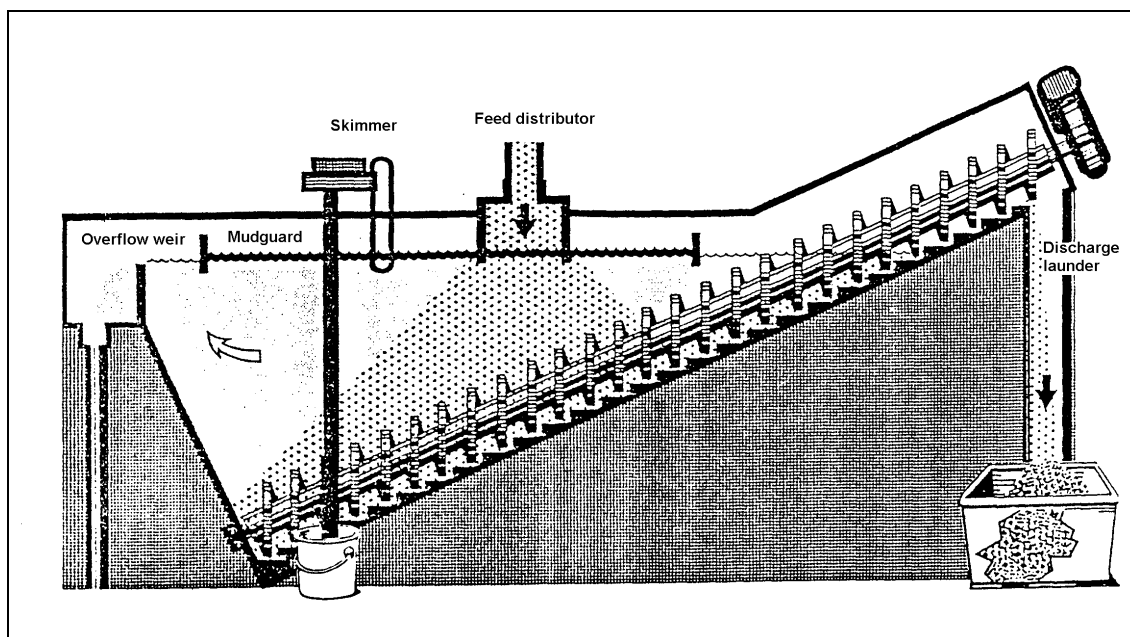
The achievable reduction depends on tank size, particle size distribution, addition of flocculating agents and oil content. Settling tanks can reduce suspended solids from 40 - 80 mg/l down to 20 - 35 mg/l (load 4 - 15 m<sup>3</sup>/(m<sup>2</sup>h)).

Other types of gravity separators are **screw-type clarifier (or screw-type dewaterer)** and **lamella separator**. Compared to settling basins they have a more compact construction. In lamella separators (Figure D.9-3) the incoming water is led over a number of inclined plates (lamellas). The settling distance is much shorter. The settlements are forced down along the plates by gravity, while the oils move upwards along the underside of the plates and can be collected by skimming mechanisms. The purified water is discharged through an outlet, which is separated from the basin by a submerged barrier. The sediment is discharged from the bottom e.g. via a screw, which is also separated from the main basin by a submerged barrier.

Screw-type clarifiers (see Figure D.9-4) are basically settling tanks with an inclined bottom. The solids settling by gravity are transported out of the separator by a rotating screw, partially submerged in the sediment.



**Figure D.9-3: Schematic of a lamella separator**  
[Fichtner]



**Figure D.9-4: Screw-type clarifier**  
[BSW-WWT-90]

In **centrifugal separators** the scale particles are pressed to the wall by the flow. On the wall of the separation chamber, the scale particles glide slowly downward to the collecting chamber. When the collecting chamber is full, automatic elutriation starts. A disadvantage of this method is the fact that oil separation is not possible.

Oil floating on water surfaces is removed by **oil skimmers**. The oil adheres to an endless strip or hose, which is immersed in the basin. Together with this strip or hose the oil is transferred to a funnel outside of the basin where it is skimmed from the strip. A wheel can also be used instead of the endless strip.

Fine cleaning can be carried out in **gravel- or sand filters** (Figure D.9-5). The water flows through the filter medium from the top to the bottom. Thus large amounts of scale, sludge and oil are retained. Depending on the cleaning system these filters can remove all particles carried by the water down to a grain size of 1 micron. The cleaned but still thermally loaded water is cooled in cooling towers in order to achieve the right temperature for re-circulation. Gravel and sand filters need to be cleaned in order to remove particles and hydrocarbons. The filters are backwashed after a fixed period or when a defined filter resistance has been reached. Backwashing is performed with water or air. The required volume of backwash water amounts to about 1 – 3 % of the cleaned water.

Some sand filters are operated with continuous backwashing. Here the water flows through the filter medium from the bottom to the top. The sand is continuously transported upwards and constantly washed. The purified sand falls on top of the clean sand bed.

The backwash water is usually highly contaminated and is either treated in the pre-cleaning units, if necessary under addition of flocculating agents; or is treated separately in special sludge treatment units.

For **treatment of backwashing water** from the sand filters, the water is thickened in a thickener by adding flocculents and applying sedimentation techniques. The flocculent is added and mixed with the backwash water in a pre-reaction chamber. In the central chamber the sludge settles down. The purified water is discharged through an indented weir and is returned

to a sand filter system. By means of a scraper the sludge is transported to the sludge sluice, where it is discharged.

