



EUROPEAN COMMISSION

Integrated Pollution Prevention and Control (IPPC)
Reference Document on Best Available Techniques in the
Cement and Lime Manufacturing Industries

December 2001

EXECUTIVE SUMMARY

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

This BREF document has two parts, one for the cement industry and one for the lime industry, which each have 7 chapters according to the general outline.

Cement industry

Cement is a basic material for building and civil engineering construction. Output from the cement industry is directly related to the state of the construction business in general and therefore tracks the overall economic situation closely. The production of cement in the European Union stood at 172 million tonnes in 1995, equivalent to about 12% of world production.

After mining, grinding and homogenisation of raw materials; the first step in cement manufacture is calcination of calcium carbonate followed by burning the resulting calcium oxide together with silica, alumina, and ferrous oxide at high temperatures to form clinker. The clinker is then ground or milled together with gypsum and other constituents to produce cement.

Naturally occurring calcareous deposits such as limestone, marl or chalk provide the source for calcium carbonate. Silica, iron oxide and alumina are found in various ores and minerals, such as sand, shale, clay and iron ore. Power station ash, blast furnace slag, and other process residues can also be used as partial replacements for the natural raw materials.

To produce 1 tonne of clinker the typical average consumption of raw materials in the EU is 1.57 tonnes. Most of the balance is lost from the process as carbon dioxide emission to air in the calcination reaction ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$).

The cement industry is an energy intensive industry with energy typically accounting for 30-40% of production costs (i.e. excluding capital costs). Various fuels can be used to provide the heat required for the process. In 1995 the most commonly used fuels were petcoke (39%) and coal (36%) followed by different types of waste (10%), fuel oil (7%), lignite (6%) and gas (2%).

In 1995 there were 252 installations producing cement clinker and finished cement in the European Union and a total of 437 kilns, but not all of them in operation. In addition there were a further 68 grinding plants (mills) without kilns. In recent years typical kiln size has come to be around 3000 tonnes clinker/day.

The clinker burning takes place in a rotary kiln which can be part of a wet or dry long kiln system, a semi-wet or semi-dry grate preheater (Lepol) kiln system, a dry suspension preheater kiln system or a preheater/precalciner kiln system. The best available technique⁽¹⁾ for the production of cement clinker is considered to be a dry process kiln with multi-stage suspension preheating and precalcination. The associated BAT heat balance value is 3000 MJ/tonne clinker.

¹ See chapter 1.5 for qualifications about applicability and feasibility.

At present, about 78% of Europe's cement production is from dry process kilns, a further 16% of production is accounted for by semi-dry and semi-wet process kilns, with the remainder of European production, about 6%, coming from wet process kilns. The wet process kilns operating in Europe are generally expected to be converted to dry process kiln systems when renewed, as are semi-dry and semi-wet processes kiln systems.

The clinker burning is the most important part of the process in terms of the key environmental issues for the manufacture of cement; energy use and emissions to air. The key environmental emissions are nitrogen oxides (NO_x), sulphur dioxide (SO₂) and dust. Whilst dust abatement has been widely applied for more than 50 years and SO₂ abatement is a plant specific issue, the abatement of NO_x is a relatively new issue for the cement industry.

Many cement plants have adopted general primary measures, such as process control optimisation, use of modern, gravimetric solid fuel feed systems, optimised cooler connections and use of power management systems. These measures are usually taken to improve clinker quality and lower production costs but they also reduce the energy use and air emissions.

The best available techniques⁽¹⁾ for reducing NO_x emissions are a combination of general primary measures, primary measures to control NO_x emissions, staged combustion and selective non-catalytic reduction (SNCR). The BAT emission level⁽²⁾ associated with the use of these techniques is 200-500 mg NO_x/m³ (as NO₂). This emission level could be seen in context of the current reported emission range of <200-3000 mg NO_x/m³, and that the majority of kilns in the European Union is said to be able to achieve less than 1200 mg/m³ with primary measures.

Whilst there was support for the above concluded BAT to control NO_x emissions, there was an opposing view⁽³⁾ within the TWG that the BAT emission level associated with the use of these techniques is 500-800 mg NO_x/m³ (as NO₂). There was also a view⁽³⁾ that selective catalytic reduction (SCR) is BAT with an associated emission level of 100-200 mg NO_x/m³ (as NO₂).

The best available techniques⁽¹⁾ for reducing SO₂ emissions are a combination of general primary measures and absorbent addition for initial emission levels not higher than about 1200 mg SO₂/m³ and a wet or dry scrubber for initial emission levels higher than about 1200 mg SO₂/m³. The BAT emission level⁽²⁾ associated with these techniques is 200-400 mg SO₂/m³. SO₂ emissions from cement plants are primarily determined by the content of the volatile sulphur in the raw materials. Kilns that use raw materials with little or no volatile sulphur have SO₂ emission levels well below this level without using abatement techniques. The current reported emission range is <10-3500 mg SO₂/m³.

The best available techniques for reducing dust emissions are a combination of general primary measures and efficient removal of particulate matter from point sources by application of electrostatic precipitators and/or fabric filters. The BAT emission level⁽²⁾ associated with these techniques is 20-30 mg dust/m³. The current reported emission range is 5-200 mg dust/m³ from point sources. Best available techniques also include minimisation and prevention of dust emissions from fugitive sources as described in section 1.4.7.3

The best available techniques for reducing waste are to recycle collected particulate matter to the process wherever practicable. When the collected dusts are not recyclable the utilisation of these dusts in other commercial products, when possible, is considered BAT.

It is recommended to consider an update of this BAT reference document around year 2005, in particular regarding NO_x abatement (development of SCR technology and high efficiency

² Emission levels are expressed on a daily average basis and standard conditions of 273 K, 101.3 kPa, 10% oxygen and dry gas.

³ See chapter 1.5 for details and justification of split views.

SNCR). Other issues, that have not been fully dealt with in this document, that could be considered/discussed in the review are:

- more information about chemical additives acting as slurry thinners,
- numeric information on acceptable frequency and duration of CO-trips, and
- associated BAT emission values for VOC, metals, HCl, HF, CO and PCDD/Fs.

Lime industry

Lime is used in a wide range of products, for example as a fluxing agent in steel refining, as a binder in building and construction, and in water treatment to precipitate impurities. Lime is also used extensively for the neutralisation of acidic components of industrial effluent and flue gases. With an annual production of around 20 million tonnes of lime, the EU countries produce about 15% of sales-relevant world lime production.

The lime making process consists of the burning of calcium and/or magnesium carbonates to liberate carbon dioxide and to obtain the derived oxide ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$). The calcium oxide product from the kiln is generally crushed, milled and/or screened before being conveyed to silo storage. From the silo, the burned lime is either delivered to the end user for use in the form of quicklime, or transferred to a hydrating plant where it is reacted with water to produce slaked lime.

The term lime includes quicklime and slaked lime and is synonymous with the term lime products. Quicklime, or burnt lime, is calcium oxide (CaO). Slaked lime consist mainly of calcium hydroxide (Ca(OH)_2) and includes hydrated lime (dry calcium hydroxide powder), milk of lime and lime putty (dispersions of calcium hydroxide particles in water).

Lime production generally uses between 1.4 and 2.2 tonnes of limestone per tonne of saleable quicklime. Consumption depends on the type of product, the purity of the limestone, the degree of calcination and the quantity of waste products. Most of the balance is lost from the process as carbon dioxide emission to air.

The lime industry is a highly energy-intensive industry with energy accounting for up to 50% of total production costs. Kilns are fired with solid, liquid or gaseous fuels. The use of natural gas has increased substantially over the last few years. In 1995 the most commonly used fuels were natural gas (48%) and coal, including hard coal, coke, lignite and petcoke, (36%) followed by oil (15%) and other fuels (1%).

In 1995 there were approximately 240 lime-producing installations in the European Union (excluding captive lime production) and a total of about 450 kilns, most of which are other shaft kilns and parallel-flow regenerative shaft kilns. Typical kiln size lies between 50 and 500 tonnes per day.

The key environmental issues associated with lime production are air pollution and the use of energy. The lime burning process is the main source of emissions and is also the principal user of energy. The secondary processes of lime slaking and grinding can also be of significance. The key environmental emissions are dust, nitrogen oxides (NO_x), sulphur dioxide (SO_2) and carbon monoxide (CO).

Many lime plants have taken general primary measures such as process control optimisation. These measures are usually taken to improve product quality and lower production costs but they also reduce the energy use and air emissions.

The best available techniques for reducing dust emissions are a combination of general primary measures and efficient removal of particulate matter from point sources by application of fabric filters, electrostatic precipitators and/or wet scrubbers. The BAT emission level⁴ associated with the use of these techniques is 50 mg dust/m³. The best available techniques also include minimisation and prevention of dust emissions from fugitive sources as described in section 1.4.7.3

The best available techniques for reducing waste are the utilisation of dust, out-of-specification quicklime and hydrated lime in selected commercial products.

NO_x emissions depend mainly on the quality of lime produced and the design of kiln. Low-NO_x burners have been fitted to a few rotary kilns. Other NO_x reduction technologies have not been applied in the lime industry.

SO₂ emissions, principally from rotary kilns, depend on the sulphur content of the fuel, the design of kiln and the required sulphur content of the lime produced. The selection of fuels with low sulphur content can therefore limit the SO₂ emissions, and so can production of lime with higher sulphur contents. There are absorbent addition techniques available, but they are currently not applied in the lime industry.

Before an update of this reference document is carried out, it could be useful to make a survey of current abatement techniques, emissions and consumptions and of monitoring in the lime industry.

⁴ Emission levels are expressed on a daily average basis and standard conditions of 273 K, 101.3 kPa, 10% oxygen and dry gas, except for hydrating plants for which conditions are as emitted.

PREFACE

1. Status of this document

Unless otherwise stated, references to "the Directive" in this document means the Council Directive 96/61/EC on integrated pollution prevention and control. This document forms part of a series presenting the results of an exchange of information between EU Member States and industries concerned on best available techniques (BAT), associated monitoring, and developments in them. It is published by the European Commission pursuant to Article 16(2) of the Directive, and must therefore be taken into account in accordance with Annex IV of the Directive when determining "best available techniques".

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

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

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

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

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

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

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

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

Furthermore, Annex IV of the Directive contains a list of "considerations to be taken into account generally or in specific cases when determining best available techniques ... bearing in

mind the likely costs and benefits of a measure and the principles of precaution and prevention". These considerations include the information published by the Commission pursuant to Article 16(2).

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

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

3. Objective of this Document

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

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

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

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

4. Information Sources

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

5. How to understand and use this document

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

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

Chapters 1.1, 1.2, 2.1 and 2.2 provide general information on the industrial sector concerned and on the industrial processes used within the sector. Chapters 1.3 and 2.3 provide data and information concerning current emission and consumption levels reflecting the situation in existing installations at the time of writing.

Chapters 1.4 and 2.4 describes in more detail the emission reduction and other techniques that are considered to be most relevant for determining BAT and BAT-based permit conditions. This information includes the consumption and emission levels considered achievable by using the technique, some idea of the costs and the cross-media issues associated with the technique, and the extent to which the technique is applicable to the range of installations requiring IPPC permits, for example new, existing, large or small installations. Techniques that are generally seen as obsolete are not included.

Chapters 1.5 and 2.5 present the techniques and the emission and consumption levels that are considered to be compatible with BAT in a general sense. The purpose is thus to provide general indications regarding the emission and consumption levels that can be considered as an appropriate reference point to assist in the determination of BAT-based permit conditions or for the establishment of general binding rules under Article 9(8). It should be stressed, however, that this document does not propose emission limit values. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also needs to be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and levels presented in chapter 1.5 and 2.5 will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document is fully taken into account by permitting authorities.

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

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SCOPE

This BREF covers the processes involved in the production of cement and lime. The main operations covered by the descriptions are:

- Raw materials storage and preparation.
- Fuels storage and preparation.
- The kiln systems.
- Products preparation and storage.
- Packing and dispatch

Quarrying and shaft kilns for cement clinker production are not covered.

1 CEMENT INDUSTRY

1.1 General information about the cement industry

Cement is a finely ground, non-metallic, inorganic powder when mixed with water forms a paste that sets and hardens. This hydraulic hardening is primarily due to the formation of calcium silicate hydrates as a result of the reaction between mixing water and the constituents of the cement. In the case of aluminous cements hydraulic hardening involves the formation of calcium aluminate hydrates.

Cement is a basic material for building and civil engineering construction. In Europe the use of cement and concrete (a mixture of cement, aggregates, sand and water) in large civic works can be traced back to antiquity. Portland cement, the most widely used cement in concrete construction, was patented in 1824. Output from the cement industry is directly related to the state of the construction business in general and therefore tracks the overall economic situation closely.

As Figure 1.1 shows, world cement production has grown steadily since the early 1950s, with increased production in developing countries, particularly in Asia, accounting for the lion's share of growth in world cement production in the 1990s.

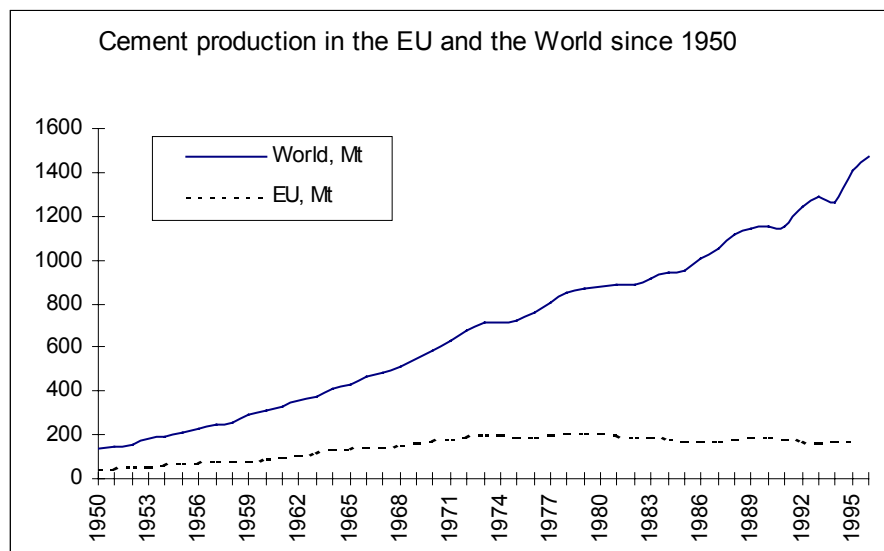


Figure 1.1: Cement production in the EU and the world 1950-1995
[Cembureau]

In 1995 world production of cement stood at 1420 million tonnes. Table 1.1 shows the distribution of cement production by geographic regions.

	1995		1995
China	30%	USA	5%
Japan	7%	Other America	8%
Other Asia	23%	Africa	4%
European Union	12%	Former USSR	4%
Other Europe	6%	Oceania	1%

Table 1.1: World cement production by geographic regions in 1995
[Cembureau report, 1997]

Producers in the European Union have increased cement output per man/year from 1700 tonnes in 1970 to 3500 in 1991. This increase in productivity is a result of the introduction of larger scale production units. These use advanced operation automation and therefore require fewer, but higher qualified, staff. The number of people employed in the cement industry in the European Union is now less than 60000. Figure 1.2 shows the estimated workforce of the cement industry in the EU 15 between 1975-1995.

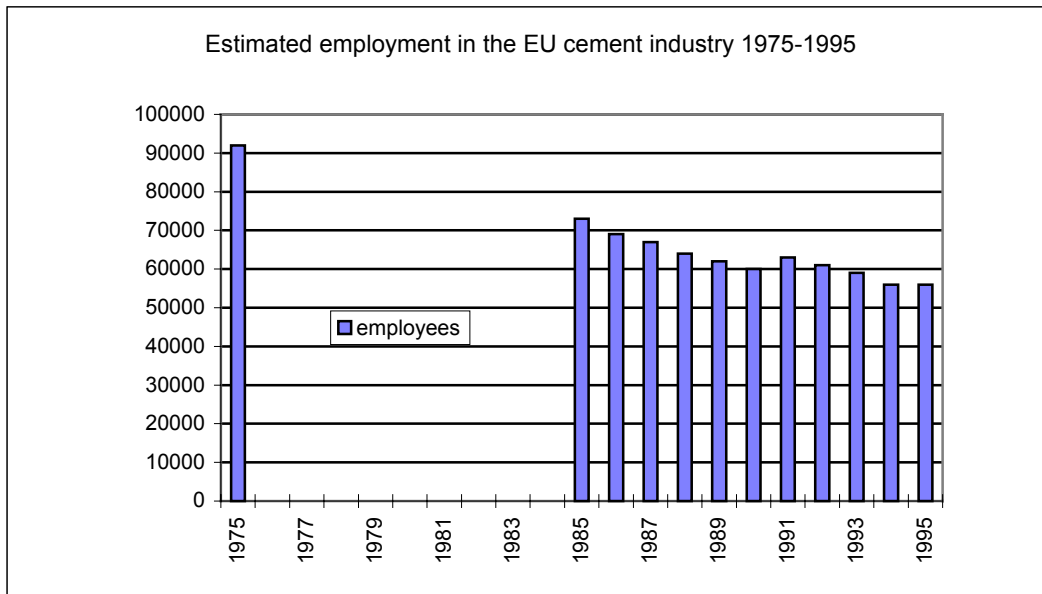


Figure 1.2: Cement industry in the EU, estimated employment 1975-1995
(pre-1991 figures do not include employees from the former East Germany)
[Cembureau]

In 1995 cement production in the European Union totalled 172 million tonnes and consumption 168 million tonnes. 23 million tonnes of cement were imported and 27 million tonnes exported. These figures include trade between EU countries.

There is generally little import and export of cement, mainly as a result of the high cost of road transport. World foreign trade in cement still accounts for only about 6-7% of production, most of which is transported by sea. Road deliveries of cement generally do not exceed distances of 150 km. Consequently, as shown in Figure 1.3, the rate of consumption equals the rate of production for many EU member states, with the exception of Greece and Denmark, which exports approximately 50% of their cement production.

The world's five largest cement producers are the four West European groups; Holderbank, Lafarge, Heidelberger and Italcementi, together with Cemex from Mexico. Apart from producing cement, these companies have also diversified into several other building materials sub-sectors such as aggregates, concrete products, plasterboard, etc.

Transport costs make markets for cement predominantly local. However, some global trade does exist and in some cases it is economically viable to ship cement around the world. International competition is mainly a threat for individual plants, and within the EU increasing imports from Eastern Europe do affect local market conditions.

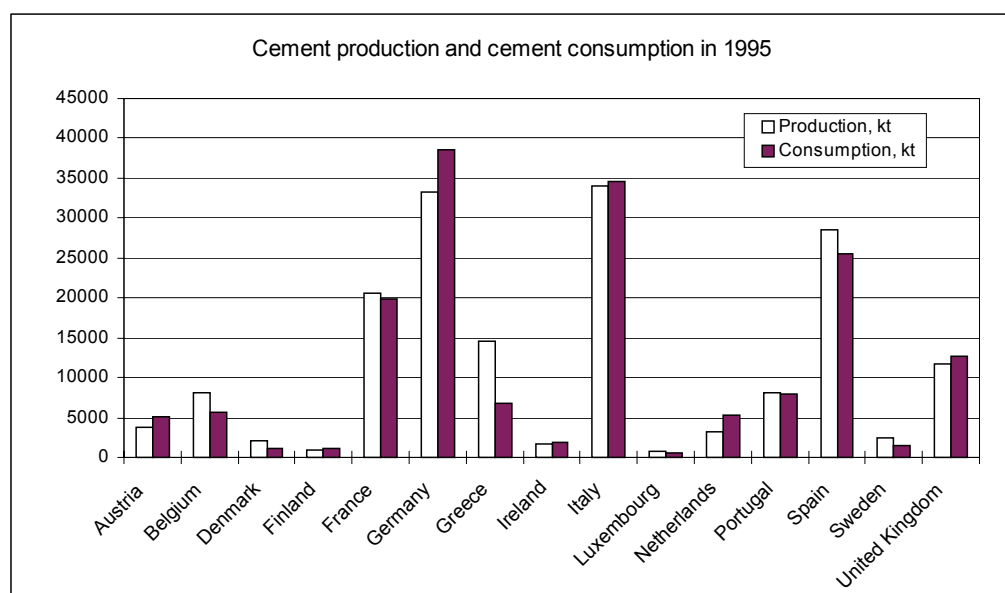


Figure 1.3: Cement production, incl. clinker for export, and cement consumption in the EU 1995
[Cembureau report, 1997], [Göller]

In 1995 there were 252 installations producing cement clinker and finished cement in the European Union. In addition there are a further 68 grinding plants (mills) without kilns. See Table 1.2.

Country	Cement Plants (with kilns)	Cement Plants (with cement mills only)
Austria	11	1
Belgium	5	3
Denmark	1	-
Finland	2	-
France	38	5
Germany	50	20
Greece	8	-
Ireland	2	-
Italy	64	29
Luxembourg	1	1
Netherlands	1	2
Portugal	6	1
Spain	37	5
Sweden	3	-
United Kingdom	23	1
Total	252	68

Table 1.2: Number of cement plants in EU countries 1995
[Cembureau report, 1997], [Schneider]

There is a total of 437 kilns in the countries of the EU, but not all are currently in operation. In recent years typical kiln size has come to be around 3000 tonnes/day, and although kilns of widely different sizes and ages exist, very few kilns have a capacity of less than 500 tonnes per day.

At present, about 78% of Europe's cement production is from dry process kilns, a further 16% of production is accounted for by semi-dry and semi-wet process kilns, with the remainder of European production -about 6%- now coming from wet process kilns. The choice of manufacturing process is primarily motivated by the nature of the available raw materials.

The draft European standard (prEN 197-1) for common cements lists 27 different Portland cement types into 5 groups. In addition, there is a range of special cements produced for particular applications. Table 1.3 shows the percentages of each type of cement supplied to domestic markets in 1994.

	1994
Portland-composite cement	44%
Portland cement	43%
Blastfurnace cement	7%
Pozzolanic cement	5%
Other cements	1%

Table 1.3: Domestic deliveries by cement type in the EU and European Economic Area
[Cembureau report, 1997]

The cement industry is an energy intensive industry with energy typically accounting for 30-40% of production costs (i.e. excluding capital costs). Traditionally, the primary fuel used is coal. A wide range of other fuels are also used, including petroleum coke, natural gas and oil. In addition to these fuel types, the cement industry has been using various types of waste as fuel for more than 10 years.

	1995
Petcoke	39%
Coal	36%
Fuel oil	7%
Lignite	6%
Gas	2%
Different types of waste	10%

Table 1.4: Fuel consumption by the European cement industry
[Cembureau report, 1997]

The emissions from cement plants which cause greatest concern are nitrogen oxides (NO_x), sulphur dioxide (SO₂) and dust. Other emissions to be considered are carbon oxides (CO, CO₂), volatile organic compounds (VOCs), polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs), metals, and noise.

The cement industry is a capital intensive industry. The cost of a new cement plant is equivalent to around 3 years' turnover, which ranks the cement industry among the most capital intensive industries. The profitability of the cement industry is around 10% as a proportion of turnover (on the basis of pre-tax profits before interest repayments).

1.2 Applied processes and techniques

The basic chemistry of the cement manufacturing process begins with the decomposition of calcium carbonate (CaCO_3) at about $900\text{ }^\circ\text{C}$ to leave calcium oxide (CaO , lime) and liberate gaseous carbon dioxide (CO_2); this process is known as calcination. This is followed by the clinkering process in which the calcium oxide reacts at high temperature (typically $1400\text{-}1500\text{ }^\circ\text{C}$) with silica, alumina, and ferrous oxide to form the silicates, aluminates, and ferrites of calcium which comprise the clinker. The clinker is then ground or milled together with gypsum and other additives to produce cement.

There are four main process routes for the manufacture of cement; the dry, semi-dry, semi-wet and wet processes:

- In the **dry process**, the raw materials are ground and dried to raw meal in the form of a flowable powder. The dry raw meal is fed to the preheater or precalciner kiln or, more rarely, to a long dry kiln.

- In the **semi-dry process** dry raw meal is pelletised with water and fed into a grate preheater before the kiln or to a long kiln equipped with crosses.

- In the **semi-wet process** the slurry is first dewatered in filter presses. The filter cake is extruded into pellets and fed either to a grate preheater or directly to a filter cake drier for raw meal production.

- In the **wet process**, the raw materials (often with high moisture content) are ground in water to form a pumpable slurry. The slurry is either fed directly into the kiln or first to a slurry drier.

Figure 1.4 shows an overview of a dry process precalciner route.

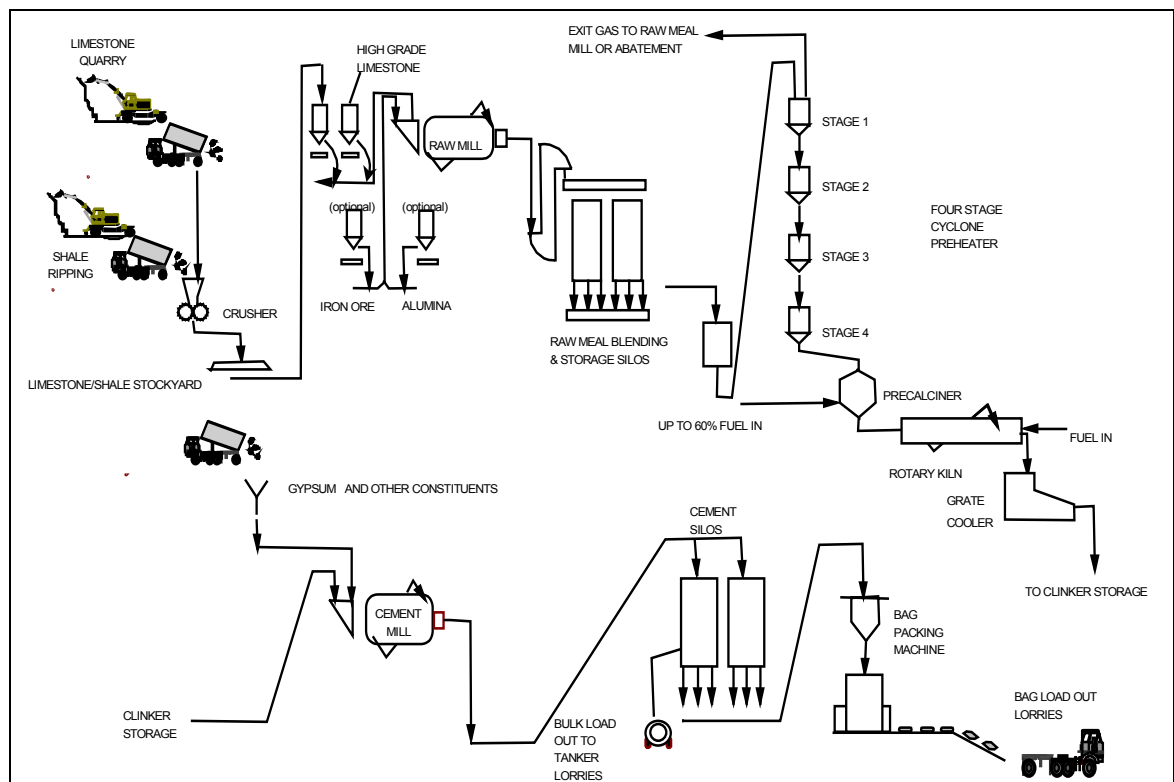


Figure 1.4: Typical precalciner dry process

Based on figure in [UK IPC Note, 1996]

The choice of process is to a large extent determined by the state of the raw materials (dry or wet). A large part of world clinker production is still based on wet processes. However, in

Europe, more than 75% of production is based on dry processes thanks to the availability of dry raw materials. Wet processes are more energy consuming, and thus more expensive. Plants using semi-dry processes are likely to change to dry technologies whenever expansion or major improvement is required. Plants using wet or semi-wet processes normally only have access to moist raw materials, as is the situation in Denmark and Belgium, and to some extent in the UK.

All processes have the following sub-processes in common:

- Winning of raw materials
- Raw materials storage and preparation
- Fuels storage and preparation
- Clinker burning
- Cement grinding and storage
- Packing and dispatch

1.2.1 Winning of raw materials

Naturally occurring calcareous deposits such as limestone, marl or chalk provide the source for calcium carbonate. Silica, iron oxide and alumina are found in various ores and minerals, such as sand, shale, clay and iron ore. Power station ash, blast furnace slag, and other process residues can also be used as partial replacements for the natural raw materials, depending on their chemical suitability. Table 1.5 shows the types of waste most frequently used as raw materials in the production of cement in Europe today.

Fly ash	Blast furnace slag	Silica fume
Iron slag	Paper sludge	Pyrite ash
Phosphogypsum (from flue gas desulphurisation and phosphoric acid production)		

Table 1.5: Types of waste frequently used as raw materials in the European cement industry
[Cembureau]

Winning of nearly all of the natural raw materials involves quarrying and mining operations. The materials are most often obtained from open surface quarries. The operations necessary include rock drilling, blasting, excavation, hauling and crushing.

Main raw materials, like limestone, chalk marl and shale or clay, are extracted from quarries. In most cases the quarry is close to the plant. After primary crushing the raw materials are transported to the cement plant for storage and further preparation. Other raw materials, such as bauxite, iron ore, blast furnace slag or foundry sand, are brought in from elsewhere.

1.2.2 Raw material storage and preparation

Preparation of the raw material is of great importance to the subsequent kiln system both in getting the chemistry of the raw feed right and in ensuring that the feed is sufficiently fine.

1.2.2.1 Raw materials storage

The need to use covered storage depends on climatic conditions and the amount of fines in the raw material leaving the crushing plant. In the case of a 3000 tonnes/day plant these buildings may hold between 20000 and 40000 tonnes of material.

The raw material fed to a kiln system needs to be as chemically homogeneous as practicable. This is achieved by controlling the feed into the raw grinding plant. When the material from the quarry varies in quality, initial preblending can be achieved by stacking the material in rows or layers along the length (or around the circumference) of the store and extracting it by taking cross-sections across the pile. When the material from the quarry is fairly homogeneous, simpler stacking and reclaiming systems can be used.

