Best Available Techniques Reference Document on the Production of Sulphuric acid

(Final)

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Preface

The European Sulphuric Acid Association (ESA) and the European Fertilizer Manufacturer Association (EFMA) have prepared recommendations on Best Available Techniques (BAT) in response EU Directive on integrated pollution and control (IPPC Directive) . This recommendation (Based **of Report EUR 13006 EN)**
has been prepared by ESA and EFMA experts drawn from member companies. They cover the production processes of Sulphuric acid and Oleum and reflect industry perception of what techniques are generally considered to be feasible and present achievable emission levels associated with the manufacturing of the products.

The recommendation use the same definition of BAT as that given in the proposed IPPC Directive . BAT covers both the technologie used and the management practices necessary to operate a plant efficiently and safely . They focus primarily on the technological processes , since good management is considerd to be independent of the process route. The industry recognises, however, that good operational practices are vital for effective environmental management and that the principles of Responsible Care should be adhered to by all companies.

Two sets of BAT emission levels are given :

- For existing production units where pollution prevention is usually obtained by revamps or end–of-pipe solutions
- For new plants where pollution prvention is integrated in the process design.

The emission levels refer to emissions during normal operations of typical sized plants.Other levels may be more appropriate for smaller or larger units and high emissions may occur in start-up and shut-down operations and in emergencies.

Only the more significant types of emissions are covered and the emission levels given do not include fugitive emissions and emissions due to rainwater.
The emission levels are given both in concentration values (ppm or mg /m³) and in load values (emission per ton sulphuric acid with 100 weight %). It should be noted that there is not necessarity a direct link between the concentration values and the load values.
The recommendation is that given emission levels should be used as reference levels for the establishment of regulatory authorisations . Deviations should be allowed as governed by :

- Local environmental requirements ,given that the global and inter-regional environments are not adversely affected
- Practicalities and costs of achieving BAT
- Production constraints given by product range, energy source and availability of raw materials.

If authorisation is given to exceed these BAT emission levels, the reasons for the deviation should be documented locally.
Existing plants should be given ample time to comply with BAT emission levels and care should be taken to reflect the technological differences between new and existing plants when issuing regulatory authorisations, as discussed in this recommendation.
A wide variety of methods exist for monitoring emissions. The emission levels given are subject to some variance, depending on the method chosen and the precision of the analysis. It is important when issuing regulatory authorisations, to identify the monitoring method(s) to be applied. Differences in national practice may give rise to differing results, as the methods are not internationally standardised. The given emission levels should not, therefore, be considered as absolute but as references which are independent of the methods used.

ESA would also advocate a further development for the authorisation of sulphuric acid plants. The plants can be complex, with the integration of several production processes and they can be located close to other industries. Thus there should be a shift away from authorisation governed by concentration values of single point emission sources. It would be better to define maximum allowable load values from an entire operation, e.g. from a total site area. However, this implies that emissions from single units should be allowed to exceed the values in the BAT recommendation, provided that the total load from whole complex is comparable with that which can be deduced from there. This approach will enable plant management to find the most-effective environmental solutions and would be the benefit of our common environment.
Finally, it should be emphasised that each individual member company of ESA is responsible for deciding how to apply the guiding principles of the BAT Reference Document on the Production of Sulphuric Acid.

1. General Information

1.1 General information about the sulphuric acid industry

More sulphuric acid is produced than any other chemicals in the world. In western Europe in 1997 over 19 million tonnes were produced, the total production world-wide being estimated around 150 million tons. About half of this output is produced in North America, Western Europe and Japan [20],[21].

In Million tonnes H_2SO_4	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**
World sulphuric acid production	145,7	132,5	137,9	148,9	151,3	155,6
World sulphuric acid consumption	147,1	132,8	138,8	150,1	153,3	157,5

The output of sulphuric acid at base metal smelters today represents about 20 % of all acid production. Whereas in 1991 smelter acid production amounted to 27,98 millions tonnes, it is calculated that the output in the following decade will have grown to reach 44,97 millions tonnes in 2001. Smelter acid will be more than 25% of world sulphuric acid production compared to some 18% in 1991.

Production of Sulphuric acid in the countries of the european community :

In Million tonnes H2SO4	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**
Belgium/Luxembourg	1,836	1,535	1,515	2,174	2,067	2,160
Finland	1,351	1,361	1,373	1,376	1,479	1,570
France	3,132	2,515	2,227	2,382	2,263	2,242
Germany	3,800	3,515	3,380	3,530	3,978	3,496
Greece	0,620	0,588	0,630	0,515	0,615	0,675
Italy	1,725	1,423	1,228	1,344	1,588	1,590
Netherlands	1,080	1,000	1,073	1,113	1,060	1,040
Norway	0,587	0,564	0,585	0,609	0,594	0,666
Spain	2,420	2,176	2,348	2,265	2,786	2,810
Sweden	0,567	0,497	0,518	0,485	0,620	0,630
United Kingdom	1,568	1,269	1,225	1,293	1,196	1,205

Sulphuric acid is produced in all countries of Europe; the major producers are Germany, Spain, France, Belgium and Italy, those countries accounting for 70% of the total European production. It is used directly or indirectly in nearly all industries and is a vital commodity in any national economy. In fact, sulphuric acid is so widely used that its consumption rate, like steel production or electric power, can be used to indicate a nation's prosperity.

Most of its uses are actually indirect in that the sulphuric acid is used as a reagent rather than an ingredient. The largest single sulphuric acid consumer by far is the fertiliser industry. Sulphuricacid is used with phosphate rock in the manufacture of phosphate fertilisers. Smaller amounts are used in the production of ammonium and potassium sulphate.
Substantial quantities are used as an acidic dehydrating agent in organic chemical and petrochemical processes, as well as in oil refining.In the metal processing industry, sulphuric acid is used for pickling and descaling steel; for the extraction of copper, uranium and vanadium from ores; and in the non-ferrous metal purification and plating. In the inorganic chemical industry, it is used most notably in the production of titanium dioxide.

Certain wood pulping processes for paper also require sulphuric acid, as do some textile and fibers processes (such as rayon and cellulose manufacture) and leather tanning.

Other end uses for sulphuric acid include: effluent/ water treatment, plasticisers, dyestuffs, explosives, silicate for toothpaste, adhesives, rubbers, edible oils, lubricants and the manufacture of food acids such as citric acid and lactic acid.

Probably the largest use of sulphuric acid in which this chemical becomes incorporated into the final product is in organic sulphonation processes, particularly for the production of detergents. Many pharmaceuticals are also made by sulphonation processes.

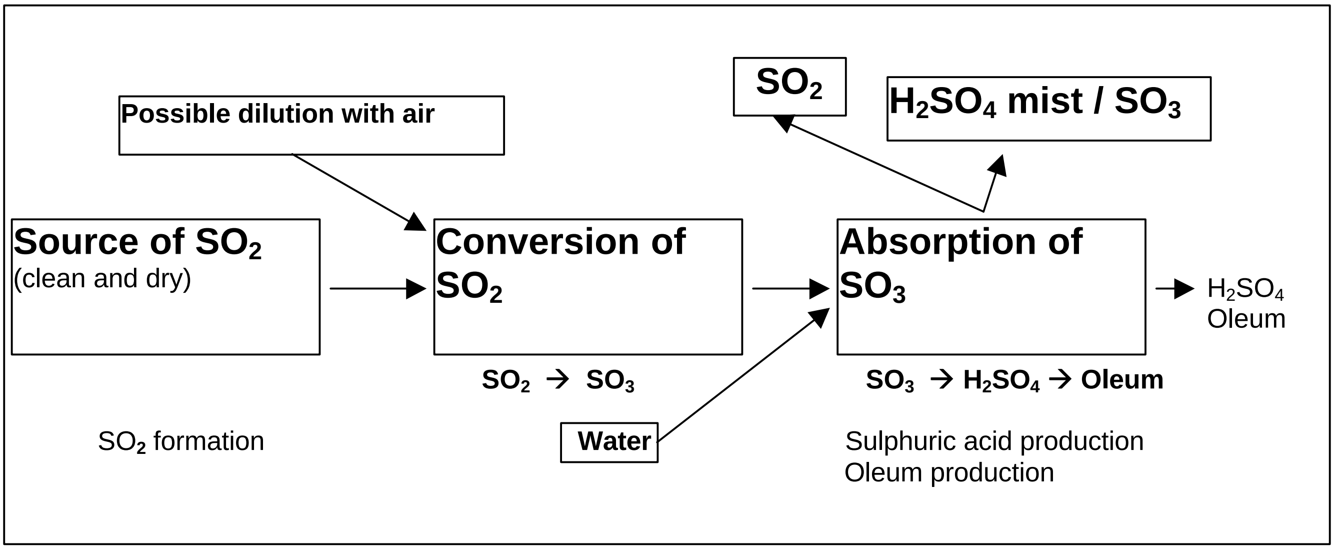
1.2 Limits to other industries

Many processes of sulphuric acid production have been developed according to the large number of sources of raw materials (SO_2), and their specific characteristics**.** The present document deals also with the production of Oleum.

It is possible to draw a general diagram of sulphuric acid production distinguishing the two fundamental steps of the process (see figure 1.2):

(a) Conversion of SO_2 into SO_3
(b) Absorption of SO_3

Figure 1.2



2. Applied Processes and Techniques

2.1 Raw material preparation (incl. storage and handling)

2.1.1 Sulphur storage and handling

Liquid sulphur is a product of the desulphurisation of natural gas by the Claus-Process and raw oil , further source is the cleaning of coal fluegas. The third way is the melting of nature solid sulphur (Frash-process). This way isn't in frequent use because there are many difficulties in removing the contaminants.
A typical analysis of molten sulphur (quality: bright yellow) is the following:

a)	Ash	max. 0,015 % weight
b)	Carbon	max. 0,02 % weight
c)	Hydrogen sulphide	ca. 1 – 2 mg / kg
d)	Sulphur dioxide	0 mg / kg
e)	Arsenic	max. 1 mg / kg
f)	Mercury	max. 1 mg / kg
g)	Water	max. 0,05 % weight

Liquid sulphur will be batched in ships, railcars and trucks made of mild steel. There is special equipment for all loading and unloading facilities.

Liquid sulphur is stored in insulated and steam heated mild steel tanks. To avoid static charges and reduce agitation in the tank, it is equipped with submerged fill lines. The ventilation of the tanks is conventionally free. A further fact is less de-gasing of hydrogen sulfide and sulphur dioxide. All pipes and pumps are insulated and steam heated. The normal temperature level of the storage and the handling is about 125 – 145 °C.

2.1.2 Ores storage and handling

2.1.2.1 Pyrite

Normally pyrite is produced in a flotation process, which means that the concentrate is relatively fine grinded with a moisture content dependent of how much energy is spent in the drying step. The analyses are variable within following ranges :

Element		Content	Content in one specific pyrite
Sulphur	weight %	30 - 52	50 – 52
Iron	weight %	26 - 46	45
Copper	weight %	up to 2,7	max. 0,10
Zinc	weight %	up to 3,0	max. 0,10
Arsenic	weight %	up to 10,0	max. 0,06
Water	weight %	5 - 9	5

and a number of other metals in small quantities. The right column shows the analyses of one certain pyrite.

Storage and transporting of pyrite should be done covered to avoid dust. If one has to store outside two problems will come up depending on the climate;

- under dry conditions one can expect dust problems. A dusty atmosphere, especially inside buildings can with the right conditions cause a fire or an explosion.
- under wet conditions, water in contact with pyrite becomes acidic. This water has to be picked up and treated before leading it to the recipient. With too high moisture content the pyrite will give clogging problems in the internal transport system at the plant.

2.1.2.2 Metal sulphide Ores

Approximately 85% of primary copper is produced from sulphur ores and therefore sulphur is in a sense a by-product of the majority of copper processes.
Copper ore concentrates are produced in the flotation process and consist mainly of copper pyrites or chalcopyrite ($CuFeS_2$) but may also contain pyrite, chalconite, burnite, cuprite and other minerals. A typical concentrate composition is 26-30 % Cu, 27-29 % Fe and 28-32 % S.
Copper concentrates are usually processed by pyrometallurgical methods. Ores and concentrates are delivered to site by road, rail or ship. Copper concentrates are usually stored in closed building. For the intermediate storage and the preparation of the blend silo systems are used. For the unloading, storage and distribution of solid material dust collection and abatement systems are used extensively.

Zinc and Lead, are for a major part produced starting from sulphur ores and so sulphuric acid is also a final product by treating this ores in metallurgical processes.
This basic ores are in a first step treated in a flotation process to become concentrates, which are shipped for basic metal recuperation to Smelters.
The concentrates are primary usually processed by metallurgical methods to desulfurise.
Ores and concentrate are delivered to site by road, train or ship.

Depending on local situations, the storage on site, original in open air, is evaluating to a covered building storage's.
In every case for intermediate storage in the process and the preparation of the blend, silo systems and dust collections systems, as baghouses for instance, are used to avoid dust propagation.

2.1.3 Organic spent acids

Spent acids stemming from different operations such as steel pickling, titanium dioxide production (see chapter 2.1.6) or organic sulphonation reactions have such a variety of compositions that it is not possible to spell out a set of general rules for preparation, storage and handling. In fact each case is a particular one and has to be handled on individual basis with special consideration given to dilution and contained impurities which affect all operations. Experience and know-how are of paramount importance.

Spent acids come mainly from organic chemical production . Sulphuric acid is mainly used as catalyst and needs to be replaced with fresh concentrated acid when diluted or / and saturated with organics. Alkylation process for refineries , nitration and sulphonation processes for chemical industry generate a large amount of spent acids which, after regeneration , become clean acid able to be recycled in any process.

Storage and handling :

Spent acids can be received by barges , road and rail tankers. Chemical analysis and physical tests are performed before unloading to be sure the product is on line with the acceptation contract , and to avoid any chemical reaction in the storage when mixing spent acids issued from different processes. Storage vessels are located inside containing dikes. Because of the risks relative to the organics vapour pressure ,to some dissolved sulphur containing products and to NOx potential emissions, the storage gas phases are connected to the thermal decomposition furnace , through non flamable systems. Nitrogen is used for blanketting the gas phase to avoid any oxygen intrusion.
Construction material depend on the spent acid strength. Feeding the furnace is achieved with corrosion resistant pumps and pipes .

2.1.4 H_2S or other Sulphur containing gases

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2.1.5 SO_2-gases from different sources

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2.1.6 Sulphate salts

Ferrous sulphate is obtained in large quantities as its heptahydrate **[$FeSO_4 . 7 H_2O$]** during the regeneration of pickling liquors or as a side product in the TiO_2 process via the sulphate route.

2.2 Material processing

2.2.1 Conversion of SO_2 into SO_3

The design and operation of sulphuric acid plant are focused on the following gas phase chemical equilibrium reaction with a catalyst:

$SO_2 + 1/2\ O_2 \Leftrightarrow SO_3 \quad \Delta H = -99$ kJ/mole

This reaction is characterised by the conversion rate, which is defined as follows:

$$\text{conversion rate} = \frac{SO_2\text{ in} - SO_2\text{ out}}{SO_2\text{ in}} \times 100\ (\%)$$

Both thermodynamic and stoechiometric considerations are taken into account in maximising the formation of SO_3. In deciding how to optimise the equilibrium, usually the Lechatelier-Braun Principle, which states that when an equilibration system is subjected to stress, the system will tend to adjust itself in such a way as to partly relieve the stress, is taken into account. The stresses are, for instance, a variation of temperature, of pressure, or of concentration of a reactant.