If the arising sludge contains too much water, a press can be used for further dewatering. Such a press can be designed as a chamber filter press, a membrane filter press or a solid bowl centrifuge. The filtered water is recirculated to the thickener. [EUROFER HR]

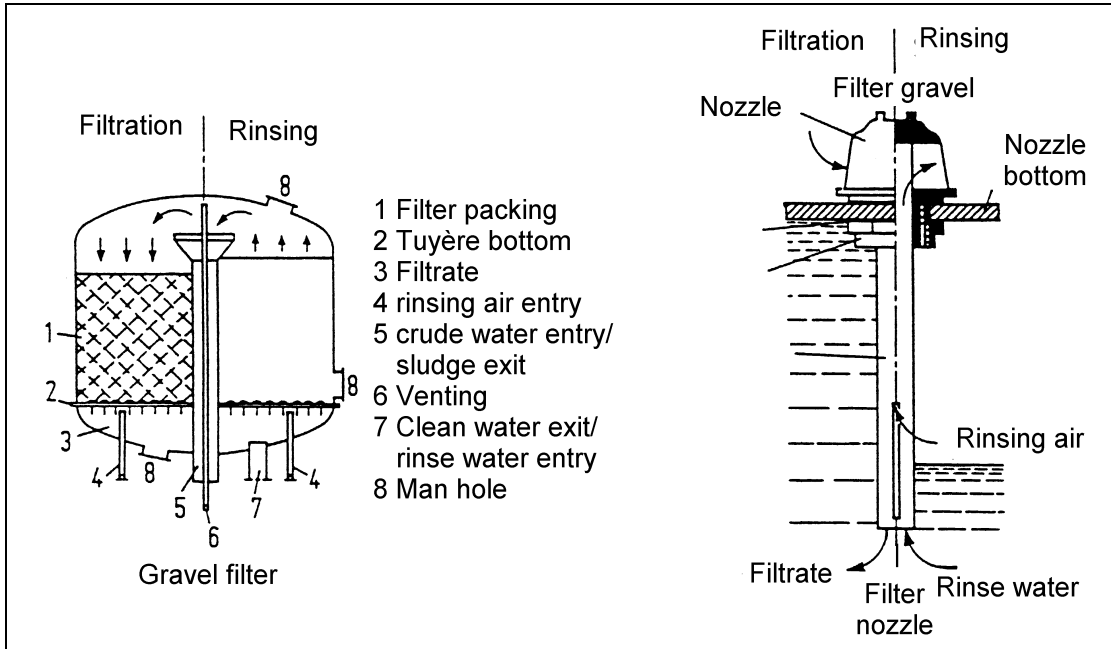


Figure D.9-5: Example of a gravel filter with indication of backwash operation [Theobald]

Another option for fine cleaning the pre-cleaned waste water is filters that consist of **cylindrical, wire-netting filtering elements** (see Figure D.9-6).

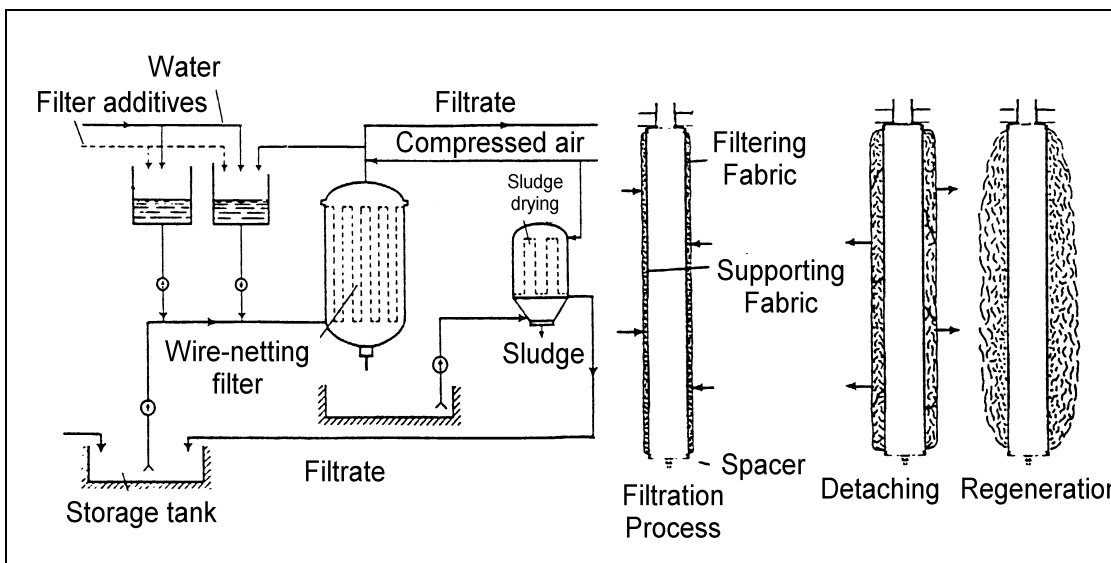


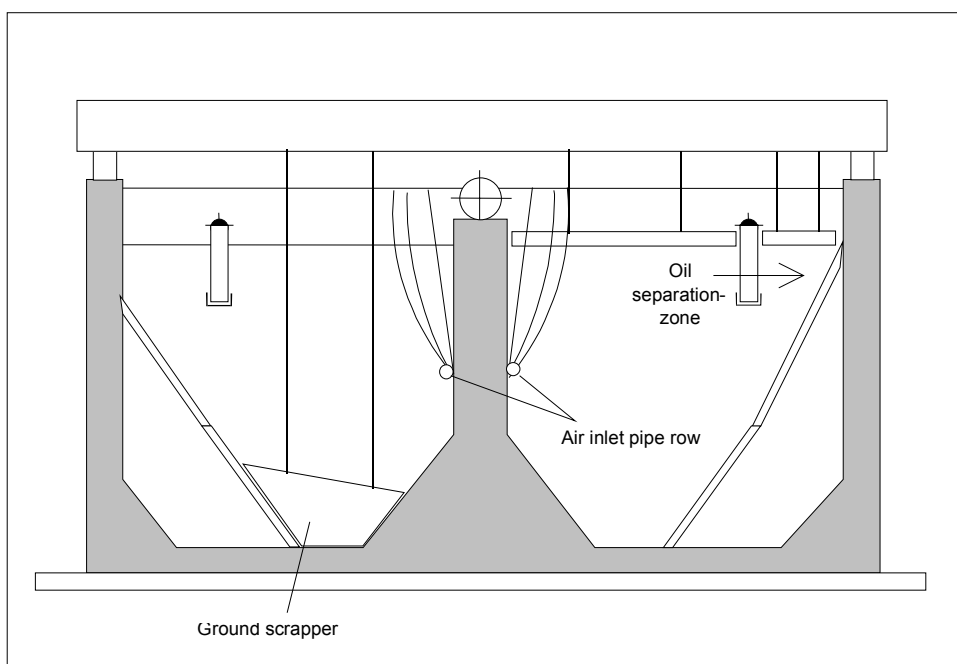
Figure D.9-6: Example of wire-netting filters with indication of backwash operation [Theobald]

Operation cycles of these filters are divided into:

- starting phase during which a layer of filtration aid is built up on the fine meshed filters
- filtering phase during which further filtration aid is added to keep the filtrate and sludge layer permeable
- backwashing phase during which the filters are cleaned by reversing the flow direction.