Raw materials used in relatively small quantities, mineral additions for example, may alternatively be stored in silos or bunkers. Any raw materials with potentially harmful properties, such as fly ash and phosphogypsum, must be stored and prepared according to individual specific requirements.

1.2.2.2 Grinding of raw materials

Accurate metering and proportioning of the mill feed components by weight is important for achieving a consistent chemical composition. This is essential for steady kiln operation and a high-quality product. Metering and proportioning is also an important factor in the energy efficiency of the grinding system. The predominant metering and proportioning equipment for raw material feed to mills is the apron feeder followed by the belt weigh feeder.

Grinding of raw materials, dry and semi-dry kiln systems

The raw materials, in controlled proportions, are ground and mixed together to form a homogeneous blend with the required chemical composition. For dry and semi-dry kiln systems, the raw material components are ground and dried to a fine powder, making use mainly of the kiln exhaust gases and/or cooler exhaust air. For raw materials with a relatively high moisture content, and for start up procedures, an auxiliary furnace may be needed to provide additional heat.

Typical dry grinding systems used are:

- tube mill, centre discharge;
- tube mill, airswept;
- vertical roller mill
- horizontal roller mill (only a few installations in operation so far).

Other grinding systems are used to a lesser extent. These are:

- tube mill, end discharge in closed circuit;
- autogenous mill;
- roller press, with or without crusher drier.

The fineness and particle size distribution of the product leaving a raw grinding system is of great importance for the subsequent burning process. The target given for these parameters is achieved by adjusting the separator used for classifying the product leaving the grinding mill. For dry classification, air separators are used. The newest generation, rotor cage type separators, have several advantages. These are:

- lower specific energy consumption of the grinding system (less over-grinding),
- increased system throughput (efficiency of particle separation), and
- more favourable particle size distribution and product uniformity.

Grinding of raw materials, wet or semi-wet kiln system

Wet grinding is used only in combination with a wet or semi-wet kiln system. The raw material components are ground with added water to form a slurry. To achieve the slurry fineness required, in order to comply with modern quality demands, closed circuit milling systems are the main option.

The wet process is normally preferred whenever the raw material has a moisture content of more than 20% by weight. Raw materials such as chalk, marl or clay, which are sticky and of high inherent moisture content, are soft and as a first stage of preparation they may be ground in a wash mill. Water and crushed material are fed to the wash mill and broken down into slurry by shearing and impact forces imparted by the rotating harrows. When sufficiently fine, the material passes through screens in the wall of the wash mill and is pumped to storage. To achieve the required slurry fineness further grinding in a tube mill is usually required, especially if an additional raw material such as sand is to be added.

To reduce kiln fuel consumption, water addition during the raw material grinding is controlled so that the amount used is the minimum necessary to achieve the required slurry flow and pumpability characteristics (32 to 40% w/w water). Chemical additives may act as slurry thinners permitting the water content to be reduced.

Raw meal or slurry homogenisation and storage

Raw meal or slurry leaving the raw grinding process requires further blending/homogenisation to achieve optimum consistency of the raw mix prior to being fed to any type of kiln system. The raw meal is homogenised and stored in silos, the raw slurry in either tanks or silos.

For raw meal transport to storage silos pneumatic and mechanical systems are used. Mechanical conveyors normally require a higher investment cost but have much lower operating costs than pneumatic conveying systems. A combination of air-slide or screw/chain conveyors with a belt bucket elevator is nowadays the most commonly used conveying system.

1.2.3 Fuel, storage and preparation

Various fuels can be used to provide the heat required for the process. Three different types of fuels are mainly used in cement kiln firing; in decreasing order of importance these are:

- pulverised coal and petcoke;
- (heavy) fuel oil;
- natural gas.

The main ash constituents of these fuels are silica and alumina compounds. These combine with the raw materials to become part of the clinker. This needs to be allowed for in calculating the raw material proportion and so it is desirable to use fuel with a consistent, though not necessarily low, ash content.

The main fuels used in the European cement industry are petcoke and coal (black coal and lignite). Cost normally precludes the use of natural gas or oil, but the selection of fuels depends on the local situation (such as availability of domestic coal). However, the high temperatures and long residence times in the kiln system implies considerable potential for destruction of organic substances. This makes a wide variety of less expensive fuel options possible, in particular different types of wastes.

In order to keep heat losses at minimum, cement kilns are operated at lowest reasonable excess oxygen levels. This requires highly uniform and reliable fuel metering and fuel presentation in a form allowing easy and complete combustion. These conditions are fulfilled by all liquid and gaseous fuels. For pulverised solid fuels, good design of hoppers, conveyors and feeders is essential to meet these conditions. The main fuel input (65-85%) has to be of this easily combustible type, whereas the remaining 15-35% may be fed in coarse crushed or lump form.

1.2.3.1 Storage of fuels

Raw coal and petcoke are stored similarly to raw materials; thus, in many cases, in covered stores. Outside storage in large, compacted stockpiles is used for long-term stocks. Such stockpiles may be seeded with grass to prevent rainwater and wind erosion. Drainage to the ground from outside storage has shown to be a problem. However, sealed concrete floors under the stockpiles make it possible to collect and clean the water that drains off. Normal good practice in terms of compaction and stockpile height needs to be observed when storing coal of relatively high volatile-matter content in order to avoid the risk of spontaneous ignition when stored for long periods.

Pulverised coal and petcoke are stored exclusively in silos. For safety reasons (i.e. the danger of explosions being triggered by smouldering fires and static electricity spark-overs) these silos have to be of the mass flow extraction type and have to be equipped with standard safety devices.

Fuel oil is stored in vertical steel tanks. These are sometimes insulated to help keep the oil at pumpable temperature (50 to 60 °C). They may also be equipped with heatable suction points to maintain the oil at the correct temperature locally.

Natural gas is not stored at the cement plant. The international high pressure gas distribution network acts as a gas storage facility.

1.2.3.2 Preparation of fuels

Solid fuel preparation (crushing, grinding and drying) is usually carried out on site. Coal and petcoke are pulverised to about raw meal fineness in grinding plants using equipment similar to the raw-material grinding plants. The fineness of the pulverised fuel is important, too fine and flame temperatures can be excessively high, too coarse and poor combustion can occur. Low volatility or low volatiles content solid fuel will need finer grinding. If sufficient hot air for drying is not available from the kiln or from the cooler, an auxiliary furnace may be needed. Special features have to be incorporated to protect the equipment from fires and explosions.

Three main types of coal milling and grinding systems are used:

- tube mill, airswept;
- vertical roller or ring-ball mill;
- impact mill.

Ground solid fuel may be fired directly into the kiln, but in modern installations it is usually stored in silos to allow the use of more thermally efficient burners (indirect firing) using low primary air.

Solid fuel grinding, storage and firing systems have to be designed and operated so as to avoid the risk of explosion or fire. The primary requirements are to control air temperatures properly, and to avoid the accumulation of fine material in dead spots exposed to heat.

Fuel oil preparation: In order to facilitate metering and combustion the fuel oil is brought to 120-140 °C, resulting in a viscosity reduction to 10-20 cSt. Additionally, the pressure is increased to 20-40 bar.

Natural gas preparation: Prior to combustion the gas pressure has to be brought from the pipeline pressure of 30-80 bar down to plant network pressure of 3-10 bar and then reduced again to the burner supply pressure of around 1 bar (overpressure). The first pressure reduction step is accomplished in the gas transfer station where consumption metering also takes place. To avoid freezing of the equipment as a result of the Joule-Thompson effect the natural gas is preheated before passing through the pressure reduction valve.

Alternatively, the pressure reduction can be accomplished by passing the gas through a gas expansion turbine connected to a power generator. Thus some of the energy required for gas compression can be recovered.

1.2.3.3 Use of waste as fuel

Wastes, that are fed through the main burner, will be decomposed in the primary burning zone, at temperatures up to 2000 °C. Waste fed to a secondary burner, preheater or precalciner will be burnt at lower temperatures, which not always is enough to decompose halogenated organic substances.

Volatile components in material that is fed at the upper end of the kiln or as lump fuel can evaporate. These components do not pass the primary burning zone and may not be decomposed or bound in the cement clinker. Therefore the use of waste containing volatile metals (mercury, thallium) or volatile organic compounds can result in an increase of the emissions of mercury, thallium or VOCs when improperly used.

Table 1.6 lists the types of waste most frequently used as fuels in Europe today.

Used tyres	Waste oils	Sewage sludge
Rubber	Waste woods	Plastics
Paper waste	Paper sludge	Spent solvents

Table 1.6: Types of waste frequently used as fuels in the European cement industry
[Cembureau]

Preparation of different types of waste for use as fuel is usually performed outside the cement plant by the supplier or by waste-treatment specialists organisations. This means they only need to be stored at the cement plant and then proportioned for feeding to the cement kiln. Since supplies of waste suitable for use as fuel tend to be variable whilst waste material markets are rapidly developing, it is advisable to design storage/preparation plants to be multi-purpose.

1.2.4 Clinker burning

This part of the process is the most important in terms of emission potential and of product quality and cost. In clinker burning, the raw meal (or raw meal slurry in the wet process) is fed to the rotary kiln system where it is dried, pre-heated, calcined and sintered to produce cement clinker. The clinker is cooled with air and then stored.

In the clinker burning process it is essential to maintain kiln charge temperatures of between 1400 to 1500 °C and gas temperatures of about 2000 °C. Also, the clinker needs to be burned

under oxidising conditions. Therefore an excess of air is required in the sintering zone of a cement clinker kiln.

Since the rotary kiln was introduced around 1895 it has become the central part of all modern clinker producing installations. The vertical shaft kiln is still used for production of lime, but only in a few countries is it in use for production of cement clinker, and in these cases only at small-scale plants.

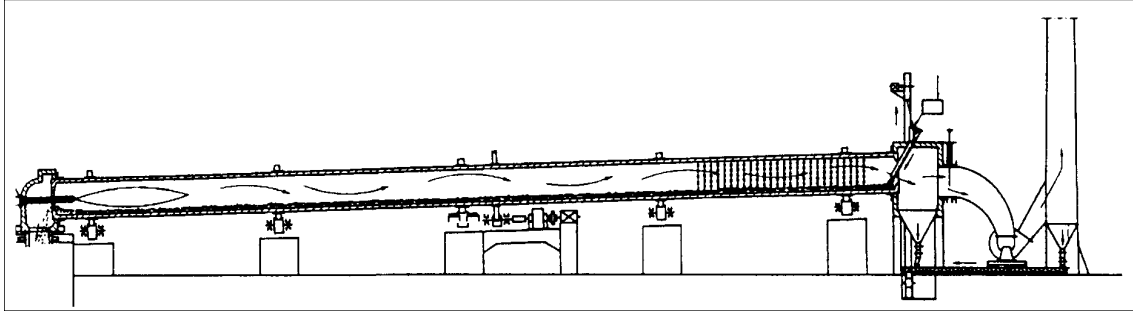


Figure 1.5: Long wet rotary kiln with chains
[Cembureau report, 1997]

The first rotary kilns were long wet kilns, as shown in Figure 1.5 above, where the whole heat consuming thermal process takes place in the kiln itself. With the introduction of the dry process, optimisation led to technologies which allowed drying, preheating and calcining to take place in a stationary installation rather than in the rotary kiln.

The rotary kiln consists of a steel tube with a length to diameter ratio of between 10:1 and 38:1. The tube is supported by two to seven (or more) support stations, has an inclination of 2.5 to 4.5% and a drive rotates the kiln about its axis at 0.5 to 4.5 revolutions per minute. The combination of the tube's slope and rotation causes material to be transported slowly along it. In order to withstand the very high peak temperatures the entire rotary kiln is lined with heat resistant bricks (refractories). All long and some short kilns are equipped with internals (chains, crosses, lifters) to improve heat transfer.

Transient buildups of material can occur around the inner surface of the kiln depending on the process and raw materials etc. These are known as rings and can occur at the feed end (gypsum rings), near the sintering zone (clinker rings) or the product exit end (ash rings). The latter two types can break away suddenly and cause a surge of hot, poor quality material to leave the kiln which may be reprocessed or have to be rejected as waste. The cyclones and grates of preheater kilns may also be subject to build up of material which can lead to blockages.

Kiln firing

The fuel introduced via the main burner produces the main flame with flame temperatures around 2000 °C. For process-optimisation reasons the flame has to be adjustable within certain limits. In a modern indirectly fired burner, the flame is shaped and adjusted by the primary air (10-15% of total combustion air).

Potential feed points for supplying fuel to the kiln system are:

- via the main burner at the rotary kiln outlet end;
- via a feed chute at the transition chamber at the rotary kiln inlet end (for lump fuel);
- via secondary burners to the riser duct;
- via precalciner burners to the precalciner;

- via a feed chute to the precalciner (for lump fuel);
- via a mid kiln valve in the case of long wet and dry kilns (for lump fuel).

Coal/petcoke firing plants are of both indirect- and direct-firing types. Direct-firing plants operate without fine-coal storage and fine-coal metering. The pulverised fuel is blown directly into the kiln with the mill sweeping air acting as carrier and as (flame shaping) primary air. Direct firing plants have a number of drawbacks. In particular kiln-system heat losses are around 200-250 MJ/tonne clinker (6 to 8% higher on modern kiln systems). Thus direct firing is seldom installed today.

Fuel oil is, at adequate viscosity and pressure, discharged via an atomiser nozzle into the kiln in order to form e.g. the main flame. Flame shaping is mainly accomplished via multi-primary air channel burners with the oil atomiser head in a central location.

Kiln burners for natural gas, too, are designed according to the multi-channel principle, the gas thereby replacing not only coal or fuel oil, but also primary air.

1.2.4.1 Long rotary kilns

Long rotary kilns (Figure 1.5) can be fed with slurry, crushed filter cakes, nodules or dry meal and are thus suitable for all process types. The largest long kilns have a length-to-diameter ratio of 38:1 and can be more than 200 m long. These huge units produce around 3600 tonnes/day using the wet process (Belgium, US, former Soviet Union). Long rotary kilns are designed for drying, preheating, calcining and sintering, so that only the feed system and cooler have to be added. The upper part of the long kilns is equipped with chain curtains and fixed installations to improve heat transfer.

Wet process kilns, used since 1895, are the oldest type of rotary kilns in use for producing cement clinker. Wet raw material preparation was initially used because homogenisation was easier with liquid material. Wet kiln feed typically contains 32 to 40% water. This is necessary to maintain the liquid properties of the feed. This water must then be evaporated in the specially designed drying zone at the inlet section of the kiln where a significant portion of the heat from fuel combustion is used. This technology has high heat consumption with the resulting emission of high quantities of combustion gas and water vapour.

Long dry kilns were developed in the US based on batch type dry homogenising systems for raw material preparation. Because of the high fuel consumption only a few have been installed in Europe.

1.2.4.2 Rotary kilns equipped with preheaters

Rotary kilns equipped with preheaters have a typical length-to-diameter ratio of between 10:1 and 17:1. There are two types preheaters : grate preheaters and suspension preheaters.

Grate preheater technology

Grate preheater technology, perhaps better known as the Lepol kiln, was invented in 1928. It represented the first approach to letting part of the clinkering process take place in a stationary installation outside the kiln. This allowed the rotary kiln to become shorter and so reduced the heat losses and increased energy efficiency.

In the grate preheater (see Figure 1.6a) nodules made from dry meal on a noduliser disc (semi-dry process) or from wet slurry filter cakes in an extruder (semi-wet process) are fed onto a horizontal travelling grate which travels through a closed tunnel. The tunnel is divided into a hot gas chamber and a drying chamber by a partition with an opening for the grate. A fan draws the exhaust gas from the rotary kiln into the top of the preheater, through the nodules layer in the hot gas chamber, and then through the cyclones of the intermediate dust collector. In these cyclones large dust particles, which would otherwise cause wear to the fan, are removed. The next fan then draws the gas into the top of the drying chamber, through the moist layer of nodules, and finally pushes it out into the dust collector. In order to achieve optimum thermal efficiency, the semi-wet grate preheaters can be equipped with triple-pass gas systems, and cooler waste air is used for raw material drying. The maximum unit size to have been built is 3300 tonnes/day for a semi-wet kiln system.

The rotary kiln exhaust gas enters the preheater with a temperature of 1000-1100 °C. As it flows through the layer of material in the hot gas chamber, the exhaust gas cools down to 250-300 °C, and it leaves the drying chamber at 90-150 °C. The material to be burnt reaches a temperature of about 150 °C in the drying chamber and 700-800 °C in the heating chamber.

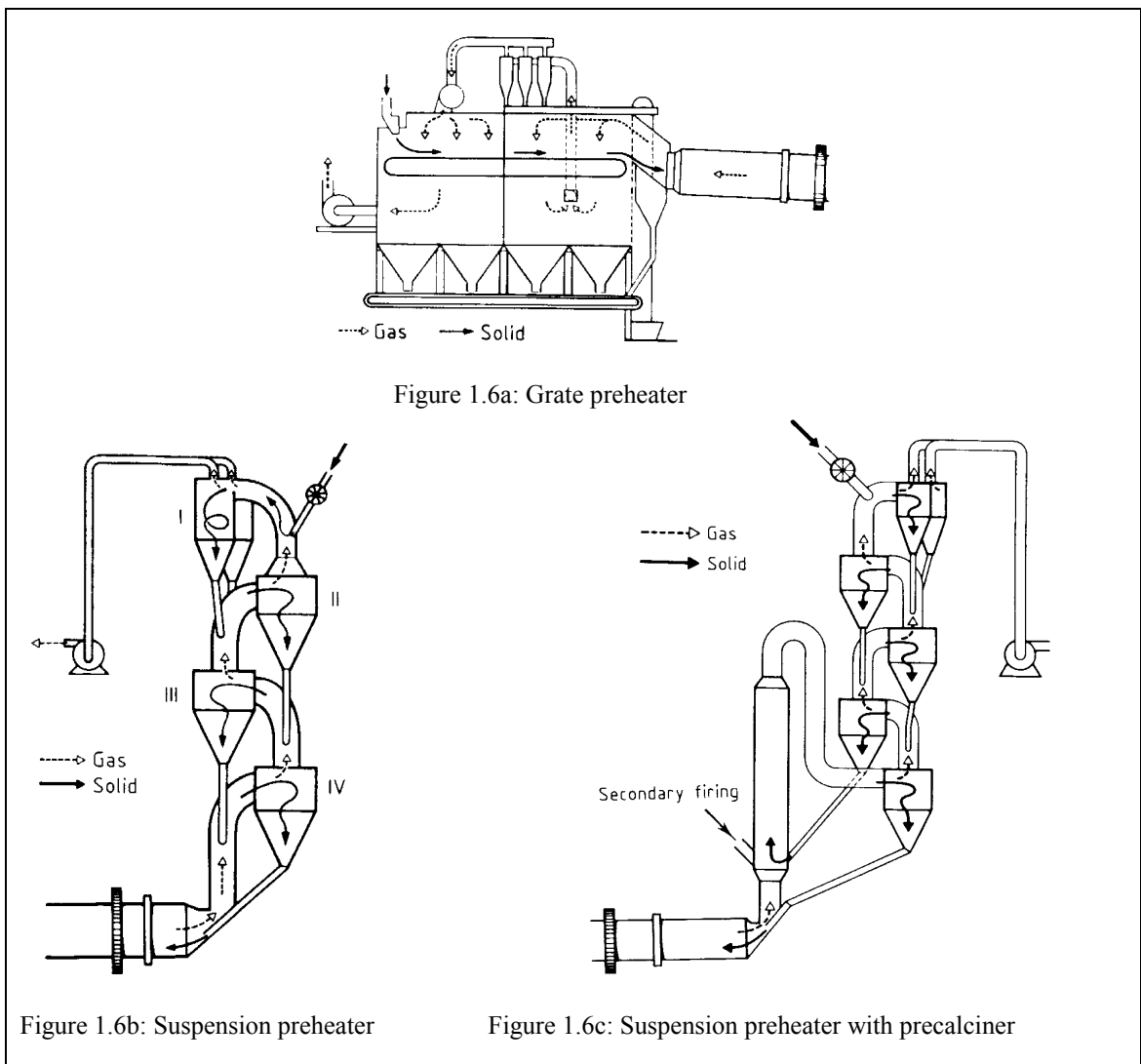


Figure 1.6: Schematic diagrams of different preheaters
[Ullmann's, 1986]

Suspension preheater technology

The invention of the suspension preheater in the early 1930s was a significant development. Preheating and even partial calcination of the dry raw meal (dry/semi-wet processes) takes place by maintaining the meal in suspension with hot gas from the rotary kiln. The considerably larger contact surface allows almost complete heat exchange, at least theoretically.

Various suspension preheater systems are available. They usually have between four and six cyclone stages, which are arranged one above the other in a tower 50-120 m high. The uppermost stage may comprise two parallel cyclones for better dust separation. The exhaust gases from the rotary kiln flow through the cyclone stages from the bottom upward. The dry powdery raw material mixture is added to the exhaust gas before the uppermost cyclone stage. It is separated from the gas in the cyclones and rejoins it before the next cyclone stage. This procedure repeats itself at every stage until finally the material is discharged from the last stage into the rotary kiln. This alternate mixing, separation, and remixing at higher temperature is necessary for optimal heat transfer.

Shaft preheaters

A considerable number of shaft preheaters were built following the introduction of suspension preheater technology, given its theoretically superior heat exchange properties. However, the difficulty of ensuring an even distribution of meal to gas meant that actual performance was far worse than expected, and technology using shaft stages alone was eventually abandoned in favour of hybrid systems with cyclone stages or pure multi-stage cyclone preheaters. Some of those hybrids are still in operation, however most of them have been converted to pure cyclone preheaters.

A shaft stage is considerably less sensitive to build-up problems than a cyclone stage, which can be an advantage for the bottom stage in cases where excessive quantities of circulating elements (chlorides, sulphur, alkalis) are present. Hybrid preheaters with a bottom shaft stage are still available for new plants.

Typical capacities of shaft preheater kilns were up to 1500 tonnes/day, whereas hybrid systems can produce 3000 tonnes/day or more.

Four stage cyclone preheater

The four-stage cyclone preheater kiln system (see Figure 1.6b) was standard technology in the 1970s when many plants were built in the 1000 to 3000 tonnes/day range. The exhaust gas, which has a temperature of around 330 °C is normally used for raw material drying.

When the meal enters the rotary kiln, calcination is already about 30% completed. Severe problems have in the past been encountered with four stage preheaters in cases where inputs of circulating elements (chlorides, sulphur, alkalis) from the feed and/or fuel were excessive. Highly enriched cycles of these elements lead to build-ups in cyclone and duct walls, which frequently cause blockages and kiln stops lasting several days. Kiln gas bypass, i.e. extraction of part of the particulate laden gas stream leaving the kiln so that it bypasses the cyclone system, is a frequently used solution to the problem. This bypass gas is cooled to condense the alkalis and then passed through a dust collector before discharge. Whilst in some regions it is necessary, for the control of clinker alkali levels, to send the bypass dust and part of the kiln dust to landfill, in all other cases it is fed back into the production process.

Almost all four-stage suspension preheaters operate with rotary kilns with three supports. This has been the standard design since around 1970. Kilns with diameters from 3.5 to 6 m have been built with length to diameter ratios in the range 13:1 to 16:1. Mechanically simpler than the long wet and dry kilns, it is probably the most widely used kiln type today.

1.2.4.3 Rotary kilns with preheater and precalciner

The precalcination technique has been available to the cement industry since about 1970. In this procedure the heat input is divided between two points. Primary fuel combustion occurs in the kiln burning zone. Secondary burning takes place in a special combustion chamber between the rotary kiln and the preheater. In this chamber up to 60% of the total fuel can be burnt in a typical precalciner kiln. This energy is basically used to calcine the raw meal, which is almost completely calcined when it enters the kiln. Hot air for combustion in the calciner is ducted from the cooler. Material leaves the calciner at about 870 °C.

Figure 1.6c shows this procedure applied to a kiln with a suspension preheater. In principle, secondary burning can also be applied in a kiln with a grate preheater. For a given rotary kiln size precalcining increases the clinker capacity.

Kiln systems with five cyclone preheater stages and precalciner are considered standard technology for new dry process plants.

The size of a new plant is primarily determined by predicted market developments, but also by economy of scale. Typical unit capacity for new plants in Europe today is from 3000 to 5000 tonnes/day. Technically, larger units with up to 15000 tonnes/day are possible, and three 10000 tonnes/day kilns are currently in operation in Asian markets.

Earlier precalciner systems had only four preheater stages with accordingly higher exhaust gas temperature and fuel consumption. Where natural raw material moisture is low, six-stage preheaters can be the preferred choice, particularly in combination with bag-filter dedusting.

Where excessive inputs of circulating elements are present, a kiln gas bypass is required to maintain continuous kiln operation. However, due to the different gas flow characteristics, a bypass in a precalciner kiln is much more efficient than in a straight preheater kiln.

In spite of the fact that the meal enters the kiln 75 to 95% calcined, most precalciner kilns are still equipped with a rotary kiln with a calcining zone, i.e. with an L/D ratio of 13:1 to 16:1 as in the case of the straight preheater kilns.

1.2.4.4 Shaft kilns

A few shaft kilns are used for cement production in Europe. Kilns of this type consist of a refractory-lined, vertical cylinder 2-3 m in diameter and 8-10 m high. They are fed from the top with raw meal pellets and fine grained coal or coke. The material being burnt travels through a short sintering zone in the upper, slightly enlarged part of the kiln. It is then cooled by the combustion air blown in from the bottom and leaves the lower end of the kiln on a discharge grate in the form of clinker.

Shaft kilns produce less than 300 tonnes/day of clinker. They are only economic for small plants, and for this reason their number has been diminishing.

1.2.4.5 Kiln exhaust gases

In all kiln systems the exhaust gases are finally passed through an air pollution control device (electrostatic precipitator or bag filter) for separation of the dust before going to the main stack.

In the dry processes the exhaust gases can be at a relatively high temperature and may provide heat for the raw mill when it is running (compound operation). If the raw mill is not running (direct operation), the gases are normally cooled with water sprays in a conditioning tower before going to the dust collector, both to reduce their volume and to improve their precipitation characteristics.

CO-trips

Carbon monoxide can arise from any organic content in the raw materials and, occasionally, due to the incomplete combustion of fuel. The contribution from the raw materials, due to preheating, will be exhausted with the kiln gases.

Control of CO levels is critical in cement (and lime) kilns when EPs are used for particulate abatement, to ensure concentrations are kept well below the lower explosive limit. If the level of CO in the EP rises (typically to 0.5% by volume) then the electrical system is tripped (switched off) to eliminate the risk of explosion. This leads to unabated particulate releases from the kiln. CO trips can be caused by unsteady state operation of the combustion system. This sometimes occurs when feeding solid fuels, so solid-fuel feeding systems must be designed to prevent surges of fuel into the burner. The moisture content of solid fuels is a particularly critical factor in this respect and must be carefully controlled to prevent hold ups or blockages in the fuel preparation and feeding systems.

1.2.4.6 Clinker coolers

The clinker cooler is an integral part of the kiln system and has a decisive influence on performance and economy of the pyroprocessing plant. The cooler has two tasks: to recover as much heat as possible from the hot (1450 °C) clinker so as to return it to the process; and to reduce the clinker temperature to a level suitable for the equipment downstream.

Heat is recovered by preheating the air used for combustion in main and secondary firing as close to the thermodynamic limit as possible. However, this is hindered by high temperatures, the extreme abrasiveness of the clinker and its wide granulometric range. Rapid cooling fixes the mineralogical composition of the clinker to improve the grindability and optimise cement reactivity.

Typical problems with clinker coolers are thermal expansion, wear, incorrect air flows and poor availability, which work against the above requirements. There are two main types of coolers: rotary and grate.

Rotary coolers

The tube cooler

The tube cooler uses the same principle as the rotary kiln, but for reversed heat exchange. Arranged at the outlet of the kiln, often in reverse configuration, i.e. underneath the kiln, a second rotary tube with its own drive is installed. After kiln discharge, the clinker passes a transition hood before it enters the cooler, which is equipped with lifters to disperse the product

into the air flow. Cooling air flow is determined by the air required for fuel combustion. Apart from the speed, only the internals can influence the performance of the cooler. Optimisation of lifters must consider heat exchange (dispersion pattern) versus dust cycle back to the kiln.

The planetary (or satellite) cooler

The planetary (or satellite) cooler is a special type of rotary cooler. Several cooler tubes, typically 9 to 11, are attached to the rotary kiln at the discharge end. The hot clinker enters through openings in the kiln shell arranged in a circle at each point where a cooler tube is attached. The quantity of cooling air is determined by the air required for fuel combustion and enters each tube from the discharge end, allowing counter-current heat exchange. As for the tube cooler, internals for lifting and dispersing the clinker are essential. There are no variable operating parameter. High wear and thermal shock, in conjunction with dust cycles, mean high clinker exit temperatures and sub-optimum heat recovery are not unusual. Clinker exit temperature can only be further reduced by water injection into the cooler tubes or onto the shell.

Because it is practically impossible to extract tertiary air, the planetary cooler is not suitable for precalcination. Secondary firing with up to 25% fuel in the kiln riser area is possible, however.

Grate coolers

Cooling in grate coolers is achieved by passing a current of air upwards through a layer of clinker (clinker bed) lying on an air-permeable grate. Two ways of transporting the clinker are applied: travelling grate and reciprocating grate (steps with pushing edges).

Since the hot air from the aftercooling zone is not used for combustion, it is available for drying purposes, e.g. raw materials, cement additives or coal. If not used for drying, this cooler waste air must be properly dedusted.

Travelling grate coolers

In this type of cooler, clinker is transported by a travelling grate. This grate has the same design features as the preheater grate (Lepol). Cooling air is blown by fans into compartments underneath the grate. Advantages of this design are an undisturbed clinker layer (no steps) and the possibility of exchanging plates without a kiln stop. Due to its mechanical complexity and poor recovery resulting from limited bed thickness (caused by the difficulty of achieving an effective seal between the grate and walls), this design ceased to be used in new installations around 1980.