For SO_2/SO_3 systems, the following methods are available to maximise the formation of SO_3:

- Heat removal, a decrease in temperature will favour the formation of SO_3 since this is an exothermic process
- Increase oxygen concentration
- remove SO_3 (as in the case of the double absorption process)
- raise system pressure
- Select a catalyst, in order to reduce the working temperature (equilibrium)
- Longer reaction time

Optimum overall system behaviour requires a balance between reaction velocity and equilibrium. However, this optimum depends also on the SO_2 concentration in the raw gas and on its variability in time. Consequently, each process is more or less specific for a particular SO_2 source.

2.2.2 Absorption of SO_3

Sulphuric acid is obtained from the absorption of SO_3 and water into H_2SO_4 (with a concentration of at least 98%).

The efficiency of the absorption step is related to:

- The H_2SO_4 concentration of the absorbing liquid (98.5 - 99.5%)
- The range of temperature of the liquid (normally 70 °C - 120 °C)
- The technique of the distribution of acid
- The raw gas humidity (mist passes the absorption equipment)
- The mist filter
- The temperature of incoming gas
- The co-current or counter-current character of the gas stream in the absorbing liquid

SO_3 emissions depend on:

- The temperature of gas leaving absorption
- The construction and operation of the final absorber
- The device for separating H_2SO_4 aerosols
- The acid mist formed upstream of the absorber through the presence of water vapour

2.3 Product finishing

2.3.1 Dilution of absorber acids

The acid produced, normally 95,5% - 96,5% or 98,5% - 99,5%, is diluted with water or steam condense down to the commercial concentrations : 25%, 37%, 48% ,78%, 96% and 98% H_2SO_4 .The dilution can be made in batch process or continuously through inline-mixing.

2.3.2 SO2-Stripping

The warm acid produced is blown with little air in a colum or in a tower to reduce the remaining SO_2 in the acid to < 20 mg SO_2 /kg. The SO_2 containing air returns to the process.

2.3.3 Purification

Sulphuric acid can be soiled by start up of acid plants after long repair . Acid is then clouded by insoluble iron sulphate or silicate of bricks or packages. Filtration of acid is possible with conventional methods.
Filter elements in the filling lines for car or railway loading is necessary for quality reasons.

2.3.4 Denitrification

For the denitrification of sulfuric acid and oleum different methods are known.The chemicals reduce nitrosylsulphuric acid ($NOHSO_4$) or nitrate to N_2 or N_xO_y .The reactant must be dosed in stoichiometric amounts .See the following table 2.3.4.:

Method of denitrification	**special conditions**	**effect**	**In tail gas**
Urea	Absorber/tanks	+ /only <80% acid	N_2
Dihydrazindisulfate 40%	Absorber/tanks	+++ /acid and oleum	N_2,N_2O
Amidosulfonic acid 15% Hydroxylammoniumsulfat	Absorber/tanks	+++ /only 50-99,5%acid	N_2
SO_2 saturated acid	78% H_2SO_4/ separated tower	+++ /only acid/ water balance	NOx

2.3.5 Decolourisation

Acid produced from smelter plants or from acid regeneration plants can contain hydrocarbons or carbonaceous material , which is absorbed in sulphuric acid .This causes a 'black' colour .The decolourisation is known as "acid bleaching".

Method of decolourisation	**special conditions**	**effect**
Hydrogenperoxide-solution <60%	Absorber/tanks	+++ /acid and oleum

2.4 Use of auxiliary chemicals /materials

2.4.1 Catalysts

When producing sulphuric acid by the contact process an important step is to produce sulphur trioxide by passing a gas mixture of sulphur dioxide and oxygen over a catalyst (Eq. 1).

$$SO_2 + \frac{1}{2} O_2 = SO_3 \quad - \Delta H \qquad (1)$$

Without a catalyst this reaction needs a very high temperature to have a realistic rate. The equilibrium is however in favour of SO_2 -formation at higher temperatures which makes the conversion very poor.

Of all substances tested for catalytic activity toward sulphur dioxide oxidation only vanadium compounds, platinum and iron oxide have proven to be technically satisfactory. Today vanadium pentoxide is used almost exclusively.

Commercial catalysts contain 4-9 wt % vanadium pentoxide, V_2O_5 , as the active component, together with alkali-metal sulphate promoters. Under operating conditions these form a liquid melt in which the reaction is thought to take place. Normally potassium sulphate is used as a promoter but in recent years also caesium sulphate has been used. Caesium sulphate lowers the melting point, which means that the catalyst can be used at lower temperatures. The carrier material is silica in different forms.

The catalyst components are mixed together to form a paste and then usually extruded into solid cylindrical pellets, rings or star-rings which are then baked at elevated temperatures. Ring (or star-ring) shaped catalysts, which are mostly used today, give a lower pressure drop and are less sensitive to dust blockage.

The lower temperature limit is 410-430 °C for conventional catalysts and 380-390 °C for caesium doped catalysts. The upper temperature limit is 600-650 °C above which, catalytic activity can be lost permanently due to reduction of the internal surface.

The average service life for the catalyst is about 10 years. Service life is generally determined by catalyst losses during screening of the catalyst which must be done from time to time to remove dust [1], [2].

2.5 intermediate and final product storage

Due to very low vapour pressure of H_2SO_4 in normal temperature conditions, there is no air pollution problem connected with the storage, handling and shipping of sulphuric acid.

The handling of pure SO_3 and oleum requires safety procedures and management in order to avoid atmospheric pollution in the case of accidental release.

With regard to the ancillary operations referred to above, important considerations are as follows:

- The receipt, handling and storage of powdered raw materials should be carried out so as to minimise the emission of dust. Liquid and gaseous feeds should be carefully contained to prevent the emission of odorous fumes or gases.

- Oleum and SO_3 storage and handling operations, which are often linked with H2SO4 production, should be installed with means of controlling fume emissions. Venting should be directed towards acid tanks or scrubbing systems. Installations should be built by following the best engineering practice. The emissions can condense and solidify in cool areas so this must be very carefully guarded against to prevent over-pressurisation of storage tanks.

- During storage and handling of sulphuric acid, leaks may have an impact on the soil or on waters. Precautions have to be taken in order to reduce the possibility and the gravity of these leaks.
  Minimum requirements: see [3].

2.6 Energy generation / consumption, other specific ‘utilities’

The process steps: sulphur - burning, sulphidic – ores - roasting, SO2 - conversion and SO3 -absorption are exothermic processes , this means that from technical point of view installations for removing energy are of great importance for the production of sulphuric acid. This is coupled most effectively with energy winning in different levels and forms. Energy winning is dependent on the process strategy for the target products, for the local conditions, for a possible relationship to other productions.
The age of production units decides over energy generation / consumption because materials of construction and specific buildings fix the technical possibilities for energy optimisation.
The most energy efficiency shows the sulphur burning process in conjunction with double absorption.

The different energy-winning techniques are:

-all techniques of steam generation as known from electrical power generation with
special apparatus as super-heater , economiser , steam boiler for sulphur burning

-steam generation by the inter-pass absorption with temperatures from 110°C to 180°C and steam pressures from 1,5 bar_{abs} to 11 bar_{abs}.

-steam turbines with power generation up to 15 MWh (1250 t H_2SO_4 100% Plant/ day)

-water preheating in the end absorption from 40°C to 80°C.

For the optimisation of the process (e.g. saving costs and winning energy) special programs are used.

An essential characteristic of a conventional cold-gas plant (metallurgical gases) is that almost all the energy is discharged as waste heat at low temperature. Double absorption processes based on metallurgical gases, differ from hot-gas plants based on sulphur combustion in that cold feed gases must be heated to the converter-inlet temperature using the energy liberated in the oxidation of sulphur dioxide. See Annex 3.2.

At a feed-gas concentration 8,5 % SO_2 and a dryer inlet temperature of 30-40°C about 2,7 GJ of thermal energy is liberated per ton of sulphuric acid (5,4 GJ in the case of sulphuric acid produced from elemental sulphur). This corresponds to a thermal output of 31 Mw for a 1000t/d plant. About 45 % of the total energy is discharged through the intermediate absorber acid cooling system, 23% through the final absorber acid cooling system and about 22% through the dryer-acid cooling system.

In terms of heat recovery, in a conventional cold-gas double-absorption plant for processing relatively low-grade sulphur dioxide containing feed gases, there is no excess high - temperature heat that can be used for generation high-pressure steam. However, where the sulphuric acid plant is linked to a modern smelter, high SO_2 is available and to increase the output of high pressure steam, low temperature heat from the absorber acid circuits can be used for preheating the boiler feed water.

2.7 Gas cleaning of metallurgical off-gases

SO_2 containing gases from all metallurgical processes are cleaned before the contact process from the following components:

- fumes or aerosols formed by condensation of volatile metal components such as Zn, Pb, Sb. Bi, Cd and their chlorides, sulphates and oxides ,
- volatile gaseous metals such as As, Se, Hg and their compounds,
- gaseous non-metals compounds such as HF, HCl, SO_3, CO.

After cleaning, a minor amount of them are absorbed in sulphuric acid or emitted with the tail gas over the stack. CO is oxidised to CO_2 in the contact process. All other are absorbed in sulphuric acid or emitted with the tail gas over the stack. Gases from combustion processes contains also CO_2.

Table 2.7.1 shows the different metallurgical off-gases, the main disposals and the way to cleanup

Offgas from	Main disposal	Cleanup system
”CuS” smelters	Hg, HF	ESP, Gas scrubber with $HgCl_2$or $Na_2S_3O_3$/HgS
”PbS” smelters	Hg	ESP, Gas scrubber with $HgCl_2$
”ZnS” smelters	Hg	ESP, Gas scrubber with $HgCl_2$
”Ni” smelters	Se	Gas scrubber

2.8 Handling of waste gas / stack height

The height of the exhaust stack conditions the maximum SO_2/SO_3 concentration value in the ambient air surrounding a sulphuric acid plant. It is also well known that this concentration is widely fluctuating in space and in time due to the thermo-aerodynamic conditions of the low-level atmosphere (0 to 500m), these conditions can vary due to the following factors:

- vertical temperature and humidity structure
- wind speed and direction
- turbulence of the atmosphere
- sunshine intensity etc.

Proposals of stack heights could consequently have a questionable character.

For the time being, every Member State has its own method for estimating the height of stacks. In the future, it is foreseen that a specific Technical Note on this topic will be published by the Commission.

3.Present Consumption / Emission Levels

3.1 Consumption of energy / raw materials / water input and waste

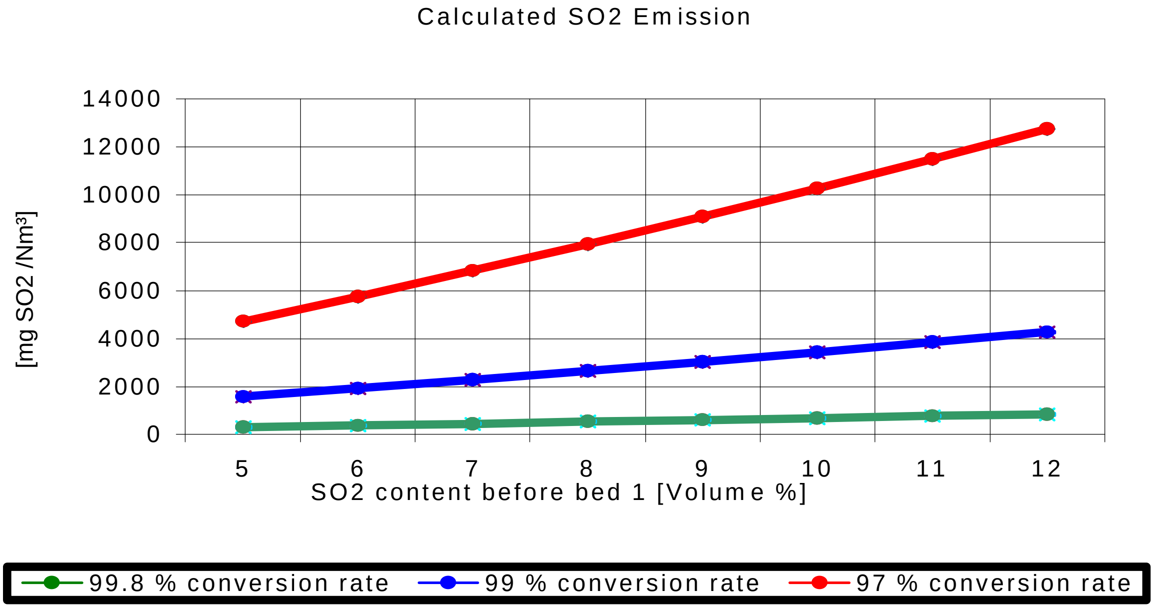
See Annex 3 for typical inputs / outputs for an 4-bed-contact-process per ton H2SO4 100%

The types of process are:

- sulphur-burner ,pyrite roasting, ”CuS” roasting, ”ZnS” roasting , ”PbS” roasting
- H_2SO_4 regeneration , ”$FeSO_4$” roasting .
- See ANNEX 3 for the different process types.

3.2 Emission Levels

**Figure 3.2.1 calculated SO_2 emissions in mg/Nm^3
in relation to the SO_2-content before bed 1**



3.3 Environmental aspects

3.3.1 emissions to air / water, waste generation

3.3.1.1 emissions to air CO_2, SOx, NOx

3.3.1.1.1 SO_3 emissions

Origins:

- Bad absorption efficiency
- Vapour pressure of sulphuric acid /Oleum

Minimization techniques:

Absorption improvements :

- absorbing tower design (velocity)
- acid distribution (flow and repartition)
- packing efficiency
- Acid temperature (vapour pressure)

3.3.1.1.2 H_2SO_4 emissions

Origins:

- Tower design
- Mist formation
- Vapour pressure

Minimization techniques:

- Droplets carry-over
- Absorbing tower design (gas velocity, acid distribution) /demisters (mesh pads or candles)
- Mistfilter
- Process control :
  - ESP efficiency
  - drying tower efficiency
  - gas temperature upstream absorption
  - NO_X content in the gases
  - acid temperature at the bottom of absorption tower.
  - acid vapour pressure (temperature)
  - High Efficiency demisters ➔ 50 mg /Nm^3 (particles > 0.5µ)

3.3.1.1.3 SO_2 emissions

Origins:

- Bad conversion efficiency
- Gas bypassing (acid cross bleed or convector)

Minimization techniques without additional process:

Gases:

- composition (O_2, SO_2, inerts…)
- velocities through catalyst and repartition
- cooling quality (heat exchangers or air cooling)
- operating pressure
- acid cross-bleeds (SO_2 stripping , SO_2 gases drying processes).
- temperature

Catalyst:

- converter design
- number of beds
- catalyst quality and quantity
- converter loading

SO_2-Minimization techniques with additional process :

- Without by-product**:** Single absorption ➔ double absorption (if gases are higher than 6 % SO_2)

- SO_2 ➔ weak H_2SO_4 possible to recycle : Activated carbon oxidation process / H_2O_2 process

- With co- or by-product:
  - NH_3 scrubbing , Co product -> **Ammonium sulphate**
  - NaOH scrubbing ,Co product -> **Sodium sulphate**
  - $Ca(OH)_2$ scrubbing ,Co product -> **Calcium sulphate (gypsum)**
  - $Mg(OH)_2$ scrubbing ,Co product -> **Magnesium sulphate**
  - Other processes – neutralization absorption, bio,..) exist but are less developped and depend on the site specificities.