Sludges obtained from backwashing can be dewatered directly and require special treatment prior to reuse (e.g. in the sinter plant) only if they have a high oil contents. [Theobald]

For a more efficient intermediate cleaning and enhanced separation of scale and oil, so-called **aerated fine scale-traps** have been developed as shown in Figure D.9-7. These combine the principles of sedimentation and flotation. The solids settle on the bottom and are removed by scrapers, while the air blown in (air bubbles) enhances the flotation of the oil.



**Figure D.9-7: Aerated fine scale-trap**  
[DFIU 98]

Furthermore, the oil adsorbed by the fine scale is 'washed off' by agitation. Due to the better separation of oil and scale and the lowered oil content of the scale, the recycling options are improved. With retaining times of 15 to 30 minutes and loads of 15 - 20 m<sup>3</sup>/(m<sup>2</sup>h), aerated fine scale-traps can achieve reduction rates of 99 % for particles > 63 µm and 20 - 80 % for particles sized 31 - 63 µm (depending on the particle size distribution). [DFIU98], [Theobald],

	<b>Inlet</b> <b>[mg/l]</b>	<b>Outlet</b> <b>[mg/l]</b>	<b>Reduction</b> <b>[%]</b>
<b>Suspended solids</b>	32.3	25.8	20.1
<b>Settleable Solids</b>	95.5	44.2	53.7
<b>Fe total</b>	43.5	24.6	43.4
<b>Hydrocarbons</b> <sup>1</sup>	2.0	1.3	35.0
Note: Source of data [StuE-111-3]			
<sup>1</sup> Determined according to DIN 38 409, part 18, 1981			

**Table D.9-1: Example of achieved emission levels for aerated fine scale-traps**

Reducing oil and grease content by using a treated fine scale-traps as a precleaning device upstream of gravel or sand filters, can improve the operation of the filters. The backwashing intervals are increased as the particle load is reduced and clogging of filters due to oil and grease is minimized. [UBA-Kloeckner-82]

Mill scale has a high magnetic susceptibility and can thus be removed by **magnetic filtration** (see example in Figure D.9-8). A coil creates a magnetic field in which the steel casing of the filter and a matrix of filament material are also magnetised (amplification); due to the high gradients small ferromagnetic particles such as mill scale fines are attracted.

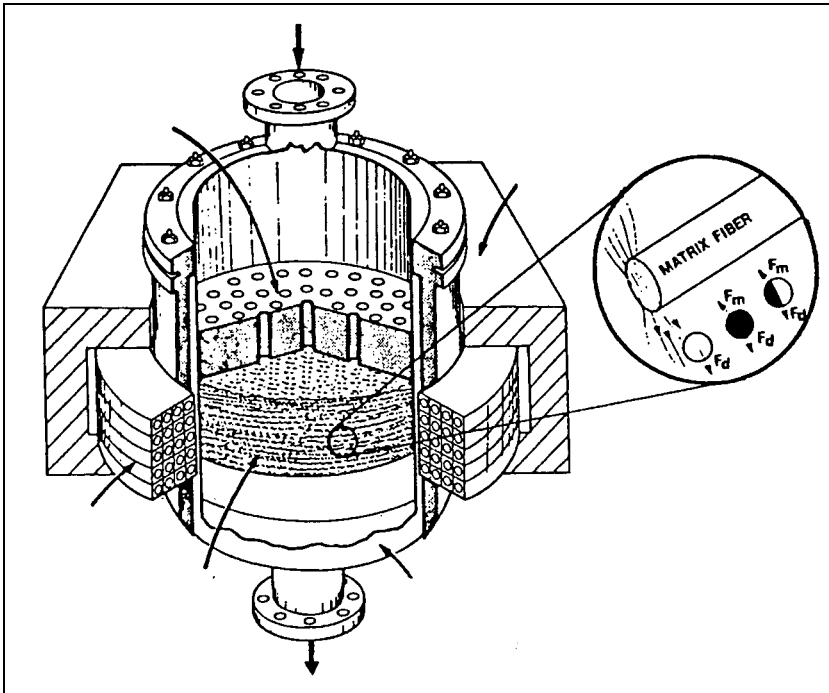


Figure D.9-8: Magnetic filtration (example high gradient MF)  
[Svedala]

## D.9.2 Cooling Systems and Cooling Water Treatment

In order to run cooling water in closed loops and thus reduce the water consumption, the cooling water has to be re-cooled and treated.

Cooling is done either by evaporation in cooling towers, heat exchangers or hybrid cooling towers. In pressure-cooled counterflow **cooling towers**, the water to be cooled is sprayed on grids in the cooling tower cells and flows over blocks into the cooling tower tray. Fans arranged laterally or on top draw in ambient air which passes the water in counterflow. Thus cooling is achieved by evaporation of water. The cooling efficiency is controlled by means of the air volume. Desalting is controlled via a measurement of the electrical conductivity. If required, the necessary amount of dispersants, sodium hypochlorite and biocide (prevention of growth of bacteria and fungi) and acid or alkali (pH-value) is added. [EUROFER HR]

In **plate heat exchangers**, plates with through-flow channels are screwed to a package. From each plate, alternatively hot waste water and cold cooling water is pumped through these channels. The heat is transferred via the plate wall. [EUROFER HR]



In **hybrid cooling towers**, a plate heat exchanger is installed in the upper part of the tower. In the lower part, the water is cooled by evaporation. Due to the heat exchanger, the air with 100 % moisture is heated and condenses as fog some time later and with less intensity.