Reciprocating grate cooler, conventional

Clinker transport in the reciprocating grate cooler is effected by stepwise pushing of the clinker bed by the front edges of alternate rows of plates. Relative movement of front edges is generated by hydraulic or mechanical (crankshaft) drives connected to every second row. Only the clinker travels from feed end to discharge end, but not the grate.

The grate plates are made from heat resistant cast steel and are typically 300 mm wide and have holes for the air to pass through them.

Cooling air is insufflated from fans at 300-1000 mmWG via compartments located underneath the grate. These compartments are partitioned from one another in order to maintain the pressure profile. Two cooling zones can be distinguished:

- the recuperation zone, from which the hot cooling air is used for combustion of the main burner fuel (secondary air) and the precalciner fuel (tertiary air);
- the aftercooling zone, where additional cooling air cools the clinker to lower temperatures.

The largest units in operation have an active surface of about 280 m² and cool 10000 tonnes/day of clinker. Typical problems with these coolers are segregation and uneven clinker distribution leading to air-clinker imbalance, fluidisation of fine clinker (red river) and also build ups (snowmen) and less than ideal life of plates.

Reciprocating grate cooler, modern

Introduction and development of modern technology reciprocating grate coolers started around 1983. The design aimed to eliminate the problems with conventional coolers thus coming a step closer to optimum heat exchange and also more compact coolers using less cooling air and smaller dedusting systems.

Key features of modern cooler technology are (depending on supplier):

- modern plates with built-in, variable or permanent, pressure drop, permeable to air but not clinker;
- forced plate aeration via ducts and beams;
- individually adjustable aeration zones ;
- fixed inlet;
- fewer and wider grates;
- roller crusher;
- heat shields.

Vertical coolers

A dust free aftercooler called a Gravity cooler or G-cooler has been developed to be installed after a planetary cooler or short grate recuperator/cooler. The cooling air never comes into contact with the clinker as heat exchange is effected by the clinker descending over transverse steel tubes in the clinker bed, which in turn are cooled by air blown through them.

1.2.5 Cement grinding and storage

1.2.5.1 Clinker storage

Clinker and other cement components are stored in silos or in closed sheds. Larger stocks can be stored in the open if the necessary precautions against dust formation are taken.

The most common clinker storage systems are:

- longitudinal store with gravity discharge (limited live stock);
- circular store with gravity discharge (limited live stock);
- clinker storage silo (high live stock; problems with ground vibrations can occur during clinker withdrawal from the silo at certain silo levels);
- clinker storage dome (limited live stock).

1.2.5.2 Cement grinding

Portland cement is produced by intergrinding cement clinker and sulphates such as gypsum and anhydrite. In blended cements (composite cements) there are other constituents, such as granulated blast furnace slag, natural or artificial pozzolanas, limestone, or inert fillers. These will be interground with the clinker or may need to be dried and ground separately. (Grinding plants may be at separate locations from clinker production plants.)

The kind of cement grinding process and the plant concept chosen at a specific site depend on the cement type to be produced. Of special importance are the grindability, the humidity and the abrasive behaviour of the compounds of the cement type produced.

Most mills work in a closed circuit, that is, they can separate cement with the required fineness from the material being ground and return coarse material to the mill.

Metering and proportioning of the mill feed

The accuracy and reliability of metering and proportioning of the mill feed components by weight is of great importance for maintaining a high energy efficiency of a grinding system. The predominant metering and proportioning equipment for the material feed to mills is the belt weigh feeder.

Grinding of cement

Due to the variety of cement types required by the market, latest-generation grinding systems equipped with a dynamic air separator predominate.

Commonly used finish grinding systems are:

- tube mill, closed circuit (mineral addition is rather limited, if not dry or pre-dried);
- vertical roller mill (best suited for high mineral additions due to its drying capacity, best suited for separate grinding of mineral addition);
- roller press (mineral addition is rather limited, if not dry or pre-dried).

Other finish grinding systems used are:

- tube mill, end discharge in open circuit;
- tube mill, end discharge in closed circuit with mechanical air separator or cyclone air separator of older generations;
- horizontal roller mill.

The working principle of *vertical roller mills* is based on the action of 2 to 4 grinding rollers supported on hinged arms and riding on a horizontal grinding table or grinding bowl. It is suited especially for simultaneous grinding and drying of cement raw materials or slag since vertical roller mills can handle relatively high moisture contents in the mill feeds. The transition time for materials through the mill is short enough to prevent pre-hydration of the cement clinker, e.g. in the case of slag cement grinding.

The *high-pressure twin roller mill* still needs a comparatively high degree of maintenance. High-pressure twin roller mills are often used in conjunction with ball mills.

A more recent development in cement grinding is the *horizontal roller mill*. This consists of a short horizontal shell supported on hydrodynamic or hydrostatic bearings. The shell is rotated via a girth gear. Inside the shell is a horizontal roller which is free to rotate and can be pressed hydraulically onto the shell. The material to be ground is fed into one or both ends of the shell,

and passes between the roller and the shell several times. The crushed material leaving the mill is transported to a separator, the oversize fraction being returned to the mill.

Grinding of mineral additions

Mineral additions are usually ground together with the clinker and gypsum. The decision to grind them separately basically depends upon the following factors:

- the percentage of mineral additives in the final product and in cement production as a whole;
- whether a spare mill system is available;
- whether there is a considerable difference in the grindability of the clinker and mineral additives;
- the moisture content of the mineral additives.

If pre-drying of mineral additives is required, drier systems can be employed using either kiln exhaust gases and/or cooler exhaust air or an independent hot gas source.

Inter-grinding systems

Any of the grinding systems mentioned for the dry/semi-dry grinding of raw materials can be used for inter-grinding mineral additives with clinker and gypsum. However, most systems place limits on the moisture content of the feed mixture - 2% maximum or 4% if a hot gas source is used. For higher moisture contents the systems require pre-drying of the mineral additives in a drier. An exception is the vertical roller system, which is capable of handling moisture contents up to 20%, but still requires a hot gas source.

Separate Grinding

For separate grinding of mineral additives the systems for the dry/semi-dry grinding of raw materials can be used. However, the same applies for the systems with regard to the moisture content of the additives mixture, and pre-drying may be required.

Separation by particle size distribution

The particle size distribution of the product leaving the cement grinding system is of great importance for the cement quality. The specification of these parameters is achieved by adjusting the separator. Latest generation separators of the rotor cage type have several advantages over previous designs, such as:

- lower specific energy consumption by the system (less overgrinding);
- increase of system throughput (efficiency);
- possibility of product cooling;
- higher flexibility for adjustments in product fineness;
- better control of particle size distribution, better product uniformity.

1.2.5.3 Storage of cement

Both pneumatic and mechanical conveying systems can be used for cement transport to storage silos. Mechanical systems normally have a higher investment cost but a much lower operating cost than pneumatic transport. A combination of air-slide or screw/chain conveyors with a chain bucket elevator is nowadays the most commonly used conveying system.

Different cements are stored separately in silos. Usually various silos are required for the storage of cements. However, new silo designs allow the storage of more than one type of cement in the same silo. The silo configurations currently used for cement storage are:

- single-cell silo with discharge hopper;
- single-cell silo with central cone;
- multi-cell silo;
- dome silo with central cone.

Compressed air is used to initiate and maintain the cement discharge process from these silos via aeration pads located at the bottom of the silo.

1.2.6 Packing and dispatch

Cement is transferred from the silos either direct into bulk road or rail (or ship) tankers, or to a bag packing station.

1.3 Present consumption/emission levels

The main environmental issues associated with cement production are emissions to air and energy use. Waste water discharge is usually limited to surface run off and cooling water only and causes no substantial contribution to water pollution. The storage and handling of fuels is a potential source of contamination of soil and groundwater.

A mass balance for the production of 1 kg of cement with the dry process, using heavy fuel oil as fuel, is shown in Figure 1.7.

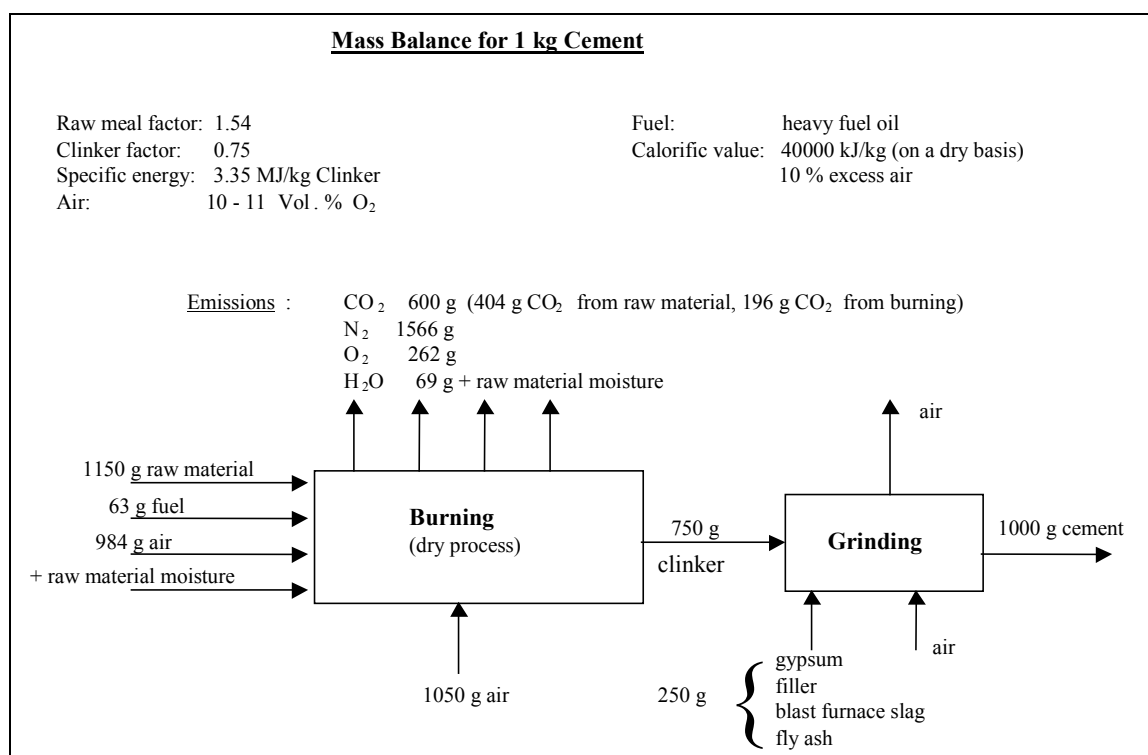


Figure 1.7: Mass balance for the production of 1 kg cement

Based on figure from [Austrian BAT-proposal, 1996]

1.3.1 Consumption of raw materials

Cement manufacture is a high volume process. The figures in Table 1.7 indicate typical average consumptions of raw materials for the production of cement in the European Union. The figures in the final column are for a plant with a clinker production of 3000 tonnes/day or 1 million tonnes/year, corresponding to 1.23 million tonnes cement per year based on the average clinker content in European cement.

Materials (dry basis)	per tonne clinker	per tonne cement	per year per Mt clinker
Limestone, clay, shale, marl, other	1.57 t	1.27 t	1568000 t
Gypsum, anhydrite	-	0.05 t	61000 t
Mineral additions	-	0.14 t	172000 t

Table 1.7: Consumption of raw materials in cement production

[Cembureau report, 1997]

1.3.2 Use of energy

The dominant use of energy in cement manufacture is as fuel for the kiln. The main users of electricity are the mills (finish grinding and raw grinding) and the exhaust fans (kiln/raw mill and cement mill) which together account for more than 80% of electrical energy usage. On average, energy costs -in the form of fuel and electricity- represent 50% of the total production cost involved in producing a tonne of cement. Electrical energy represents approximately 20% of this overall energy requirement. [Int.Cem.Rev, Jan/96]

The theoretical energy use for the burning process (chemical reactions) is about 1700 to 1800 MJ/tonne clinker. The actual fuel energy use for different kiln systems is in the following ranges (MJ/tonne clinker):

about 3000 for dry process, multi-stage cyclone preheater and precalciner kilns,
3100-4200 for dry process rotary kilns equipped with cyclone preheaters,
3300-4500 for semi-dry/semi-wet processes (Lepol-kiln),
up to 5000 for dry process long kilns,
5000-6000 for wet process long kilns, and
(3100-4200 for shaft kilns).

The electricity demand is about 90-130 kWh/tonne cement.

1.3.3 Emissions

The IPPC Directive includes a general indicative list of the main air-polluting substances to be taken into account, if they are relevant for fixing emission limit values. Relevant to cement manufacture are:

- oxides of nitrogen (NO_x) and other nitrogen compounds;
- sulphur dioxide (SO₂) and other sulphur compounds;
- dust.

Cement plant operation and literature on air pollution and abatement techniques generally focus on these three pollutants.

From the list, the following pollutants are also considered to be of concern for the production of cement:

- carbon monoxide (CO);
- volatile organic compounds (VOC).

Other pollutants from the list also to be considered in relation to the production of cement are:

- polychlorinated dibenzodioxins and dibenzofurans (PCDDs and PCDFs);
- metals and their compounds;
- HF
- HCl.

Not mentioned in the list, but considered to be relevant for cement production is carbon dioxide (CO₂). Other emissions, the effect of which is normally slight and/or local, are waste, noise and odour.

The main releases from the production of cement are releases to air from the kiln system. These derive from the physical and chemical reactions involving the raw materials and the combustion of fuels. The main constituents of the exit gases from a cement kiln are nitrogen from the combustion air; CO₂ from calcination of CaCO₃ and combustion of fuel; water vapour from the combustion process and from the raw materials; and excess oxygen.

In all kiln systems the solid material moves counter currently to the hot combustion gases. This counter current flow affects the release of pollutants, since it acts as a built-in circulating fluidised bed. Many components that result from the combustion of the fuel or from the transformation of the raw material into clinker remain in the gas phase only until they are absorbed by, or condensed on, the raw material flowing counter currently.

The adsorptive capacity of the material varies with its physical and chemical state. This in turn depends on its position within the kiln system. For instance, material leaving the calcination stage of a kiln process has a high calcium oxide content and therefore has a high absorptive capacity for acid species, such as HCl, HF and SO₂.

Emission data from kilns in operation is given in Table 1.8. The emission ranges within which kilns operate depend largely on the nature of the raw materials, the fuels, the age and design of the plant, and also on the requirements laid down by the permitting authority.

<i>Emission ranges from European cement kilns</i>			
	<u>mg/Nm³</u>	<u>kg/tonne clinker</u>	<u>tonnes/year</u>
NO _x (as NO ₂)	<200–3000	<0.4-6	400-6000
SO ₂	<10–3500	<0.02-7	<20-7000
Dust	5–200	0.01-0.4	10-400
CO	500–2000	1-4	1000-4000
CO ₂	400-520 g/Nm ³	800-1040	0.8-1.04 million
TOC	5-500	0.01–1	10-1000
HF	<0.4-5	<0.8-10 g/t	<0.8-10
HCl	<1-25	<2-50 g/t	<2-50
PCDD/F	<0.1-0.5 ng/Nm ³	<200-1000 ng/t	<0.2-1 g/year
<u>Metals:</u>			
∑ (Hg, Cd, Tl)	0.01-0.3 (mainly Hg)	20-600 mg/t	20-600 kg/year
∑ (As, Co, Ni, Se, Te)	0.001-0.1	2-200 mg/t	2-200 kg/year
∑ (Sb, Pb, Cr, Cu, Mn, V, Sn, Zn)	0.005-0.3	10-600 mg/t	10-600 kg/year

Note: Mass figures are based on 2000 m³/tonne clinker and 1 million tonnes clinker/year. Emission ranges are one-year averages and are indicative values based on various measurement techniques. O₂-content is normally 10%.

Table 1.8: Emission ranges data from European cement kilns

Based on [Cembureau report, 1997], [Cembureau], [Dutch report, 1997], [Haug], [Lohse]

Typical kiln exhaust gas volumes expressed as m³/tonne of clinker (dry gas, 101.3 kPa, 273 K) are between 1700 and 2500 for all types of kilns [Cembureau]. Suspension preheater and precalciner kiln systems normally have exhaust gas volumes around 2000 m³/tonne of clinker (dry gas, 101.3 kPa, 273 K).

There are also releases of particulates from all milling operations i.e. raw materials, solid fuel and product. There is potential for the release of particulates from any outside storage of raw materials and solid fuels as well as from any materials transport systems, including cement product loading. The magnitude of these releases can be significant if these aspects are not well engineered or maintained and being released at low level can lead to local nuisance problems.

1.3.3.1 Oxides of nitrogen

Nitrogen oxides (NO_x) are of major significance with respect to air pollution from cement manufacturing plants. On an average, the European cement kilns emit circa $1300 \text{ mg NO}_x/\text{m}^3$ (as NO_2 , dry gas, 273 K, 101.3 kPa, 10% O_2) [Ökopol report, 1998]. NO_x emission measurements at more than 50 preheater rotary cement kilns revealed a mean value of $2.1 \text{ g NO}_2/\text{kg}$ of clinker, which corresponds to $1050 \text{ mg NO}_2/\text{m}^3$ (dry gas, 273 K, 101.3 kPa, 10% O_2) in the exhaust gas [Int.Cem.Rev, Jan/96]. In an Austrian study the mean value for a calendar year was calculated from half-hour mean values for each kiln by means of continuous measurement. The mean values varied from 371–964 $\text{mg NO}_x/\text{m}^3$. All Austrian kilns use primary measures, 1 kiln has staged combustion and 1 kiln use mineralisers. The average emission of NO_x for all Austrian kilns was $680 \text{ mg NO}_x/\text{m}^3$ (11 kilns, 9 suspension preheater and 2 grate preheater (Lepol) kiln systems). [Austrian study, 1997] The NO_x emission vary with which kiln process is used, Table 1.9 shows results of emission measurements carried out in the Federal Republic of Germany by the Research Institute of the Cement Industry in the 1980s [Karlsruhe I, 1996].

Process type	NO_x emission factor [g NO_2/tonne clinker]	NO_x concentration ¹ [mg NO_2/m^3]
Cyclone preheater with heat recovery	600-3100	300-1400
Cyclone preheater without heat recovery	800-3500	500-2000
Grate preheater	800-4100	400-2100

1) Related to dry gas, 0 °C (273 K), 101.3 kPa, 10% O_2

Table 1.9: Results of NO_x measurements in Germany during the 1980s

[Karlsruhe I, 1996]

NO and NO_2 are the dominant nitrogen oxides in cement kiln exhaust gases ($\text{NO} > 90\%$ of the nitrogen oxides). There are two main sources for production of NO_x :

- Thermal NO_x : part of the nitrogen in the combustion air reacts with oxygen to form various oxides of nitrogen.
- Fuel NO_x : nitrogen containing compounds, chemically bound in the fuel, react with oxygen in the air to form various oxides of nitrogen.

Thermal NO_x forms at temperatures above 1200 °C and involves the reaction of nitrogen and oxygen molecules in the combustion air. Thermal NO_x is produced mainly in the kiln burning zone where it is hot enough to achieve this reaction. The amount of thermal NO_x produced in the burning zone is related to both burning zone temperature and oxygen content (air excess factor). The rate of reaction for thermal NO_x increases with temperature; therefore, hard-to-burn mixes which require hotter burning zones will tend to generate more thermal NO_x than kilns with easier-burning mixes. The rate of reaction also increases with increasing oxygen content (air excess factor). Running the same kiln with a higher backend oxygen content (air excess factor) will result in a higher thermal NO_x generation in the burning zone (although emissions of SO_2 and/or CO may decrease).

Fuel NO_x is generated by the combustion of the nitrogen present in the fuel. Nitrogen in the fuel either combines with other nitrogen atoms to form N_2 gas or reacts with oxygen to form fuel NO_x . In a precalciner the prevailing temperature is in the range of 850-950 °C, which is not high enough to form significant thermal NO_x , but fuel NO_x will occur. Similarly, other types of secondary firing of fuel in the back end of a kiln system, such as in the kiln riser pipe of a suspension preheater kiln or the calcining chamber of a preheater grate, may give rise to fuel NO_x . Therefore, in precalciner kilns, where up to 60% of the fuel can be burnt in the calciner, fuel NO_x formation significantly contributes to the total NO_x emission. The thermal NO_x

formation in these kilns is much lower when compared to kilns where all the fuel is burnt in the sintering zone.

Besides temperature and oxygen content (air excess factor), NO_x formation can be influenced by flame shape and temperature, combustion chamber geometry, the reactivity and nitrogen content of the fuel, the presence of moisture, the available reaction time and burner design.

1.3.3.2 Sulphur dioxide

SO_2 emissions from cement plants are primarily determined by the content of the volatile sulphur in the raw materials. Kilns that use raw materials with little or no volatile sulphur have little problems with SO_2 emissions. The emission concentration in the flue gas are below $10 \text{ mg SO}_2/\text{m}^3$ without abatement at some kilns, the SO_2 emission concentration increase with increased levels of volatile sulphur in the used raw material.

When raw materials containing organic sulphur or pyrite (FeS) are used the emissions of SO_2 can be high. SO_2 is the main (99%) sulphur compound to be released, although some SO_3 is produced and, under reducing conditions, H_2S could be evolved. Sulphur in the raw material occurring as sulphides and organically combined sulphur will evaporate, and 30% or more may be emitted from the first stage of a preheater. The gases from this unit will either be emitted directly to the atmosphere, or fed to the raw mill if it is in operation. In the raw mill, 20-70% of the SO_2 will be captured by the finely ground raw materials. Thus it is important that raw milling is optimised so that the raw mill can be operated to act as SO_2 abatement for the kiln.

Sulphur in the fuels fed to preheater kilns will not lead to significant SO_2 emissions, due to the strong alkaline nature in the sintering zone, the calcination zone and in the lower stage of the preheater. This sulphur will be captured in the clinker. The excess oxygen (1 to 3% O_2 maintained in the kiln for satisfactory cement product quality) will normally immediately oxidise any released sulphide compounds to SO_2 . In long kilns the contact between SO_2 and alkaline material is not so good, and sulphur in the fuels can lead to significant SO_2 emissions.

Despite the fact that most sulphur remains in the clinker as sulphate, SO_2 emissions can be significant from raw materials with a high volatile sulphur content and can be regarded as a major pollutant.

1.3.3.3 Dust

Traditionally the emission of dust, particularly from kiln stacks, has been the main environmental concern in relation to cement manufacture. The main sources of dust are kilns, raw mills, clinker coolers and cement mills. In all these processes large volumes of gases are flowing through dusty materials. The design and reliability of modern electrostatic precipitators and bag filters ensure dust releases can be reduced to levels where they cease to be significant; emission levels below $10 \text{ mg}/\text{m}^3$ are achieved in some installations.

Fugitive dust emissions can arise during the storage and handling of materials and solid fuels, and also from road surfaces. Particulate releases from packing and dispatch of clinker/cement can also be significant. The impact of fugitive emissions can be a local increase in levels of dust, whereas process dust emissions (generally from high stacks) can have impact on the air quality over a much larger area.

1.3.3.4 Carbon oxides (CO₂, CO)

The emission of CO₂ is estimated at 900 to 1000 kg/tonne clinker, related to a specific heat demand of approximately 3500 to 5000 MJ/tonne clinker, but also depending on fuel type. Due to cement grinding with mineral additions the emission of CO₂ is reduced when related to tonnes of cement (compare to Figure 1.7). Approximately 60% originates in the calcining process and the remaining 40% is related to fuel combustion. The CO₂ emissions resulting from the combustion of the carbon content of the fuel is directly proportional to the specific heat demand as well as the ratio of carbon content to the calorific value of the fuel. For example, a specific heat demand of 3000 MJ/tonne of clinker and the use of hard coal with a calorific value of 30 MJ/kg and a carbon content of 88% results in a CO₂ emission of 0.32 tonne per tonne of clinker, when regarding fuel part only. Using natural gas instead reduces this level by approximately 25%. [Austrian report, 1997] Emissions of combustion CO₂ have been progressively reduced, a reduction of about 30% in the last 25 years has been accomplished mainly by the adoption of more fuel efficient kiln processes.

The emission of CO is related to the content of organic matter in the raw material, but may also result from poor combustion when control of the solid fuel feed is sub-optimal. Depending on the raw material deposit, between 1.5 and 6 g of organic carbon per kg clinker are brought into the process with the natural raw material. According to Cembureau, tests using raw meals of various origins showed that between 85-95% of the organic compounds in the raw material are converted to CO₂ in the presence of 3% oxygen, but at the same time 5-15% are converted to CO. The proportion emitted as volatile organic carbon compounds (VOC) under these conditions was well below 1%. The CO concentration can be as high as 1000 mg/Nm³, even exceeding 2000 mg/Nm³ in some cases. [Cembureau report, 1997] Good hopper, transport conveyor and feeder design is essential to ensure that the feedrate of solid fuel is steady with minimal peaks. Otherwise substoichiometric combustion may occur which can lead to short term peaks of greater than 0.5% CO. These cause the additional problem that any EP abatement will have to be switched off automatically to avoid explosion.

1.3.3.5 Volatile organic compounds

In heat (combustion) processes in general, the occurrence of volatile organic compounds (and carbon monoxide) is often associated with incomplete combustion. In cement kilns, the emission will be low under normal steady-state conditions, due to the large residence time of the gases in the kiln, the high temperature and the excess oxygen conditions. Concentrations may increase during start-up or upset conditions. These events can occur with varying frequency, for example between once or twice per week to once per two or three months.

Emissions of volatile organic compounds (VOCs) can occur in the primary steps of the process (preheater, precalciner), when organic matter that is present in the raw materials is volatilised as the feed is heated. (See also section 1.2.3.3 Use of waste as fuel). The organic matter is released between temperatures of 400 and 600 °C. The VOC content of the exhaust gas from cement kilns typically lies between 10 and 100 mg/Nm³, in rare cases emissions can reach as much as 500 mg/Nm³ because of the raw material characteristics. [Cembureau report, 1997]

1.3.3.6 Polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs)

Any chlorine input in the presence of organic material may potentially cause the formation of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in heat (combustion) processes. PCDDs and PCDFs can be formed in/after the preheater and in the air pollution control device if chlorine and hydrocarbon precursors from the raw materials are available in sufficient quantities. (See also section 1.2.3.3 Use of waste as fuel). The

reformation of dioxins and furans is known to occur by de novo synthesis within the temperature window of cooling from 450 to 200 °C. Thus it is important that as the gases are leaving the kiln system they should be cooled rapidly through this range. In practice this is what occurs in preheater systems as the incoming raw materials are preheated by the kiln gases.

Due to the long residence time in the kiln and the high temperatures, emissions of PCDDs and PCDFs is generally low during steady kiln conditions. In Europe, cement production is rarely a significant source of PCDD/F emissions. Nevertheless, from the data reported in the document "Identification of Relevant Industrial Sources of Dioxins and Furans in Europe" there would still seem to be considerable uncertainty about dioxin emissions. [Materialien, 1997]

The reported data indicate that cement kilns can mostly comply with an emission concentration of 0.1 ng TEQ/Nm³, which is the limit value in the European legislation for hazardous waste incineration plants (Council Directive 94/67/EC). German measurements at 16 cement clinker kilns (suspension preheater kilns and Lepol kilns) during the last 10 years indicate that the average concentration amounts to about 0.02 ng TE/m³. [Schneider, 1996]

1.3.3.7 Metals and their compounds

Raw materials and fuels will always contain metals. The concentrations vary widely from one location to another. Metal compounds can be categorised into three classes, based on the volatilities of the metals and their salts:

1. Metals which are or have compounds that are refractory or non-volatile: Ba, Be, Cr, As, Ni, V, Al, Ti, Ca, Fe, Mn, Cu and Ag;
2. Metals that are or have compounds that are semi-volatile: Sb, Cd, Pb, Se, Zn, K and Na;
3. Metals that are or have compounds that are volatile: Hg and Tl.

[Dutch report, 1997]

The behaviour of these metals in the burning process is dependent on their volatility. Non-volatile metal compounds remain within the process and exit the kiln as part of the cement clinker composition. Semi-volatile metal compounds are partly taken into the gas phase at sintering temperatures to condense on the raw material in cooler parts of the kiln system. This leads to a cyclic effect within the kiln system (internal cycles) which builds up to the point where an equilibrium is established and maintained between input and output via the cement clinker. [Cembureau report, 1997] Volatile metal compounds condense on raw material particles at lower temperatures and potentially form internal or external cycles, if not emitted with the flue gas of the kiln. Thallium and mercury and their compounds are particularly easily volatilised and to a lesser extent so are cadmium, lead, selenium and their compounds. An internal cycle of easily volatile metal compounds is formed, when they react with the calcination feedstock or when they precipitate on the feedstock in cool areas of the calcination chamber, in the preheater, or in subsequent drying plants. Metals form an external cycle when the dust together with the condensed volatile compounds is separated in dust separators and returned to the raw meal. [Karlsruhe II, 1996]

The dusts from the production of cement contain small amounts of compounds of metals such as arsenic (As), cadmium (Cd), mercury (Hg), lead (Pb), thallium (Tl) and zinc (Zn). The main source of metal-laden dusts is the kiln system, including preheaters, precalciners, rotary kilns and clinker coolers. The metal concentration depends on the feedstock and recirculation in the kiln system. In particular, the use of coal and waste fuels may increase the input of metals into the process. As the metals entering the kiln system are of varying volatility and because of the high temperature, the hot gases in the cement kiln system contain also gaseous metal compounds. Balance investigations show that there is low retention of elements with high volatility in the clinker, resulting in an accumulation of these substances in the kiln system. [Karlsruhe II, 1996]

1.3.4 Waste

Waste produced during clinker production consists basically of unwanted rocks, which are removed from the raw materials during the preparation of the raw meal, and kiln dust removed from the by-pass flow and the stack, which is not recycled.

Filtrate from the filter presses used in the semi-wet process is fairly alkaline and contains suspended solids.

1.3.5 Noise

The heavy machinery and large fans used in cement manufacture can give rise to emissions of noise and/or vibration.

1.3.6 Odour

Odour emissions are very rarely a problem with a well operated plant. If the raw material contain combustible components (kerogens) which do not burn when they are heated in the preheater, but instead only pyrolise, emissions of hydrocarbons can occur. This hydrocarbon emission can be seen above the stack as a 'blue haze' or plume and can cause unpleasant smell around the cement plant under unfavourable weather conditions.