3.3.1.2 emissions to water

- energy release from cooling
- accidental leakage
- waste water treatment plants must be able to deal with heavy metals
- emissions of noise by air cooling
- water treatment for steam production

3.3.1.3.1 sulphuric acid spent catalysts

Methods for disposing of spent catalyst are:

a) Metal recovery
The vanadium content of the catalysts can be reclaimed for further use. This service is usually provided by the catalyst manufacturer who will have access to a reclamation operation.

The metal recycling can practice as vanadium-salts or as ferrovanadium for steel production.
In all cases of the recycling versions it is very important that the spent catalyst has a low content of arsenic.
A typical analysis for spent catalyst:

V_2O_5 : min 3 % weight
K_2O: max. 10 % weight
P: max. 0,5 % weight
Sn, Pb, As, Sb, Bi, Cu, Zn, Cd, Hg: max. 0,1 % weight

b) Landfill Disposal :
Two types of disposal are available

Fixation: The catalyst is 'fixed' in an inert matrix, usually concrete or glass (also known as vitrification) prior to controlled deposit in a suitably licensed landfill site. The fixation process is designed to prevent metals leaching into the landfill site.

Direct landfilling: The catalyst is deposited directly into a suitably licensed landfill site in compliance with national legislation. It is common practice to mix the catalyst with lime to neutralize residual acidity.

3.3.1.3.2 wastes from packing and lining

Waste from the chemical industry is always handled with care. Waste from sulphuric acid production, packing, lining and scrap-iron is always handled in the same way as waste from other chemical production plants. That means that where it is necessary, the waste is checked for impurities before decision is made how to handle it. In normal sulphuric acid production there are usually no problems

3.3.2 concerning consumption of water / energy and other resources

Sulphuric acid production is one of the few chemical processes where you normally get a lot of energy more than you use in the process. In many cases sulphuric acid plants are used as the energy source for production of other chemicals that consume energy. Schemes about the energy output from different plants se annex 3 Sulphuric acid production also has the advantage that compared with fuel and natural gas, there is no formation of carbon dioxide. You could say that the energy is green compared with other energy production due to the fact that the energy is a by-product.

These aspects had to take into account the influence of energy winning.The process is a net producer of energy , although recovery is a function of the level of quality of this energy.

3.3.2.1 concerning consumption of water

All acid plants have some system to control the use of water in the acid system for cooling and adjusting the concentration. For cooling purpose is it normally a closed water circuit, or a measurement of the pH before it is released to the recipient. The use of water in the acid system is important to ensure the right concentration in the absorption tower to prevent acid mist in the stack.

Boiler feed water for the steam production is manufactered by specially processes (Anion/ cation- exchanger and water conditioning with ammona or sodiumhydroxid ore hydrazine ore phoshates) from different water sources (ground water , drinking water,..) . The water quality (pH , conductivity,..) must be totally controlled . Ca. < 95 % of water is used for steam production , the rest boiler water (mostly alcaline) can given after neutralisation in the water drainment system. For economical reasons all uncontaminated water condensates should be collected to supplying for new steam production .

3.3.2.2 concerning consumption of energy

Consumption of energy in sulphuric acid production is always a net energy production instead of consumption. The quality of the energy produced is always a matter of what you need at the site. Different kinds of energy produced are for example: steams of different levels for chemical plants, power generation , city heating or hot water to greenhouses or fish farms.

3.3.2.3 concerning other resources

Regeneration, recycling and evaporation are different ways to prevent spent acids to become a waste and a problem for the environment. Metal roasting and a sulphuric acid plant to take the tail gas prevents sulphur dioxide to be an emission

3.3.3 accidental pollution

When chemicals are produced and handled, there is always a risk for accidental pollution. The more common a chemical is the more known are the different risks and because of this you have minimised the risk for different ways of accidental pollution. The biggest risk for accidental pollution is during transportation of the product and that is taken care of with the different regulations for transportation, ADR/RID and IMO regulations. After that there is the storage of sulphuric acid, where the plants have different systems to collect leakages depending on the guidelines for storage of acid.
Gas leaks are normally a small problem that’s handled by different control systems, monitoring systems, measuring the SO_2 content in the air.

3.3.4 centres of concern (gravity)

The most important issue is the transportation of the product and that is handled by the regulation for ADR/RID and IMO. Close to this there is the loading and unloading of sulphuric acid where there is a risk for the personnel if its handled wrong. All companies work a lot with personal safety and have different systems to ensure that its handled properly.

3.3.5 Multimedia complexity

The emissions of sulphur dioxide into air could, fall down on the soil and contribute to lower pH.

SO_2 scrubbing will create a by-product disposal problem which will have to be handled depending on the type of by-product produced ie gypsum to landfill, ammonium sulphate for sale or recycling etc...

4.Candidate BATs:

4.1 Available Techniques

Since the technique of conversion of SO_2 to SO_3 and of absorption of SO_3 depends on the concentration of SO_2 in the feed gas entering the installation and on the variability of SO_2 concentration, the general presentation of the technique of production of sulphuric acid is divided into two parts:

Sources of SO_2

- Sulphur burning
- Pyrite roasting
- Metal sulphide roasting and smelting
- Sulphuric acid regeneration
- Metal sulphate roasting
- Combustion of H_2S or other Sulphur containing gases
- Other processes

Sulphuric acid production

The acid production will be divided in two different processes: < 3 Vol.% SO2 and > 3 Vol.% SO2 poor gas processes and tail gas processes leading sulphuric acid.

Poor gas processes with > 3 Vol. % SO2:

- Single contact process
- Double contact process
- Wet Contact Process (WCP)

Tail gas processes with < 3 Vol. % SO_2:

- Modified Lead Chamber Process (MLCP)
- H_2O_2 process
- Activated Carbon
- Other processes

4.1.1 Overview of techniques applicable to sources of SO_2

The characteristics of the principal sources of SO2 dependent on the different processes are detailed in annex 3 figures 3.1 to 3.6.

Table 4.1.1 gives an overview of techniques that have a positive effect on , that is reduces the emissions from the manufacture of Sulfurdioxide.

Table 4.1.1 Techniques reducing the emissions

Techniques	Process control	Fuel selection	ESP	Filters	SOx
Sulphur burning	x			X	X
Ores roasting/smelting	X	X	X	X	X
H_2SO_4 Regeneration	X	X	X	X	X
Sulphates roasting	X	X	X	X	X
Combustion of H_2S	X	X		X	x

4.1.1.1 Combustion of Sulphur:

Combustion of sulphur, which is obtained either from natural deposits or from de-sulphurisation of natural gas or crude oil, is carried out in one-stage or two-stage sulphur combustion units at between 900 °C and 1800 °C. The combustion unit consists of a combustion chamber followed by a process gas cooler. The SO_2 content of the combustion gases is generally up to 18% by volume and the O_2 content is low (but higher than 3%).

The gases are generally diluted to 10-11% before entering the conversion process. In the inlet-gas to the converter the ratio SO_2/O_2 should not be higher than 0.8 to achieve a high conversion efficiency. This means that the highest percentage of SO_2 should not exceed 11 % in a 4-bed double contact (no Caesium) to achieve a conversion rate of 99,6 % average.

4.1.1.2 Pyrite roasting:

Nowadays fluid-bed roasters are the preferred equipment for pyrite roasting. They are much superior to other types of equipments in term of process technology, throughput rates and economy. When roasting pyrite to get SO_2-gas two by-products are also produced, iron-oxide and energy. 1 Ton acid needs 0,5 Tons pyrite.

The SO_2 content of the gases is generally 6 – 14 % and the O_2 - gas is zero.

The gases are always treated in 3-4 cleaning steps, cyclones, bag filters, scrubbers and electric precipitators with a high efficiency. Waste water from the scrubbing has to be treated before discharge. The clean gas is diluted with air to 6 -10 % and dried before entering the conversion process.

Due to the heterogeneous character of the raw material (pyrite), the SO_2 content in the gases is slightly variable over time.

4.1.1.3 Metal sulphide roasting/smelting:

Many metal sulphides (other than pyrite), when roasted during metallurgical processes, produce gases containing SO_2. It is necessary to distinguish the main ores as indicated in Table 4.1.1.4.

Table 4.1.1.3 Principal Metal Sulphides Producing SO_2

Metal Sulphide	SO_2%	Raw Gases O_2%	Process Gases SO_2%	Variability in time
ZnS containing ores	6 --- 10	6 --- 11	6 --- 10	Relatively low
CuS containing ores	1 ---20	8 --- 15	1 --- 13	Can be very high
PbS containing ores				
- sintering	2 --- 6	≈ 15	2 --- 6	Relatively high
- other lead smelters	7 --- 20	≈ 15	7 --- 13	Low to very high (Batch process)

The concentration of SO_2 in gases entering an acid plant, determines the amount of gas that must be treated per tonne of fixed sulphur. The size of the plant and the cost of fixing sulphur increase as the concentration of SO_2 diminishes. Furthermore, there is a minimum concentration of SO_2 that can be treated without increasing the number of stages in the plant.

For copper, it is typical to find not only fluctuations in the concentration of SO_2 in converters, but also important fluctuations in the gas flow. The reason for these effects of converter operation on the concentration of SO_2 is the fact that about 30% of converter operating time is used for charging and slag tapping.

4.1.1.3.1 Copper production

Pyrometallurgical copper extraction is based on the decomposition of complex iron-copper sulphide minerals into copper sulphides, followed by selective oxidation, separation of the iron portion as slag, and final oxidation of the remaining copper sulphide.

These steps are known as roasting, smelting and converting (the present-day tendency is to carry out the first two in a single process). The Flash Smelting process is currently one of the most widely used pyrometallurgical processes.

Converters are used extensively, to blow air, or oxygen-enriched air through the copper matte to produce blister copper. Virtually all the sulphur from the concentrates finishes as SO_2. A concentrate of $CuFeS_2$ produces almost one tonne of sulphur (2 tonnes of SO_2) per tonne of copper extracted. To avoid air pollution, these gases are processed to obtain sulphuric acid, oleum or liquid SO_2.
The development of copper recovery processes has been dominated by two objectives. One is to economise on energy, making the maximum use of reaction heat obtained from the processes. The other has been the need to decrease the gas volume, and increase the concentration of SO_2 in metallurgical gases by the use of oxygen enrichment, to improve environmental controls. The gas purification follows during which the gas is cooled, and the dust and contained SO_3 are eliminated by scrubbing, cooling and electrostatic cleaning. After that, the clean SO_2 gases are converted to sulphuric acid through the contact process.

4.1.1.3.2 Zn Production

Zn production is based on the treatment of Zn-concentrates, mainly sulphides, with an average composition of sulphide sulphur : 30 -33%, Zn : 50 - 60%, Fe : 1 -12%, Pb : 0,5 - 4 % and Cu : 0,1 - 2%.These concentrates are desulphurised in a first step.

After the desulphurisation step the product (calcine) is treated for Zn-recovery mainly in a Hydrometallurgical Process and for a minor part also in a Pyrometallurgical Process. The Hydro way consists of leaching this calcine, purifying the enriched Zn-solution with subsequently pure Zn-metal recovered by electrolysis.
In the Pyrometallurgical way, conditioned calcine is reduced in a shaft furnace (ISF) with condensing of Zn-vapours in a splash condenser. This crude Zn is further refined in a destillation column.
More specifically the preliminary desulphurisation step, happens mainly in a fluidized bed roaster or alternativelly in a sinter plant. The SO_2 content of the gases is about 5 to 10 %. After heat recovery in a waste heat boiler with production of steam, the gases are dedusted in ESP, cooled down in scrubbing towers, and subsequently demercurified in a specific scrubbing-process. In a double contact process, a single one for older plants, the cleaned SO_2 gases are treated and converted to sulphuric acid .

4.1.1.3.3 Lead Production

Primary lead is produced predominantly from Pb- and Pb-Zn concentrates. To a smaller extent from other sources, such as complex Pb-Cu concentrates. Concentrate compositions may therefore vary between rather wide ranges: 10 - 80 % Pb, 1 - 40 % Zn, 1 -20 % Cu, 1 - 15 % Fe, 15 - 35 % S.
For an optimum recovery of the various metals present in the feed, rather different processes have been developed, and are used.

Whatever smelting technique is used, desulphurisation is always one of the objectives of the first treatment stages. It is carried out on belt sinter machines in those cases where a shaft furnace is the actual smelting step. Or in flash or bath smelting furnaces in the other processes.

From this variety of feed materials and consequently of techniques, it should be clear that the characteristics of the SO_2-containing gas will differ largely from case to case.From continuous operations, such as sinter machines, the SO_2-concentration can be kept fairly constant. Depending on the actual feed mix it can be between 6 and 9 %.
From batch operations, it will obviously be very variable, between 0 and 15%, depending on the process stage. Average concentrations may be among 2.5 and 10 %,depending on the actual feed mix, and applied technique.

The gas cleaning circuit will always include ESP and scrubbers. Energy recovery can be practised in some cases of bath smelting; a specific mercury removal step, on the gas or on the acid, may be necessary in others.The double absorption process is largely used, specially when $S0_2$- concentrations are high and constant.When low and very varying SO_2-concentrations are inevitable, or where those streams can not be integrated in more steady gas streams from other processes on the site, single absorption still is more appropriate.

4.1.1.4 Regeneration of Sulphuric Acid

Thermal decomposition of spent sulphuric acids to sulphur dioxide is achieved in a furnace at temperature in the range of 1000°C. Spent acids issue from processes where H_2SO_4 or oleum are used as a catalyst (alkylation ,nitration ,sulfonation,...) or from other processes where H_2SO_4 is used to clean , to dry , to remove water.

Gas phase thermolysis of sulphuric acid is represented by the overall equation:

$H_2SO_4 \text{ --> } SO_2 + H_2O + ½ O_2 \quad \Delta H = +202$ kJ/mole

Spent acids are atomized in very small droplets to get a good thermal decomposition. Energy is brought by the organics from the spent acids and by additional energy from natural gas,fuel oil or coke. Combustion air preheating reduces the amount of fuel needed.Furnaces can be horizontal (fixed or rotating)or vertical.

SO_2 content in the gases mainly depends on the composition of the spent acids; water and organics content affect the gas composition. It can vary from 2 to 15%.Sulphur, pure or waste, can generaly be fed to adjust SO_2 content and to try to avoid too high variations. Most part of the combustion gases energy is recovered as steam in a Waste Heat Boiler. Downstream, the gases are cleaned, demisted and dried before going to the converter. The ratio O_2/SO_2 is important to get a conversion rate of SO_2 to SO_3 as high as possible. Upsteam of the converter, the gases are reheated to the ignition temperature through gas/gas heat exchangers with the conversion heat. A double absorption process can be used only if the SO_2 content of the gases is high enough (about 8%) at the converter inlet.

Conversion rates:

Single absorption

SO_2 content at the converter inlet **8**% with O_2/SO_2 ratio of 1,1 **: 98 %**
SO_2 content at the converter inlet from **5 to 8%** with O_2/SO_2 ratio of 1,1 **: 97 to 98%**
SO_2 content at the converter inlet below **5%** with O_2/SO_2 ratio of 1,1 **: 96 to 97%**

Double absorption

When achievable, leads to conversion rates from **99 to 99.6%**

For new plants, the double absorption is considered as the BAT. For existing plants,a single absorption can be advantageously combined with an ammonia scrubber, the by-product obtained being either sold on the market or recycled in the furnace.

4.1.1.5 Sulphate roasting:

Decomposition of sulphates, par example iron sulphate, is carried out in multiple-hearth furnaces, rotary kiln or fluid bed furnaces at over 700 °'C with addition of elemental sulphur, pyrite, coke, plastic, tar, lignite, hard coal or oil as fuel compensator. The SO_2 content of the gases obtained is dependent on the type of fuel; after cleaning and drying, the SO_2 content is about 6%. The variability in time of the SO_2 content is high.