In the planning and installation of circuit-type water treatment plants with cooling towers, the geographical situation of the respective mill has to be taken into consideration. Due to the water evaporation in the recooling process, climatic conditions can be affected by the constant formation of fog and by so-called industrial snow, especially in central Europe. [EUROFER HR]



# **ANNEXES**



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## **Best Available Technique Reference Document on Ferrous Metals Processing**

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## **ANNEX I. MONITORING**

On issues specific to the ferrous metals processing sector, it was reported during the 2<sup>nd</sup> TWG meeting that there are difficulties in measuring acid fumes (especially HF and in low concentration ranges) and on measuring fugitive emissions.

It was also mentioned that for discontinuous sampling, the sampling period and number of samples taken should be sufficient to demonstrate that the results are reflective of the actual performance.

No further information on monitoring was submitted.





## ANNEX II. LEGISLATION

No other information on legislation regarding the ferrous metals processing than that presented in this annex was submitted. In cases where the legislation of certain Member States is missing, that information was not made available to the Bureau.

### 1. HELCOM and PARCOM Recommendations

In the following HELCOM and PARCOM recommendations regarding ferrous metals processes are summarized:

#### HELCOM Recommendation 11/7

1. As of January 1st 1995 dust emissions from processes (including rolling, furnaces in rolling mills and cutting) in the iron and steel industry should be avoided or collected and filtered before being allowed to enter into the atmosphere.
2. Fugitive emissions from all processes should be avoided as far as technically feasible e.g. by encapsulation, evacuation hoods combined with good housekeeping practices.
3. Fabric filters or technology environmentally equivalent should be used for dust cleaning e.g. in sintering plants, for secondary gases from blast furnaces and basic oxygen furnaces, in electric arc furnaces and at cutting and grinding operations.

When these technologies are used the particulate matter content of the filtered gases should, as a guiding value, not exceed  $10 \text{ mg/m}^3$  (ndg). In any case, the particulate matter content of the filtered gases should not exceed  $50 \text{ mg/m}^3$  (ndg).

4. A good process and device control and regular monitoring should be maintained in order to keep emissions low. From 1987 dust emissions shall be continuously monitored if the particulate emission is  $5 \text{ kg/h}$  or more or the cadmium emission is  $5 \text{ g/h}$  or more and that installations with a particulate emission of  $2$  to  $5 \text{ kg/h}$  shall be equipped with measuring instruments which continuously determine waste gas opacity, e.g. optical transmission.

#### HELCOM Recommendation 17/5

##### 1. General requirements

- process water, polluted cooling water and polluted stormwater should be treated separately from unpolluted cooling water at each plant
- installation of closed water systems should be developed for process water and polluted cooling water in order to reach a circulation rate of at least 95 %
- production processes, utilization of by-products, waste- and storm-water treatment technology should be developed in order to minimise discharges
- internal and external measures should be taken to minimise accidental discharges (e.g. installation of sufficient storage capacity for untreated waste waters)
- sludges should be disposed of in a manner causing minimal environmental hazard, preferably by treating and entering the sludges to the blast furnace, sintering plant or electric arc furnace

##### 2. Requirements to the effluent of the plant

After having fulfilled the general requirements under 1, the following limit values should not be exceeded as annual mean values:

**Hot Rolling:** Suspended Solids 50 g/t (or 1 t/a) Oil 10 g/t (or 0.2 t/a for existing plants only)  
**Cold Rolling:** Suspended Solids 10 g/t Oil 5 g/t

### HELCOM Recommendation 13/6

Definition of best environmental practice

### PARCOM Recommendation 92/3 concerning limitation of pollution from new secondary steel production and rolling mills

Contracting parties to the convention for the prevention of marine pollution from land-based sources agree that:

Measures should be taken to reduce NO<sub>x</sub> emissions at pickling plants where nitric acid is used and NO<sub>x</sub> emissions (as NO<sub>2</sub>) exceed 5 tonnes /year. The measures should aim at a reduction rate of at least 70 %.

At least 95 % process water (i.e. water from direct cooling) should be recirculated from hot rolling and continuous casting machines.

The discharges of suspended solids (s.s.) and oil in bleed from process water systems from hot rolling should not exceed 50 g/tonne processed steel for suspended solids and 10 g/tonne for oil.

Before discharging spent oil emulsions from cold rolling, treatment by e.g. ultrafiltration should be carried out. The discharges from cold rolling should not exceed 10 g/tonne for s.s. and 5 g/tonne processed steel for oil. For plants with integrated waste water systems the total annual discharge should not exceed the sum of the annual production multiplied with the values above for each process.

Waste water flow from pickling should be reduced as far as possible. Discharges of metals from pickling plants should be limited as follows:

Ni	1	mg/l
Cr-tot	1	mg/l
Cr (VI)	0.1	mg/l
Zn	2	mg/l
Cd	0.2	mg/l

(maximum concentration of metals in effluent water in unfiltered samples)

In pickling plants using more than 20 tonnes of nitric acid per year, measures should be taken in order to reduce the nitrate discharges by applying acid regeneration, or equally efficient method.

Recovery of metals from all zinc-rich (zn concentration above 16 %) filter dust and filterdust from all stainless steel production should be carried out.

### PARCOM Recommendation 90/1 of 14 June 1990 on the definition of the best available technology for secondary iron and steel plants

The Paris Commission agrees that as a minimum the following measures constitute the best available technology for secondary iron and steel plants:

- Fabric filters for dust cleaning or equally efficient arrestment system at cutting, grinding and scarfing operations
- Regeneration of pickling baths and closing of rinse water systems
- Addition of hydrogen peroxide to pickling baths containing nitric acid or any equivalent measure which enables reduction on NO<sub>x</sub> to the atmosphere

- Sedimentation combined with filtration of waste water from continuous casting and rolling. Recirculation or re-use of the water.
- Metal recovery from filter dust.