Burning of sulphur containing fuels and/or use of sulphur containing raw materials can lead to odour emissions (a problem especially encountered in shaft kilns).

1.3.7 Legislation

In general, emission limits for the cement industry are related to the three main pollutants NO_x , SO_2 and dust. Some countries have additional limits for metals, HCl, HF, organic compounds and PCDD/Fs. An overview of current legislation in the EU is given in Annex A.

Emission limits for cement industry are in general expressed as daily means and/or half hour values and generally apply for stable conditions.

1.3.8 Monitoring

To control kiln process, continuous measurements are recommended for the following parameters:

- pressure,
- temperature,
- O₂-content
- NO_x,
- CO, and possibly when the SO_x concentration is high
- SO₂ (it is a developing technique to optimise CO with NO_x and SO₂)

To accurately quantify the emissions, continuous measurements are recommended for the following parameters (these may need to be measured again if their levels can change after the point where they are measured to be used for control):

- exhaust volume (can be calculated but is regarded by some to be complicated),
- humidity (can be calculated but is regarded by some to be complicated),
- temperature,
- dust,
- O₂,
- NO_x,
- SO₂, and
- CO

Regular periodical monitoring is appropriate to carry out for the following substances:

- metals and their compounds,
- TOC,
- HCl,
- HF,
- NH₃, and
- PCDD/Fs

Measurements of the following substances may be required occasionally under special operating conditions:

- BTX (benzene, toluene, xylene),
- PAH (polyaromatic hydrocarbons), and
- other organic pollutants (for example chlorobenzenes, PCB (polychlorinated biphenyls) including coplanar congeners, chloronaphthalenes, etc.).

It is especially important to measure metals when wastes with enhanced metals contents are used as raw materials or fuels.

It is appropriate to have measured all these substances on at least one occasion to provide data when applying for the plant's first IPPC permit.

1.4 Techniques to consider in the determination of BAT

In this chapter techniques are discussed that may have a positive effect on (i.e. reduce) emissions arising during the manufacture of cement. A short description, applicability, general emission levels (or reduction potential) and cost information are given when available/appropriate. In addition to these emission-reduction techniques, the consumption of raw materials and the use of energy are discussed in this chapter.

A technique to reduce energy use and emissions from the cement industry, expressed per unit mass of cement product, is to reduce the clinker content of cement products. This can be done by adding fillers, for example sand, slag, limestone, fly-ash and pozzolana, in the grinding step. In Europe the average clinker content in cement is 80-85%. Many manufacturers of cement are working on techniques to further lower the clinker content. One reported technique claims to exchange 50% of the clinker with maintained product quality/performance and without increased production cost. Cement standards define some types of cement with less than 20% clinker, the balance being made of blast furnace slag.

1.4.1 Consumption of raw materials

Recycling of collected dust to the production processes lowers the total consumption of raw materials. This recycling may take place directly into the kiln or kiln feed (alkali metal content being the limiting factor) or by blending with finished cement products.

The use of suitable wastes as raw materials can reduce the input of natural resources, but should always be done with satisfactory control on the substances introduced to the kiln process.

1.4.2 Use of energy

Kiln systems with 5 cyclone preheater stages and precalciner are considered standard technology for ordinary new plants, such a configuration will use 2900-3200 MJ/tonne clinker [Cembureau report, 1997]. To optimise the input of energy in other kiln systems it is a possibility to change the configuration of the kiln to a short dry process kiln with multi stage preheating and precalcination. This is usually not feasible unless done as part of a major upgrade with an increase in production. The application of the latest generation of clinker coolers and recovering waste heat as far as possible, utilising it for drying and preheating processes, are examples of methods which cut primary energy consumption.

Electrical energy use can be minimised through the installation of power management systems and the utilisation of energy efficient equipment such as high-pressure grinding rolls for clinker comminution and variable speed drives for fans.

Energy use will be increased by most type of end-of-pipe abatement. Some of the reduction techniques described below will also have a positive effect on energy use, for example process control optimisation.

1.4.3 Process selection

The selected process will affect the releases of all pollutants, and will also have a significant effect on the energy use. For new plants and major upgrades a dry process kiln with multi-stage preheating and precalcination is considered to be state of the art. The wet process kilns

operating in Europe are generally expected to convert to the dry process when renewed [Dutch report, 1997], and so are semi-dry and semi-wet processes.

1.4.4 General techniques

1.4.4.1 Process control optimisation

Optimisation of the clinker burning process is usually done to reduce the heat consumption, to improve the clinker quality and to increase the lifetime of the equipment (the refractory lining, for example) by stabilising process parameters. Reduction of emissions, such as NO_x, SO₂ and dust, are secondary effects of this optimisation. Smooth and stable kiln operation close to design values for process parameters is beneficial for all kiln emissions. Optimisation includes measures like homogenising the raw material, ensuring uniform coal dosing and improving the cooler's operation. To ensure that the feed rate of solid fuel is steady with minimal peaks, it is essential with good designs of hopper, transport conveyor and feeder, such as a modern, gravimetric solid fuel feed system.

NO_x reduction is caused by the reduced flame and burning temperatures and the reduced consumption of fuel, as well as zones with a reducing atmosphere in the kiln system. Control of oxygen content (excess air) is critical to NO_x control. Generally the lower the oxygen content (excess air) at for instance a cement kiln back end, the less NO_x is produced. However this has to be balanced against increases in CO and SO₂ at lower oxygen levels. [UK IPC Note, 1996] NO_x reductions of up to 30% have been reported [Cembureau report, 1997].

The SO₂ reduction is caused by the reduced SO₂ volatility at lower flame and burning temperatures and the oxidising atmosphere in the kiln, together with stable kiln operation. The effect of kiln optimisation on SO₂ emission is considerable for long wet and dry kilns and marginal for preheater kilns. SO₂ reductions of up to 50% have been reported. [Cembureau report, 1997]

Avoidance of kiln upsets and of CO-trips when EPs are applied, reduces dust emissions, and in doing so also reduces emissions of any substances adsorbed to the dust, for example metals. Modern control systems with faster measuring and control equipment can allow higher switch-off criteria than the typically applied 0.5% v/v CO, and thereby reduce the number of CO-trips.

Kiln optimisation is applicable to all kilns and can include many elements ranging from instruction/training of the kiln operators up to installation of new equipment such as dosing systems, homogenisation silos, preblending beds and new clinker coolers. The cost of these measures varies widely, from 0 to about 5 million euros. [Cembureau report, 1997]

Several cement equipment suppliers have developed expert automatic control systems based usually on the control of the burn by monitoring NO_x levels [UK IPC Note, 1996]. The investment required for a computer-based high level control system is about 300000 euros, additional investment may be necessary to install the required measuring and dosing systems at the plant. [Cembureau report, 1997]

Kiln optimisation is primarily done to reduce operating costs, increase capacity and improve product quality. The operating cost of an optimised kiln is usually reduced compared to the non-optimised state. The savings result from reduced fuel and refractory consumption, lower maintenance cost and higher productivity among other factors. [Cembureau report, 1997]

1.4.4.2 Choice of fuel and raw material

Careful selection and control of substances entering the kiln can reduce emissions. For example, limiting the sulphur content of both raw materials and fuels can reduce releases of SO₂. The same is valid for raw materials and fuels containing other substances, for example nitrogen, metals and organic compounds. There are, however, some differences between different kiln systems and feeding points. For example, fuel sulphur is not a problem for dry preheater and precalciner kiln systems, and all organic compounds in fuels fed through the main burner will be completely destroyed.

Limiting the chlorine content of input materials reduces formation of alkaline chlorides (and other metal chlorides), which can cause build-ups and upset kiln conditions and therefore can impair the performance of electrostatic precipitators, which in turn causes increased dust emissions. High alkali materials may also require some of the dust to be bled off, rather than be recycled within the kiln system, to avoid high alkali contents in the final product. In this case, use of low alkali materials can allow the dust to be returned to the process, thus reducing the waste generated by the process.

1.4.5 Techniques for controlling NO_x emissions

Table 1.10 gives an overview of techniques that have a positive effect on, i.e. reduce, the emissions of NO_x arising during the manufacture of cement. The table is a summary and should be read in conjunction with the corresponding paragraph below.

Technique	Kiln systems applicability	Reduction efficiency	Reported emissions		Reported costs ³	
			mg/m ³ ¹	kg/tonne ²	investment	operating
Flame cooling	All	0-50 %	400-	0.8-	0.0-0.2	0.0-0.5
Low-NO _x burner	All	0-30 %			0.15-0.8	0
Staged combustion	Precalciner	10-50 %	<500-1000	<1.0-2.0	0.1-2	0
	Preheater				1-4	0
Mid-kiln firing	Long	20-40 %	No info.	-	0.8-1.7	No info.
Mineralised clinker	All	10-15 %	No info.	-	No info.	No info.
SNCR	Preheater and Precalciner	10-85 %	200-800	0.4-1.6	0.5-1.5	0.3-0.5
SCR – data from pilot plants only	Possibly all	85-95 %	100-200	0.2-0.4	ca. 2.5 ⁴ 3.5-4.5 ⁵	0.2-0.4 ⁴ No info. ⁵

1) normally referring to daily averages, dry gas, 273 K, 101.3 kPa and 10% O₂

2) kg/tonne clinker: based on 2000 m³/tonne of clinker

3) investment cost in 10⁶ euros and operating cost in euros/tonne of clinker, normally referring to a kiln capacity of 3000 tonne clinker/day and initial emission up to 2000 mg NO_x/m³

4) costs estimated by Ökopol for a full scale installation (kiln capacities from 1000 to 5000 tonne clinker/day and initial emissions from 1300 to 2000 mg NO_x/m³), operating costs ca. 25% lower than for SNCR

5) costs estimated by Cembureau for a full scale installation

Table 1.10: Overview of techniques for controlling NO_x

1.4.5.1 Primary measures to control NO_x emissions

Many cement plants have taken general primary optimisation measures, such as process control measures, improved firing technique, optimised cooler connections and fuel selection, and these also reduce NO_x emissions.

Some modern well-optimised preheater kiln systems and preheater/precalciner kiln systems are achieving less than 500 mg NO_x/m³ with either primary measures only or combined with staged combustion. Raw materials quality (the burnability of the raw mix) and kiln system design may be reasons for not being able to achieve this level.

Flame cooling

Addition of water to the fuel or directly to the flame reduces the temperature and increases the concentration of hydroxyl radicals. This can have a positive effect on NO_x reduction in the burning zone, reduction efficiency from 0-50% has been reported. Additional heat is required to evaporate the water, which causes slight additional CO₂ emissions (approximately 0.1-1.5%) compared to the total CO₂ emission of the kiln. [Cembureau report, 1997] Water injection can cause kiln operation problems.

For a kiln capacity of 3000 tonne clinker/day the investment cost is estimated at 0.0-0.2 million euros and the operating cost at 0.0-0.5 euros/tonne clinker [Cembureau].

Low-NO_x burner

Designs of low-NO_x burners vary in detail but essentially the coal (fuel) and air are injected into the kiln through concentric tubes. The primary air proportion is reduced to some 6-10% of that required for stoichiometric combustion (typically 20-25% in traditional burners). Axial air is injected at high momentum in the outer channel. The coal may be blown through the centre pipe or the middle channel. A third channel is used for swirl air, its swirl being induced by vanes at, or behind, the outlet of the firing pipe

The net effect of this burner design is to produce very early ignition, especially of the volatile compounds in the fuel, in an oxygen-deficient atmosphere, and this will tend to reduce the formation of NO_x. NO_x reductions of up to 30% are achievable in successful installations [Int.Cem.Rev., Oct/97] but the application of low-NO_x burners is not always followed by a reduction of the NO_x emissions. Low-NO_x burners can be applied to all rotary kilns, in the main kiln as well as in the precalciner, and emission levels of 600-1000 mg/Nm³ have been reported [Dutch report, 1997]. The investment cost for a new low-NO_x burner is about 150000 to 350000 euros for a kiln capacity of 3000 tonne clinker/day. [Cembureau report, 1997][Dutch report, 1997] If the existing firing system uses direct firing it must be changed to an indirect firing system to allow combustion with low primary air flow, this will mean an investment cost of about 600000 to 800000 euros for a kiln capacity of 3000 tonne clinker/day. [Cembureau report, 1997]

1.4.5.2 Staged combustion

Staged combustion is applied at cement kilns supplied with several combustion stages. This technique is mostly carried out with specially designed precalciners. The first combustion stage takes place in the rotary kiln under optimum conditions for the clinker burning process. The second combustion stage is a burner at the kiln inlet, which produces a reducing atmosphere that decomposes a portion of the nitrogen oxides generated in the sintering zone. The high temperature in this zone is particularly favourable for the reaction which reconverts the NO_x to elementary nitrogen. In the third combustion stage the calcining fuel is fed into the calciner with an amount of tertiary air, producing a reducing atmosphere there, too. This system reduces the generation of NO_x from the fuel, and also decreases the NO_x coming out of the kiln. In the fourth and final combustion stage the remaining tertiary air is fed into the system as 'top air' for residual combustion. [Dutch report, 1997]

Calciners currently in use differ from one another essentially in the location of the fuel input, the way in which the fuel, kiln feed and tertiary air are distributed, and the geometric configuration. [Dutch report, 1997]

Staged firing technology can in general only be used with kilns equipped with a precalciner. Substantial plant modifications are necessary in cyclone preheater systems without precalciners. If this cannot be combined with an increase in production capacity the manufacturers offer a solution with so-called 'small' tertiary air ducting and calciner. In this case only a small proportion of about 10-25% of the total heat needed from the kiln is passed through the calciner, but this is sufficient to produce a reducing zone for decomposing nitrogen oxides. [ZKG, 10/1996]

Some modern well optimised plants achieve emission levels below 500 mg NO_x/Nm³ with multi-staged combustion. Emissions of CO and SO₂ can increase if the combustion process is not completed in the precalciner [Cembureau report, 1997] and problems with CO and clogging have been reported when attempting high efficiencies [Cembureau]. Possible reductions in NO_x by up to 50% are specified by the suppliers of the different staged firing systems. However, it is difficult to maintain the guaranteed values for this level of NO_x abatement while at the same time limiting the CO emissions. [ZKG, 10/1996]

The investment cost for installing staged combustion at a precalciner kiln is 0.1-2 million euros, the cost depending on the design of the existing calciner [Cembureau]. The investment cost for a precalciner and the tertiary duct for a 3000 tonne/day preheater kiln with a grate cooler into a precalciner kiln is about 1 to 4 million euros. The investment cost for the transformation of a 3000 tonne/day preheater kiln with a satellite cooler into a precalciner kiln with a grate cooler is about 15 to 20 million euros. [Cembureau report, 1997]

Lump fuel (for example tyres) firing is a possible variant of the staged combustion technique as a reducing zone is created when the lump fuel is burned. In preheater/precalciner kilns the lump fuel can be introduced at the kiln inlet or at the precalciner. Lump fuel firing is reported to have a positive effect on NO_x reduction. However, it is very difficult to produce a controlled reducing atmosphere with lump fuel firing. [Cembureau report, 1997]

1.4.5.3 Mid-kiln firing

In long wet and long dry kilns the creation of a reducing zone by firing lump fuel can reduce NO_x emissions. As long kilns usually have no access to a temperature zone of about 900 to 1000 °C, mid-kiln firing systems have been installed at some plants in order to be able to use waste fuels that cannot pass the main burner (for example tyres). [Cembureau report, 1997]

Mechanical design considerations mean that the fuel can only be injected intermittently, once per kiln revolution. To maintain continuity of heat input, solid, slow burning fuels such as tyres or other waste fuels in containers may be used. A few of such installations exist and NO_x reductions of 20-40% have been reported in some cases. The rate of burning of such secondary fuels can be critical. If it is too slow, reducing conditions can occur in the burning zone, which may severely affect product quality. If it is too high, the kiln chain section can be overheated – resulting in the chains being burnt out. [Int.Cem.Rev., Oct/97]

Capital costs may be in the region of 0.8-1.7 million euros for the kiln conversion and fuel handling equipment, and the annual labour and maintenance costs may be of a similar order [Int.Cem.Rev., Oct/97].

1.4.5.4 Mineralised clinker

The addition of mineralisers to the raw material is a technology to adjust the clinker quality and allow the sintering zone temperature to be reduced. By lowering the burning temperature, NO_x -formation is reduced. The NO_x reduction might be between 10 and 15%, but reductions of up to 50% has been reported [Cementa AB, 1994].

Calcium fluoride is one example of a mineraliser, but excessive additions could lead to an increase in HF releases.

1.4.5.5 Selective non-catalytic reduction (SNCR)

Selective non-catalytic reduction (SNCR) involves injecting $\text{NH}_2\text{-X}$ compounds into the exhaust gas to reduce NO to N_2 . The reaction has an optimum in a temperature window of about 800 to 1000 °C, and sufficient retention time must be provided for the injected agents to react with NO . The right temperature window is easy to obtain in suspension preheater kilns, precalciner kilns and possibly in some Lepol kilns. At the moment no full scale installation of SNCR in Lepol kilns exists, but very promising results from pilot investigations in Germany are known [Göller]. In long wet and dry process kilns it might be very difficult, or impossible, to obtain the right temperature and retention time needed. The most common $\text{NH}_2\text{-X}$ agent is ammonia water of about 25% NH_3 . [Cembureau report, 1997] Other possible reduction agents which can be employed on an industrial scale are ammonia gas, urea solutions, nitrolime or cyanamide and similar other substances [Int.Cem.Rev., Jan/96]. Experience shows that for most applications ammonia water is the best agent for SNCR at preheater and precalciner kiln systems [Cembureau report, 1997].

Further development in the use of SNCR technology is necessary if the plant is already equipped with a staged combustion system. Simultaneous use of these technologies requires the temperatures, residence times and gas atmosphere in the reaction section to be adjusted to suit one another. [ZKG, 10/1996]

There are 18 full-scale SNCR installations in operation in the EU and EFTA countries, as presented in Annex B.

Most SNCR installations operating today are designed and/or operated for NO_x reduction rates of 10-50% (with NH_3/NO_2 molar ratios of 0.5-0.9) and emission levels of 500-800 $\text{mg NO}_x/\text{m}^3$, which is sufficient to comply with current legislation in some countries. Installations designed and/or operated for higher reduction rates will do better. Two plants, see below for more details, with SNCR installations delivered by two different suppliers, which both guaranteed 80% reduction, are achieving reduction rates of 80-85% which corresponds to emissions of less than 200 $\text{mg NO}_x/\text{m}^3$. With SNCR installations operating at reduction rates of 80-85% daily average concentrations of less than 500 mg/m^3 are theoretically achievable, also when initial levels are above 2000 mg/m^3 .

It is important to maintain the temperature range mentioned above, if the temperature falls below this level unconverted ammonia is emitted (so-called NH_3 slip) and at significant higher temperatures the ammonia is oxidised to NO_x . NH_3 slip may also occur at elevated NH_3/NO_2 molar ratios, i.e. from a molar ratio of about 1.0-1.2. NH_3 slippage has in other sectors of industry sometimes resulted in the formation of aerosols of ammonia chlorides and ammonia sulphates which has passed through the filter and become visible as a white plume above the exhaust gas stack. Investigations have shown that considerably lower aerosol levels are produced by cement plants. [World Cement, March 1992] Unused ammonia may be oxidised and transformed into NO_x in the atmosphere and NH_3 slippage may also result in ammonia enriched dust which may not be recycled to the cement mill [Cembureau]. The possible NH_3

slip should be taken into account in the design of SNCR installations. Emissions of carbon monoxide (CO) and nitrous oxide (N₂O) may also occur [World Cement, March 1992]. Additional heat is required to evaporate the water, which causes a small increase in CO₂ emissions. The transport and storage of ammonia is a potential danger for the environment and requires additional safety measures. [Cembureau report, 1997] By storing a 25% ammonia water solution, some of the problems with ammonia are avoided.

The NO_x reduction efficiency increases with the NH₃/NO₂ molar ratio. However, the NO_x reduction rate cannot simply be increased at will, as higher dosage might cause NH₃ slippage. At one plant, a four-stage cyclone preheater kiln system with a maximum clinker throughput of 2000 tonnes/day, a molar ratio of around 1.0 produced a NO_x reduction rate of up to 80%, without any escape of NH₃. Correct operation (appropriate control system, optimised injection of NH₃-water) of the SNCR system does not entail any higher ammonia emissions than normal. [Int.Cem.Rev., Jan/96]

Two Swedish plants, dry process cyclone preheater/precalciner kilns, installed SNCR in 1996/97. A reduction of 80-85% has been achieved at both kilns when applying a NH₃/NO molar ratio of 1.0-1.1 and so far a small increase of NH₃ is estimated, no N₂O and no increase in CO emissions have been measured and no traces of any NH₃ have been found in the cement. One of the kilns is 20 years old with a capacity of 5800 tonnes clinker/day and initial NO_x levels about 1100 mg/Nm³ (as NO₂, dry gas), the investment cost was about 1.1 million euros (0.55 million euros for the SNCR installation and another 0.55 million euros for the ammonia water storage) and the operating cost is about 0.55 euros/tonne of clinker. The total cost (investment + operating costs) is less than 0.6 euros/tonne of clinker. The other kiln has a capacity of 1900 tonnes clinker/day and initial NO_x levels of 750-1350 mg/Nm³ (as NO₂), the investment cost was about 0.55 million euros and the operating cost is about 0.3 euros/tonne of clinker. [Cementa AB][Junker]

The driving force for these plants to invest in high-performing SNCR installations was the Swedish policy about NO_x emission. According to this policy any investment in abatement that has a total cost (investment + operating) less than 4.5 euros (40 SEK) per kilo of abated NO_x (as NO₂) may be acceptable.

For a 3000 tonnes/day preheater kiln with initial NO_x emission of up to 2000 mg/m³ and with NO_x reduction up to 65% (i.e. 700 mg NO_x/m³) the investment cost for SNCR using ammonia water as the reducing agent is 0.5-1.5 million euros, the cost being very influenced by local regulations on the storage of ammonia water. The operating cost for the same kiln is 0.3-0.5 euros/tonne of clinker, the cost mainly determined by the cost of the injected ammonia. [Cembureau report, 1997]

1.4.5.6 Selective catalytic reduction (SCR)

SCR reduces NO and NO₂ to N₂ with the help of NH₃ and a catalyst at a temperature range of about 300-400 °C. This technology is widely used for NO_x abatement in other industries (coal-fired power stations, waste incinerators). In the cement industry, basically two systems are being considered: low dust exhaust gas and high dust exhaust gas treatment. Low dust exhaust gas systems require reheating of the exhaust gases after dedusting, resulting in additional cost. High dust systems are considered preferable for technical and economical reasons. [Cembureau report, 1997][Dutch report, 1997] Up to now SCR is only tested on preheater and semi-dry (Lepol) kiln systems, but it might be applicable to other kiln systems as well.

Large NO_x emission reductions are potentially achievable by SCR high dust systems (85-95%) [Cembureau report, 1997]. Pilot plant trials on small portions (3%) of the exhaust gas in Austria, Germany, Italy and Sweden have shown promising results. The NO_x emission levels

were approximately 100-200 mg/m³ with no loss of catalyst activity, except for one recent trial in Austria that has reported considerable abrasion of the catalyst after a working period of about 5000 hours which shortened the lifetime of this type of catalyst to less than one year [Göller]. Full-scale production runs will have to be carried out in order to remove the technical and economic uncertainties related to upscaling of the SCR technique. The main uncertainties are related to the high dust concentration in the gases (up to 500 g/Nm³), the catalyst dust removal techniques, lifetime of catalysts and total investment costs. [Cembureau]

As the catalysts remove hydrocarbons as well, SCR will in general also reduce VOC and PCDD/Fs. According to one supplier, new pilot projects for NO_x reduction are being developed in which specific catalysts are applied for the additional reduction of VOC and CO emissions. [Dutch report, 1997]

Considering the high reduction potential, the successful pilot tests and the fact that SCR is state-of-the-art technology for comparable installations; SCR is an interesting technique for the cement industry. There are at least three suppliers in Europe that offers full scale SCR to the cement industry with performance levels of 100-200 mg/m³. However, SCR capital expenditure is still considered to be higher than for SNCR. [Dutch report, 1997]

Feasibility studies have been carried out in Austria, Germany, the Netherlands and Sweden, for example. The estimated costs for the SCR technique in the cement industry varies a lot, with the production costs and lifetime of the catalyst being mayor variables. A full-scale SCR demonstration plant is being built in Germany with governmental financial support. This first full-scale plant (Solnhofen Zementwerke) will be in operation in the end of 1999. A full-scale SCR plant is also under consideration in Austria, this too with governmental financial support [Göller].

In a report from Austrian UBA the total cost for achieving 100-200 mg/Nm³, referred to 10% O₂, is estimated at less than 2.3 euros/tonne clinker for an 850 tonne clinker/day kiln [Austrian report, 1998].

A Dutch study shows that an SCR installation at the Dutch cement plant would have a cost of about 2500 euros per tonne of abated NO_x. The Netherlands has a NO_x policy which considers costs up to 5000 euros per tonne of abated NO_x as reasonable. Accordingly, The Netherlands regards SCR to be a cost effective NO_x abatement technique for its cement industry. [de Jonge]

Cementa AB in Slite, Sweden, has a 5800 tonne clinker/day dry process suspension preheater/precalciner kiln. They have been operating a pilot high dust SCR, downstream of an SNCR, for about a year and have investigated how much a full scale SCR installed downstream the SNCR would cost (this means initial NO_x levels into the SCR of less than 200 mg/m³). The estimated investment cost is about 11.2 million euros and the operating cost about 1.3 euros/tonne of clinker, giving a total cost of 3.2 euros/tonne of clinker. The cost per additional kilo of abated NO_x would be 5.5-7.3 euros for the SCR. This cost is too high and not reasonable according to the company. But the Swedish EPA argues that the average cost per kilo of abated NO_x would be less than 4.5 euros for the combined SNCR and SCR installations. This may be an acceptable cost according to the Swedish policy about NO_x emission. [Junker]

In a report compiled for DG XI, Ökopol estimates the total cost for achieving 200 mg/Nm³ at between 0.75 euros/tonne clinker (5000 tonne clinker/day kiln, initial NO_x emission level of 1300 mg/Nm³) and 1.87 euros/tonne clinker (1000 tonne clinker/day kiln, initial NO_x emission level of 2000 mg/Nm³). The calculations are based on an investment cost of ca. 2.5 million euros and operating costs ca. 25% lower than for SNCR, which were provided by suppliers and pilot plant operators. In the calculations, an exchange of catalyst after 5 years were taken into account. [Ökopol report, 1998]

Cembureau estimates the investment cost for a 3000 tonne clinker/day preheater kiln at 3.5-4.5 million euros, remarking that investment costs indication are only known from supplier not including the plant modifications [Cembureau report, 1997].

According to one supplier the total cost (investment + operating costs) for the high dust SCR process is approximately 1.5-2.5 euros/tonne of clinker. For the low dust SCR process the total cost was estimated at approximately 5 euros/tonne of clinker. [Dutch report, 1997]

1.4.6 Techniques for controlling SO₂ emissions

The first step with respect to SO₂ control is to consider primary process optimisation measures, including the smoothing of kiln operation, choice of oxygen concentration and choice of raw materials and fuels. Increasing the oxygen content in long kilns is decreasing the SO₂ level and increasing the NO_x level. A balance to protect the environment should be sought by optimising NO_x/SO₂/CO by adjusting the backend oxygen content. In those cases where these measures are not enough additional end-of-pipe measures can be taken. Table 1.11 gives an overview of techniques that have a positive effect on, that is reduce, the emissions of SO₂ arising from the manufacture of cement. The table is a summary and should be read in conjunction with the corresponding paragraph below.

Technique	Kiln systems applicability	Reduction efficiency	Reported emissions		Cost ³	
			mg/m ³ ¹	kg/tonne ²	investment	operating
Absorbent addition	All	60-80%	400	0.8	0.2-0.3	0.1-0.4
Dry scrubber	Dry	up to 90%	<400	<0.8	11	1.4-1.6
Wet scrubber	All	>90%	<200	<0.4	6-10	0.5-1
Activated carbon	Dry	up to 95%	<50	<0.1	15 ⁴	no info.

1) normally referring to daily averages, dry gas, 273 K, 101.3 kPa and 10% O₂

2) kg/tonne clinker: based on 2000 m³/tonne clinker

3) investment cost in 10⁶ euros and operating cost in euros/tonne clinker

4) this cost also includes an SNCR process, referring to a kiln capacity of 2000 tonne clinker/day and initial emission of 50-600 mg SO₂/m³

Table 1.11: Overview of techniques for controlling SO₂

1.4.6.1 Absorbent addition

The addition of absorbents such as slaked lime (Ca(OH)₂), quicklime (CaO) or activated fly ash with high CaO content to the exhaust gas of the kiln can absorb some of the SO₂. Absorbent injection can be applied in dry or wet form. [Dutch report, 1997] For preheater kilns it has been found that direct injection of slaked lime into the exhaust gas is less efficient than adding slaked lime to the kiln feed. The SO₂ will react with the lime to CaSO₃ and CaSO₄, which then enters the kiln together with the raw material and is incorporated into the clinker. [Dutch report, 1997][Cembureau report, 1997] This technique is suitable for cleaning gas streams with moderate SO₂ concentrations and can be applied at an air temperature of over 400 °C. The highest reduction rates can be achieved at temperatures exceeding 600 °C. It is recommended to use a Ca(OH)₂ based absorbent with a high specific surface area and high porosity. [Dutch report, 1997] Slaked lime does not have a high reactivity, therefore Ca(OH)₂/SO₂ molar ratios of between 3 and 6 have to be applied. [Cembureau report, 1997] Gas streams with high SO₂ concentrations require 6-7 times the stoichiometric amount of absorbent, implying high operation costs. [Dutch report, 1997]

SO₂ reductions of 60 to 80% can be achieved by absorbent injection in suspension preheater kiln systems. With initial levels not higher than 400 mg/m³ it is theoretically possible to achieve

around 100 mg/m³. No plant has implemented this technique to achieve this level of reduction, yet. Most plants in Europe have emission limit values that correspond to actual emissions, and thus require no abatement. For initial levels up to 1200 mg/m³ it is possible to achieve around 400 mg/m³ with absorbent addition. At initial levels above 1200 mg/m³ adding slaked lime to the kiln feed is not cost effective. [Dutch report, 1997] There might be a risk of higher sulphur recirculation and kiln instability as higher levels of sulphur are returned to the kiln when this technique is applied [Cembureau].