During the first step, the heptahydrate is dehydrated at 130-200 °C by flue gases in spray dryers or fluid-bed dryers to a monohydrate or mixed hydrate. In a second step, the material is decomposed at about 900 °C.

The gases thus obtained contain about 7% by volume of sulphur dioxide. Today it is common practice for ferrous sulphate to be decomposed in a fluid-bed pyrite roasting furnace at 850 °C or more. Elemental sulphur, coal or fuel oil may be used as supplementary fuels. The sulphur dioxide containing gas leaving the furnace is cooled in a waste heat boiler to about 350 - 400 °C and is subsequently passed to the gas cleaning system. The cleaned gases are fed to the sulphuric acid plant.
A mixture of (metallic or ammonium) sulphates and eventually sulphuric acid resulting from the concentration of acidic wastes of titanium oxide production or from organic sulfonations can similarly be processed in a fluid bed reactor or a furnace.
In individual cases, ferrous sulphate is also decomposed in multiple-hearth furnaces with flue gases from fuel oil or natural gas combustion.

4.1.1.6 Combustion of sulphur containing gases:

Combustion of Hydrogen Sulphide (H_2S) or similar gases is achieved in a fixed furnace at about 1000°C . Combustion heat is higher than with sulphur combustion.
2 different ways are used to process the gases to SO_3 and H_2SO_4 :

- Dry process where the water is eliminated by condensation and then drying and the gases are processed like in the spent acid regeneration process
- Wet process in which the gases are processed with all the water steam. At the end of the process,the absorption tower is replaced by a condenser where the control of temperature allows to produce 96% H_2SO_4 ,the most part of water being rejected to the atmosphere.

The conversion rates can be compared to sulphur burning plants.

4.1.1.7 Tail gas scrubbing

SO_2 abatement by scrubbing consists in a chemical reaction between SO_2 and a basic liquid solution.
This operation is achieved generaly in a Gas/Liquid contact packed tower or a scrubber . A liquid circulation loop is operated from the bottom to the top of the tower,where the liquid is distributed above the packing.
The gases enter the bottom part of the tower ,contact and react with the basic liquid solution on the packing.
SO_2 content in the outlet gases is achieved by controling the pH of the solution, by adding more or less basic concentrated solution into the liquid circulation loop.
Depending on the inlet and outlet SO_2 content and the basic product (ammonia, caustic soda, magnesium or calcium hydroxides , ...) , one or two reaction steps can be needed.
The resulting by-products (ammonium, sodium, magnesium, calcium,..sulphate, sulphite and bisulphite) can be sold or have to be disposed of.

4.1.2 Overview of techniques applicable to the Sulphuric Acid Production

This section refers to existing plants which may (or may not) be up-graded,although not reaching the specifications of new plants.

4.1.2.1 Overview

The six process routes are the principal process routes that are available.
The following data on production processes have been presented in detail in the previous paragraphs and are summarised here in Table 4.1.2.1 (a) using an O_2/SO_2 ratio of about 1 ± 0,2 (possibly 0,8 to 3).

Table 4.1.2.1 (a) Sulphuric Acid Production Processes for New Plants

NEW PLANTS	SO_2 content in feed gas (% vol)	Conversion rate daily average (%)	State of the art emission for new plants SO_3 [2]
Single contact	6 ---10 3 --- 6	98,5% [4] 97,5% to 98,5%	0,4 kg / t [5]
Double contact	6 ---12	99,6% [1]	0,1 kg / t [5]
Wet contact process	0,05 --- 7	98,0%	< 10 ppmv SO_3
Process based on NO_x	0,05 --- 8	nearly 100% [3]	No data
H_2O_2 Process		> 99,0%	Very low

[1] when sulphur burning
[2] SO_3 + H_2SO_4 expressed as SO_3
[3] possible emissions of NO_x
[4] for existing plants the conversion rate is 98%
[5] per ton of acid produced

Table 4.1.2.1 (b) gives an overview of techniques that have a positive effect on , that is reduces the emissions from the manufacture of sulphuric acid

Table 4.1.2.1 (b) Techniques reducing the emissions

Techniques	**Process control**	**Single contact**	**Double Contact**	**Catalysts**	**Filters**	**SOx**	**NOx**
Sulphur burning	x		X	x	X	X	X
Ores roasting	X	X	X	X	X	X	
H_2SO_4 Regeneration	X	X	X	X	X	X	X
Sulphates roasting	X		X	X	X	X	
Incineration of H_2S	X	X	X	X	X	x	X

4.1.2.2 Single contact process (single absorption):

The contact process without intermediate absorption is nowadays only used in new plants to process SO_2 gases with low and widely varying SO_2 contents.

The SO_2-containing gases, which have been carefully cleaned and dried, are oxidised to sulphur trioxide in the presence of catalysts containing alkali and vanadium oxides. The sulphur trioxide is absorbed by concentrated sulphuric acid in absorbers, where if necessary preceded by oleum absorbers. In the absorbers, the sulphur trioxide is converted to sulphuric acid by the existing water in the absorber acid.
The absorber acid is kept at the desired concentration of approximately 99% by wt. by adding water or dilute sulphuric acid as shown in **Figure 4.1.2.2 "Single absorption process for spent acid regeneration".**

The single contact process is generally used with SO_2, content inlet gases of 3 to 10%; in new plants, the conversion efficiency is about 98,5% as a daily average and can be upgraded till 99,1 % depending on good design and use of specially adapted doped Cs-catalyst.

In existing plants, it is difficult to obtain better than 98,0% conversion, however, in some existing plants, a conversion efficiency of 98,5% can be achieved.

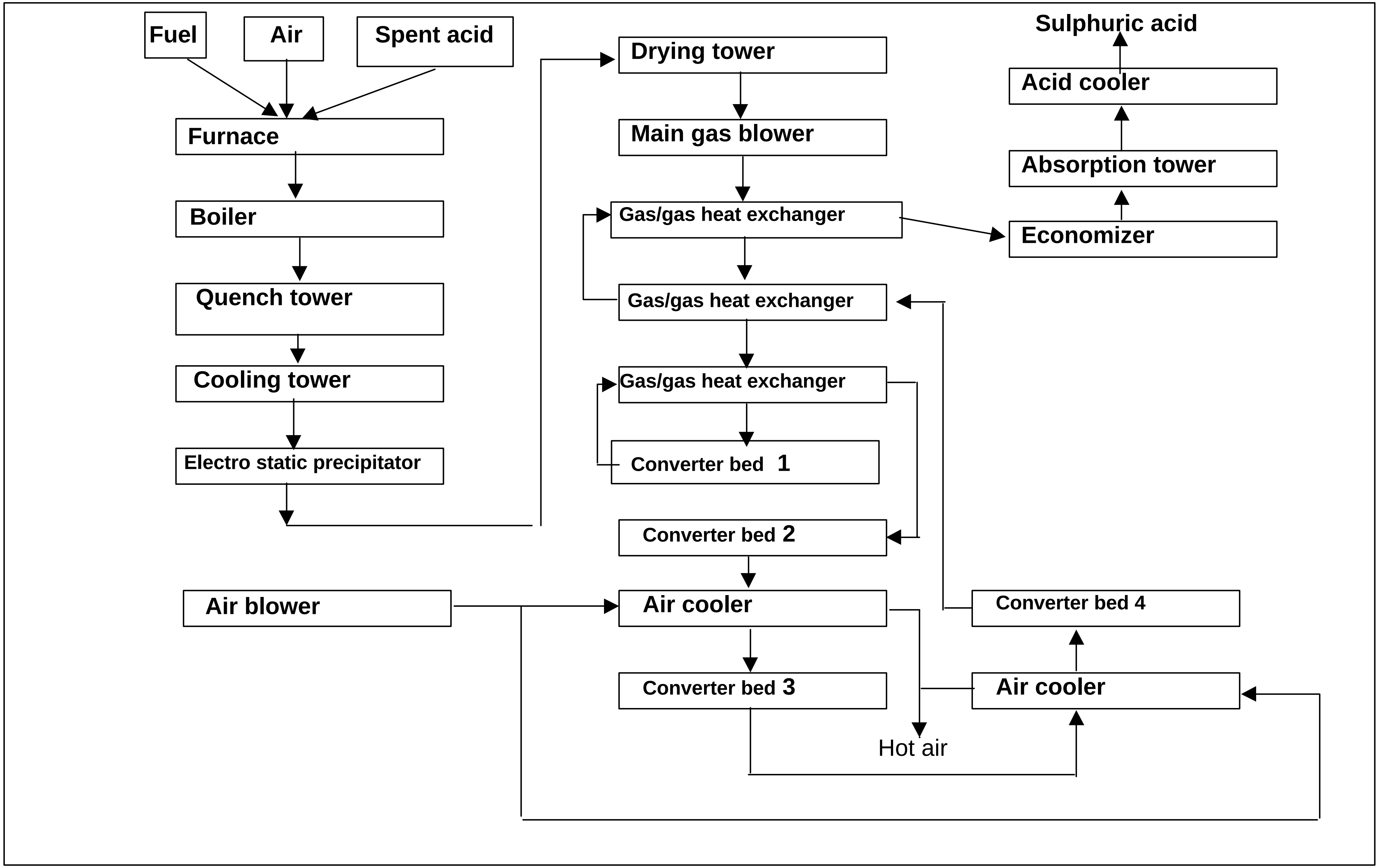


Fig.4.1.2.2 „ Single absoption process for spent acid regeneration“

4.1.2.3 Double contact process (double absorption):

In the double contact process, a primary conversion efficiency of 80% to 93%, depending on the arrangement of the contact beds and of contact time, is obtained in the primary contact stage of a converter preceding the intermediate absorber. After cooling the gases to approx. 190°C in a heat exchanger, the sulphur trioxide already formed is absorbed in the intermediate absorber by means of sulphuric acid with a concentration of 98,5 to 99,5% by weight. The intermediate absorber is preceded by an oleum absorber if required. The absorption of the sulphur trioxide brings about a considerable shift in the reaction equilibrium towards the formation of SO_3, resulting in considerably higher overall conversion efficiencies when the residual gas is passed through one or two secondary contact beds. The sulphur trioxide formed in the secondary stage is absorbed in the final absorber.

The double contact processes including double absorption are seen in Figure 4.1.2.3 (a,b,c) with the different raw materials sulphur, non-ferrous ores and pyrite.

In general, SO_2 feed gases containing up to 12 Vol.% SO_2 are used for this process. The conversion efficiency in new plants can achieve about 99.6 % as a daily average in the case of sulphur burning.

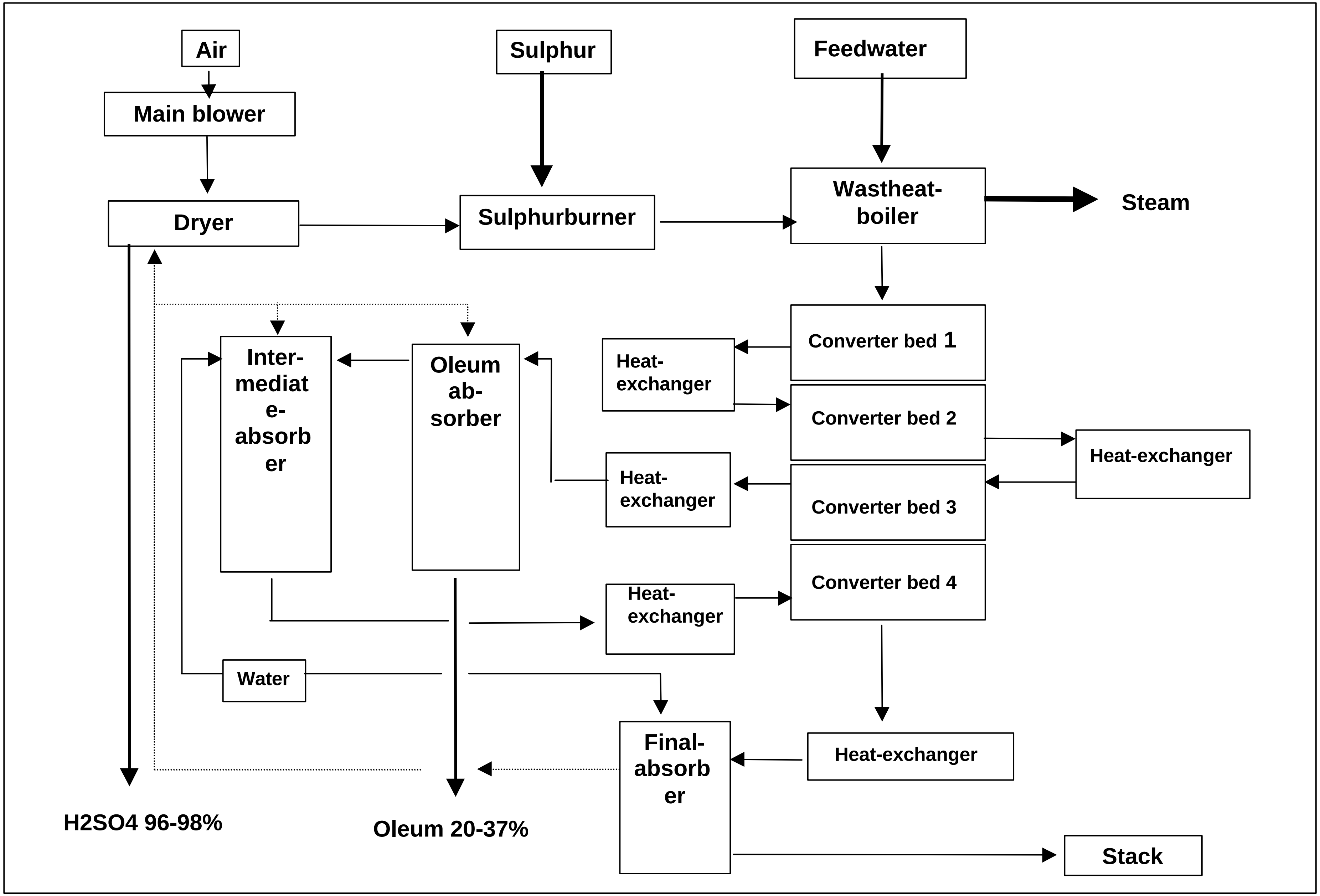
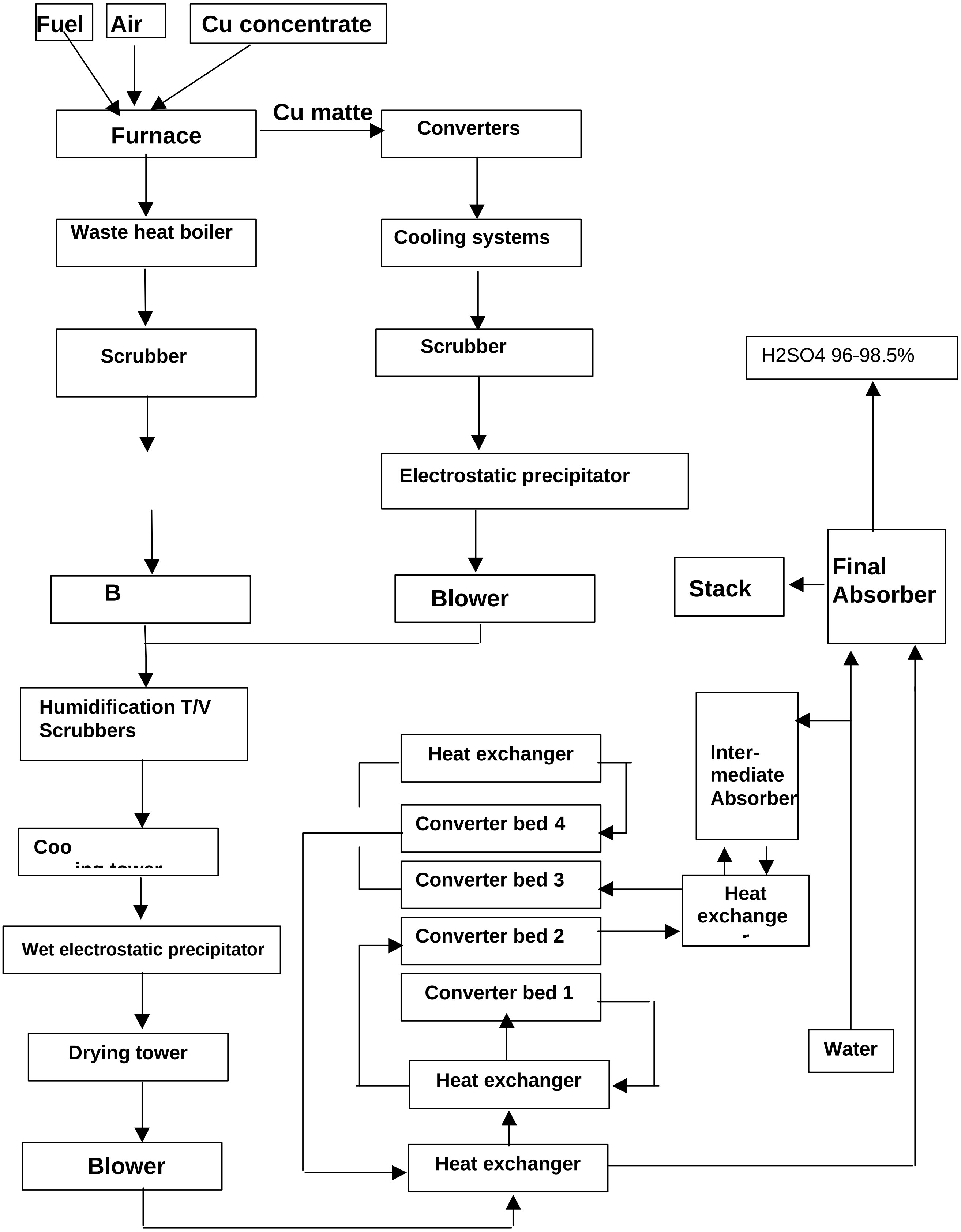