## 2. GENERAL AUSTRIAN EMISSION LIMITS VALUES INTO AIR

(see also ordinance Nr. 160)

### 2.1. Installations for Heating / Reheating / Heat Treatment

(see BGBl. II Nr. 160, page 727, para. 5)

SO <sub>2</sub> emission limit value, using coke oven gas	300 mg/Nm <sup>3</sup>
NO <sub>x</sub> emission limit value, using preheated air	750 mg/Nm <sup>3</sup> (calc. as NO <sub>2</sub> )
NO <sub>x</sub> emission limit value, not using preheated air	500 mg/Nm <sup>3</sup> (calc. as NO <sub>2</sub> )
O <sub>2</sub> reference value for gas or liquid fuels is 5 % (details see page 726 of the ordinance)	

### 2.2 Installations for Acid Surface Treatment

(see BGBl. II Nr. 160, page 727, para. 7)

SO <sub>2</sub> emission limit value	300 mg/Nm <sup>3</sup>
NO <sub>x</sub> emission limit value	500 mg/Nm <sup>3</sup> (calc. as NO <sub>2</sub> )
O <sub>2</sub> reference value for gas or liquid fuels is 3 %, for solid fuels 6 % (details see page 726 of the ordinance)	

The above limit value are half hourly mean values and have to be applied to new plants. Old plants have to reach these values 5 years later, after this ordinance is entering into force, that means in June 2002. More details are listed in the ordinance.

### 2.3 General Austrian Emission Limits into Water

Waste water Emission Limit Values for hot / cold metal treatment (rolling, forging, pressing, drawing,..); for more details see page 2835 – 2838 of the ordinance (BGBl. 345/1997)

	Hot forming (pp. 2835)		Cold forming (pp. 2836)	
	running water	public discharge channel	running water	public discharge channel
<b>General Parameter</b>				
<b>Temperature</b>	30 °C	35 °C	30 °C	35 °C
<b>Fish toxicity G<sub>F</sub></b>	2	no affect on biological degradation	4	no affect on biological degradation
<b>Filter out matter</b>	50 mg/l	200 mg/l	50	200
<b>pH value</b>	6.5 – 8.5	6.5 – 9.5	6.5 – 8.5	6.5 – 9.5
<b>Inorganic parameter</b>	mg/l	mg/l	mg/l	mg/l
<b>Chromium as Cr</b>	0.5	0.5	0.5	0.5
<b>Chromium-VI as Cr</b>			0.1	0.1
<b>Iron as Fe</b>	2.0	2.0	2.0	2.0
<b>Copper as Cu</b>			0.5	0.5
<b>Nickel as Ni</b>	0.5	0.5	0.5	0.5
<b>Zinc as Zn</b>	1.0	1.0	1.0	1.0
<b>Fluoride as F</b>			30	30
<b>Nitrate as N</b>			20	-
<b>Nitride as N</b>			1.5	10
<b>Ammonium as N</b>	5.0	5.0		-
<b>Phosphor as P</b>	2.0		2.0	-
<b>Organic parameter</b>	mg/l	mg/l	mg/l	mg/l
<b>Chem. Oxygen demand, CSB calc. as O<sub>2</sub></b>	75		200	-
<b>Sum of organic comp.</b>	10	20	10	20

Table 2-1: Waste water Emission Limit Values

This ordinance was entering into force in 1998 for new plants. Old plants have to fulfil the requirements within the next 7 years, which means until 2005. For further information related to monitoring see §3 and 4 of the ordinance.

### 3. CURRENT GERMAN LEGISLATION RELEVANT FOR FERROUS METAL PROCESSING ACTIVITIES

Important regulations relevant to ferrous metals processing activities in Germany are laid down in the BImSchG (Federal Immission Control Act), the WHG (Federal Water Act) and the KrW-/AbfG (Waste Avoidance, Recycling and Disposal Act for the Promotion of Closed Substance Waste Management and Ensuring Environmental Compatible Waste Disposal). Germany uses a segregated media licensing system for different environmental media, but the final decision on an installation is reached by the assessment of environmental impacts to all media by the local authorities. Also noise requirements are considered in the licensing procedure. Germany aims at favouring pollution prevention in the licensing procedure. The „precautionary principle“ has a legal status which permits the setting of standards. Legal standards are not subject to any negotiation in the licensing process in Germany.

In compliance with the federal structure of Germany, the implementation of environmental laws and decrees is under the responsibility of the federal states (Bundesländer), which may implement the administrative procedure differently. For new plants, that are regarded as relevant with respect to emissions and releases into the environment, also an environmental impact assessment is required during the licensing procedure (cf. Gesetz über die Umweltverträglichkeitsprüfung, UVPG).

Area	Legal Basis	Regulations and ordinances
Transport	Verkehrsrecht	Gefahrgutverordnung Straße Gefahrgutverordnung Schiene Gefahrgutverordnung Binnenschifffahrt
Health and safety at work	Chemikaliengesetz (ChemG)  Gewerbeordnung	Chemikalienverbotsordnung Gefährstoffverordnung TA Lärm Arbeitsstättenverordnung und -richtlinien
Emissions	Bundes-Immissionsschutzgesetz (BImSchG)  Wasserhaushaltsgesetz (WHG)	Bundes-Immissionsschutzverordnungen Bundes-Immissionsschutzverwaltungsvorschriften TA Luft TA Lärm Katalog wassergefährdender Stoffe Abwasserverwaltungsvorschriften Indirekteinleiterverordnungen der Länder
Waste	Abfallgesetz (AbfG)  Kreislaufwirtschaftsgesetz (KrW.-/AbfG)	Abfall- und Reststoffüberwachungsverordnung Abfallbestimmungsverordnung Reststoffbestimmungsverordnung TA Abfall TA Siedlungsabfall

**Table 3-1: Legal basis and regulations alongside the product line**

Table 3-1 gives an overview of the German legal basis and regulations for environmental protection in Germany alongside the product line. In the following, a selection of most important acts, regulations and requirements concerning air and water quality for ferrous metals processing activities is presented.

### 3.1 German regulations concerning air quality

The basic law for air pollution control and noise abatement in Germany is the Federal Immission Control Act (Bundes-Immissionsschutzgesetz, BImSchG). It primarily aims towards the protection of the medium air, but it also applies to the media water and land in case pollution is introduced via the air. The BImSchG is complemented by 21 ordinances and the Technical Instructions on Air Quality (TA Luft). Especially the TA Luft specifies in more detail requirements to be met by installations subject to licensing. The next sections present important acts and ordinances of German air pollution prevention in more detail.

#### 3.1.1 Federal Immission Control Act (Bundes-Immissionsschutz-gesetz, BImSchG)

The BImSchG is the legal instrument for monitoring air pollution. Immission as defined within the law comprises air pollutants, and also noise, vibration, light, heat, radiation and associated factors affecting humans as well as animals, plants or other things. This concept already implements the idea of cross-media effects to a certain extent. The BImSchG requires federal authorities to issue ordinances identifying the types of facilities, which are subject to licensing, set licensing requirements for these facilities, and impose emission limit values and technical control requirements for all facilities, whether licensed or not.