Absorbent addition is in principle applicable to all kiln systems [Dutch report, 1997], although it is mostly used in suspension preheaters. There is at least one long wet cement kiln injecting dry NaHCO₃ to the exhaust gas before the EP to reduce peak emissions of SO₂ [Marchal]. Lime addition to the kiln feed reduces the quality of the granules/nodules and causes flow problems in Lepol kilns.

Absorbent addition is currently in use at several plants to ensure that the current limits are not exceeded in peak situations. This means that in general it is not in continuous operation, but only when required by specific circumstances. [Dutch report, 1997] With an initial SO₂ concentration of up to 3000 mg/Nm³, a reduction of up to 65% and a slaked lime cost of 85 euros/tonne, the investment cost for a 3000 tonne clinker/day preheater kiln is about 0.2-0.3 million euros and the operating costs about 0.1-0.4 euros/tonne of clinker. [Cembureau report, 1997]

1.4.6.2 Dry scrubber

To reduce very high SO₂ emissions (more than 1500 mg/Nm³) a separate scrubber is required. One type of dry scrubber uses a venturi reactor column to produce a fluidised bed consisting of a blend of slaked lime and raw meal. The intensive contact between gas and absorbent, the long residence time and the low temperature (close to the dew point) allow efficient absorption of SO₂. The gas leaving the venturi is loaded with absorbent which is collected in an electrostatic precipitator. A portion of the collected absorbent is returned to the scrubber, and the other portion is added to the kiln inlet and duly converted into clinker. [Cembureau report, 1997]

An SO₂ reduction of 90% may be achieved, that corresponds to a clean gas content of 300 mg SO₂/m³ when the initial SO₂ concentration is 3000 mg/m³. A dry scrubber will also reduce emissions of HCl and HF. Dry scrubbers can be fitted to all dry kiln types. For an initial SO₂ concentration of up to 3000 mg/Nm³ and a slaked lime cost of 85 euros/tonne, the investment cost for a 3000 tonne clinker/day preheater kiln is about 11 million euros and the operating costs approximately 1.6 euros/tonne of clinker. The additional sulphur content of the clinker reduces the amount of additional gypsum required by the cement mill. When the contribution of gypsum replacement is included in the cost evaluation the operating cost is reduced to about 1.4 euros/tonne of clinker. [Cembureau report, 1997]

There is only one sulphur dry scrubber in operation at a cement plant in Europe (and possibly worldwide), at the HCB-Untervaz plant in Switzerland. This kiln system is a 4 stage suspension preheater kiln with planetary cooler and has a maximum capacity of 2000 tonnes clinker/day. The unabated emission levels would be around 2500 mg SO₂/Nm³ (dry gas, 10% O₂) in direct operation and up to 2000 mg SO₂/Nm³ in compound operation. The abated average emission level 1998 was 385 mg SO₂/Nm³. [Cembureau]

1.4.6.3 Wet scrubber

The wet scrubber is the most commonly used technique for flue gas desulphurisation in coal fired power plants. The SO_x is absorbed by a liquid/slurry sprayed in a spray tower or is bubbled through the liquid/slurry. The absorbent can be calcium carbonate, hydroxide or oxide. There are five wet scrubbers currently in use in the European cement industry, all of them spray towers. The slurry is sprayed in counter current to the exhaust gas and collected in a recycle tank at the bottom of the scrubber where the formed sulphite is oxidised with air to sulphate and forms calcium sulphate dihydrate. The dihydrate is separated and used as gypsum in cement milling and the water is returned to the scrubber. [Cembureau][Cembureau report, 1997][Cementa AB, 1994][Coulburn]

The SO_2 reduction achieved can be more than 90%. Cementa AB operates a 5800 tonne clinker/day preheater kiln and has an initial SO_2 concentration in the flue gas of 1200-1800 mg/m^3 , Castle cement operates a 2500 tonne clinker/day preheater kiln and has an initial SO_2 concentration in the flue gas of about 800-1400 mg/m^3 as daily averages with peak values of more than 2000 mg/m^3 at times. They are both below 200 mg/m^3 with the scrubber in operation. [Cembureau][Cementa AB][Junker]

The wet scrubber also significantly reduce the HCl, residual dust, metal and NH_3 emissions [Cementa AB, 1994]. A wet scrubber can be fitted to all kiln types. The investment cost for Castle Cement's scrubber (including plant modifications) is reported at 7 million euros and the operating cost is about 0.9 euro/tonne of clinker [Cembureau]. For Cementa AB the investment cost was about 10 million euros and the operating cost is about 0.5 euros/tonne of clinker [Cementa AB]. With an initial SO_2 concentration of up to 3000 mg/Nm^3 and a kiln capacity of 3000 tonne clinker/day the investment cost is 6-10 million euros and the operating costs 0.5-1 euros/tonne of clinker. [Cembureau]

1.4.6.4 Activated carbon

Pollutants such as SO_2 , organic compounds, metals, NH_3 , NH_4 compounds, HCl, HF and residual dust (after an EP or fabric filter) may be removed from the exhaust gases by adsorption on activated carbon. If NH_3 is present, or added, the filter will remove NO_x as well. The activated carbon filter is constructed as a packed-bed with modular partition walls. The modular design allows the filter sizes to be adapted for different gas throughputs and kiln capacity. The used activated coke is periodically extracted to a separate silo and replaced with fresh adsorbent. By using the saturated coke as fuel in the kiln, the trapped substances are returned to the system and to a large extent become fixed in the cement clinker. [Cembureau report, 1997], [Cementa AB, 1994], [Dutch report, 1997]

The only activated carbon filter installed at a cement works in Europe is that at Siggenthal, Switzerland. The Siggenthal kiln is a 4-stage cyclone preheater kiln with a capacity of 2000 tonne clinker/day. Measurements showed high removal efficiencies for SO_2 , metals and PCDD/Fs. During a 100 days trial, the SO_2 concentrations at the filter inlet varied between 50 and 600 mg/m^3 , whereas the outlet concentrations were always significantly below 50 mg/m^3 . Dust concentrations dropped from 30 mg/m^3 to significantly below 10 mg/m^3 . [Dutch report, 1997]

An activated carbon filter can be fitted to all dry kiln systems. The system at Siggenthal also includes an SNCR process and the city of Zürich financed about 30% of the total investment cost of approximately 15 million euros. The investment in this abatement system was made to enable the cement work to use digested sewage sludge as fuel. [Dutch report, 1997], [Cementa AB, 1994]

1.4.7 Techniques for controlling dust emissions

There are three main point sources of dust emissions from cement plants. These are kiln systems, clinker coolers and cement mills. Various dedusting devices have been used in the past for these three duties but nowadays only electrostatic precipitators, EPs, or fabric filters are installed. Fugitive dust releases from handling and storage of materials, and the crushing and grinding of raw materials and fuels can also be significant. Table 1.12 gives an overview of available data. The table is a summary and should be read in conjunction with the corresponding paragraph below.

EPs and fabric filters both have their advantages and disadvantages. Both types have a very high dedusting efficiency during normal operation. During special conditions such as high CO concentration, kiln start up, kiln shut down or switching from compound operation (raw mill on) to direct operation (raw mill off) the efficiency of EPs can be significantly reduced while the efficiency of fabric filters is not affected. Fabric filters therefore have a higher overall efficiency if they are well maintained and filter bags are replaced periodically. A disadvantage of fabric filters is that used filter bags are waste and have to be disposed of according to national regulations. [Cembureau report, 1997]

Technique	Applicability	Reported emissions		Cost ³	
		mg/m ³ ¹	kg/tonne ²	investment	operating
Electrostatic precipitators	All kiln systems	5-50	0.01-0.1	2.1-4.6	0.1-0.2
	clinker coolers	5-50	0.01-0.1	0.8-1.2	0.09-0.18
	cement mills	5-50	0.01-0.1	0.8-1.2	0.09-0.18
Fabric filters	All kiln systems	5-50	0.01-0.1	2.1-4.3	0.15-0.35
	clinker coolers	5-50	0.01-0.1	1.0-1.4	0.1-0.15
	cement mills	5-50	0.01-0.1	0.3-0.5	0.03-0.04
Fugitive dust abatement	All plants	-	-	-	-

1) for kiln systems normally referring to daily averages, dry gas, 273 K, 101.3 kPa and 10% O₂

2) kg/tonne clinker: based on 2000 m³/tonne clinker

3) investment cost in 10⁶ euros and operating cost in euros per tonne of clinker for reducing the emission to 10-50 mg/m³, normally referring to a kiln capacity of 3000 tonne clinker per day and initial emission up to 500 g dust/m³

Table 1.12: Overview of techniques for controlling dust

1.4.7.1 Electrostatic precipitators

Electrostatic precipitators generate an electrostatic field across the path of particulate matter in the air stream. The particles become negatively charged and migrate towards positively charged collection plates. The collection plates are rapped or vibrated periodically, dislodging the material so that it falls into collection hoppers below. It is important that EP rapping cycles are optimised to minimise particulate reentrainment and thereby minimise the potential to affect plume visibility. EPs are characterised by their ability to operate under conditions of high temperatures (up to approximately 400 °C) and high humidity.

Factors affecting efficiency are flue gas flow rate, strength of the electric field, particulate loading rate, SO₂ concentration, moisture content and shape and area of the electrodes. In particular, performance can be impaired by build-up of material forming an insulating layer on the collection plates and so reducing the electric field. [Dutch report, 1997] This can happen if there are high chlorine and sulphur inputs to the kiln process, forming alkali metal chlorides and sulphates. The alkali metal chlorides forms very fine dust (0.1-1 µm) and have high specific dust resistivity (between 10¹²-10¹³ Ω cm) forming insulating layers on the electrodes and so leading to problems in dust removal. This has been observed and studied particularly in the iron and steel industry. Problems of high dust resistances can be solved by water injection in

evaporation coolers. [Karlsruhe II, 1996] Another way of solving the problem is to use fabric filters.

In sinter plants (iron and steel industry) this fine dust of alkali metal chlorides is the reason why well designed and operated common EPs normally can not achieve emitted dust concentrations below 100-150 mg/m³. The same problem with alkali metal chlorides and a malfunctioning EP have been encountered at a cement plant in Austria, when burning pre-treated plastic waste (1.3% Cl) as part of the fuel.

Sufficiently dimensioned electrostatic filters, together with good air conditioning and optimised EP cleaning regime, can reduce levels down to 5-15 mg/m³ as monthly average (dry gas, 273 K, 10% O₂) [Austrian report, 1997]. Existing EP installations can often be upgraded without the need for total replacement thereby limiting costs. This may be done by fitting more modern electrodes or installing automatic voltage control on older installations. In addition it may be possible to improve the gas passage through the EP or add supplementary stages. At one cement works EPs bought in 1979 to achieve levels of 50 mg/m³ were upgraded and now achieve levels of below 30 mg/m³ [Cementa AB]. Besides dust, the EP also removes substances that adsorb to the dust particles, such as dioxins and metals if present.

For the overall performance of electrostatic precipitators, it is important to avoid CO-trips. See section 1.4.4.1 Process control optimisation.

The available literature indicates no restrictions on the applicability of EPs to the various types of processes used in the cement industry. [Dutch report, 1997] EPs are, however, not installed any more for cement mill dedusting because of the relatively high emissions at startups and shut downs.

The investment cost for a new EP for a kiln with a capacity of 3000 tonne clinker/day, initial emission level of up to 500 g/m³ and clean gas dust content of 10-50 mg/m³ is about 1.5-3.8 million euros, and an extra 0.6-0.8 million euros for the conditioning tower and filter fan if required. The operating cost for the same kiln EP is about 0.1-0.2 euros/tonne of clinker. For clinker cooler for a kiln capacity of 3000 tonne clinker/day, initial emission level of up to 20 g/m³ and clean gas dust content of 10-50 mg/m³ and cement ball mill with a capacity of 160 tonne cement/hour, initial emission level of up to 300 g/m³ and clean gas dust content of 10-50 mg/m³ the investment cost for an EP is about 0.8-1.2 million euros and the operating cost 0.09-0.18 euros/tonne of clinker. [Cembureau report, 1997]

1.4.7.2 Fabric filters

The basic principle of fabric filtration is to use a fabric membrane which is permeable to gas but which will retain the dust. Initially, dust is deposited both on the surface fibres and within the depth of the fabric, but as the surface layer builds up the dust itself becomes the dominating filter medium. Gas for treatment can flow either from the inside of the bag outwards or vice versa. As the dust cake thickens, the resistance to gas flow increases. Periodic cleaning of the filter medium is therefore necessary to control the gas pressure drop across the filter. The most common cleaning methods include reverse air flow, mechanical shaking, vibration and compressed air pulsing. The fabric filter should have multiple compartments which can be individually isolated in case of bag failure and it should be sufficient of these to allow adequate performance to be maintained if a compartment is taken off line. There should be 'burst bag detectors' on each compartment to indicate the need for maintenance when this happens.

The use of modern fabric filters can reduce dust emissions to below 5 mg/m³ (dry gas, 273 K, 10% O₂) [Austrian report, 1997]. Besides dust, the fabric filter also removes substances that adsorb to the dust particles, such as dioxins and metals if present.

The available literature indicates no restrictions on the applicability of fabric filters to the various types of processes used in the cement industry. [Dutch report, 1997] High temperature applications will result in the need for more exotic fabric types than are 'normally' supplied. However a good range of these is available.

The investment required to fit a new fabric filter to a kiln with a capacity of 3000 tonne clinker/day, initial emission level of up to 500 g/m³ and clean gas dust content of 10-50 mg/m³ is about 1.5-3.5 million euros, and an extra 0.6-0.8 million euros are required for the conditioning tower and filter fan if required. Conditioning towers are only needed for low temperature applications with for example polyacrylnitril bags. The operating cost for the same kiln fabric filter is about 0.15-0.35 euros/tonne of clinker. A pulse jet fabric filter with air to air heat exchanger and filter fan for a grate clinker cooler for a kiln capacity of 3000 tonne clinker/day, initial emission level of up to 20 g/m³ and clean gas dust content of 10-50 mg/m³ cost about 1.0-1.4 million euros and the operating cost is about 0.10-0.15 euros/tonne of clinker. For a cement ball mill with a capacity of 160 tonne cement/hour, initial emission level of up to 300 g/m³ and clean gas dust content of 10-50 mg/m³ the investment cost for a pulse jet fabric filter is about 0.3-0.5 million euros including filter fan, and the operating cost 0.03-0.04 euros/tonne of clinker. [Cembureau report, 1997]

1.4.7.3 Fugitive dust abatement

Fugitive emission sources mainly arise from storage and handling of raw materials, fuels and clinker and from vehicle traffic at the manufacturing site. A simple and linear site layout is advisable to minimise possible sources of fugitive dust. Proper and complete maintenance of the installation always has the indirect result of reducing fugitive dust by reducing air leakage and spillage points. The use of automatic devices and control systems also helps fugitive dust reduction, as well as continuous trouble-free operation. [Cembureau report, 1997]

Some techniques for fugitive dust abatement are:

- Open pile wind protection. Outdoor storage piles of dusty materials should be avoided, but when they do exist it is possible to reduce fugitive dust by using properly designed wind barriers.
- Water spray and chemical dust suppressors. When the point source of dust is well localised a water spray injection system can be installed. The humidification of dust particles aids agglomeration and so help dust settle. A wide variety of chemical agents is also available to improve the overall efficiency of the water spray.
- Paving, road wetting and housekeeping. Areas used by lorries should be paved when possible and the surface should be kept as clean as possible. Wetting the roads can reduce dust emissions, especially during dry weather. Good housekeeping practices should be used in order to keep fugitive dust emissions to a minimum.
- Mobile and stationary vacuum cleaning. During maintenance operations or in case of trouble with conveying systems, spillage of materials can take place. To prevent the formation of fugitive dust during removal operations, vacuum systems should be used. New buildings can easily be equipped with stationary vacuum cleaning systems, while existing buildings normally are better fitted with mobile systems and flexible connections.
- Ventilation and collection in fabric filters. As far as possible, all material handling should be conducted in closed systems maintained under negative pressure. The suction air for this purpose is then dedusted by a fabric filter before emitted into the atmosphere.
- Closed storage with automatic handling system. Clinker silos and closed fully automated raw material storage are considered the most efficient solution to the problem of fugitive dust generated by high volume stocks. These types of storage are equipped with one or more fabric filters to prevent fugitive dust formation in loading and unloading operations. [Cembureau report, 1997]

1.4.8 Controlling other emissions to air

1.4.8.1 Carbon oxides (CO₂, CO)

All measures that reduce fuel energy use also reduce the CO₂ emissions. The selection, when possible, of raw materials with low organic matter content and fuels with low ratio of carbon content to calorific value reduces CO₂ emissions.

The selection, when possible, of raw materials with low content of organic matter also reduces the emission of CO.

1.4.8.2 Volatile organic compounds and PCDD/PCDFs

Under normal circumstances emissions of VOCs and PCDD/PCDFs are generally low. Materials with high content of volatile organic compounds should not, if a choice is possible, be fed into the kiln system via the raw material feeding route and fuels with high content of halogens should not be used in a secondary firing. To minimise the possibility of PCDD/F reformation it is important that the kiln gases are cooled through the window of 450 to 200 °C as quickly as possible.

If elevated concentrations of VOCs and/or PCDD/PCDFs occur, adsorption on activated carbon can be considered.

1.4.8.3 Metals

It should be avoided to feed materials with high content of volatile metals into the kiln system.

Accumulation of metals, especially thallium, in the internal and external cycles of a cement kiln system results in an increase in emissions with increasing kiln operating time. This can be reduced by partly or completely interrupting these cycles. However, the close interconnection between internal and external cycles means it is sufficient to interrupt only the external cycle. This can be done by discarding the dust collected in the dust collector, instead of returning it to the raw meal. When its chemical composition is suitable, this discarded cement kiln dust can be added directly to the cement milling stage. [Karlsruhe II, 1996] As the emitted metals (except part of the mercury) are to a large extent bound to dust, abatement strategies for metals are covered by abatement strategies for dust. One way to minimise mercury emissions is to lower the exhaust temperature. Non-volatile elements remain within the process and exit the kiln as part of the cement clinker composition. When high concentrations of volatile metals (especially mercury) occur, absorption on activated carbon is an option.

1.4.9 Waste

Collected dust should be recycled to the production processes whenever practicable. This recycling may take place directly into the kiln or kiln feed (alkali metal content being the limiting factor) or by blending with finished cement products. Alternative uses may be found for material that cannot be recycled.

1.4.10 Noise

Best available techniques for reduction of noise will not be described in this document.

1.4.11 Odour

Unpleasant smells caused by hydrocarbon emissions can be avoided by after-burning, use of an activated carbon filter or by feeding the raw material responsible to the hot zone of the kiln.

If odour is caused by sulphur compounds, a change of fuel and/or raw material can be a solution, also see section 1.4.6.

1.5 Best available techniques for the cement industry

In understanding this chapter and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector; for the manufacture of cement these are energy use and emissions to air. The emissions to air from cement plants include nitrogen oxides (NO_x), sulphur dioxide (SO₂) and dust;
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this chapter that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous chapter. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this chapter could be used to judge the current performance of an existing installation or to judge a proposal for a new installation and thereby assist in the determination of appropriate "BAT-based" conditions for that installation. It is foreseen that new installations could be designed to perform at or even better than the general "BAT" levels presented here. It is also considered that many existing installations could reasonably be expected, over time, to move towards the general "BAT" levels or do better.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

Emission levels given below are expressed on a daily average basis and standard conditions of 273 K, 101.3 kPa, 10% oxygen and dry gas.

Process selection

The selected process has a major impact on the energy use and air emissions from the manufacture of cement clinker.

- For new plants and major upgrades the best available technique for the production of cement clinker is considered to be a dry process kiln with multi-stage preheating and precalcination. The associated BAT heat balance value is 3000 MJ/tonne clinker.

General primary measures

The best available techniques for the manufacturing of cement includes the following general primary measures:

- A smooth and stable kiln process, operating close to the process parameter set points, is beneficial for all kiln emissions as well as the energy use. This can be obtained by applying:
 - Process control optimisation, including computer-based automatic control systems.
 - The use of modern, gravimetric solid fuel feed systems.
- Minimising fuel energy use by means of:
 - Preheating and precalcination to the extent possible, considering the existing kiln system configuration.
 - The use of modern clinker coolers enabling maximum heat recovery.
 - Heat recovery from waste gas.
- Minimising electrical energy use by means of:
 - Power management systems.
 - Grinding equipment and other electricity based equipment with high energy efficiency.
- Careful selection and control of substances entering the kiln can reduce emissions.
 - When practicable selection of raw materials and fuels with low contents of sulphur, nitrogen, chlorine, metals and volatile organic compounds.

Oxides of Nitrogen

The best available techniques for reducing NO_x emissions are the combination of the above described general primary measures and:

- Primary measures to control NO_x emissions
 - Flame cooling
 - Low-NO_x burner
- Staged combustion
- Selective non-catalytic reduction (SNCR)

Staged combustion and SNCR are not yet used simultaneously for NO_x reduction.

The BAT emission level associated with the use of these techniques is considered to be in the range 200-500 mg NO_x/m³ expressed as NO₂ on a daily average basis. (See comments below on consensus in TWG). The ease with which individual installations can achieve emissions within this range varies greatly and is discussed below, therefore it is not presumed that all kilns can or should achieve these emission levels by a given date. The use of SNCR introduces an active control mechanism which can be expected to result in less variation in emission levels over time, whereas kilns without SNCR may achieve these levels only over longer averaging periods.

Some modern well-optimised suspension preheater kiln systems and suspension preheater/precalciner kiln systems are achieving NO_x emission levels of less than 500 mg/m³ with either primary measures only or combined with staged combustion. Raw material quality and kiln system design may be reasons for not achieving this emission level.

With SNCR the achievable NO_x emission level can in the best of cases be less than 200 mg/m³ if the initial level is not higher than about 1000-1300 mg/m³ (80-85% reduction), although the majority of installations are today operated to achieve an emission level of 500-800 mg/m³ (10-50% reduction). The possible NH₃ slip should be taken into account in the design of SNCR installations.

On a sector level the majority of kilns in the European Union is said to be able to achieve less than 1200 mg/m³ with primary measures. By applying SNCR at moderate reduction efficiencies of about 60% this could reduce the NO_x emission level to less than 500 mg/m³.

To fit SNCR, an appropriate temperature window has to be accessible. The right temperature window is easy to obtain in suspension preheater kiln systems, in suspension preheater/precalciner kiln systems and possibly in some Lepol kiln systems. At the moment no full scale installation of SNCR in Lepol kilns exists, but promising results from pilot plants have been reported. In long wet and dry process kilns it might be very difficult, or impossible, to obtain the right temperature and retention time needed. At present, about 78% of Europe's cement production is from dry process kilns and an overwhelming majority of these kilns are suspension preheater kiln systems or suspension preheater/precalciner kiln systems.

There was some consensus reached within the TWG regarding the best available techniques to control NO_x emissions. Whilst there was support for the above concluded BAT, there was an opposing view that the emission level associated with the use of BAT is 500-800 mg NO_x/m³ (as NO₂). Although there are 15 kilns using SNCR techniques at relatively low efficiencies to obtain emission levels below 800 mg NO_x/m³ this view is based upon limited experience with application of SNCR at higher reduction efficiencies and the consequent uncertainty regarding additional ammonia emissions which may occur at high ammonia-water injection rates. The

fear is that ammonia slippage may result in visible and persistent emissions of dust formed of ammonia sulphates and ammonia chlorides. Additionally unused ammonia may subsequently transform into NO_x in the atmosphere and unused ammonia may prevent recovered dust from being reused in cement. Whilst a few modern cement plants are able to obtain long-term NO_x emission levels below 500 mg/m^3 , the industry view is that at the sector level plants would have to combine primary measures and either staged combustion or SNCR to reach emission levels below 800 mg/m^3 , and these techniques can only be applied to certain kiln systems.

There was also a view that selective catalytic reduction (SCR) is BAT with an associated emission level of $100\text{-}200 \text{ mg NO}_x/\text{m}^3$ (as NO_2), based upon SCR being regarded as an available and economically viable technique. This conclusion is drawn from feasibility studies and successful pilot tests. There are at least three suppliers in Europe that offers full scale SCR to the cement industry with performance levels of $100\text{-}200 \text{ mg/m}^3$. However, the first full scale SCR installation in the cement industry will not be in operation until the end of 1999.

Oxides of Sulphur

The best available techniques for reducing SO_x emissions are the combination of the above described general primary measures and:

- For initial emission levels not higher than about $1200 \text{ mg SO}_2/\text{m}^3$:
 - Absorbent addition.
- For initial emission levels higher than about $1200 \text{ mg SO}_2/\text{m}^3$:
 - Wet scrubber.
 - Dry scrubber.

The BAT emission level associated with the use of these techniques is in the range $200\text{-}400 \text{ mg/m}^3$ expressed as SO_2 on a daily average basis.

SO_2 emissions from cement plants are primarily determined by the content of the volatile sulphur in the raw materials. Kilns that use raw materials with little or no volatile sulphur have SO_2 emission levels well below this level without using abatement techniques.

For initial levels up to 1200 mg/m^3 it is possible to achieve around 400 mg/m^3 with absorbent addition. Absorbent addition is in principle applicable to all kiln systems, although it is mostly used in suspension preheaters.

The techniques dry scrubber and wet scrubber have proven their efficiency in a few plants where the raw materials have a high content of volatile sulphur. The cost for these techniques is rather high and it will be a local decision whether the environmental benefits justify the cost. A wet scrubber can achieve a level of less than $200 \text{ mg SO}_2/\text{m}^3$, irrespective of initial concentration. The SO_2 reduction achieved with dry scrubbing is up to 90%, that corresponds to a clean gas content of $300 \text{ mg SO}_2/\text{m}^3$ when the initial SO_2 concentration is 3000 mg/m^3 . A wet scrubber can be fitted to all kilns, and a dry scrubber can be fitted to all dry kilns.

Dust

The best available techniques for reducing dust emissions are the combination of the above described general primary measures and:

- Minimisation/prevention of dust emissions from fugitive sources as described in section 1.4.7.3.
- Efficient removal of particulate matter from point sources by application of:
 - Electrostatic precipitators with fast measuring and control equipment to minimise the number of CO trips
 - Fabric filters with multiple compartments and ‘burst bag detectors’

The BAT emission level associated with these techniques is 20-30 mg dust/m³ on a daily average basis. This emission level can be achieved by electrostatic precipitators and/or fabric filters at the various types of installations in the cement industry.

Waste

The recycling of collected particulate matter to the process wherever practicable, is considered to constitute BAT. When the collected dusts are not recyclable the utilisation of these dusts in other commercial products, when possible, is considered BAT.

1.6 Emerging techniques in the cement industry

1.6.1 Fluidised bed cement manufacturing technology

The new cement sintering technology by means of the fluidised bed cement kiln system is a project subsidised by the Ministry of International Trade and Industry in Japan since 1986. A pilot plant with the capacity of 20 tonnes clinker/day has been operated for six years, between 1989 and 1995, by Sumitomo Osaka Cement Co. Ltd at Toshigi Factory in Japan. A 200 tonnes clinker/day large scale pilot plant was constructed in the end of 1995.

The configuration of the 20 tonnes clinker/day fluidised bed cement kiln system is shown in. The system consists of a suspension preheater (SP), a spouted bed granulating kiln (SBK), a fluidised bed sintering kiln (FBK), a fluidised bed quenching cooler (FBK) and a packed bed cooler.

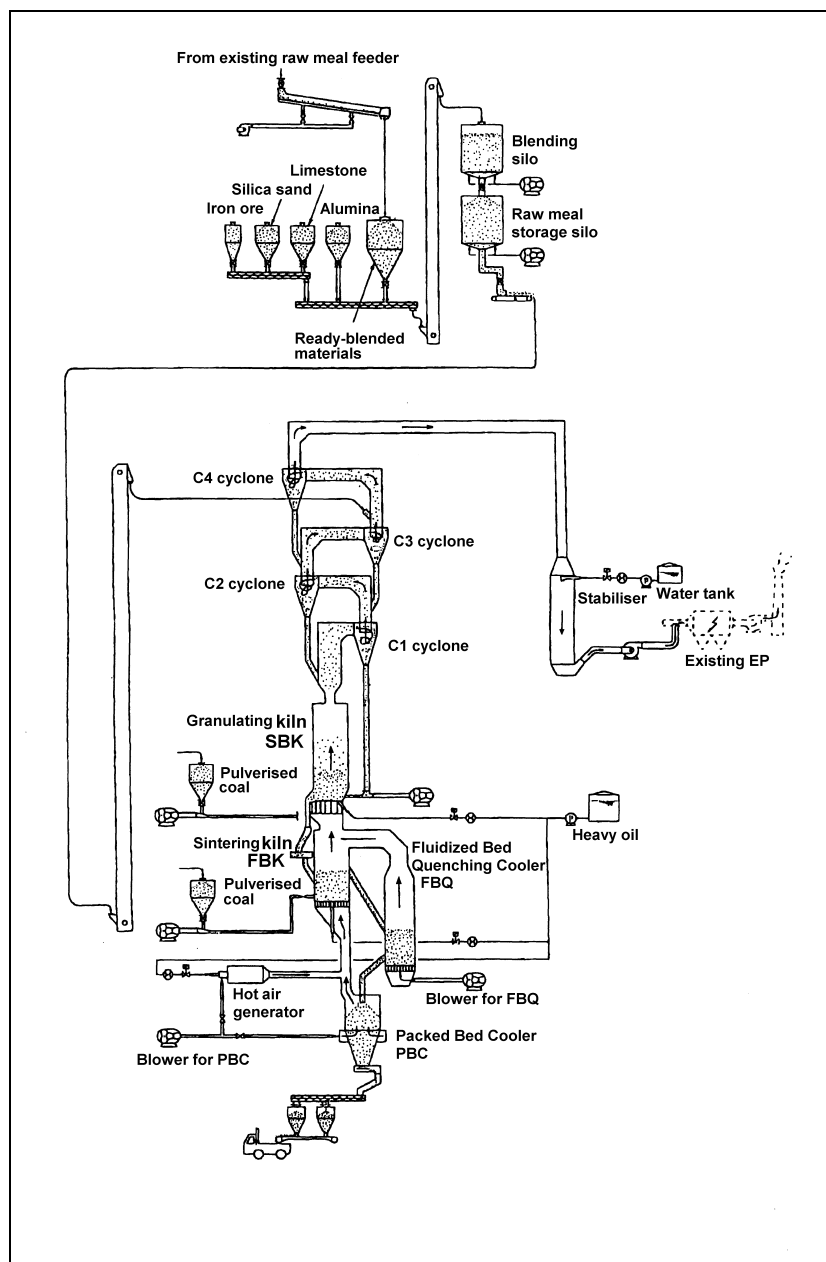


Figure 1.8: Fluidised bed cement kiln
[Japan Cement Association, 1996]

The suspension preheater is a conventional 4-stage cyclone preheater which preheats and calcines the raw meal. The granulating kiln is granulating the raw meal into granules of about 1.5-2.5 mm diameter at a temperature of 1300 °C. In the sintering kiln the sintering of the granules is completed at a temperature of 1400 °C. The fluidised bed quenching cooler quickly cools the cement clinker from 1400 to 1000 °C. Finally, the cement clinker is cooled down to about 100 °C in the packed bed cooler.