Figure 4.1.2.3 (a) „Sulphuric acid plant (double catalysis) based on Sulphur combustion“


Fuel
Air
Cu concentrate
Furnace
Cu matte
Converters
Waste heat boiler
Cooling systems
Scrubber
Scrubber
H2SO4 96-98.5%
Electrostatic precipitator
B
Blower
Stack
Final Absorber
Humidification T/V Scrubbers
Heat exchanger
Inter-mediate Absorber
Converter bed 4
Coo
ing tower
Converter bed 3
Heat exchange
Converter bed 2
Wet electrostatic precipitator
Converter bed 1
Water
Drying tower
Heat exchanger
Blower
Heat exchanger

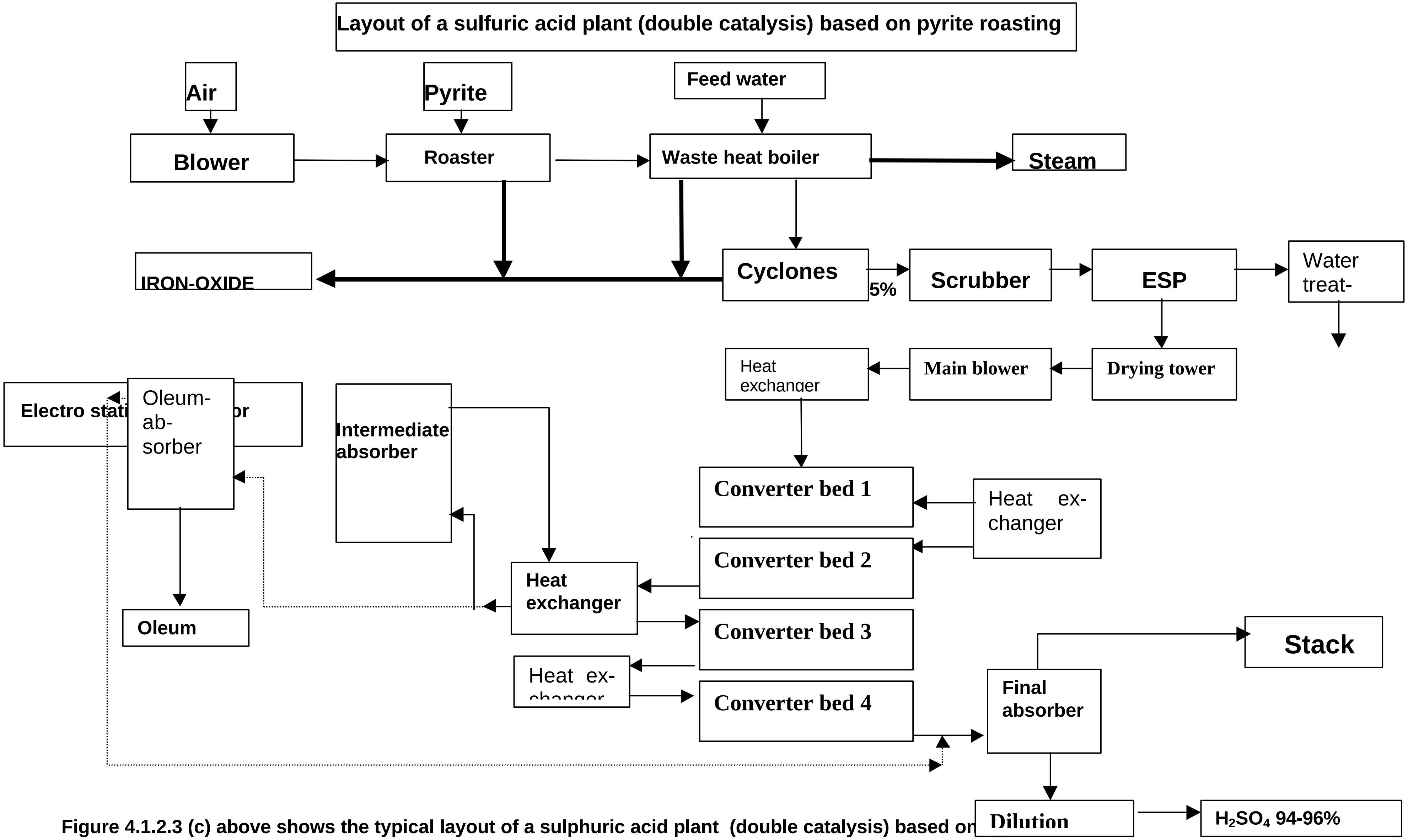


Figure 4.1.2.3 (c) above shows the typical layout of a sulphuric acid plant (double catalysis) based on

4.1.2.4 Wet Contact Process (WCP):

This process is not sensitive to the water balance and has been used to treat off-gas from a molybdenum smelter as well as being installed in two de-sulphurisation plants (one in a Flue Gas De-sulphurisation system, the other on an industrial boiler) currently under construction. An earlier version of the WCP technology was used to treat lean hydrogen sulphide gases. For all gas feeds, sulphurous components in the gas are converted to sulphuric acid without the need to dry the gas first.[33].

When treating roaster off-gas, the off-gas is cleaned in a standard purification system and then fed through a blower, which provides the pressure necessary to overcome the pressure drop across the system. The gas is preheated initially in the tower and, secondly, in a heat exchanger. It is next fed to a converter, where sulphur dioxide is oxidised over a catalyst to sulphur trioxide. Depending on the conditions, a cooled reactor or an adiabatic reactor is used.
Sulphur trioxide-containing gas is then cooled in a gas-gas heat exchanger. Consequently, part of the sulphur trioxide reacts with the water vapour in the gas to form sulphuric acid vapour. Finally, the sulphuric acid vapour is condensed and concentrated, without acid mist formation, in a multi-tube falling film condenser. Cooling is provided by the cold feed gas supplied to the shell side.
The only utilities required are cooling water for the acid coolers, electricity for the blower and fuel to enable autothermal operation if the feed gas contains below about 1.5-2.0% SO_2.
The conversion efficiency is about 98,5 % as daily average.

4.1.2.5 Pressure process:

As the oxidation of SO_2 is favoured by pressure, Pressure Contact Processes have been developed in which the sulphur combustion, sulphur dioxide conversion and sulphur trioxide absorption stages are effected at elevated pressure. Several parameters can influence the conversion efficiency , by modifying the chemical equilibrium. The pressure is one of them and displace the equilibrium to the right . One plant ,a double-absorption plant with a capacity of 550 - 575 tonnes per day of H_2SO_4 in France, has been designed with the pressure process in the early 70's, and is still in operation . Usual sulphuric acid processes are operated at pressures in a range of 0.2 to 0.6 bar.

Compared with the conventional double-absorption process, two especial advantages have been claimed for the pressure contact process:

- The position of the, chemical equilibrium in the sulphur dioxide oxidation reaction is more favourable, allowing a higher conversion efficiency to be attained with a reduced amount of catalyst. The plant is reported to have achieved 99,80-99,85% conversion. The tail gas sulphur dioxide content is reported to be reduced to about 200-250 ppm SO_2. However, the high temperatures in the sulphur furnace increase the rate of formation of nitrogen oxide.

- On account of the lower operating volumes of the converter gases, smaller equipment can be used. This reduces material and site area requirements, and it raises the capacity limit of shop-fabricated equipment. The resulting capital cost savings are said to be about 10-17% in comparison with current double-absorption plants. It should be mentioned, however, that in some countries these savings would be nullified by the cost of conforming to the requirements for extra wall thickness and higher-grade materials of construction laid down in the safety regulations relating to pressure vessels.

The principal disadvantages of the pressure contact process in comparison with the conventional double-absorption process is that it consumes more power and produces less steam.

4.1.2.6 Other processes

Other processes are defined as processes building sulphuric acid but not in economical view . They are not suitable for great productions for different reasons.

4.1.2.6.1 Unsteady state oxidation process:

This new method of SO_2 oxidation is based on a periodic reversal of the direction of the reaction mixture flow over the catalyst bed.

The process was developed at the Institute of Catalysis of the former USSR. Basically a large bed of catalysis is used as both a reversing, regenerating heat exchanger and as a catalytic reactor for the SO_2 oxidation reaction. Cold SO_2 gas is fed into the catalysis bed and is heated by the heat stored in the bed to catalyst ignition temperature. At this point the conversion reaction proceeds, producing heat. The heat is absorbed by catalyst and the bed, increasing its temperature front comes close to the exit side of the bed, the flow through the reactor is reversed. Flow reversals are made every 30-120 minutes. The main advantage of the unsteady state process is that the operating line for bed one would be almost vertical, giving one bed conversion of about 80-90% at a low exit temperature.
The process is auto-thermal at low (0.5-3%) SO_2 gas strengths.

The process is in operation in several plants in Russia and other East European countries.

4.1.2.6.2 H_2O_2 Process:

The conversion of SO_2 to SO_3 can be achieved by the use of H_2O_2 by a sulphuric acid concentration of 70 %. Conversion efficiency is higher than 99% but the cost of H_2O_2 makes this an expensive process for sulphuric acid production. However, since the process leaves no waste, it is very useful for tail gas scrubbing where especially difficult local conditions cannot tolerate the emission even from an installation as efficient as the best contact plant. The H_2O_2 is used either directly or is produced by electrolysing H_2SO_4 to peroxydisulphuric acid in the "Peracidox" process.

4.1.2.6.3 The Modified Lead Chamber Process

The Modified Lead Chamber Process is able to treat gases with low SO_2-content (as low as 0,05%) up to 8%. The process is also able to treat gases containing a mixing of SO_2 and $NO_{x. From}$ the chemical point of view, the process is a development of lead chamber sulphuric acid technology, in which nitrogen oxides are used to promote sulphuric acid production directly from sulphur dioxide through the formation of an intermediate, nitrosyl sulphuric acid. Widely used in the early 1900s, this technology has been largely superseded by the contact process.

After dust removal and purification, the sulphur dioxide-containing gas is fed through a denitrification system, where final traces of nitrogen oxides remaining in the sulphuric acid are removed, and then through the Glover tower, where the bulk of the nitrogen oxides are removed from sulphuric acid. Sulphur dioxide is absorbed from the gas stream next in sulphuric acid (59 to 66%) in a packed tower. In both the Glover and absorption towers, the gas flow is counter current to the liquid f low .The final step of the process is removal of nitrogen oxides from the gas stream by absorption in sulphuric acid (74%), so forming nitrosyl sulphuric acid. Absorption is achieved in three stages in a specially designed packed vessel through which the gas flows horizontally. This vessel allows multiple absorption without dead space between stages. (This design is also employed for final removal of nitrogen oxides from sulphuric acid). The absorber has dividing walls that are permeable to the gas between each stage. Packing is placed between the dividing walls.
Regulation of the NO/NO_2 ratio, which is important for the absorption of nitrogen oxides, is achieved by adjusting the amount of nitrosyl sulphuric acid fed to the Glover tower. If necessary the nitrogen oxide's balance is maintained by adding nitric acid to the Glover tower. For SO_2 content of 0,5 to 8%, the conversion efficiency is about 100% but emissions of NO_x occur (up to 1 g/m3 N of $NO + NO_2$).
Since 1974, Ciba-Geigy has been developing such a process specifically designed for processing gases with about 0.5-3% volume SO_2.

4.2 Environmental Performance

The main pollutants emitted are:

- SO_2 resulting from the uncompleted character of the reaction of oxidation
- SO_3 resulting from the uncompleted absorption of SO_3
- droplets of H_2SO_4 resulting from absorption
- H_2SO_4 vapour from scrubbing.

According to the source of SO_2 and the process of H_2SO_4 production, many other pollutants can be (or could be) emitted as traces, such as NO_x ($NO + NO_2$) in all processes but mainly in the process based on NO_x

- NO and NO_2 in the Modified Lead Chamber Process
- Heavy metals (for example, Mercury) when certain ores are treated.

4.2.1 Monitoring of Pollution

Two approaches are used to monitor emissions:

- monitoring the process: temperature of contact layers, SO_2 content entering the contact and behind the intermediate absorption

- monitoring of the emissions

4.2.1.1 Monitoring of SO_2 emissions:

Continuous emission monitoring equipment for SO_2 is available and suitable for sulphuric acid plants and should be installed on all plants. Dual range instruments are available so that the much higher SO_2 emission concentration during start-up can be monitored as well as the relatively low concentration in the emission during steady operation. Emission monitor records should be retained and the competent authorities should consider the appropriate statistical analysis or reporting which is required.

For the analytical methods for the determination of SO_2 – samples see [4],[7],[10],[11]. For online-sampling and measuring see [8],[9].

Measurement problem:

SO_2 concentration; Span 0 – 1000 ppm   Matrix: air, H_20, H_2SO_4 [30ppm], NO_X [50ppm]

The method for the solution of the problem is usually done with a commercial photometer. For the mentioned measuring range and matrix an IR or UV photometer can be used (IR measurment needs a water compensation). There are two kinds of photometer available.