Especially article 5(1)3 BImSchG aims at the avoidance and minimisation of wastes and residues. The paragraph emphasises the cross-media effects of industrial production.

The concept of "state of the art technology" defined in the BImSchG is similar to the one of BAT:

*State of the art as used herein shall mean the state of development of advanced processes of facilities or modes of operation which is deemed to indicate the practical suitability of a particular technique for restricting emission levels. When determining the state of the art, special consideration shall be given to comparable processes, facilities or modes of operation that have been successfully proven in practical operation. (Article 3 paragraph 6 BImSchG)*

In principle, "state of the art technology" is stated in terms of emission limits set by the licensing authority, the choice of technology to comply with the emission limit levels is left to industry. Necessary precautions against harmful effects on the environment are to be taken in particular by using control measures corresponding to the state of the art. Depending on the mass flow, some substances have to be measured continuously (eg. SO<sub>x</sub>, NO<sub>x</sub>, and particulates). Some relevant ordinances as well as selected requirements of the BImSchG are briefly presented in the following.

##### 3.1.1.1 Ordinance on installations subject to licensing (4. BImSchV)

The 4. BImSchV (Ordinance on installations subject to licensing) lists all installations that are subject to licensing under the BImSchG. According to this ordinance (cf. Annex, row 1, N° 3.5 and 3.6) installations for the rolling of metals and for scarfing have to undergo a formal licensing procedure, regardless if they are new installations or substantial alterations to location, nature or operation of existing installations.

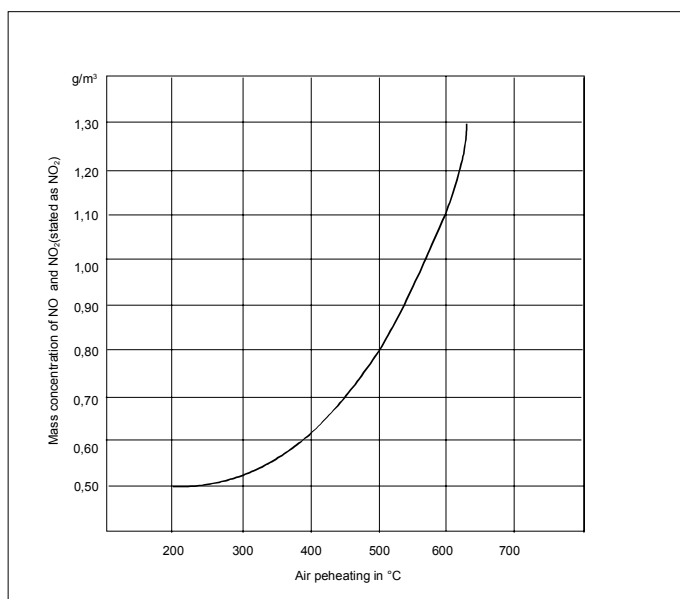
##### 3.1.1.2 Technical Instructions on Air Quality (TA Luft)

The Technical Instructions on Air Quality (TA Luft) have been set up as general administrative regulations related to §48 BImSchG. The TA Luft further specifies the requirements to be met by installations subject to licensing. It prescribes limit values for most air pollutants as well as structural and operational requirements designed to limit diffuse emissions. Specific regulations for ferrous metals processing activities by the TA Luft, directing at the avoidance and minimisation of air pollution, are laid down in N° 3.3.3.6.1 (plants for rolling metals, heating and heat treatment furnaces) in N° 3.3.3.9.1. (galvanising installations), and in N° 3.3.3.10.1

(installation for surface treatment of metals using HNO<sub>3</sub>). Requirements set out are listed in Table 3-2.

N° in TA Luft	Reference	Specification
3.3.3.6.1 (rolling)	Reference quantity	Emissions values refer to a volume content of oxygen in waste gas of 5 out of 100
3.3.3.6.1 (rolling)	Nitrogen oxides *)	Emissions of nitrogen monoxide and nitrogen dioxide in the waste gas of plants operating air preheating of 200°C or more must not exceed the mass concentration given in the figure below (Fig. 8-1), given as nitrogen dioxide; possibilities, to control emissions by fuel engineering and other state of the art measures are to be employed.
3.3.3.6.1 (rolling)	Sulphur oxides	If burnable gases are used in an interrelated production between an iron and steel works and a coking plant, sulphur oxide emissions may not exceed the emission value according to enclosure 1 to §16, 13 <sup>th</sup> BImSchV.
3.3.3.9.1 (galvanising)	Waste gas cleaning	Installations for galvanising, using fluxes, are to be equipped with waste gas capturing devices like encapsulation or hoods; waste gases need to be ducted to a waste gas cleaning facility.
3.3.3.9.1 (galvanising)	Dust	Dustlike emissions in waste gases must not exceed 10mg/m <sup>3</sup> (STP).
3.3.3.9.1 (galvanising)	Chlorine compounds	Emissions of gaseous inorganic chlorine compounds in waste gas must not exceed 20mg/m <sup>3</sup> (STP), given as hydrogen chloride.
3.3.3.9.1 (galvanising)	Emission measurements	The result of a single measurement is to be determined by several dipping processes; measuring time corresponds to the sum of single dipping times and shall cover usually ½ hour; dipping time is the period between the 1 <sup>st</sup> and the last contact of the galvanised piece with the galvanising bath.

**Table 3-2: Technical requirements**



**Figure 3-1: NO<sub>x</sub> emission limits TA Luft**

\*) The German *Länderausschuß für Immissionsschutz (LAI)* agreed on the 6<sup>th</sup> and 8<sup>th</sup> Mai of 1991 in Bayreuth to put in concrete terms the making dynamic of the TA Luft for heating and heat treatment furnaces and settled the following emission values for NO<sub>x</sub>:

new plants - 500mg/m<sup>3</sup>

existing plants with combustion air preheating

- up to 450°C: 500mg/m<sup>3</sup>

- over 450°C: target value 500mg/m<sup>3</sup>

In case of using coke oven gas:

- investigation of the individual case with a target value of 500mg/m<sup>3</sup>

Since the TA Luft was enacted in 1986, local authorities sometimes demand stricter emission limit values.