The cement clinker produced in the fluidised bed kiln are of the same or better quality as the clinker from a commercial plant. The NO_x emission is 115-190 mg/m³ when heavy oil is used and 440-515 mg/m³ when pulverised coal is used as fuel (converted to 10% O₂). According to a feasibility study of a 3000 tonne clinker/day plant the heat use can be reduced by 10-12% compared with a suspension preheater rotary kiln with grate cooler, it is therefore expected that the CO₂ emission can be reduced by 10-12%.

The final target of the technical development of the fluidised bed cement kiln system are (in accordance with the feasibility study on a 3000 tonne clinker/day plant and based on the results from the 20 tonnes/day pilot plant):

1. Reduction of heat use by 10-12%.
2. Reduction of CO₂ emission by 10-12%.
3. A NO_x emission level of 380 mg/m³ or less (converted to 10% O₂).
4. To maintain the current SO_x emission level.
5. Reduction of construction cost by 30%.
6. Reduction of installation area by 30%.

1.6.2 Staged combustion combined with SNCR

In theory, a combination of staged combustion and SNCR could be comparable to SCR in performance, that is NO_x emission levels of 100-200 mg/m³. This combination is considered very promising by suppliers but is not yet proven.

1.7 Conclusions and recommendations

The experts nominated to the Technical Working Group by Member States, Norway, European Environmental Bureau and European Industry (Cembureau - The European Cement Association) have all taken part in this exchange of information.

There is quite a lot of general information available about cement manufacturing. The general emission and consumption levels and the applied production and abatement techniques have been no problem to collect. When it comes to plant specific information, or figures for the very best and/or very worse performances it has been more difficult or impossible to get the information.

There is some cost data available but in general it is not known what exactly is included or how it is calculated. Therefore costs given in this document are more indications of magnitudes than exact figures.

SCR technology may be close to being implemented in the cement sector. The first full scale plant will be in operation in Germany in the end of 1999, and one installation is under consideration in Austria. At the end of year 2000, according to the current timetable, results from the commissioning and long time trials of the performance will be available from the German installation.

It is recommended to consider an update of this BAT reference document around year 2005, in particular regarding NO_x abatement (development of SCR technology and high efficiency SNCR). Other issues, that have not been fully dealt with in this document, that could be considered/discussed in the review are:

- more information about chemical additives acting as slurry thinners,
- numeric information on acceptable frequency and duration of CO-trips, and
- associated BAT emission values for VOC, metals, HCl, HF, CO and PCDD/Fs.

2 LIME INDUSTRY

2.1 General information about the Lime industry

Lime is used in a wide range of products, each suited to particular market requirements. For example, lime and its derivatives are used as a fluxing agent in steel refining, as a binder in building and construction, and in water treatment to precipitate impurities. Lime is also used extensively for the neutralisation of acidic components of industrial effluent and flue gases.

There is evidence that the use of quicklime and hydrated lime in construction was widespread as early as 1000 B.C. among many civilisations, including the Greeks, Egyptians, Romans, Incas, Mayas, Chinese, and Mogul Indians. The Romans knew of its chemical properties and used it, for example, for bleaching linen and medicinally as limewater.

Quicklime, or burnt lime, is calcium oxide (CaO) produced by decarbonisation of limestone (CaCO₃). Slaked lime are produced by reacting, or “slaking”, quicklime with water and consist mainly of calcium hydroxide (Ca(OH)₂). Slaked lime includes hydrated lime (dry calcium hydroxide powder), milk of lime and lime putty (dispersions of calcium hydroxide particles in water). The term lime includes quicklime and slaked lime and is synonymous with the term lime products. Lime is, however, sometimes used incorrectly to describe limestone products which is a frequent cause of confusion.

World production of lime grew steadily from just under 60 million tonnes in 1960 to a peak of almost 140 million tonnes in 1989. Output of lime dipped in the mid-1970s and early 1980s, due to the general economic recessions at the time, and the most recent world recession led to a drop in production to 120 million tonnes in 1995, as shown in Figure 2.1. The numbers shown do not give the complete picture, however, as a significant portion of total lime production takes place at the point of use (i.e. captive lime production within, among others, iron and steel, kraft pulp and sugar industries) and so does not enter the market. The European Lime Association, EuLA, estimates the total world production of lime, including captive lime, at 300 million tonnes.

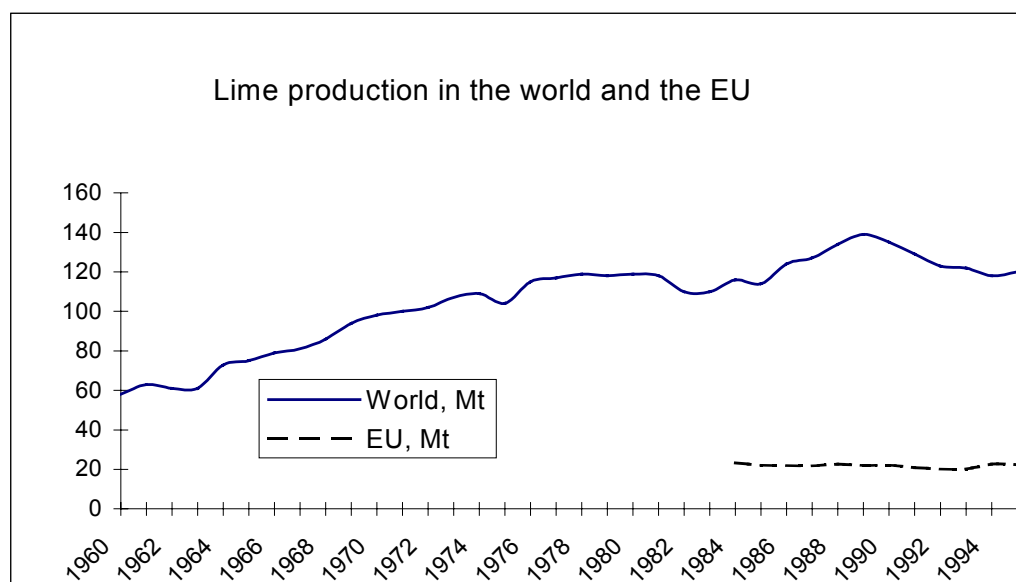


Figure 2.1: Sales-relevant lime production in the world and the EU 1960,1984-1995
[EC Mineral Yearbook, 1995 and 1997]

With an annual production of around 20 million tonnes of lime, the EU countries produce about 15% of sales-relevant world lime production. In most EU countries the lime industry is characterised by small and medium-sized companies. There has, however, been a growing trend towards concentrations in recent years, with a small number of large international companies having gained a considerable market share. Nevertheless, there are still more than 100 companies operating in the European Union.

Germany, Italy and France are the largest producers of lime in the EU, together accounting for about two thirds of the total volume. The production of lime in countries of the EU is shown in Figure 2.2.

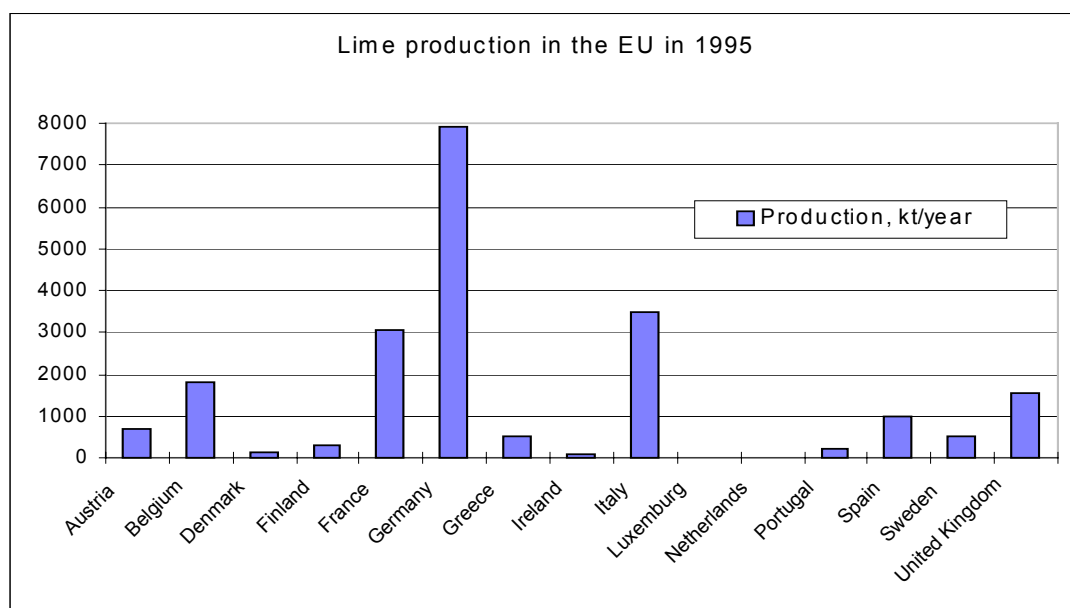


Figure 2.2: Sales-relevant lime production in the EU countries 1995

[EC Mineral Yearbook, 1997], [EuLA]

The production of lime in the EU countries dropped in the end of the 1980s, only to increase again at the beginning of 1994. This was a consequence of changes in patterns of consumption. One of the main users of lime, the iron and steel industry, reduced its specific lime consumption per tonne of steel from 100 kg to 40 kg. However, around the middle of the 1990s the growing use of lime for environmental protection brought sales figures back up again.

Total lime consumption in the EU has stagnated because sectors with increasing demand, such as water treatment and flue gas desulphurisation, only partially compensate for decreased demand in the traditional steel and metallurgy sectors. In the medium-term the EU market for lime should remain stable, but may be affected by imports from Eastern Europe.

The consumption of sales-relevant lime in the EU countries by different sectors is shown in Table 2.1. Details of the captive lime production are not available, but the estimated total consumption of captive and sales relevant lime in 1996 in Europe by the biggest users was:

Iron and steel making	6-10 million tonnes per year
Kraft pulping	4 million tonnes per year
Sugar industry	2 million tonnes per year

Lime is a low-cost but bulky material, so it tends to be transported only over relatively short distances. Exports of lime from the EU only amount to a few per cent of the production. The main exporting country in the EU is Belgium, which exports nearly 50% of its lime production.

	1995	
Steel making and non-ferrous metals processing	40%	ca.
Construction and public works	20%	
Agriculture	12%	
Chemistry-petrochemistry	10%	
Environmental applications	8%	
Sugar industry	5%	
Soil stabilization in construction	3%	
Paper and cardboard industry	2%	

Table 2.1: Lime consumption by sectors in the EU countries 1995 (not including captive lime)
[EC Mineral Yearbook, 1997]

There are approximately 240 lime-producing installations in the European Union (excluding captive lime production), which are distributed across the Member States as shown in Table 2.2.

Country	Lime Plants
Austria	7
Belgium	6
Denmark	2
Finland	4
France	19
Germany	67
Greece	44
Ireland	4
Italy	32
Luxembourg	0
Netherlands	0
Portugal	12
Spain	26
Sweden	6
United Kingdom	9
Total	238

Table 2.2: Number of non-captive lime plants in EU Member States in 1995
[EuLA], [Bournis, Symeonidis], [Gomes], [Göller], [Junker], [Jørgensen]

There is a total of about 450 kilns (excluding captive lime kilns) in the EU, most of which are other shaft kilns and parallel-flow regenerative shaft kilns (See Table 2.3). Typical kiln size lies between 50 and 500 tonnes per day. Only about 10% of kilns have a capacity of less than 50 or more than 500 tonnes per day.

Country	Rotary	Annular shaft	Regener. shaft	Other shaft	Other kilns	Total
Austria	0	2	6	3	1	12
Belgium	8	5	14	0	2	29
Denmark	2	0	0	0	0	2
Finland	5	0	0	0	0	5
France	4	21	20	18	1	64
Germany	7	31	12	74	12	136
Greece	1	2	1	39	1	44
Ireland	1	0	1	3	0	5
Italy	0	5	25	30	0	60
Luxembourg	0	0	0	0	0	0
Netherlands	0	0	0	0	0	0
Portugal	0	0	2	1	9	12
Spain	4	1	21	16	0	42
Sweden	5	0	3	2	0	10
UK	8	0	7	10	1	26
Total	45	67	114	196	27	449

Table 2.3: Number of operational lime kilns, not including captive kilns, in EU Member States 1995
[EuLA], [Aspelund], [Bournis, Symeonidis], [Gomes], [Junker], [Slavin]

Different types of lime are used for a wide variety of applications. A distinction is made between calcium limes, dolomitic limes and hydraulic limes. Calcium limes are by far the largest category and are supplied in lump, ground and hydrated forms. Dolomitic limes are more specialised products and are supplied in smaller quantities in lump, ground, hydrated and dead-burned forms. Hydraulic limes are partially hydrated and contain cementitious compounds, and are used exclusively in building and construction. The estimated distribution of different types of lime in terms of percentages of total production of burnt lime in 1995 is shown in Table 2.4.

	1995
Fine ground lime	50%
Lump lime	30%
Hydrated lime	16%
Deadburnt dolomite	2.5%
Hydraulic lime	1.5%

Table 2.4: Estimated distribution of different types of lime in the EU in 1995
[EuLA]

Each specific type of lime has a certain reactivity and the type of lime used is therefore governed by the requirements of the application and the specific process. A distinction is drawn between hard burnt, medium burnt and soft burnt limes. Soft burnt limes are those with the highest reactivity. The properties of limes also depend on the limestone feed material, the type of kiln and the fuel used. For example, coke-fired shaft kilns generally produce quicklime with a medium to low reactivity, whereas gas-fired parallel-flow regenerative kilns usually produce a high reactivity lime.

The lime industry is a highly energy-intensive industry with energy accounting for up to 50% of total production costs. Kilns are fired with solid, liquid or gaseous fuels. The use of natural gas has grown substantially over the last few years. Table 2.5 shows the distribution of the fuel types used in the EU in 1995.

	1995
Natural gas	48%
Coal ¹⁾	36%
Oil	15%
Other	1%

1) including hard coal, coke, lignite and pet coke

Table 2.5: Distribution of fuels used by the European lime industry in 1995
[EuLA]

The main releases from lime production are atmospheric releases from the kiln. These result from the particular chemical composition of the raw materials and fuels used. However, significant releases of particulates can occur from any part of the process, notably the hydrator. Potentially significant emissions from lime plants include carbon oxides (CO, CO₂), nitrogen oxides (NO_x), sulphur dioxide (SO₂) and dust.

2.2 Applied processes and techniques in lime manufacturing

The lime making process consists of the burning of calcium and/or magnesium carbonates at a temperature between 900 and 1500 °C, which is sufficiently high to liberate carbon dioxide, and to obtain the derived oxide ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$). For some processes significantly higher burning temperatures are necessary, for example dead-burned dolomite.

The calcium oxide product from the kiln is generally crushed, milled and/or screened before being conveyed to silo storage. From the silo, the burned lime is either delivered to the end user for use in the form of quicklime, or transferred to a hydrating plant where it is reacted with water to produce hydrated or slaked lime.

Lime processes mainly contains the following basic steps, which are illustrated in Figure 2.3:

- Wining of limestone
- Limestone storage and preparation
- Fuels storage and preparation
- Calcination of limestone
- Quicklime processing
- Quicklime hydration and slaking
- Storage, handling and transport

The paragraphs 2.2.1-2.2.8 are to a large extent based on information from [TO, 1997].

2.2.1 Wining of limestone

The raw material for lime production is limestone or, to a lesser extent, dolomite or dolomitic limestone. Dolomite and dolomitic limestone are mixtures of calcium carbonate and up to 44% magnesium carbonate. While limestone deposits are relatively abundant in many countries, only a small proportion are suitable for commercial extraction.

High purity limestone or dolomite is quarried, crushed, and in some cases washed. It is then screened and transported to the kiln. Limestone is normally obtained by surface quarrying, generally adjacent to the lime plant, but in some cases sea dredging or even underground mining are used. A typical mining process includes:

- Removal of the overburden (i.e., the soil, clay and loose rock overlying the deposit).
- Blasting of rock.
- Loading and transportation of the blasted rock to the crushing and screening plant.

2.2.2 Limestone preparation and storage

Limestone is crushed to the appropriate size range, which is normally 5 to 200 mm depending upon the kiln used. Primary crushers receive quarry rocks as large as one metre in diameter and reduce their size down to 100-250 mm. Crushed stone from the primary crushers is transported via conveyors to vibrating screens, where large pieces are separated and recycled while those passing through are used as kiln charge, or may be fed into the secondary crushers located further down the process line.

Secondary crushers yield pebbles of 10 to 50 mm, which after screening are transported on belt conveyors and/or bucket elevators to limestone storage silos or compartments for storage prior to feeding the dryer or the lime kiln.

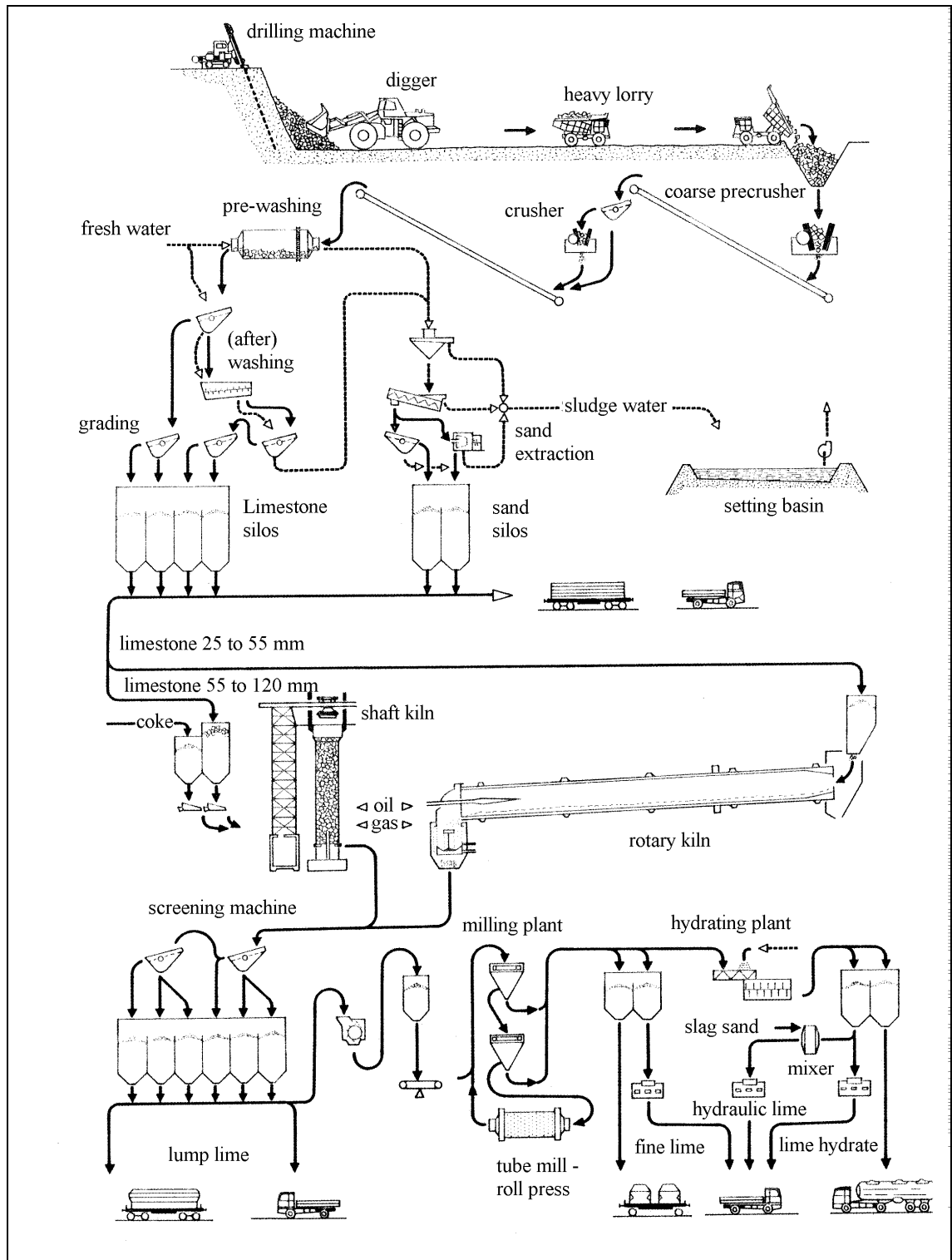


Figure 2.3: Overview of a lime manufacturing process
[EuLA]

Depending on the nature of the rock (hardness, lamination, size etc.) various types of primary crushers are used, such as: jaw crushers, gyratory crushers and impact crushers. As the kiln charge does not have to be very fine, jaw and impact crushers are also often used as secondary crushers, as are hammer mills. Sometimes crushing plants are located at the quarry and are mobile.

The particle size distribution must be compatible with the requirements of the kiln. This generally requires the stone to be positively screened to give a size distribution of, ideally 2 to 1, or at least 3 to 1.

Washing is sometimes used to remove natural impurities such as silica, clay and the very fine particles of limestone. This washing aids the burning process by leaving free space between the stones for combustion air circulation, thus reducing the amount of excess air and saving electrical energy. Techniques for piling the limestone, for better cleaning, have been developed.

Screened sizes of limestone are stored in bunkers and in outdoor stockpiles. Fine grades are usually stored in sealed bunkers.

In a very limited number of installations (for example, where the calcium carbonate is in the form of a sludge or filter cake), it is necessary to dry the feed material. This is generally done by using the surplus heat from kiln exhaust gases.

2.2.3 Fuels, storage and preparation

In lime burning, the fuel provides the necessary energy to calcine the lime. It also interacts with the process, and the combustion products react with the quicklime. Many different fuels are used in lime kilns. The most common in the EU is natural gas, but coal, coke and fuel oil are also widely used. Table 2.6 shows fuels used in lime-burning. Most kilns can operate on more than one fuel, but some fuels cannot be used in certain kilns. Fuels markedly affect the heat usage, output and product quality. Some fuels require a special refractory kiln lining.

Type of fuel	Widely used	Sometimes used	Rarely used
Solid	Bituminous coal Coke	Anthracite Lignite Pet coke	Peat Oil shales
Liquid	Heavy fuel oil	Medium fuel oil	Light fuel oil
Gaseous	Natural gas	Butane/propane Producer gas	Town gas
Unconventional		Wood/sawdust, Used tyres, Paper, Plastic, etc.	Biomass, Waste liquid and solid fuels

Table 2.6: Fuels used in lime-burning
[EuLA]

The choice of fuel(s) for a lime-burning operation is important for the following reasons:

- the cost of fuel per tonne of lime may represent 40 to 50% of the production cost,
- an inappropriate fuel can cause major operating costs, and
- the fuel can influence the quality of the lime, notably the residual CO₂ level, the reactivity, and the sulphur content.

In addition, the choice of fuel can affect the levels of emissions of carbon dioxide, carbon monoxide, smoke, dust, sulphur dioxide and oxides of nitrogen, all of which have an environmental impact.

The fuel should be prepared as required for the injection system, which can be of direct or indirect firing type. In the case of solid fuels, this involves delivery at the appropriate particle size for the installed handling system. In the case of liquid and gaseous fuels, the required pressure and (as appropriate) temperature need to be maintained.

2.2.4 Calcining of limestone

The lime burning process typically involves:

1. providing sufficient heat at above 800 °C to heat the limestone and to cause decarbonation, and
2. holding the quicklime for the requisite time at a sufficiently high temperature (typically in the range 1200 to 1300 °C to adjust reactivity).

A large variety of techniques and kiln designs have been used over the centuries and around the world. Although sales of lime kilns in recent years have been dominated by a relatively small number of designs, many alternatives are available, which may be particularly suitable for specific applications. Stone properties such as strength before and after burning, dust generation and product quality must be considered when choosing kiln technology. Many lime producers operate two or more types of kiln, using different sizes of limestone feed, and producing different qualities of lime. The main characteristics of some types of lime kiln are summarised in Table 2.7.

Kiln type	Fuels ^a	Output range (tonnes/day)	Range of feed stone size (mm)
Shaft			
Mixed feed	S	60-200	20-200
Double-inclined	G,L,S	10-160	20-100
Multi-chamber	G,L,S	40-225	20-150
Annular	G,L,S	80-600	10-250
Parallel-flow reg. (standard)	G,L,S	100-600	25-200
Parallel-flow reg. (finelime)	G,S	100-300	10-30
Other shaft - central burner	G,S	40-80	40-150
- external chambers	G,L	40-120	80-350
- beam burner	G,L,S	50-800	20-175
- internal arch	G,L,S	15-250	25-120
Rotary			
Long	G,L,S	160-1500	dust-60
Preheater	G,L,S	150-1500	0-60 ^b
Other kilns			
Travelling grate	G,L,S	80-130	15-45
“Top-shaped”	G,L,S	30-100	5-40
Fluidised bed	G,L	30-150	0-2
Flash calciner	G,L	300-1500	0-2
Rotating hearth	G,L,S	100-300	10-40
^a G=Gaseous, L=Liquid, S=Solid			
^b cyclone preheater 0-2 mm, shaft preheater 10-60 mm, grate preheater 10-50 mm			

Table 2.7: Characteristics of some types of lime kiln
[EuLA], [UK Report 1996]

Since the “oil crisis” of 1972, there have been a number of pressures on lime producers to replace existing kilns, in particular:

- a) variable and, at times, high fuel prices,
- b) fierce competition (arising from spare capacity), which has forced down the market price of lime,
- c) a preference for quicklime with more consistent quality and particularly with high reactivity, low CaCO_3 and low sulphur content, and
- d) increasingly stringent environmental standards both for the workplace and for atmospheric emissions.

Heat transfer in lime burning can be divided into three stages:

- a) *Preheating zone*. Limestone is heated from ambient to above $800\text{ }^\circ\text{C}$ by direct contact with the gases leaving the calcining zone (i.e. products of combustion, excess air and CO_2 from calcination).
- b) *Calcining zone*. Fuel is burned in preheated air from the cooling zone and (depending on the design) in additional “combustion” air added with the fuel. This produces a temperature of over $900\text{ }^\circ\text{C}$ and causes dissociation of the limestone into quicklime and carbon dioxide.
- c) *Cooling zone*. Quicklime leaving the calcining zone at $900\text{ }^\circ\text{C}$ is cooled by direct contact with “cooling” air, part or all of the combustion air, which in return is preheated.

These zones are illustrated in Figure 2.4 for a vertical shaft kiln

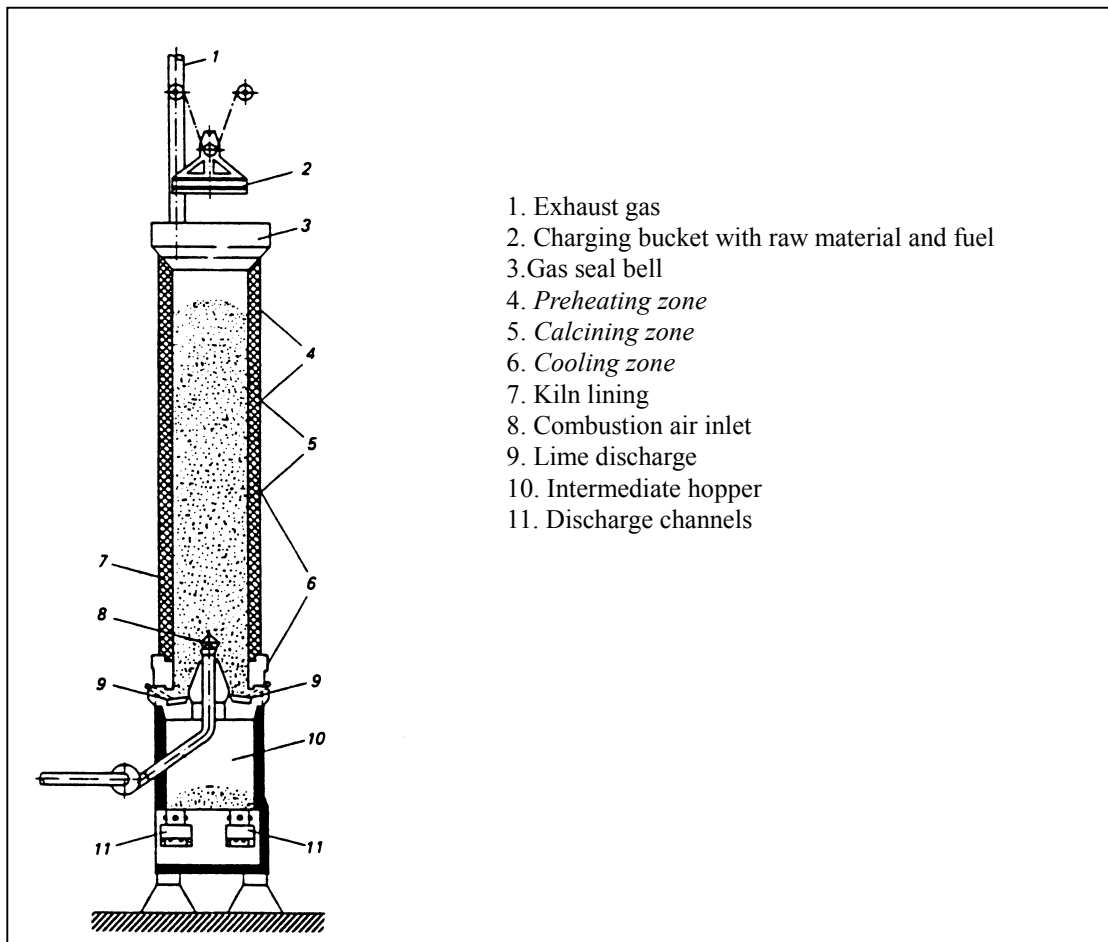


Figure 2.4: Vertical shaft kiln.