- Inline photometer (only IR) are able to measure the gas concentration inside the gas pipeline, if the matrix is transparent for the optics (e.g. no fog).
- Online photometer with sample preparation. The second method is the normal method. Because of corrosion one has to choose suitable materials for the sample preparation and the measuring cell.

The sample preparation occurs in two ways.

- Hot sample preparation keeps the sample and the whole sampling equipment (filter, pipeline, pump, measuring cell) above the dewpoint (~ 150°C).
- Cold sample preparation uses a cooler to dry the sample gas to a fixed dewpoint (~5°C).

Any method of SO_2 measurement needs a certain maintenance for high availability and reliability. Appropriate plans with intervals for inspection and service should be done, including information for maintanance in the case of breakdown.

The accuracy of the analyzers lies in between 1 or 2 %. The over all precision of a complet system lies in between 2 or 5 %. For special purpose (e.g. enviromental protection) one has to observe statutory conditions for the analyzer and sampling system. Registration and storage of the concentration values is done in an additional system (e.g. PCS, special datalogger).

Provision should be made for zero and calibration checks of emission monitors, and for alternative testing in the event of breakdown or suspected malfunctioning of the monitoring equipment. The regular observation of monitors by plant operators for detecting abnormalities in the process operation is as important an aspect of monitoring as is the compliance function, and should be encouraged by the competent authorities.[32]

4.2.1.2 Monitoring of mist emissions in the stack:

There is at present no known equipment available for carrying out reliable continuous monitoring of sulphur tri-oxide.
Meanwhile, sulphur trioxide together with sulphuric-acid - mist can be measured by manual sampling and chemical analysis. See method [4] .The analytical problem separation between SO_3/H_2SO_4 and SO_2 is excellent solved in the method of 'Specht' by using boiling aqueous hydrogen chloride for absorption of SO_3/H_2SO_4 .

Sampling points for the above measurements under iso-kinetic conditions should be provided. They must be easily accessible and kept in good condition so that they can be used at very short notice. Sealable openings 20 to 50mm diameter are generally considered as suitable, provided that a sampling probe can be inserted into the exhaust gas stream, except in cases when standardised methods require use of larger openings.

4.2.2 General Techniques

4.2.2.1 Process control optimisation

Operational controls could include means for:

- Warning of absorber acid feed failure
- Warning of absorber acid feed over-temperature and controls of temperature along the conversion tower
- Indication of sulphur feed rate and air flow rate
- Detection of acid leaks in acid coolers (pH-meter) and controlling level of acid reservoir
- Acid-concentration > 98,5%
- Emergency plant trips
- pH-control on cooling water systems

To aid start-up the following will be necessary:

- Efficient catalyst preheating facilities, vented to the chimney. At least, two catalyst stages must be above "strike" temperature before sulphur dioxide is admitted to contact the catalyst
- Optimisation of absorber acid strength and temperature before sulphur is admitted to the burner
- Use of additional controls to ensure that sulphur cannot enter the system during shut-down
- Before a long shut-down period the catalyst bed should be efficiently purged of SO_2 / SO_3

4.2.2.2 Fuels and raw materials selection

4.2.2.2.1 Sulphur

Sulphur with low contents of ash, water and suphuric acid must be preferred .

4.2.2.2.2 Energy for heating systems

For the start-up of sulphuric-acid plants heating systems are necessary. Where direct combustion is applied, low sulphur fuels are preferable.

4.2.3 Techniques to control emissions of SO2

Table 4.2.3.(a) gives an overview of techniques that have a positive effect on, that is reduce, the emissions of SO2 for the manufacturing of Sulphuric acid. Most sulphuric acid plants have taken general primary optimisation measures, like process control measures.

Techniques	Applicability In processes	Emission Level referring to 11% SO_2 and 1000 t/d = 100.000 Nm³/h		Cost (in addition to the basic installation)		Additional effects
		mg SO_2 /m³ tail gas	Kg SO_2 / ton H2SO_4 100%	investment	Operating	
Contact process						

Single absorption + 5 th bed	all s.a.	< 5000	< 10	1 to 3 M EUR	0.2 EUR/ton	
Double absorption + 5 th bed	all d.a.	< 1000	< 2.5	1 to 3 M EUR	0.2 EUR/ton	
Single absorption + Caesium catalyst in the last bed	all s.a.	< 4500	< 9	35 k EUR	0	
Double absorption +Caesium catalyst in the lastbed	all d.a.	< 900	< 2.3	35 k EUR	0	
Single to double absorption	s.a.	< 1000	2.6	6.5 M EUR	3.8 EUR/ton	
Tail gas scrubbing						
Sodiumhydroxide	all	< 200	< 2	6 M EUR	4,5 EUR/ton	Sodium salt to be disposed of
Ammoniumhydroxide	all	< 200	< 2	6 M EUR	4.4 EUR/ton	Ammonium salt to be disposed of
Calcium hydroxide	all	< 200	< 2	6 M EUR	4.0 EUR/ton	Gypsum to be disposed of
Activated Carbon	all	< 1000	< 2	5.5 M EUR	4.0 EUR/ton	Dilute sulphuric acid
Hydrogen peroxide treatment after end absorption	all	< 200	< 2	4,5 M EUR	6 EUR/ton	Dilute Sulphuric acid

4.2.4 Techniques to control emissions of SO_3 and H_2SO_4

Table 4.2.4.(a) gives an overview of techniques that have a positive effect on, that is reduce, the emissions of H_2SO_4 (as sum of SO_3 and H2SO$_4$) for the manufacturing of Sulphuric acid. Most sulphuric acid plants have taken general primary optimisation measures, like process control measures.

Techniques	Applicability	Emission Level		Additional cost		Additional effects
		mg H_2SO_4 /Nm³ tail gas	Kg / ton H_2SO_4 100%	Investment	Operating	
Wire-mesh	Large droplets (1μ-20μ)	< 100				Not efficient on mists
High efficency candle type filter after absorbers	0,1 μ to 2 μ droplets	< 50	< 0,03	0,5 M EUR	30 EUR/yr	-increased energy consumption - production loss - capacity loss - plume suppression
Scrubbing	all	< 10	0,015	As in table 4.2.3.	As in table 4.2.3.	- waste generation as in table 4.2.3. - plume reduction

4.3 Economic Performance

The estimated Investment Costs for a 1000 TPD H_2SO_4 sulphuric acid process plant are:

- Double absorption with 11 % SO_2 , 4-bed double contact without Caesium catalyst : 20 to 30 M EUR
- Single absorption with 3 – 6 % SO_2 ,4-bed single contact without Caesium catalyst : 18 to 25 M EUR

Operating cost:

The economical considerations base on a price of sulphuric acid between 30 and 60 EUR / ton H_2SO_4

4.3.1 Additional processes

If process optimizations are not sufficient to reach the SO_2 emission administrative limit, it will be needed to create an additional process.The "Best Available Technique" for it will be mainly depending on the site or company opportunities.

For example : NH_3 scrubbing could be the BAT on a fertilizer site $Ca(OH)_2$ scrubbing could be the BAT if gypsum can be used in plaster or cement industries.Double absorption will be the BAT if no by or co-product can be accepted.

Additional process impacts:

Capital costs: On a basis of a 500 TPD H_2SO_4 production facility, corresponding to an SO_2 reduction of 5 TPD to the atmospher, we can consider the following figures :

Process	**Costs**
Changing Single to Double Absorption (If the existing converter can be used as it is)	4.5 M EUR
H_2O_2 oxydation process	3 M EUR
OH - Scrubbing processes	4 M EUR

These figures could be modified according to the specificities of each facility.

Operating costs:

Typ of costs	**Double absorption**	**H_2O_2**	**OH-Scrubbing**
Fixed costs / year			
Personel	0	1 person	6 persons
Maintenance	135 k EUR	90 k EUR	120 k EUR
Variable costs/ year			
Electricity	130 k EUR	100 k EUR	100 k EUR
Raw materials	- 60 k EUR	540 k EUR	120 k EUR
Co-product disposal	0	0	- 10 k EUR
Total costs / year	**205 k EUR**	**730 k EUR**	**330 k EUR**

SO_2 reduction leads to a cost of 110 to 440 EUR for each ton of SO_2 abated, depreciation excluded.

In conclusion , it appears that double absorption is an interesting way of reduction when :

- . the plant configuration (mainly the converter) and compacity allows the transformation
- . there is no valuable use of any by-product.

According to the process selected , the SO_2 reduction leads to an additional cost per ton of H_2SO_4 produced , including depreciation over 10 years, of :

• Double absorption	3.8 EUR
• H_2O_2 abatement	6 EUR
• OH abatement (as NH_3)	4.4 EUR (for a selling price of the by-product at 0 EUR)

(**Hypothesis :** Estimated price for :

Electricity :	38 EUR/MWH
H_2O_2	610 EUR/T (100%)
OH as NH_3	122 EUR/T)

5. Best Available Techniques

Article 2.11 in Council Directive 96/61/EC concerning integrated pollution prevention and council says:
‘best available techniques’ shall mean 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 an the impact on the environment as whole.

Candidate best available techniques are identified and described in chapter 4.The selection of BAT is made in this chapter, based on the information given in chapter 4 considering achievable emission levels, applicability and cost of the techniques.

The present technical note does not deal in detail with the storage and handling of raw materials (sulphur, pyrites, ore, spent acid, sulphates, etc.) used to produce SO_2.

Part 4 has presented the different sources of SO_2, the techniques of conversion of SO_2 to SO_3 best adapted to each kind of source. These techniques of conversion have their own typical conversion rate and consequently their SO_2 emission concentration expressed in kg SO_2/ ton H_2SO_4 or mg SO_2/Nm^3 or ppm SO_2/ H_2SO_4 (measurements of concentration and flow rate).

The process conditions and the SO_2 concentration in the gas entering the converter determine the conversion efficiencies which directly influences the SO_2 emission concentration (see figure 3.2.1).

The SO_3 and H_2SO_4 content in the tail gases depends on the raw material and process. The content of gaseous SO_3 and H_2SO_4 mist of tail gases is essentially a function of the temperature and concentration of the irrigation acid in the final absorber.

The following BAT's are presented for new plants due to the fact that it is generally not possible to change the source of SO_2 or to change or modify the conversion process. For existing plants, only tail gas scrubbing can be generally considered as a BAT taking into account that addition of a tail gas scrubbing to a double absorption is considered as entailing excessive costs (see 4.3) and could be justified only by severe local considerations.

5.1 BAT for the different types of sulphuric acid processes

5.1.1 Sulphur Burning

Due to the high concentration of SO_2 and stability over time, the BAT proposed is without doubt the double contact process. To get the highest possible conversion efficiency in this process there are two alternatives:

- To select a Caesium-promoted catalysts with a lower working temperature in one or several layers, usually in the last layer. Four layers are normally sufficient. A Cs-promoted catalyst is about three times more expensive than the usual catalyst.
- Alternatively you can increase the catalyst-volume with a cheaper normal catalyst in four layers.The better method is to add a fifth layer.

In both alternatives a conversion efficiency of 99.6 % (daily average except start-up and shut down conditions) could be achieved in new plants.

5.1.2 Metal Sulphide Roasting/Smelting

5.1.2.1 Pyrite Roasting:

Although the stability over time is slightly variable, the BAT should be the double contact process with a conversion efficiency of about 99,5 to 99,6 depending on the quality of the pyrite (daily average excluding start up and shut-down conditions): To get the highest possible conversion efficiency one has the same two options as for sulphur burning (see 5.1.)

5.1.2.2 Zinc Roasting :

As the range of SO_2-content after possible dilution is about 6 to 13% and the variability over time is low, the double contact process can be used as a BAT with a conversion efficiency of about 99,6% (daily average except start-up and shut-down conditions) when using gases with SO_2 content >8%.

5.1.2.3 Copper Smelting:

When the SO_2 content in gases is high (6 - 13% after possible dilution) and the variability over time is low, the double contact process can be considered as BAT with a conversion efficiency of about 99,6% (daily average except start-up and shutdown conditions).

When the SO_2 content in gases is low (1 - 6%) and the variability over time is high, the single contact process can be considered as BAT with a conversion efficiency of about 98,5% (daily average except start-up and shut-down conditions).

When the SO_2 content is 5 - 10% and the variability over time is high, the double contact process can be considered as BAT with a conversion efficiency of about 99,5% (daily average except start-up and shut-down conditions).

When a plant experiences the full range of variability, the efficiency will vary between 98 and 99,5%. Similar circumstances will permit an achievable SO_2 level, in terms of converter throughput based on 100% H_2SO_4 acid of between 3 - 6 kg SO_2/ t H_2SO_4 due to fluctuating absorption conditions.

Off-Gas Specific Process Composition :
The key to a correct purification of metallurgical gases lies in continuous, stable operation of the purification process, normally in an acid plant. The gas flows, which are susceptible to wide fluctuations in volume and concentration, are to some degree incompatible with this criterion. Fluctuations can be minimised by carrying out the conversion process in various converters, or by mixing the gases with the more concentrated flow coming from the smelting stage. This produces gas flows with a concentration range that is adequate to maintain the autothermal process. This is the procedure followed in modern copper smelters that use Outokumpu flash smelting furnaces and Pierce Smith converters.

5.1.2.4 Lead Smelting:

In the case of sintering lead ores, the variability is relatively high and SO_2 content can be very low, the single contact process but also the wet Process and the process based on NO_x can be considered as BAT with a conversion efficiency of about 98.5, 98 and 100% respectively. This low or variable SO_2 – content is due to a down-draught sintering which limit SO_2 emissions. In other cases (lead smelters), the SO_2 can be much higher and less variable over time. In this case the double contact process can be considered as a BAT with a conversion efficiency of about 99,5% (daily average except start-up and shutdown conditions).

It has not been possible to arrive at precise limits for the chosen BAT. Apart from costs, conversions and theoretical considerations, also local regulations will have to be taken into account to decide the right BAT. The Technical note on BAT on heavy metals covers this point and it is recommended that this document should be consulted on this issue.

5.1.3 Sulphuric Acid Regeneration

The ratio O_2/SO_2 is important to get a conversion rate of SO_2 to SO_3 as high as possible. Upsteam the converter the gases are reheated to the ignition temperature through Gas/gas heat exchangers with the conversion heat. A double absorption process can be used only if the SO_2 content of the gases is high enough (about 8%) at the converter inlet. The conversion rates for different SO_2-concentrations are seen below :

Single absorption

SO_2 content at the converter inlet **8% with O_2/SO_2 ratio of 1.1 : 98 %**
SO_2 content at the converter inlet from **5 to 8% with O_2/SO_2 ratio of 1.1 : 97 to 98%**
SO_2 content at the converter inlet below **5% with O_2/SO_2 ratio of 1.1 : 96 to 97%**

Double absorption
When achievable , leads to conversion rates from **99 to 99.6%**

For new plants, the double absorption is considered as the BAT. For existing plants,a single absorption can be advantageously combined with an ammonia scrubber, the by product obtained being either sold on the market or recycled in the furnace.

5.1.4 Metal Sulphate Roasting

The conclusions are exactly the same as those for sulphuric acid regeneration.

5.1.5 Combustion of H_2S and Other S-Containing Gases

The conclusions are the same as those for sulphuric acid regeneration.