### 3.1.1.3 Technical Instruction on Noise Abatement (TA Lärm)

The Technical Instruction on Noise Abatement (TA Lärm) sets limits for noise emissions by the operation of a facility, specified for various areas. The construction, operation or altering of a facility is granted only if the emission limits allowed for a specific area are not exceeded and if state-of-the-art noise protection measures are employed.

### 3.1.2 German regulations concerning the water quality

With respect to water management, each discharge, wherever it is located, has to comply with the Federal Water Act (Wasserhaushaltsgesetz, WHG). The WHG is the legal instrument for water pollution control, analogous to the BImSchG for control of air pollution. Regulations of the WHG cover waste water streams generated by various industrial processes, including ferrous metals processing activities. According to the WHG, the use of surface, coastal, and ground waters requires approval of the competent authority. Water protection legislation in Germany is implemented by the Ordinance on Waste Water (Abwasserverordnung, AbwV) and by general administrative regulations concerning minimum requirements to be met by discharges, irrespective of the quality of the receiving medium. Generally, frame regulations for water protection are provided on a federal level, but the federal states also add to water legislation by complementary regulations. The WHG is furthermore complemented by the discharge levy act (Abwasserabgabengesetz: AbwAG). Tariffs are related to the mass and possible hazard of the discharged waste water according to Table 8-3. For discharge of sewage, that exceeds the mentioned threshold values for concentrations or annual freights, the discharging party has to pay a fee related to the given units of measurement.

Hazardous Substances	Units of measurement (relating to a unit of hazard)	Threshold values	
		Concentrations	Annual freights
Oxydizable substances (given as COD)	50 kg Oxygen	20 mg/l	250 kg
Phosphor	3 kg	0.1 mg/l	15 kg
Nitrogen	25 kg	5 mg/l	125 kg
Organic Halogen compounds as AOX	2 kg Halogen, calculated as Cl	100 µg/l	10 kg
Mercury & compounds.	20 g	1 µg/l	0.1 kg
Cadmium & compounds	100 g	5 µg/l	0.5 kg
Chromium & compounds	500 g	50 µg/l	2.5 kg
Nickel & compounds	500 g	50 µg/l	2.5 kg
Lead & compounds	500 g	50 µg/l	2.5 kg
Copper & compounds	1000 g	100 µg/l	5 kg
Fish toxicity	3,000 m <sup>3</sup> discharges / G <sub>F</sub>	G <sub>F</sub> =2 (dilution factor for non-lethality for fishes of the discharge)	

Table 3-4: Thresholds according to the discharge levy act

Minimum requirements are placed on sewage lines from certain legally fixed sources. Annex 24a of the AbWV (Abwasserverordnung, AbWV) deals inter alia with ferrous metals processing activities. This Annex applies inter alia to waste water generated by the following processes: continuous casting, hot forming, hot production of tubes, cold production of strip, cold production of tubes, sections, bright steel, wire, continuous surface treatment of semi finished and finished steel products. In section 2.1.2 of that Annex requirements are stated to minimise the level of harmful substances in the waste water. Table 8-7 provides important restrictions established by the AbWV, especially for warm and cold forming. Excluded from this regulation is waste water from cooling systems for the indirect cooling of industrial processes and process water treatment. Waste water obtained by these activities is subject to the provisions laid down in Annex 31, AbWV. Table 8-8 gives relevant requirements to discharges of this Annex 31. If the stated values are not observed, approval for the discharge of waste water will be denied. Effluents of batch galvanising installations also need to comply with the provisions of Annex 40, AbWV.

Hazardous Substances / Process	Hot forming	Hot production of tubes	Cold production of strip	Cold production of tubes, ...	Cont. surface treatment
Chemical Oxygen Demand COD	40 mg/l	200 mg/l	200 mg/l	300 mg/l	300 mg/l
Iron	5 mg/l	5 mg/l	3 mg/l	5 mg/l	5 mg/l
Hydrocarbons	5 mg/l	10 mg/l	10 mg/l	10 mg/l	5
Nitrogen from nitrite (NO <sub>2</sub> -N)	-	-	5 mg/l	5 mg/l	-
Total phosphorus	-	-	2 mg/l	2 mg/l	2 mg/l
Fluoride	-	-	30 mg/l	30 mg/l	-
Lead	-	-	-	-	0.5 mg/l
Chromium, total	0.2 mg/l	0.5 mg/l	0.5 mg/l	0.5 mg/l	0.5 mg/l
Chromium VI	-	-	0.1 mg/l	0.1 mg/l	0.1 mg/l
Copper	-	-	-	-	0.5
Nickel	0.2 mg/l	0.5 mg/l	0.5 mg/l	0.5 mg/l	0.5 mg/l
Zinc	2 mg/l	2 mg/l	2 mg/l	2 mg/l	2 mg/l
Tin	-	-	-	-	2 mg/l
Cyanide	-	-	-	-	0.2 mg/l
Fish toxicity as thinning factor	2	2	6	6	6
AOX	-	-	-	-	1 mg/l

**Table 3-5: Requirements to discharges from the iron and steel production (Annex 24, AbWV)**

Most federal state constituted complementary regulations for indirect discharges. These Directives usually are applicable to industrial plants, as long as no federal regulations are provided. However, as most plants concerned are directly discharging waste water and therefore have to comply with the corresponding regulations for direct discharge, the Directives on Indirect Discharges are of minor interest.

Hazardous Substances	Minimal Requirements
Chemical Oxygen Demand COD	40 mg/l
Phosphor compounds, given as P	3 mg/l
Zinc	4 mg/l
AOX	0.15 mg/l
Available residual chlorine	0.3 mg/l
Chromium compounds	must not be contained
Mercury compounds	must not be contained
Nitrite	must not be contained
Metal organic Compounds (Metal-Carbon-Compound)	must not be contained

**Table 3-6: Requirements to discharges from cooling systems of industrial processes (Annex 31, AbWV)**



### 3.1.3 German regulations concerning the waste management and disposal of hazardous materials

Waste legislation in Germany is laid down in the Act on Waste Prevention and Treatment (Abfallgesetz, AbfG). It is applied to the use and storage of waste, i.e. to substances to be disposed of by the processor or to substances whose proper treatment is necessary to protect the environment. Additional requirements refer to waste from particular installations.