[VDI Draft Guidelines 2583, 1984]

Most of the kilns currently used are based on either the shaft or the rotary design. There are a few other kilns based on different principles. All of these designs incorporate the concept of the

three zones. Whereas shaft kilns usually incorporate a preheating zone, some other lime kilns, namely rotary and fluidised bed kilns, are nowadays operated in connection with separate preheaters. Two main types of preheaters are used; vertical shaft and travelling grate.

Most kiln systems are characterised by the counter-current flow of solids and gases, which has implications for the resulting pollutant releases.

2.2.4.1 Shaft kilns

Figure 2.4 shows a schematic diagram of a shaft kiln. The major problem with traditional shaft kilns is obtaining uniform heat release and movement of the burden across the shaft. Fuel injected at a wall usually does not penetrate more than 1 m into a packed bed. This limits the kiln width (or diameter) to 2 m. Uniform heat release can be achieved in larger shafts by:

- use of the mixed feed technique
- use of central burners or lances,
- injecting the fuel via tuyères which penetrate approximately 1 m into the kiln,
- injection of the fuel underneath arches, or
- injection of air or recycled kiln gas above the fuel.

In general, shaft kilns have relatively low heat use rates because of efficient heat transfer between the gases and the packed bed. However, they retain most of the sulphur in the fuel so low-sulphur fuel is required to produce a low-sulphur product. Older designs tend to produce quicklime with a low to moderate reactivity and a relatively high CaCO_3 content. Modern designs incorporate features which enable highly reactive lime to be produced with low CaCO_3 levels.

Before describing specific designs of vertical shaft kilns, it is appropriate to consider three important features which are common to all designs, namely charging, drawing and combustion.

Charging of raw material

Single point charging of lump raw material, especially to shaft kilns, can lead to problems in kiln operation. Larger stones tend to roll down the conical heap towards the walls, while the smaller fractions concentrate along the axis of the kiln. As a result, there is a gradation in the resistance to flow of kiln gases from a high level around the central axis to progressively lower levels towards the walls. This results in a greatly reduced flow of gases through the central part of the kiln and as a result part of the burden tends to be under-calcined.

A variety of devices have been developed to mitigate this effect and to minimise the asymmetry of the charging system. In the fixed plate and cone arrangement, the position of the cone and strike plate, relatively to the feed chute and to each other, can be adjusted to produce a more-or-less uniform profile around the kiln. Inevitably, fines tend to concentrate on either side of the feed chute centre line, but the effect on the kiln operation is small. The rotating hopper and bell system is more sophisticated and produces both a more uniform profile and a better dispersion of fines in an annular ring around the kiln.

For mixed feed kilns it is essential that the fuel is dispersed uniformly across the kiln. Therefore rotating hopper and bell systems are used, in which the bell may be fitted with extensions, which typically consist of four quadrants, one deflecting part of the charge towards the centre of the kiln, a second deflecting it further out, and with the third and fourth quadrants deflecting it progressively further away from the axis of the kiln. After each charge, the hopper

and the apron are rotated by a fraction of revolution so that, on average, a uniform distribution is obtained.

Drawing of lime

In most cases the drawing system determines the velocity at which the limestone burden descends through the kiln. The drawing system should produce a uniform movement of the burden. Simple systems, using a single discharge point and a conical table, work satisfactorily while the burden moves freely. However, when there is a tendency for part of the kiln to stick or when fused lumps of lime bridge between the table and the wall of the cooling zone, lime is preferentially drawn from the free-flowing parts of the kiln, resulting in further over-heating in the problem area.

A better system uses four discharge points without a central table. If there is a tendency for part of the kiln to stick, the feeder(s) under that part can be operated at a faster rate than the others to help re-establish free movement. Similarly, if one feeder becomes blocked, appropriate action can be taken. Multiple discharge points can also assist with diagnosing problems within a kiln. By operating each in turn, the lime from different segments can be tested separately to identify if a particular segment is under or over-burned.

Still more sophisticated drawing mechanisms are used, such as;

- a) hydraulically driven quadrants,
- b) a rotating eccentric plate, and
- c) a rotating spiral cone with steps and a slope designed to take lime uniformly across the shaft.

This design is used on some mixed-feed kilns.

Combustion

In all combustion processes there is an optimum air to fuel ratio which gives the highest efficiency of combustion. A ratio lower than optimum results in incomplete combustion and increased levels of carbon monoxide, while a higher ratio results in the products of combustion being diluted and cooled by the additional quantities of air.

Combustion within the packed bed in vertical lime kilns is particularly problematical as mixing of gasified fuel and air under these conditions is more difficult. From the viewpoint of combustion efficiency, the fuel and air should, ideally, be distributed uniformly across the shaft. However, regardless of the firing system, variations in the air-fuel ratio occur.

Various techniques have been used to moderate temperatures in the calcining zone. Use of an overall deficiency of air is effective but increases fuel usage and can cause the emission of dark smoke. Recirculation of kiln gases is practised with some kilns to moderate kiln temperatures, particularly at the walls. In the annular shaft and parallel-flow regenerative kilns part or all of the combustion gases pass down part of the shaft in co-current flow with the lime. This results in a comparatively low temperature in the finishing section of the calcining zone.

Mixed-feed shaft kiln

Modern mixed-feed shaft kilns use limestone with a top size in the range of 50 to 150 mm and a size ratio of approximately 2:1. The most widely used fuel is a dense grade of coke with low reactivity and low ash content. The coke size is only slightly smaller than that of the stone so that it moves with it rather than trickling through the interstices. The stone and the coke are mixed and charged into the kiln in such a way as to minimize segregation.

The quality of the quicklime tends to be moderate, with the reactivity being considerably lower than that obtained by rotary kilns at the same CaCO_3 level. The retention of sulphur from the fuel is high.

Double-inclined shaft kiln

The double-inclined kiln is shown in Figure 2.5. It is essentially rectangular in cross-section, but incorporates two inclined sections in the calcining zone. Opposite each inclined section, off-set arches create spaces into which fuel and preheated combustion air is fired via combustion chambers.

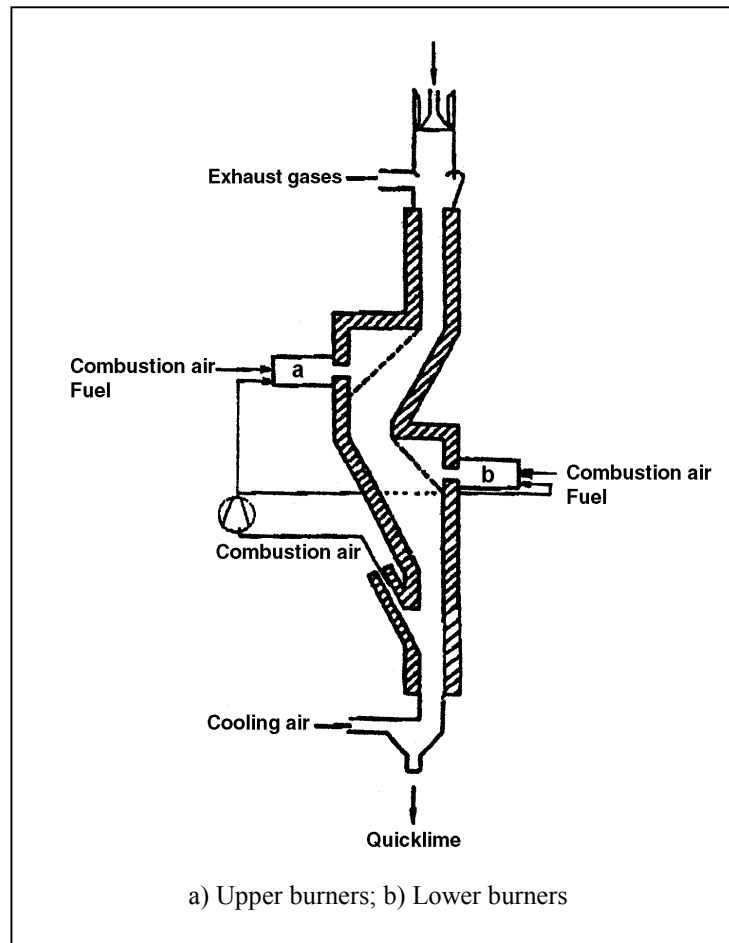


Figure 2.5: Double-inclined shaft kiln.

Based on figure from [Ullmann's, 1990]

Cooling air is drawn into the base of the kiln where it is preheated, withdrawn and re-injected via the combustion chambers. The tortuous paths for both the gases and the burden, coupled with firing from both sides, ensures an efficient distribution of heat. A range of solid, liquid and gaseous fuels can be used, although they should be selected with care to avoid excessive build-ups caused by fuel ash and calcium sulphate deposits.

The kiln can produce a reactive low-carbonate product.

The multi-chamber shaft kiln

This is a development of the double-inclined kiln. It consists of 4 or 6 alternately inclined sections in the calcining zone, opposite each of which is an offset arch. The arches serve the same purpose as in the double-inclined kiln.

Cooling air is preheated by lime in the cooling zone and is withdrawn, de-dusted and re-injected via the combustion chambers.

A feature of the kiln is that the temperature of the lower combustion chambers can be varied to control the reactivity of the lime over a wide range. The kiln can be fired with solid, liquid and gaseous fuels (or a mixture).

Annular shaft kiln

The major feature of the annular shaft kiln Figure 2.6a, is a central cylinder which restricts the width of the annulus, and together with arches for combustion gas distribution ensures good heat distribution. The central column also enables part of the combustion gases from the lower burners to be drawn down the shaft and to be injected back into the lower chamber. This

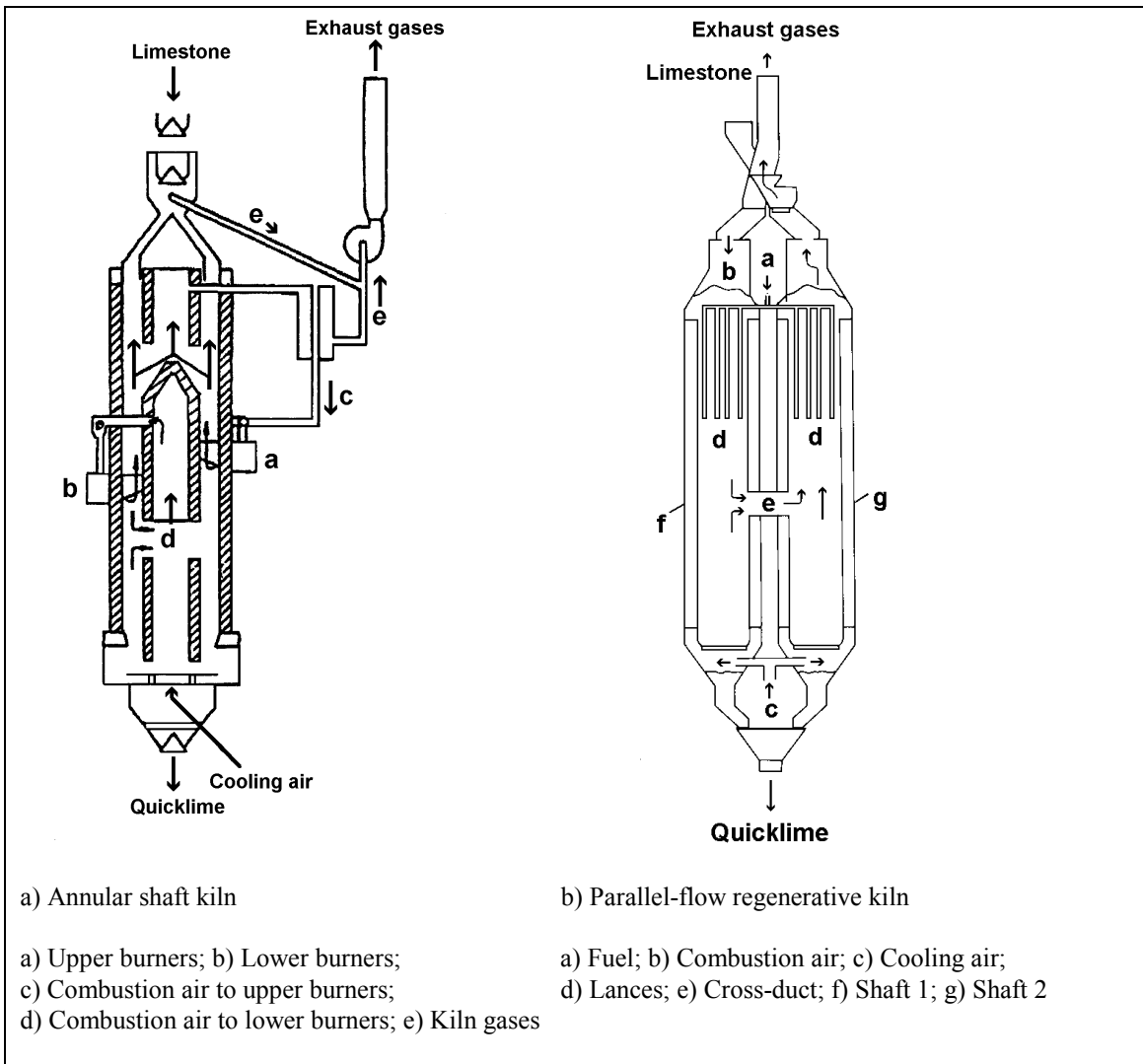


Figure 2.6: a) Annular shaft kiln; b) Parallel-flow regenerative kiln.
 Based on figures from [Ullmann's, 1990]

recycling moderates the temperature at the lower burners and ensures that the final stages of calcination occur at low temperature. Both effects help to ensure a product with a low CaCO_3 level and a high reactivity. The annular shaft kiln can be fired with gas, oil or solid fuel. The exhaust gases have a high CO_2 concentration.

Parallel-flow regenerative kiln

The parallel-flow regenerative (or Maerz) kiln is shown in Figure 2.6b. Its characteristic feature is that it consists of two interconnected cylindrical shafts. Some early designs had three shafts, while others had rectangular shafts, but the operating principles are the same.

Batches of limestone are charged alternately to each shaft and pass downwards through a preheating/regenerative heat exchange zone, past the fuel lances and into the calcining zone. From the calcining zone they pass to the cooling zone.

The operation of the kiln consists of two equal periods, which last from 8 to 15 minutes at full output.

In the first period, fuel is injected through the lances in shaft 1 and burns in the combustion air blown down this shaft. The heat released is partly absorbed by the calcination of limestone in shaft 1. Air is blown into the base of each shaft to cool the lime. The cooling air in shaft 1, together with the combustion gases and the carbon dioxide from calcination, pass through the interconnecting cross-duct into shaft 2 at a temperature of about $1050\text{ }^\circ\text{C}$. In shaft 2, the gases from shaft 1 mix with the cooling air blown into the base of shaft 2 and pass upwards. In so doing, they heat the stone in the preheating zone of shaft 2.

If the above mode of operation were to continue, the exhaust gas temperature would rise to well over $500\text{ }^\circ\text{C}$. However, after a period of 8 to 15 minutes, the fuel and air flows to shaft 1 are stopped, and “reversal” occurs. After charging limestone to shaft 1, fuel and air are injected to shaft 2 and the exhaust gases are vented from the top of shaft 1.

The method of operation described above incorporates two key principles:

- a) The stone-packed preheating zone in each shaft acts as a regenerative heat exchanger, in addition to preheating the stone to calcining temperature. The surplus heat in the gases is transferred to the stone in shaft 2 during the first stage of the process. It is then recovered from the stone to the combustion air in the second. As a result, the combustion air is preheated to about $800\text{ }^\circ\text{C}$.
- b) The calcination of the quicklime is completed at the level of the cross-duct at a moderate temperature of about $1100\text{ }^\circ\text{C}$. This favours the production of a highly reactive quicklime, which may, if required, be produced with a low CaCO_3 content.

Because the kiln is designed to operate with a high level of excess air (none of the cooling air is required for combustion), the level of CO_2 in the exhaust gases is low -about 20% by volume (dry).

The kiln can be fired with gas, oil or solid fuel (in the case of solid fuel, its characteristics must be carefully selected). A modified design (the “finelime” kiln) is able to accept a feedstone in the range 10 to 30 mm, provided that the limestone is suitable.

Other shaft kilns

This group includes a number of designs not described above. In these designs fuel is introduced through the walls of the kiln, and is burned in the calcining zone, with the combustion products moving upwards in counter-current to the lime and limestone. In some designs, the fuel is partially combusted in external gasifiers. In others, it is introduced via devices such as a central burner, beam burner or injected below internal arches.

2.2.4.2 Rotary kilns

Long rotary kiln

The traditional/long rotary kiln consists of a rotating cylinder (up to 140 m long) inclined at an angle of 1 to 4 degrees to the horizontal. Limestone is fed into the upper end and fuel plus combustion air is fired into the lower end. Quicklime is discharged from the kiln into a lime cooler, where it is used to preheat the combustion air. Various designs of lime cooler are used, including "planetary" units mounted around the kiln shell, travelling grates and various types of counter-flow shaft coolers.

Many kilns have internal features to recover heat from the kiln gases and to preheat the limestone. These include:

- a) chains (in kilns fed with calcium carbonate sludge),
- b) metal dividers and refractory trefoils, which effectively divide the kiln into smaller tubes,
- c) lifters which cause the stone to cascade through the gases, and
- d) internal refractory dams, which increase the residence time of the burden.

The design of burner is important for the efficient and reliable operation of the kiln. The flame should be of the correct length, too short and it causes excessive temperatures and refractory failure, too long and it does not transfer sufficient radiant heat in the calcining zone with the result that the back-end temperature rises and thermal efficiency decreases. The flame should not impinge on the refractory.

Rotary kilns can accept a wide range of feed stone sizes from 60 mm down to dust. An interesting feature of the tumbling bed in the kiln is that larger stones migrate towards the outside of the bed, while smaller stones concentrate at the centre of the bed. This results in the larger stones being exposed to higher temperatures than the smaller stones, with the result that over-calcination of the finer fractions can be avoided. Indeed, it is frequently necessary to incorporate "mixers" or steps into the refractory lining to mix the bed and to ensure that the finer fractions are fully calcined. Because of the ease with which they can be controlled, rotary kilns can produce a wider range of reactivities and lower CaCO_3 levels than shaft kilns. The variability of reactivity, however, tends to be greater than that of shaft kilns. Relatively weak feedstones, such as shell deposits, and limestones that break up, are unsuitable as feed to shaft kilns but may prove to be suitable for rotary kilns.

Rotary kilns can be fired with a wide range of fuels. As heat transfer in the calcining zone is largely by radiation, and as the infra-red emissivities increase in the sequence gas, oil and solid fuel, the choice of fuel can have a marked effect on heat usage. Values as high as 9200 MJ/tonne quicklime have been observed for simple gas-fired kilns, while a similar coal-fired kiln may have a heat usage of 7500 MJ/tonne quicklime. The use of internal fittings can reduce those heat usages to below 6700 MJ/tonne quicklime. Radiation and convection losses from the kiln are high relative to other designs of lime kiln.

A feature of rotary kilns is the formation of "rings". These consist of an accumulation of material on the refractory in a part of the kiln which has the appropriate temperature for a semi-

liquid phase to form. Such rings can form from ash in coal-fired kilns and from calcium sulphate deposits. Alkalis (sodium and potassium oxides), clay and lime can contribute to the build-ups, which can be troublesome. In the case of coal-firing, fine grinding of the fuel can significantly reduce the rate of build-up.

Another feature of rotary kilns is that sulphur from the fuel, and, to a lesser extent from the limestone, can be expelled from the kiln in the kiln gases by a combination of controlling the temperature and the percentage of CO in the calcining zone. Thus low sulphur limes can be produced using high sulphur fuels, subject to any emission limits for SO₂ in the exhaust gases.

Preheater rotary kiln

Modern rotary kilns are fitted with preheaters, see Figure 2.7, and are generally considerably shorter than the conventional rotary kiln (e.g. 40 to 90 m). The heat use decreases because of reduced radiation and convection losses as well as the increased heat recovery from the exhaust gases. Thus, with coal firing, net heat uses of less than 5200 MJ/tonne quicklime are reported.

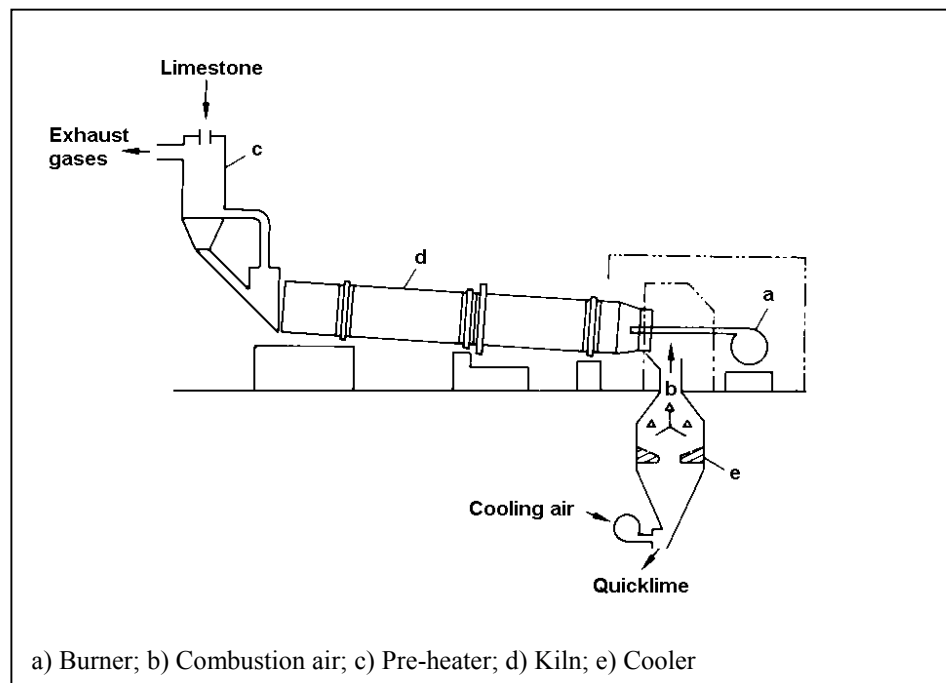


Figure 2.7: Preheater rotary lime kiln.

[Ullmann's, 1990]

A number of preheater designs have been developed, including vertical shafts and travelling grates. The preheater should be selected on the basis of the size and properties of the feedstone. Most can accept a bottom size of 10 mm; some have used stones down to 6 mm, and some cannot tolerate weak stones or stone that is prone to breaking up.

While the elimination of sulphur is more difficult with preheater kilns, there are a number of ways in which it can be achieved:

- establishing a purge of SO₂ by taking some of the kiln gases around the preheater (at the cost of increased heat use),
- operating the kiln under reducing conditions and introducing additional air at the back end (only works with certain designs of preheater), and

- c) adding sufficient finely divided limestone to the feed for it to preferentially absorb SO_2 and so that it is either collected in the back-end dust collector, or is screened out of the lime discharged from the cooler.

2.2.4.3 Other kilns

Various designs of lime kilns have been developed, based on the technology used in modern cement kilns. One of the driving forces for developing new designs of kiln is that substantial quantities of calcium carbonate are available in finely divided form. The sugar and paper/wood pulp industries, for example, produce a mixture of calcium carbonate and organic matter which can be calcined and recycled, and many limestone quarries produce a surplus of fine stone, which, in principle, would be suitable for calcination (although it is often contaminated with clay).

Travelling grate kiln

For limestone in the size range 15 to 45 mm, an option is the "travelling grate" (or CID) kiln (developed in Germany). It consists of a rectangular shaft preheating zone, which feeds the limestone into a calcining zone. In the calcining zone the limestone slowly cascades over five oscillating plates, opposite which are a series of burners. The lime passes to a rectangular cooling zone. The CID kiln can burn gaseous, liquid or pulverised fuels and is reported to produce a soft-burned lime with a residual CaCO_3 content of less than 2.3%. The four kilns built to date have capacities of 80 to 130 tonnes/day of quicklime.

The top-shaped Kiln

Another relatively new development, which accepts feedstone in the 10 to 25 mm range, is the "top-shaped" lime kiln (developed in Japan). This consists of an annular preheating zone from which the limestone is displaced by pushing rods into a cylindrical calcining zone. Combustion gases from a central, downward facing burner, fired with oil and positioned in the centre of the preheating zone are drawn down into the calcining zone by an ejector. The lime then passes down into a conical cooling zone. The kiln is reported to produce high quality quicklime, suitable for steel production and precipitated calcium carbonate. Kiln capacities are up to 100 tonnes/day of quicklime, heat use is 4600 MJ/tonne of lime. It is reported that, because of its relatively low height, the kiln can accept limestones with low strengths.

Gas suspension calcination process

Gas suspension calcination, GSC, is a new technology for minerals processing, such as the calcination of limestone, dolomite and magnesite from pulverised raw materials to produce highly reactive and uniform products. Most of the processes in the plant, such as drying, preheating, calcination and cooling, are performed in gas suspension. Consequently, the plant consists of stationary equipment and few moving components, as shown in Figure 2.8.

The amount of material present in the system is negligible, which means that after a few minutes of operation the product will conform to specifications. There is no loss of material or quality during start-up and shut-down so there is no sub-grade product. The GSC process produces a product with high reactivity, even when calcined to a high degree. The material to be processed in gas suspension must have a suitable fineness, practical experience has shown that 2 mm particle size should not be exceeded.

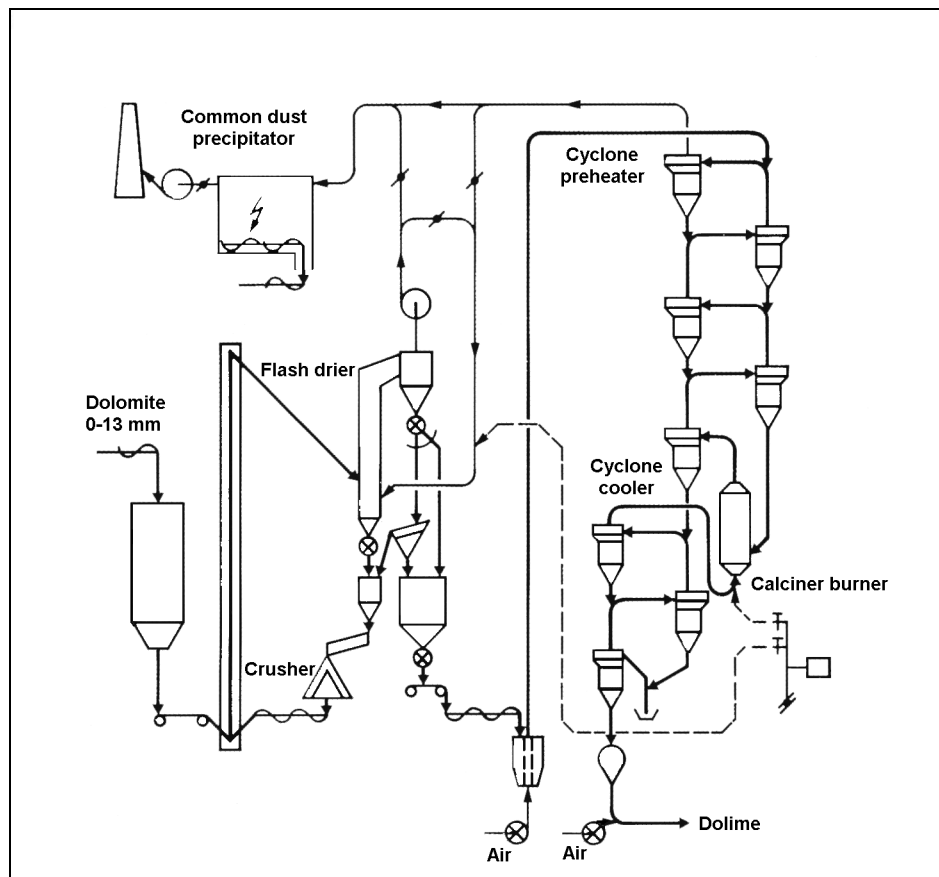


Figure 2.8: Gas suspension calcination process
Process diagram of Norsk Hydro's GSC plant

A GSC plant for the production of dolomitic lime has been in continuous operation at Norsk Hydro, Porsgrunn, Norway, since August 1986. Some performance figures for the balanced operation of GSC and crushing/drying are presented below:

Plant capacity	430 tonnes/day
Fuel consumption	4800 MJ/tonne product
Power consumption	33 kWh/tonne product

Rotating hearth kiln

This type of kiln, now almost obsolete, was designed to produce pebble lime. It consists of an annular travelling hearth carrying the limestone charge. The limestone is calcined by multiple burners as it rotates on the annular hearth. The combustion air is preheated by surplus heat in exhaust gases and/or by using it to cool the quicklime. Due to the reduced abrasion compared with rotary and shaft kilns, rotating hearth kilns produce a high proportion of pebble lime.