5.2 BAT for contact processes

5.2.1 In respect of SO_2 emissions

Figure 5.2.1 BAT limits for SO_2 emissions dependent from process type and absorption type

process type for manufacturing sulphuric acid	range for SO_2 conc. Vol. % SO_2	single absorption kg SO_2 / t H_2SO_4	double absorption * kg SO_2 / t H_2SO_4	double absorption + Bed 5 or Bed 4 Caesium* kg SO_2 / t H_2SO_4	single absorption + tailgas scrubbing with usage byprod. kg SO_2 / t H_2SO_4
sulphur burning	6-12	6,7 - 13,3	1,5 - 3.9	1,0 - 2,6	<2
pyrite roasting	8-10		2,6 - 3,9	1,5 - 3	<2
zinc/lead ores roasting	4 - 9	7-12	1,7 - 3,3	1,5 - 2,5	<2
		(4 - 6 % SO_2)	(6 - 12 % SO_2)		
copper smelting	3 - 13	6,5 - 20	1,2 - 3,3	1,2 - 2,5	<2
lead/copper smelting	2,7	6 - 10			<2
organic spent acid regeneration	2 - 10	10 - 27	2,6 - 6,6	1,5 - 4,5	<2
metal sulphate roasting	8 - 12		1,6 - 3,3	1,3 - 2,6	-

- Not achievable for low SO_2 Gas content

5.2.2 In respect of H_2SO_4 emissions

Figure 5.2.2 BAT limits for H_2SO_4 emissions dependent from process type and absorption type

process type for manufacturing sulphuric acid	range for SO_2 conc.	single absorption	double absorption	double absorption + Bed 5 or Bed 4 cesium	single absorption + tailgas scrubbing with usage byprod.
	Vol. % SO_2	kg H_2SO_4* / t H_2SO_4	kg H_2SO_4* / t H_2SO_4	kg H_2SO_4* / t H_2SO_4	kg H_2SO_4* / t H_2SO_4
sulphur burning	6 - 12	< 0,1	< 0,1	< 0,1	< 0,1
pyrite roasting	8 - 10	0,2	0,2		
zinc/lead ores roasting	4 - 9	0,15 - 0,3	0,1 - 0,16		
		(4 - 6 %SO2)	(6 - 12 %SO2)		
copper smeltting	3 - 13	0,06 - 0,35	0,05 - 0,2		
lead/ copper smeltting	2,7	0,15			
organic spent acid regeneration	2 - 10	0,05 - 0,2	0,05 - 0,2		0,01 - 0,03
metal sulphate roasting	8 - 12		0,065 - 0,13	0,065 - 0,13	

*) $H_2SO_4 = SO_3 + H_2SO_4$

5.2.3 In respect of energy output

Figure 5.2.3 BAT limits for energy outputs dependent from process type and absorption type [16]

process type for manufacturing sulphuric acid	range for SO_2 conc.	single absorption	double absorption
	Vol. % SO_2	MJ / t H_2SO_4	MJ / t H_2SO_4
sulphur burning	6 - 12		2500
pyrite roasting	8 - 10		4500
zinc/ lead ores roasting	4 - 9		600
		(4 - 6 %SO_2)	(6 - 12 %SO_2)
copper smelting	3 - 13	2000 - 2900	2000 - 2900
lead /copper smelting	2,7	900	
organic spent acid regeneration	2 - 10	2500	2500

5.2.4 The role of scrubbing and tail gas processes

Tail gas scrubbing produces sulphites and sulphates, which possibly entail problems of reasonable disposal of wastes. They are applicable if par example Sodium bisulphite, Ammonium sulphate or gypsum are produced as marketable by products near the sulphuric acid plant.

5.2.5 energy consideration on plants with double and single absorption

The energy considerations are carried out with the different SO_2-concentrations 5% and 11% Vol. and for single / double absorption process . The starting inlet gas is dry SO_2-Gas from 20° C .The end product is sulphuric acid from 98,0 % and 25°C. The energy (+ supply,- removal) values are given as MJ / t H_2SO_4 100%. The temperature point in the region of 180°C is the gas dewpoint .In newer techniques is energy recoverable until to 120°C.

- Five cases are calculated:11 % SO_2 Double contact (3 + 2)
- 11 % SO_2 Double contact (2 + 2 + heat recovery system)
- 11 % SO_2 Double contact (2 + 2)
- 5 % SO_2 Double contact (2 + 2)
- 5 % SO_2 Single contact (4 beds)

Table 5.2.5 Energy considerations on plants with double absorption

11% SO_2 Double contact (3+2)	**theoret. conv.%**	**MJ / t H_2SO_4**	**Energy status**	**Energy Level**
Gasinlet 80°C --> 430°C		972	recovering	Heat exchanger
Bed 1 430°C-> 582->430°C	48,80	-462	recovering	heat exchanger
Bed 2 430°C-> 520->430°C	77,60	-273	recovering	Heat exchanger
Bed 3 430°C->478°C->180°C	92,84	-871	recovering	Heat exchanger
Interabsorption 180°C->80°C		-1353	lost	Cooling with water/air
After interabsorption 80°C -> 430°C		799	recovering	Heat exchanger
Bed 4 430°C->457->430°C	99,61	-64	recovering	Heat exchanger
Bed 5 430°C->431°C->180°C	99,78	-578	recovering	Heat exchanger
End absorption 180°C->80°C		-443	lost	Cooling with water/air
Sulphuric acid 25°C 98%		-97	lost	Cooling with water
		-477	recovering	
		-1893	lost	Cooling with water

11% SO_2 Double contact (2+2 + Heat recovery system)				
Gasinlet 80°C --> 430°C		972	recovering	Heat exchanger
Bed 1 430°C-> 582°C ->430°C	48,80	-462	recovering	Heat exchanger
Bed 2 430°C-> 520°C ->180°C	77,60	-998	recovering	Heat exchanger
Interabsorption 180°C		-659	recovering	Heat exchanger
After interabsorption 180°C->430°C		598	recovering	Heat exchanger
Bed 3 430°C->457°C ->430°C	99,61	-192	recovering	Heat exchanger
Bed 4 430°C->436°C ->180°C	99,78	-617	recovering	Heat exchanger
End absorption 180°C->80°C		-883	lost	Cooling with water/air
Outlet sulphuric acid 25°C / 98%		-112	lost	Cooling with water
		-1357	recovering	
		-995	lost	Cooling with water

11% SO_2 Double contact (2 + 2)				
Gasinlet 80°C --> 430°C		972	recovering	Heat exchanger
Bed 1 430°C-> 582°C ->430°C	48,80	-462	recovering	Heat exchanger
Bed 2 430°C-> 520°C ->180°C	77,60	-998	recovering	Heat exchanger
Interabsorption 180°C -> 80°C		-1167	loss	Cooling water/air
After interabsorption 80°C->430°C		830	recovering	Heat exchanger
Bed 3 430°C->457°C ->430°C	99,61	-192	recovering	heat exchanger
Bed 4 430°C->436°C ->180°C	99,78	-617	recovering	heat exchanger
End absorption 180°C->80°C		-623	lost	cooling with water/air
Outlet sulphuric acid 25°C / 98%		-103	lost	cooling with water
		-465	recovering	
		-1893	lost	cooling with water

5% SO_2 Double contact (2 + 2)	**theoret. conv.%**	**MJ / t H_2SO_4**	**Energy status**	**Energy level**
Gasinlet 80°C --> 430°C		946	recovering	heat exchanger
bed 1 430°C-> 538°C ->430°C	72,91	-315	recovering	heat exchanger
bed 2 430°C-> 461°C ->180°C	93,52	-789	recovering	heat exchanger
Interabsorption 180°C -> 80°C		-718	loss	cooling water/air
after interabsorption 80°C->430°C		875	recovering	heat exchanger
bed 3 430°C->441°C ->430°C	99,85	-27	recovering	heat exchanger
bed 4 430°C->430°C ->180°C	99,88	-631	recovering	heat exchanger
end absorption 180°C->80°C		-347	lost	cooling with water/air
Outlet sulphuric acid 25°C / 98%		-43	lost	cooling with water
		60	recovering	
		-1108	lost	cooling with water

5% SO2 Single contact (4 bed)				
Gasinlet 80°C --> 430°C		946	recovering	heat exchanger
bed 1 430°C-> 538°C ->430°C	72,91	-315	recovering	heat exchanger
bed 2 430°C-> 461°C ->430°C	93,52	-89	recovering	heat exchanger
bed 3 430°C->437°C ->430°C	98,24	-20	recovering	heat exchanger
bed 4 430°C->431°C ->180°C	98,88	-703	recovering	heat exchanger
end absorption 180°C->80°C		-347	lost	cooling with water/air
Outlet sulphuric acid 25°C / 98%		-43	lost	cooling with water
		-180	recovering	
		-390	lost	cooling with water

1KWh = 3,6*MJ

5.2.6 Effect of the emission / consumption level

The production and consumption of sulphuric acid is influenced through the following arguments:

1. Costs of sulphuric acids
2. Costs of transport
3. Quality of the different acids – the reason of consumption
4. safety by transport , storage and emissions
5. The environmental regulation at the location of production
6. The future development of regeneration of spent acids.

A flowsheet for sulphuric acid production, consumption and remain should clear the different influences:

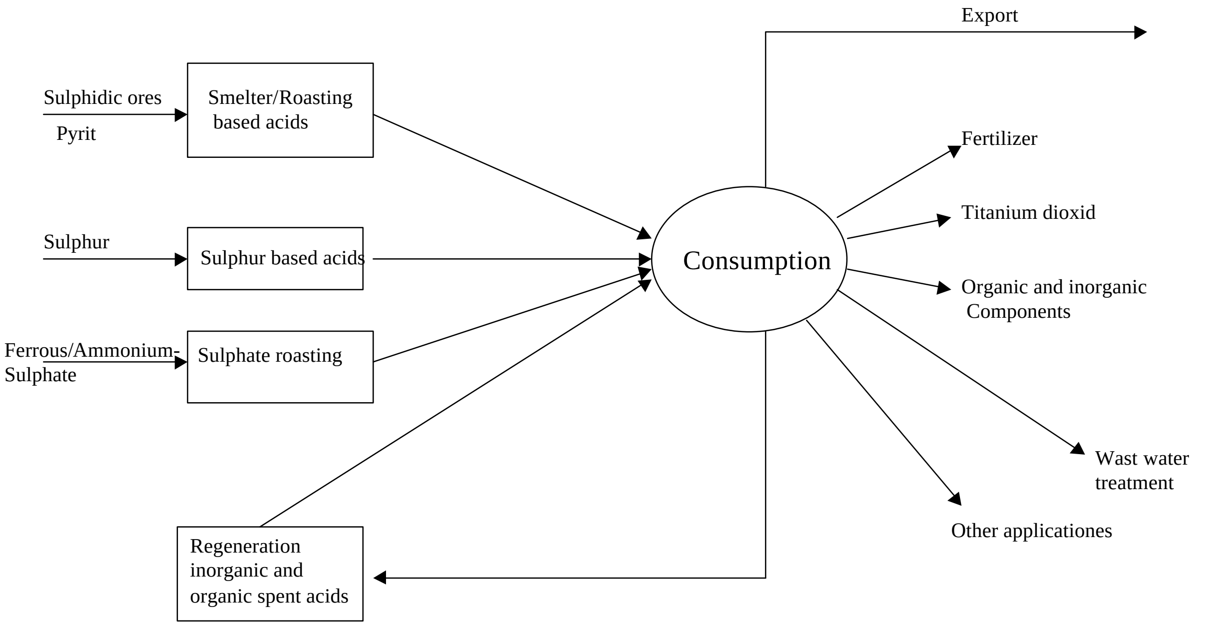


Table 7.1 Pattern of european sulphuric acid production and remain

5.3 Cross Media Impact

SO_2 emissions minimization to the atmosphere can lead to different impacts, depending on the route of reduction.

The metal sulphide sector will emphasis that sulphuric acid production is not the prime objective of the process, which remains the production of non-ferrous metal. Sulphuric acid production is stemmimg from the necessity to reduce of SO_2 emision.

5.3.1 Tail gas Scrubbing

Tail gas scrubbing transfers the SO_2 from tail gases to a by-product which can be in liquid solution or solid. Disposal of this by-product on the soil or in water (sea/river) can be considered as a pollution transfer. A conclusion can be that this kind of technique must be associated with a recycling or usage of the by-product on site or on a customer site with a certain perennity.

5.3.2 Caesium catalyst

Usage of large amounts of Caesium catalyst will have an impact on Caesium production and disposal in spent catalyst.

5.3.3 Electricity

About all the processes for SO_2 reduction lead to an increase in electricity consumption, mainly due to pressure drop increase. This point impacts the needed electricity generation and can have some consequencies on CO_2, SO_2, dust emissions from electricity power stations.

5.3.4 Cooling water effect to the atmosphere

On a sulphuric acid plant ,the most part of the conversion energy is recovered as steam, but absorption energy needs to be disposed of, totaly or partialy, and generaly with cooling water. Cooling water system can be open when large amounts of water are available, or through an atmospheric cooling tower. In both cases, the recovered energy is transformed to water evaporation to the atmosphere.

6. Emerging Techniques

Sulphuric acid had been produced for many years and is the biggest handled chemical produced in the world. Most of developements was done in the last 100 years. Proven techniques give only little room for improvements .Sulphuric acid production is a mature industry ; hence there are little room for further improvement in the process itself. It was pointed out, however, that there were some developments in the material used in the construction of the plants or their design, like double shell. These are mainly designed to reduce accidental pollution.

Other developements was in the following fields:

- Energy recovery from primer energy
- Product quality in view of content of NOx and SO_2 can cause emission problems by the customer, so NOx have to be destroyed and SO_2 stripped with air,
- Demisters with very high efficiency.

Now it is more a question of optimising sections in the different process stages depending on site requirement and local conditions.

7. Conclusions and Recommendations

7.1 Conclusions

Today two main different families of Sulphuric Acid production plants can be considered :

- Plants built before 1970
- Plants built after 1970

The first family has been designed on a Single Absorption process basis, with associated conversion rates in the range of 96 to 98.5 %. The second family is operating on the Double Absorption process, with conversion rates in the range of 99 to 99.7%. In these 2 families it has been noticed that large differences exist, mainly depending on the upstream process generating the SO_2 containing gases:
Some processes generate $S0_2$ rich and non variable gases (Sulphur burning for exemple) leading to the highest conversion rates. Some others generate SO_2-poor and/or -variable gases with corresponding lowest conversion rates (spent acids regeneration for example).It is in certain cases impossible to achieve a Double Absorption process.

For the metalurgical acid plants, the conversion efficiency depends on the fluctuations of the SO_2 concentration at the inlet of the plant.

The situation in Western Europe after 1990 is demonstrated in the following tables 7.1 and 7.2 .

Table 7.1.1 : List of plants built after 1990 in Western Europe :

Location	Process type	Costs	Company	Capacity t H_2SO_4 /day	Year of start up	Emission level	Ref.
			Rhone-Poulenc				*)
Hamburg, Ge	Cu Smelter acid (5 - 8,4 % SO_2)	5.bed : 1 M EUR	Norddeutsche Affinerie	918 t/d	1991	< 800 mg SO_2 / Nm^3	[25]
Helsingborg, Sw	Sulphur burning 17,5 % SO_2 H_2O_2 scrubbing tower,5. Bed,	36 M EUR	Kemira Kemi	1.000 t/d	1992	< 0,9 kg SO_2 / t H_2SO_4	[26]
Harjavalta, Fi	Copper and nickel based smelter acid 7-12% SO_2	33 M EUR	Outokumpu extension	2430 t /d H2SO4	1995	< 4500 t SO_2 /y	[27]
Tessenderlo, Be	Sulphur burner, 11,5% SO_2, heat recovery system		Tessenderlo Chemie	1000 t/d	1992	300 ppm SO_2	[28]
Leuna, Ge	Sulphur burner 5. bed		Domo		1996	99,9 % conversion rate	[29]
Huelva Spain	Cu Smelter acid (5 – 10.2 % SO_2)	39 M EUR	Atlantic Copper	1270 t/d	1996	>99.6 %	
Ludwigshafen Ge	Sulphur burner,		BASF	900 t/d		0,65 kg SO_2/ t H_2SO_4	
Le Havre	Sulphur burner, double absorption 11,5 % SO_2		Milllennium	800 t/d	1992	2,6 kg SO_2 /t H_2SO_4	
Huelva			Fertiberia	2400 t/d	2000		
Worms,Ge	Spent acid regeneration; H_2SO_4/ NH_4SO_4	53 M Euro	Rhöm GmbH	500 t/d	1994		[30]

***)Practice from a large producer:** Only for Rhone-Poulenc group in Europa, during the last 10 years; 5 plants representating a production capacity about 3600 TPD have been transformed or are going to be transformed to achieve the equivalent of Double Absorption process: 2 of them from SA to DA, 3 of them with additional SO_2 abatement.