Legislation laying down measures aiming towards „avoidance, utilisation and disposal“ of waste is set down in the Recycling and Waste Management Act (Kreislaufwirtschafts- und Abfallgesetz, KrW-/AbfG), which came into force in October 1996 and is the most important part of the new AbfG. It broadens the entire national waste concept and sets new priorities with regard to the avoidance of and the duty to utilise waste. The KrW-/AbfG also codifies manufacturer's product responsibility.

For administrative procedures, technical guidelines on waste (TA Abfall) and on municipal waste (TA Siedlungsabfall) are of relevance. Furthermore, an administrative instruction, technical guideline on special wastes (TA Sonderabfall), regulates the handling of special waste. Facilities for treating waste have to fulfil requirements regulated in special decrees, based on Art. 5 BImSchG.

A working group of the federal states on waste (Länderarbeitsgemeinschaft Abfall, LAGA) issued a categorisation of waste types, comprising 589 types of waste, of which 333 have priority for control (*LAGA-Abfallartenkatalog*). This catalogue was valid till 12/31/1998 and has been replaced by the European waste catalogue (EWC) in the following. To facilitate the change from the LAGA catalogue to the EWC, the German *LAGA* worked out an interim catalogue (*LAGA-Umsteigekatalog*). Table 8-9 summarises the classification of selected relevant substances generated within ferrous metals activities.

Type of Waste	LAGA Waste Key <sup>1</sup>	EWC Waste Key / remarks
Scale	351 02	120199
Dismantled refractories	31103	100206
Eisenhaltiger Staub ohne schädli. Beim.	35101	120102
Ferrous scrap	35103	170405
Zinc dross	35309	170404
Iron hydroxide	51309	110104, 190201
Iron chloride (FeCl <sub>3</sub> )	51519	060305
Spent pickle	52102	060101, 060102, 060103, 060105, 110105
Cooling agents	54401	120110
Rolling mill sludge	54701	130501
Sludge from oil separation	54703	130502

**Table 3-7: Selected LAGA/EWC numbers for wastes resulting from selected FMP activities**

<sup>1</sup> Classification with reservation



**GLOSSARY****Substances**

Ca	Calcium
Ca(OH) <sub>2</sub>	Calcium hydroxide
CaCl <sub>2</sub>	Calcium chloride
Cd	Cadmium
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
Cr	Chromium
Cu	Copper
Fe	Iron
FeCl <sub>2</sub>	Iron chloride
Fe <sub>2</sub> O <sub>3</sub>	Iron oxide, ferric oxide
FeO <sub>x</sub>	
HCl	Hydrochloric Acid
HF	Hydrofluoric Acid
Hg	Mercury
H <sub>2</sub> SO <sub>4</sub>	Sulphuric acid
Mn	Manganese
N <sub>2</sub>	Molecular nitrogen
NaCl	Sodium chloride
NO <sub>2</sub> <sup>-</sup>	Nitrite
NO <sub>x</sub>	Nitrogen Oxides
Na <sub>2</sub> SO <sub>4</sub>	Sodium sulphate
Ni	Nickel
NH <sub>3</sub>	Ammonia
NH <sub>4</sub> Cl	
NO	Nitric oxide
NO <sub>2</sub>	Nitrogen dioxide
Pb	Lead
SO <sub>2</sub>	Sulphur dioxide
Zn	Zinc
ZnCl <sub>2</sub>	Zinc chloride

**Units**

euro	currency unit of EU (participating Member States)
Pa	Pascal
°C	Degree centigrade/Celsius
g	gram
kg	kilogram
t	metric tonne (1000kg)
min	minutes
mm	millimetre
cm	centimetre
m	metre
m <sup>2</sup>	square metre
m <sup>3</sup>	cubic metre
Nm <sup>3</sup>	m <sup>3</sup> at 273K, 101.3kPa, dry
kWh	kilowatt hour
kWth	kilowatt thermal
J	joule
s	second
h	hour
d	day
y	year
t/d	tonnes per day
t/y	tonnes per year
bar	10 <sup>5</sup> Pa
l	litre
vol%	Percentage of the volume
Mt/a	Million of tonnes per annum

**Prefixes**

μ	micro	10 <sup>-6</sup>
m	milli	10 <sup>-3</sup>
c	centi	10 <sup>-2</sup>
k	kilo	10 <sup>3</sup>
M	mega	10 <sup>6</sup>
G	giga	10 <sup>9</sup>

<b>Abbreviations</b>
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∅	Average
BAT	Best available technique as defined in Article 2(11) of the IPPC Directive
BF	Blast Furnace
BFG	Blast Furnace Gas
BOF	Basic Oxygen Furnace
BREF	BAT reference document
CC	Continuous coating/continuous coated
COD	Chemical oxygen demand indicating the amount of chemically oxidisable organic matter in the waste waters
COG	Coke Oven Gas
CR	Cold rolling/cold rolled
EIPPCB	European Integrated Pollution Prevention and Control Bureau
EP	Electrostatic Precipitator
€ or EUR	European currency unit
FF	Fabric Filter
FMP	Ferrous metals processing
HC	Hydrocarbon
HN <sub>x</sub> gas	Nitrogen-hydrogen mixture
HOWAQ	Hot water quench
HR	Hot rolling/hot rolled
HTC	Hourly technical capacity
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
IEF	Information exchange forum
n.a.	Not available
NG	Natural gas
PCDD/F	Polychlorinated Dibenzo-p-Dioxins/Furans
ppm	Parts per million
SCR	Selective non-catalytic reduction
SNCR	Selective non-catalytic reduction
SS	Suspended solids (in waste water)
TSS	Total suspended solids (in wastewater)
TWG	Technical working group
VOC	Volatile organic compounds

<b>Definitions of terms</b>
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Mixed acid/mixed liquor	HCl used for pickling of steel and for stripping of galvanized steel
Mixed acid	A mixture of nitric and hydrofluoric acids, used to pickle stainless steel
Stripping	De-zincing of steel by immersion in acid (HCl)



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