Table 7.1.2 : Project List of “new” plants in Western Europe :

Location	Company	Capacity	Year of start up	Ref.
Aviles,Sp	Asturiana de Zinc S.A.	n.a	1998	[31]
Sweden	Boliden	910 t/d	2000	
Porto Maghera,It	Enichem	540 t/d	n.a.	
Sardinia,It	Sarlux	339 t/d	n.a.	
Budel	Budelco	1185 t/d	n.a.	

Innovative techniques with environmental performance better than the listed techniques are not possible :

- practically is with a conversion rate from 99,9 % the Zero – Emission level reached,
- maximum recovery of energy is technically possible .

Sulphuric acid is one of the oldest industrial chemicals. As an industry we have under a long period made a lot of improvements concerning emissions and energy recovery.Today all sulphuric acid industries in Western Europe have taken a big responsibility to cut sulphur emissions down to a very low level. In order to improve the environment it is better to invest money to prevent the” Green House” effect for example. Producing energy from sulphur there is no carbon dioxide.

All new plants with stable **and high** sulphur dioxide concentrations (> 6 %), are built with the double contact process and with high energy standard. Most of the old plants are improved to a good conversion rate and a high energy standard.

Depending on these facts our conclusion for gases with 6 – 12 % is a double absorption process with an average conversion rate of at least 99,6 %.On the other side for poor gases or fluctuating gases were a double absorption process is not feasible for practical an theoritical reasons, a single absorption process can be further on considered as BAT.In this case and with optimal design a conversion rate of 99% can be achieved.

7.2 Recommendations

On these basis of chapter 7.1, our recommendations are the followings :

1. **For new plants**, Double Absorption process has to be considered as the BAT, when achievable. Average conversion rate corresponding to this technique is at least 99.6% for non variable and rich gases (more than 6 %). It is possible to improve this conversion rate by 0.2% when using Caesium catalyst. But this quite new catalyst is very expensive (3 to 4 times the normal one) and can be used when local constraints are very severe.

2. **For plants operating on a Single Absorption process**, different ways can be considered: -

- Caesium catalyst in the last bed (conversion at least 99 %)
- Transforming Single to Double Absorption process
- SO_2 abatement by scrubbing with neutralizing compound
- SO_2 abatement with Hydrogen peroxide H_2O_2,

and the BAT will depend on: -

- Site location and opportunities
- Technical possibilities
- Environmental considerations
- Economical criteria

When achievable on a technical basis, transformation to Double Absorption process can be considered as the BAT. When Single to Double Absorption is not possible or when there is a possible enhanced value for the by-product resulting from the scrubbing (ammonium, sodium magnesium, calcium .... Salts solutions), can be considered as the BAT for old and new plants.
To further limit emiision, depending on local legislations, environmental considerations and economical data, tail gas scrubbing can be a solution. In this case, it has also to be taken into account the possible enhanced value for by-products, so in specific cases only single absorption can be considered as BAT.

For tail gas processes with lower sulphur dioxide content or fluctuating concentration it is always a matter of process and there it must be decided for each plant. Depending from local conditions the recommendation are tail gas treatments with ammonia or calcmilk or sodiumhydroxide as described.This level is normally reached by double contact and double absorption, but this must always be decided at the plant, depending on that all sites have different possibilities due to local conditions.

3**. For plants where Double Absorption is not achievable** because of the gas quality and where there is no possible use of a neutralization by-product , processes able to operate on very poor gases have to be considered for the BAT, with the condition of recycling the by-product (usualy sulphuric acid more or less diluted) in the plant. These processes can be: -

- Abatement by scrubbing with H_2O_2
- Activated carbon process

In conclusion to SO_2 emissions minimization from Sulphuric Acid plants, we can recommend to take in account for the BAT, for old as for new plants :

- site opportunities
- the process generating SO_2.

For SO_3 and H_2SO_4 mists emissions , the progresses made during the last years in designing the absorbing towers, and the high efficiency demisting systems allow to consider these emissions are possible to keep at very low levels, as low as 50 mg/Nm3. This could be the BAT .

8. Annexes

ANNEX 1: Literature

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ANNEX 2: Glossary

ADR:	Accord européen realtif au transport international des marchandises Dangereuses par Route
RID:	Règlement concernant le transport International ferroviaire des marchandises Dangereuses
DA:	Double absorption
ESP:	Electro static precipitator
EUR:	Euro
IMO:	International Maritime Organisation
IR:	Infrared
ISF:	Imperial Smelting Furnace (blast furnace for Zn-Pb concentrates)
k EUR:	Thousand of Euro
M EUR:	Million of Euro
MWH:	Megawatt hour
ppm:	Part per million
ppmv:	Part per million in volume
PCS:	Process control system
SA:	Single absorption
TPD:	Ton per day
UV:	Ultraviolet
WCP:	Wet contact process

ANNEX 3: Inputs and Outputs

3.1.1 Sulphur burning plants with Single Absorption

Inputs	Amount	Unit	Comments	
. SO2	6 – 12	%	degree of variability	Low
. O2	9 – 15	%	degree of variability	Low
. CO2	0	%	degree of variability	No
. Water (in the gas)	10	mg/Nm^3		

Outputs	Amount	Unit	Comments
Energy	2500	MJ	net balance
Emissions to air			
. SO_2 *	6,7 – 13,3	Kg/t ***	
SO3 *	0,03	Kg/t ***	
. $H2SO_4$ *	0,03	Kg/t ***	
. NOx **	< 30	mg/Nm^3	
. CO_2	0	%(vol)	
Emissions to water	0		no emission to water
Solid emisions	10	g/t	spent catalyst
Conversion rate	98 – 99	%	
Emission with the final product			
. As	< 0,01	ppm	
. Hg	< 0,01	ppm	
. Se	< 0,01	ppm	
. F	< 0,01	ppm	
. SO2	< 30	ppm	
. NOx	< 30	ppm	
. HCl	< 1	ppm	
. organic carbon	< 1	ppm	

* : expressed in SO2
** : expressed in NO2
*** : in Kg per tonne of sulphuric acid 100%

3.1.2 Sulphur burning plants with Double Absorption

Inputs	Amount	Unit	Comments	
. SO_2	6 – 12	%	degree of variability	Low
. O_2	9 – 15	%	degree of variability	Low
. CO_2	0	%	degree of variability	No
. Water (in the gas)	10	mg/Nm^3		

Outputs		Amount	Unit	Comments
Energy		2500	MJ	net balance
Emissions to air				
. SO_2	*	1.5 – 3.9	Kg/t ****	
. SO_3	**	0,1	Kg/t ****	
. H_2SO_4	**	0,1	Kg/t ****	
. NOx	***	< 30	mg/Nm^3	
. CO_2		0	%(vol)	
Emissions to water		0		no emission to water
Solid emisions		10	g/t	spent catalyst
Conversion rate		99,2 – 99,6	%	
Emission with the final product *****				
. As		< 0,01	ppm	
. Hg		< 0,01	ppm	
. Se		< 0,01	ppm	
. F		< 0,01	ppm	
. SO2		< 30	ppm	
. NOx		< 30	ppm	
. HCl		< 1	ppm	
. organic carbon		< 1	ppm	

* : expressed in SO2
** : expressed in H2SO2
*** : expressed in NO2
**** : in Kg per tonne of sulphuric acid 100%
**** : those values may not be met with certain raw material

3.2 Pyrite roasting

	Amount	Unit	Comments
INPUTS			
SO_2	8 - 10	%	
O_2	8 - 11	%	
CO_2	0	%	
H_2O	0	%	
degree of variability			slightly over time
OUTPUTS			
Energy	~4500	MJ/t ***	net balance incl. roasting process
Emission to air			
SO_2*	3,0	Kg/t ***	
SO_3*	0,2	Kg/t ***	
H_2SO_4*	n.a.	Kg/t ***	
NO_X**	~210	mg/Nm3	
CO_2	0	%(vol)	
Emission to water			no emission to water
Solid emissions	~40	g/t ***	spent catalyst
Conversion rate	99,4-99,6	%	
Emission with the final product			dependent of the analyses of the pyrite
As	0,01	ppm	The figures are examples from one
Hg	0,03	ppm	specific pyrite, see 2.1.2.1.
Se	0,05	ppm	.
F	n.a.	ppm	
SO_2	13	ppm	
NO_X	n.a.	ppm	
HCl	n.a.	ppm	
Organic carbon	0	ppm	

* : expressed in SO_2

** : expressed in NO_2

*** : per tonne of sulfuric acid 100%

3.3 Zn , Pb smelter Sulphuric acid plants (..... ZnS-roasting)

		single Abs.		double Abs.	
Input					
	% SO_2	4 ~ 6		5 ~ 9	
	% O_2	6 ~12		6 ~11	
	% CO_2	x		X	
	% H_2O	x		X	
	variability in time	low		Low	
	Energy (1kWh = 3,6 MJ) MJ/t.H_2SO_4			~ 600	
Output	Air emission at stack	kg/t H_2SO_4	mgNO_x/ Nm³	kg/t H_2SO_4	mgNO_x/ Nm³
	SO_2	7 ~12	x	1,7 ~3,3	x
	SO_3	0,1~ 0,2	x	0,05 ~0,08	x
	NO_X		150		150
	H_2SO_4	0,05 ~0,1	x	0,05 ~0,08	x
	Conversion SO_2/SO_3	98 ~99 %		99,5 ~ 99,7%	
	H_2O emission	no contaminants		no contaminants	
	Spent Catalyst	20 ~ 40 g/t.H_2SO_4 to recycle in process		20 ~ 40 g/t.H_2SO_4 to recycle in process	
	H_2SO_4				
	Hg	max 1 ppm			
	As	max 0,5 ppm			
	Se	max 0,2 ppm			
	SO_2	< 50 ppm			
	NO_2	5 ~30 ppm			
	Org C	max 1 ppm			
	Energy steam in Roasting Proces MJ/t.H_2SO_4	3500			
	(waste)heat in acid production : MJ/t.H_2SO_4	1000 ~ 2000			
	Net Balance (In-Out)	3900 ~4900			

3.4 “ Complex (Pb , Cu) S batch – treatment “

Input		single Abs.		double Abs.	
	% SO_2	2,70%	on dry		
	% O_2	2,50%	on dry		
	% CO_2	20,00%	on dry		
	% H_2O	45%			
	variability in time	extremely,			
	Energy (1kWh = 3,6 MJ) MJ/t.H_2SO_4	900			
Output	Air emission at stack	kg/t H_2SO_4	mgNO_2/ Nm³	kg/t H_2SO_4	mgNO_2/ Nm³
	SO_2	6 ~10			x
	SO_3	see H_2SO_4			x
	NO_2		100		
	H_2SO_4	0,15			x
	Conversion SO_2/SO_3	99,0 - 99,2 %			
	H_2O emission	none			
	Spent Catalyst	20 ~ 40 g/t.H_2SO_4			
	H_2SO_4				
	Hg	<1 ppm			
	As	<0,2 ppm			
	Se	<0,5 ppm			
	SO_2	90 ppm			
	NO_2	150 ppm			
	Org C	40 ppm			
	Energy steam in Production Proces MJ/t.H_2SO_4	depending on S-content			
	(waste)heat in acid production : MJ / t.H_2SO_4	1000 ~ 2000			
	Net Balance (In-Out)	~1000-2000			

3.5 Copper smelter Sulphuric Acid Plant

Inputs	Unit	Double Absorption	Single Absorption	**Comments**
. SO_2	%	5-13	3-10	degree of variability: High
. O_2	%	8-16	11-18	degree of variability: High
. CO_2	%	0-3	0-3	degree of variability: High
. Water (in the gas)	% (vol)	5-7	5-7	
Process water	m³/t	0-0.2	0-0.2	

Outputs	Unit			Comments
Energy	MJ	2000 -2900	2000 -2900	net balance
Emissions to air				
. SO_2 *	Kg/t ***	1.2 - 3.3	6.5 - 20	
. SO_3 * + H_2SO_4*	Kg/t ***	0.05 - 0.2	0.06 - 0.35	
. H_2SO_4 *	Kg/t ***			
. NOx **	mg/Nm³			Variability : High, depending of smelter O_2 enrichment
. CO_2	%(vol)	0 - 4	0 - 4	
Emissions to water				no emission to water
Solid emisions				
spent catalyst	g/t	20 - 40	20 - 40	5-10% of the installed catalyst and per screening operation
Conversion rate	%	99.5 - 99.8	97- 99	
Emission with the final product				
. As	ppm	< 1	Similar to double absorption	
. Hg	ppm	< 1	"	
. Se	ppm	<0.5	"	
. F	ppm	0 - 2	"	
. SO_2	ppm	<30	"	
. NOx	ppm	<40	"	Variability : High, depending of smelter O2 enrichment
. HCl	ppm	<5	"	
. organic carbon	ppm	traces	"	Influenced by the smelter fuel combustion burner type (<50)

* : expressed in SO_2
** : expressed in NO_2
*** : in Kg per tonne of sulphuric acid 100%

3.6 Spent acid regeneration

Inputs	Amount	Unit	Comments
. SO_2	7	%	degree of variability 2 –10 %
. O_2	8	%	degree of variability 5 – 15%
. CO_2	5	%	degree of variability 1 – 10%
. Water (in the gas)	10	mg / Nm³	

Outputs	Amount	Unit	Comments
Energy	2500	MJ	net balance
Emissions to air			
. SO_2 *	2,6 to 2,7	Kg/t ***	DA : 2,6 to 6,6 SA : 10 to 27
. SO_3 *	0,03	Kg/t ***	
. H_2SO_4 *	0,03	Kg/t ***	
. NOx **	0 to 50	mg/Nm³	
. CO_2	4	%(vol)	
Emissions to water	0		no emission to water
Solid emisions	0	g/t	spent catalyst
Conversion rate	96 to 99,6	%	DA : 99 to 99,5 SA : 96 to 98,5
Emission with the final product			
. As	< 0,01	Ppm	
. Hg	< 0,01	Ppm	
. Se	< 0,01	Ppm	
. F	< 0,01	Ppm	
. SO_2	< 30	Ppm	
. NOx	< 30	Ppm	Depends on the spent acid type
. HCl	< 1	Ppm	
. organic carbon	< 1	Ppm	

* : expressed in SO_2
** : expressed in NO_2
*** : in Kg per tonne of sulphuric acid 100%

ND : not determined

3.7 Scheme energy output from a sulphur burner double absorption plant (Bayer)

The plant has a capacity of 625 tons sulphuric acid 100% per day. The inlet SO_2 concentration bed 1 is 10,5 %.