2.2.5 Quicklime processing

The objective of processing run-of-kiln (ROK) quicklime is to produce a number of grades with the particle sizes and qualities required by the various market segments. A number of unit processes are used, including screening, crushing, pulverising, grinding, air-classifying and conveying. A well-designed lime processing plant achieves a number of objectives, namely:

- a) maximising the yield of main products,
- b) minimising the yield of surplus grades (generally fines),
- c) improving the quality of certain products, and
- d) providing flexibility to alter the yields of products in response to changes in market demand.

The processing plant should include adequate storage, both for the products and intermediates, to provide a buffer between the kiln, which is best operated on a continuous basis, and despatches which tend to be at low levels overnight and at weekends.

ROK lime is often screened (typically at about 5 mm) to remove a less pure “primary” fines fraction. If the ROK lime has a top size in excess of (say) 45 mm, it is reduced in size with the minimum production of fines. Jaw and rolls crushers are widely used for this task. The crushed ROK lime is then fed to a multi-deck screen, which produces a secondary fines fraction (e.g. less than 5 mm), and granular, or “pebble”, lime fractions (e.g. 5-15 mm and 15-45 mm). Oversize lumps (e.g., greater than 45 mm) may be crushed in a secondary crusher and recycled to the multi-deck screen.

The products are stored in bunkers, from which they can be either despatched directly, or transferred to another plant for grinding or hydrating.

Production of ground quicklime

The demand for various grades and qualities of ground quicklime has grown rapidly ever since the 1950s. Particle size requirements vary from relatively coarse products used for soil stabilisation to very finely divided products for specialist applications.

The coarser products are produced relatively cheaply in a single pass through a beater mill fitted with an integral basket. Finer products are generally produced in tube mills and vertical roller mills. In the latter case, a variable speed classifier is fitted above the mill to control the grading of the product, and recycle over-sized particles.

In the late 1980s, the high pressure roll mill was developed for the cement industry and is increasingly being used for quicklime. The product is passed through the grinding rolls, which effectively produce a flake. It is then fed to a dis-agglomerator and an air classifier which removes particles of the required fineness and recycles the coarse fraction. The power requirements of this system can be less than half those of ball mills and less than 60% of the ring-roll mills.

2.2.6 Production of Slaked lime

Slaked lime includes hydrated lime (dry calcium hydroxide powder), milk of lime and lime putty (dispersions of calcium hydroxide particles in water).

Production of hydrated lime

The hydration of lime involves the addition of water in a hydrator ($\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$). The quantity of water added is about twice the stoichiometric amount required for the hydration reaction. The excess water is added to moderate the temperature generated by the heat of reaction by conversion to steam. The steam, which is laden with particulates, passes through abatement equipment prior to discharge to atmosphere.

There are many designs of equipment but technically the hydrator, see Figure 2.9, consists of pairs of contra-rotating screw paddles which vigorously agitate the lime in the presence of water. A strong exothermic reaction takes place generating 1140 kJ per kg CaO. The average residence time of the solids in the main reactor is about 15 minutes.

The heat release causes a vigorous boiling action which creates a partially fluidised bed. Dust is entrained in the steam evolved during the process. If this dust is collected in a wet scrubber a milk of lime suspension is produced, which is normally returned to the hydrator.

After hydration the product is transferred to an air-swept classifier where the coarse and fine fractions are separated using a recycling air stream. Some or all of the coarse fraction may be ground and recycled. The fine fraction is conveyed to storage silos. From here it is either discharged to bulk transport or transferred to a packing plant where it is packed in sacks or intermediate bulk containers.

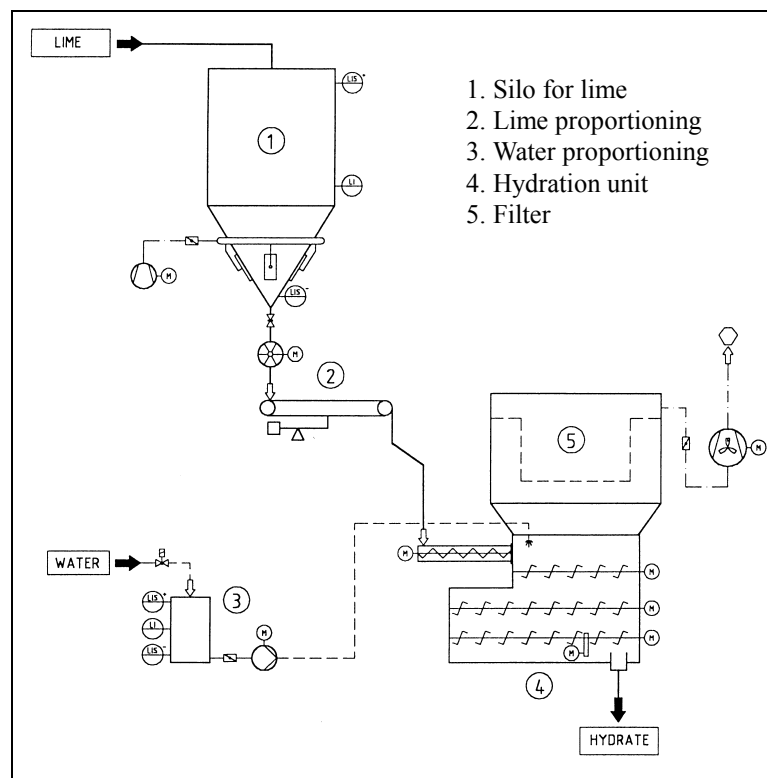


Figure 2.9: Flowsheet of a 3-stage lime hydrator
[EuLA, (Pfeiffer AG, Germany)]

Production of milk of lime and lime putty

Milk of lime and lime putty is produced by slaking of lime with excess water. Slaking is done in both batch and continuous slakers. The term milk of lime is used to describe a fluid suspension of slaked lime in water. Milks of lime may contain up to 40% by weight of solids. Milk of lime with a high solids content is sometimes called lime slurry. Lime putty is a thick dispersion of slaked lime in water. Putties typically contain 55 to 70% by weight of solids. Lime paste is sometimes used to describe a semi-fluid putty.

2.2.7 Storage and handling

Storage

Storage of quicklime

Quicklime is preferably stored in dry conditions, free from draughts to limit air slaking. Great care is exercised to ensure that water is excluded from the lime, as hydration liberates heat and causes expansion, both of which could be dangerous.

Air pressure discharge vehicles are able to blow directly into the storage bunker, which is fitted with a filter to remove dust from the conveying air. The filter should be weatherproof and watertight. The collected dust can be discharged back into the bunker. A pressure/vacuum relief device fitted to the bunker is a precautionary measure.

All storage containers can be fitted with devices which can positively seal the base of the bunker to enable maintenance work to be done on the discharge mechanism.

Where the amount of quicklime is insufficient to justify storage bunkers the product may be stored on a concrete base, preferably in a separate bay within a building to prevent excessive air slaking.

Storage of hydrated lime

Hydrated lime absorbs carbon dioxide from the atmosphere, forming calcium carbonate and water. Therefore, it is best stored in dry draft-free conditions.

Hydrate bagged in paper sacks is preferably stored under cover to avoid deterioration by moisture, and re-carbonation of the hydrated lime. When “Big bags” are used, they are also best stored under cover to prevent any damage. Pallets of bagged hydrate have been stored successfully out-of-doors; the pallet covered by a plastic sheet, the bags placed on the sheet and the pack shrink-wrapped.

Bulk hydrate is stored in silos, which must be completely weatherproof. The silo is vented via a bag filter, which should be weatherproof and be capable of handling the delivered airflow. Where the filter is fitted on top of the silo, the collected dust is discharged back into the silo. The silo top can be fitted with an inspection manhole and a pressure relief valve. A high level indicator or alarm can be fitted to prevent over-filling. It is recommended that the base of the silo be at an angle of at least 60° to the horizontal, the discharge aperture not less than 200 mm and that a positive cut-off valve is fitted to the outlet to permit equipment beneath the silo to be maintained.

Because hydrated lime is prone to “arching”, suitable arch-breaking devices, such as aeration pads, vibrators and mechanical devices, are fitted to prevent this. Conversely, precautions need to be taken to prevent “flooding” of aerated powder.

Storage of milk of lime

Many customers requiring addition of slaked lime to their process have found that milk of lime is a convenient form to store and handle. Providing certain precautions are taken, it can be handled as a liquid.

Any storage and handling system has to pay proper attention to the fact that when milk of lime is diluted with water, or when hydrated lime is dispersed in water, any carbonate hardness in the water will be deposited as calcium carbonate. Unless appropriate action is taken, this will result in scaling on the walls of pipes and on the impeller and casing of pumps. Two approaches can be adopted. Either the system can be designed to cope with scale formation, or action can be taken to prevent or minimise scaling.

It is important to prevent settling in milk of lime systems as the resulting putty can be difficult to re-disperse. Storage tanks should therefore be agitated. The degree of agitation can be low and should avoid forming a vortex, which would increase absorption of carbon dioxide from the atmosphere.

The discharge pipe from a storage vessel inevitably constitutes a dead-leg and provision can be made for back-flushing with water to remove any blockages. The storage area should be suitably banded.

Handling

Many types of equipment are suitable for transferring the product and new ones are continually being developed. The following items have been used successfully, but may not be suitable for all applications.

Skip hoists can be used for all granular and lump grades but are more suitable for particles greater than 100 mm. *Elevators* - both belt-and-bucket and chain-and-bucket elevators have been used for all grades of quicklime. *Drag-link* conveyors are suitable for granular and fine quicklime. They are generally used for horizontal or inclined transfer. *Conveyor belts* are widely used for transferring lump and granular grades horizontally and on an upward slope. *Screw conveyors* are widely used for fine quicklime. *Vibrating trough conveyors* have been used for particle sizes up to 40 mm. They operate more successfully when there is a slight downward slope from the feed to the discharge point.

Pneumatic conveying can be used for products with a maximum size up to 20 mm and often has a lower capital cost than alternatives, but the operating costs are higher. The product is fed into a rotary blowing seal connected to a blower. The pipeline bore, and volume/pressure of the blowing air, is designed taking into account the size of lime being conveyed, the transfer rate and the length/route of the pipeline. The receiving silo is equipped with an air filter and a pressure relief valve.

2.2.8 Other types of lime

2.2.8.1 Production of calcined dolomite

Dolomite is calcined in both shaft and rotary kilns. Three qualities of calcined dolomite are produced - light-burned, dead-burned and half-burned.

Light-burned dolomite is generally produced in either rotary or shaft kilns. The principles of making light-burned dolomite are similar to those of making high calcium quicklime. Less heat is used owing to the lower heat of calcination and the lower dissociation temperature of dolomite (MgCO_3).

Dead-burned dolomite is produced in two grades. A high purity grade, used for the manufacture of refractories, is made by calcining dolomite at temperatures of up to 1800 °C in either rotary or shaft kilns. A “fettling” grade is produced by the calcination of dolomite with 5 to 10% iron

oxide at 1400 to 1600 °C, usually in a rotary kiln. The exhaust gases from both of these processes are at higher temperatures than from other lime kilns; they are generally cooled to below 420 °C using heat exchangers, tempering air or injection of atomised water.

Half-burned dolomite ($\text{CaCO}_3\text{-MgO}$) is produced by the slow calcination of dolomite at about 650 °C. It is produced in relatively small quantities and Germany is the only country in Europe to manufacture it.

2.2.8.2 Production of hydraulic limes

Natural hydraulic limes are produced from siliceous or argillaceous limestones containing more or less silica, alumina and iron. Typical levels in the limestone are; SiO_2 : 4 to 16%, Al_2O_3 : 1 to 8% and Fe_2O_3 : 0.3 to 6%. The calcium plus magnesium carbonate content can range from 78 to 92%.

The limestone is generally calcined in shaft kilns which must be controlled closely to ensure that as much of the silica and alumina as possible reacts, without sintering the free lime. Typical calcining temperatures are 950-1250 °C: the required temperature rises as the cementation index increases (i.e. from feebly to eminently hydraulic limes).

The calcined lime is hydrated with sufficient water to convert the free CaO into Ca(OH)_2 . If the free CaO content is greater than 10 to 15%, the hard sintered lumps disintegrate into a powder. Otherwise, the lime must be ground before hydration. It may also be necessary to grind the hydrated product to achieve the required degree of fineness and setting rate.

“Special” natural hydraulic limes are produced by intimately blending powdered natural hydraulic limes with powdered pozzolanic or hydraulic materials. Artificial hydraulic limes are produced by intimately blending powdered hydrated limes with pulverised pozzolanic or hydraulic materials.

2.2.9 Captive lime kilns

2.2.9.1 Lime kilns in the Iron and steel industry

Most of the lime used in the iron and steel industry is for fluxing impurities in the basic oxygen furnace. Lime is also used in smaller quantities in the sinter strand process for the preparation of iron ore, in the desulphurisation of pig iron, as a fluxing agent in other oxygen steelmaking processes, in the electric arc steelmaking process and in many of the secondary steelmaking processes.

The lime kilns in the Iron and steel industry are mainly shaft kilns of different designs and capacities. They do not differ in consumption/emission patterns from non-captive lime kilns.

2.2.9.2 Lime kilns in the Kraft pulp industry

There are about 100 lime kilns in the European Paper industry. They are all rotary kilns with capacities between 30-400 tonnes of burned lime per day. Most of the kilns are long rotary kilns, but there are also some modern preheater rotary kilns.

The long rotary lime kilns are usually fed with a slurry of calcium carbonate with a water content of 30%. The basic fuel is normally natural gas or oil. In addition, non-condensable gases produced in several areas of the pulping process are usually burned, increasing the

content of H₂S, organic sulphur compounds and SO₂ in the stack gases. In some cases sawdust and gases obtained by gasification of biomass are also used as fuel.

Venturi type wet scrubbers and electrostatic precipitators (for particular matter) are normally installed to clean the exhaust gases.

2.2.9.3 Lime kilns in the Sugar industry

Most of the lime kilns in the European Sugar industry are mixed feed shaft kilns. The majority of the kilns produce 50 to 350 tonnes of quicklime per day during the sugar campaign, which, in the 1997/1998 season, lasted between 63 and 170 days, with an average of 86 days.

The quicklime and the CO₂ in the exhaust gas are both used in sugar factories. The gas produced by the kiln is captured and most of it is dedusted in a wet scrubber before use in the sugar process (carbonatation). Most of the CO₂ recombines with the milk of lime in the limed juice to give CaCO₃.

The most common fuel in sugar industry lime kilns is coke. This is mainly because the product gas contains more CO₂ (40-42% CO₂ by volume) than product gas from oil or gas fired kilns (28-32% CO₂ by volume).

The consumption levels (limestone and fuel) for sugar industry lime kilns are about the same as for the same types of lime kiln in other sectors.

2.3 Present consumption/emission levels

The main environmental issues associated with lime production are air pollution and the use of energy. The lime burning process is the main source of emissions and is also the principal user of energy. The secondary processes of lime slaking and grinding can also be of significance, while subsidiary operations (namely crushing, screening, conveying, storage and discharge) are relatively minor in terms of both emissions and energy usage.

2.3.1 Consumption of limestone

Lime production generally uses between 1.4 and 2.2 tonnes of limestone per tonne of saleable quicklime. Consumption depends on the type of product, the purity of the limestone, the degree of calcination and the quantity of waste products (dust carried from the kiln in the exhaust gases, for example).

2.3.2 Use of energy

Calcining of limestone

Typical heat and electrical power use by various types of lime kiln are shown in Table 2.8. Energy use for a given kiln type also depends on the quality of the stone used and on the degree of conversion of calcium carbonate to calcium oxide.

The heat of dissociation of calcium limestone is 3200 MJ/tonne. The net heat use per tonne of quicklime varies considerably with kiln design. Rotary kilns generally require more heat than shaft kilns. The heat use tends to increase as the degree of burning increases.

The use of electricity varies from a low range of 5-15 kWh/tonne of lime for mixed-feed shaft kilns, to 20-40 kWh/tonne for the more advanced designs of shaft kiln and for rotary kilns.

Kiln type	heat use (MJ/tonne lime)	kiln electricity use (kWh/tonne lime)
Calcium quicklime, light- and hard-burned dolomite		
Mixed feed shaft kiln	4000-4700	5-15
Double-inclined shaft kiln	4300	30
Multi-chamber shaft kiln	4000-4500	20-45
Annular shaft kiln	4000-4600	18-35
Parallel-flow regenerative shaft kiln	3600-4200	20-40
Other shaft kilns	4000-5000	10-15
Long rotary kiln ^a	6500-7500	18-25
Grate preheater rotary kilns ^a	5000-6100	35-100
Shaft preheater rotary kilns ^a	4800-6100	17-45
Cyclone preheater rotary kilns ^a	4600-5400	23-40
Travelling grate kiln	3700-4800	31-38
Gas suspension calcination	4600-5400	20-25
Fluidised bed kiln	4600-5400	20-25
Dead-burned dolomite		
Mixed feed shaft kiln	6500-7000	20
Grate preheater rotary kiln	7200-10500	35-100

a) producing reactive calcium quicklime

Table 2.8: Typical heat and electricity use by various types of lime kiln

[EuLA], [UK IPC Note, 1996], [Jørgensen]

Lime hydrating

The hydrating process is exothermic, so excess water is added to control the temperature in the hydrators. This excess water is converted into steam, which is discharged into the atmosphere, together with a small amount of air that is drawn into the hydrator to prevent moisture and dust from entering the plant/quicklime feed equipment, and to assist in the evaporation of excess water.

The energy requirements to operate the hydrators, air classifiers and conveying equipment amounts to approximately 5 to 30 kWh/tonne of quicklime.

Lime grinding

The energy use in lime grinding varies from 4 to 10 kWh/tonne of quicklime for the coarser grades (for example, those used for soil stabilisation) to 10 to 40 kWh/tonne of quicklime for the finer grades. The amount of energy required also depends on the equipment used. Fine impact mills can be used for the coarser products. Ball mills, ring-roll mills and high-pressure mills plus dis-agglomerators (with progressively lower specific energy use) are used for making finer products.

2.3.3 Emissions

Emissions to the atmosphere include nitrogen oxides (NO_x), sulphur dioxide (SO_2), carbon oxides (CO , CO_2) and dust. The emissions depend on kiln design, operating conditions, the fuel used and lime/limestone quality. The level of carbon dioxide emission is related to the chemistry of the calcination and combustion processes. Typical emissions are quoted in each section for NO_x , SO_2 , dust and CO .

2.3.3.1 Oxides of nitrogen

Shaft kilns generally emit less NO_x than rotary kilns. This is because the temperatures in shaft kilns are usually below 1400 °C, so that the formation of thermal NO_x (by reaction of nitrogen with oxygen) is comparatively lower. Additionally, the combustion processes usually produce relatively lower flame temperatures, and low-intensity mixing conditions, resulting in lower levels of fuel NO_x . Where, however, shaft kilns are used to produce hard-burned calcium limes, or dead-burned dolomite, higher levels of NO_x are produced.

In rotary kilns, the flame is better defined and flame temperatures are higher than in shaft kilns, which results in higher levels of fuel NO_x . Moreover, because of the different heat transfer processes, the maximum temperature of the kiln gases is also higher, resulting in increased thermal NO_x levels. The production of dead-burned dolomite in rotary kilns results in still higher NO_x levels.

Typical emissions of NO_x from various types of lime kiln are shown in Table 2.9.

Kiln type	mg NO _x /Nm ³ ¹	kg NO _x /tonne lime ²
Calcium quicklime, light- and hard-burned dolomite		
Mixed feed shaft kiln	<300	<1
Double-inclined shaft kiln	<500	<1.7
Multi-chamber shaft kiln	500-800	1.7-2.8
Annular shaft kiln	<500	<1.7
Parallel-flow regenerative shaft kiln	<400	<1.4
Other shaft kilns	<300	<1
Rotary kilns, soft burning	100-700	0.4-2.8
Rotary kilns, hard burning	400-1800	1.6-7
Travelling grate kiln	<300	<1
Dead-burned dolomite		
Mixed feed shaft kiln	<300	<1
Rotary kilns	2000-5000	15-45

1) Emission concentrations are one year averages, and are indicative values based on various measurement techniques. O₂ content normally 10%.

2) based on typical exhaust gas volumes (wet) of
 3500 Nm³/tonne of lime for shaft and travelling grate kilns,
 4000 Nm³/tonne of lime for rotary kilns calcining high-calcium limestone and dolomite,
 1900 Nm³/tonne of lime for mixed feed shaft kilns dead-burning dolomite, and
 8500 Nm³/tonne of lime for rotary kilns dead-burning dolomite.

Table 2.9: Typical emissions of NO_x from some types of lime kiln
 [EuLA]

2.3.3.2 Sulphur dioxide

Typical emissions of SO₂ from various types of lime kiln are shown in Table 2.10.

Kiln type	mg SO ₂ /Nm ³ ¹	kg SO ₂ /tonne lime ²
Calcium quicklime, light- and hard-burned dolomite		
Mixed feed shaft kiln	<300	<1
Double-inclined shaft kiln	<500	<1.7
Multi-chamber shaft kiln	<500	<1.7
Annular shaft kiln	<300	<1
Parallel-flow regenerative shaft kiln	<300	<1
Other shaft kilns	<300	<1
Rotary kilns, soft burning	<800 ³	<3
Rotary kilns, hard burning	<800 ³	<3
Travelling grate kiln	<300	<1
Dead-burned dolomite		
Mixed feed shaft kiln	<800	<1.5
Rotary kilns	<5000	<42.5

1) Emission concentrations are one year averages, and are indicative values based on various measurement techniques. O₂ content normally 10%.

2) Based on typical exhaust gas volumes (wet) of
 3500 Nm³/tonne of lime for shaft and travelling grate kilns,
 4000 Nm³/tonne of lime for rotary kilns calcining high-calcium limestone and dolomite,
 1900 Nm³/tonne of lime for mixed feed shaft kilns dead-burning dolomite, and
 8500 Nm³/tonne of lime for rotary kilns dead-burning dolomite.

3) May be higher with high-sulphur fuels.

Table 2.10: Typical emissions of SO₂ from some types of lime kiln
 [EuLA]

In the majority of lime burning operations most of the sulphur present in the limestone and the fuel is captured by the quicklime. In shaft kilns and fluidised bed kilns, the efficient contact between the kiln gases and the quicklime usually ensures efficient absorption of sulphur dioxide. This is also generally valid for rotary and other kilns, with packed-bed preheaters.

However, where low sulphur quicklime is produced in rotary kilns, and hard-burned calcium lime/dead-burned dolomite in either shaft or rotary kilns, part of the sulphur in the fuel and limestone is expelled as sulphur dioxide in the exhaust gases.

2.3.3.3 Dust

Calcining of limestone

Dust generation arises from finely divided particles in the limestone feed, from thermal and mechanical degradation of the lime and limestone within the kiln, and, to a lesser extent, from fuel ash. The levels of dust generation vary widely, depending on kiln design among other things, and range from 500 to over 5000 mg/Nm³, corresponding to approximately 2 to 20 kg/tonne of quicklime (based on 4000 Nm³/tonne lime). All rotary kilns are fitted with dust collection equipment, as are most shaft kilns.

Because of the wide range of exhaust gas conditions, a variety of dust collectors are used, including cyclones, wet scrubbers, fabric filters, electrostatic precipitators and gravel bed filters. After abatement, emissions typically range from 30 to 200 mg/Nm³, about 0.1 to 0.8 kg/tonne of quicklime (based on 4000 Nm³/tonne lime).

Lime hydrating

The gaseous effluent from hydrating plants is rather small in volume; levels are around 800 m³/tonne of hydrated lime, but it may contain 2 g/m³ of dust before abatement. Thus the generation of dust can be about 1.6 kg/tonne of hydrated lime. Both wet scrubbers and bag filters are used to de-dust the emission.

Emission levels after abatement range from 20 to over 200 mg/Nm³, corresponding to approximately 0.016 to 0.16 kg/tonne of hydrated lime.

Lime grinding

Air is drawn through all of the grinding equipment to remove ground lime of the required particle size. The product is separated from the air in bag filters, often preceded by cyclones. Thus, dust collection is an integral part of the process.

Emission levels typically range from 20 to 50 mg/Nm³, corresponding to 0.03 to 0.075 kg/tonne of lime (at a typical air flow of 1500 Nm³/tonne of lime).

Subsidiary operations

Subsidiary operations may include crushing, screening, conveying, slaking, storage and discharge. Dust emission is controlled by containment and, in many cases, by extracting air to keep the equipment under slight suction. The air is passed through bag filters and the collected dust is generally returned to the product.

Fugitive dust from, for example, stock piles of raw materials and solid fuels can cause problems.

2.3.3.4 Oxides of carbon

The dissociation of limestone produces up to 0.75 tonne of carbon dioxide (CO₂) per tonne of quicklime, depending on the composition of the limestone and the degree of calcination. The amount of carbon dioxide produced by combustion depends on the chemical composition of the fuel and on the heat use per tonne of quicklime, generally it is in the range 0.2 to 0.45 tonne CO₂ per tonne of quicklime.

In recent years, the emission of carbon dioxide per tonne of quicklime in most countries has been reduced, mainly by replacing old kilns with more thermally efficient designs, and by increasing the productivity (reducing the amounts of waste dust). The German and French lime industries have entered into voluntary agreements to reduce CO₂ emissions, and in the UK it has been calculated that the emission of CO₂ per tonne of lime decreased by approximately 20% in the 15 years up to 1994.

When resulting from incomplete combustion, carbon monoxide (CO) emissions generally represent a loss of efficiency. However, in some types of kiln, and when making certain products, controlled levels of carbon monoxide are necessary to produce the required combustion conditions and product quality.

Some limestones contain carbon, which can lead to higher CO emissions from the lime burning process.

Typical emissions of CO from various types of lime kiln are shown in Table 2.11.

Kiln type	g CO/Nm ³ ¹	kg CO/tonne lime ²
Calcium quicklime, light- and hard-burned dolomite		
Mixed feed shaft kiln	12-37	42-130
Double-inclined shaft kiln	<1.4	<5
Multi-chamber shaft kiln	<1.4	<5
Annular shaft kiln	<1.4	<5
Parallel-flow regenerative shaft kiln	<1.4	<5
Other shaft kilns	<14	<50
Rotary kilns, soft burning	1.2-12	5-50
Rotary kilns, hard burning	1.2-12	5-50
Travelling grate kiln	<1.3	<4
Dead-burned dolomite		
Mixed feed shaft kiln	37-63	70-120
Rotary kilns	0.6-6	5-50

1) Emission concentrations are one year averages, and are indicative values based on various measurement techniques. O₂ content normally 10%.

2) Based on typical exhaust gas volumes (wet) of
 3500 Nm³/tonne of lime for shaft and travelling grate kilns,
 4000 Nm³/tonne of lime for rotary kilns calcining high-calcium limestone and dolomite,
 1900 Nm³/tonne of lime for mixed feed shaft kilns dead-burning dolomite, and
 8500 Nm³/tonne of lime for rotary kilns dead-burning dolomite.

Table 2.11: Typical emissions of CO from some types of lime kiln
 [EuLA]

2.3.3.5 Other substances

Volatile organic compounds

Emissions of volatile organic compounds (VOCs) may occur for short periods during start-up, or upset conditions. Such events can occur with varying frequencies: between once or twice per year for rotary kilns to once per 1 to 10 years for shaft kilns. In a very limited number of cases where the limestone contains a significant amount of organic matter, volatile organic compounds can be emitted continuously.

Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)

Raw materials or fuels that contain chlorides may potentially cause the formation of polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in the heat (combustion) process of the lime kiln. Data reported in the document "Identification of Relevant Industrial Sources of Dioxins and Furans in Europe" indicate that lime production plants are of minor significance for the total PCDD/F emissions in Europe. [Materialien, 1997] Measurements collected by EuLA from 7 kilns, of which 4 are rotary kilns and 3 are shaft kilns, show dioxin levels below 0.1 ng TCDD-equivalents/Nm³. Measurements at 2 annular shaft kilns in Germany were all below 0.05 ng TE/m³ [LAI, 1994].

However, the scarcity of measurements means it can not be ruled out that individual plants may be found in Europe with a local impact [Materialien, 1997]. Significant levels of dioxins have been measured at 3 kilns, 2 rotary kilns and 1 shaft kiln, in Sweden. The measurements were made between 1989 and 1993 and the measured levels were between 4.1 and 42 ng/TCDD-equivalents (Nordic)/Nm³. All measurements of high dioxin levels have been explained either by the raw material and/or fuel content, or the less than optimum burning conditions, underlining the importance of controlling the kiln inputs and maintaining a stable kiln operation. Two of these plants use limestone with a natural content of tar, also causing high emissions of VOCs. One measurement of 12.1 ng/m³ was made at a rotary kiln after a change of fuel from coal to oil was carried out in a much shorter period of time than normal. The measurement of 42 ng/m³ was made at a rotary kiln during a full scale trial with waste oil as fuel. Because of the high dioxin value the kiln was not permitted to use this waste fuel. [Branschrapport, 1994][Junker]

Metals

Little data is available concerning metal emissions. The high purity of most limestones used for the production of calcium and dolomitic limes means metal emissions are normally low. Measurements at different types of lime kilns, collected by EuLA, show levels of cadmium, mercury and thallium well below 0.1 mg/Nm³.

2.3.4 Waste

Early designs of shaft kilns often produce two types of inferior products; an impure fine fraction (possibly mixed with fuel ash) and a fraction consisting of under-calcined lumps.

Modern kilns make very little out-of-specification product. If such product occurs, it consists principally of dust collected from the exhaust gases, and typically amounts to 0-5% of the total, depending on the characteristics of the feedstone and the quicklime. Small quantities of partially calcined material are produced when the kiln is started-up from cold, and during shut

down. Such events may occur at frequencies ranging from once per 6 months to once per 10 years.

Some hydrating plants improve the quality of hydrated lime by removing an inferior grade, consisting of a coarse, carbonate-rich fraction. These inferior grades of material are incorporated into selected products, wherever possible. Otherwise, they are disposed to landfill.

2.3.5 Noise

Charging lumps of limestone into lime kilns can result in noise at levels which require abatement. Chutes etc. may be lined internally, or externally with resilient material. Fans used to exhaust gases from the kiln and positive displacement blowers, which are sometimes used to supply combustion air, can produce pure tones which require silencing. Outlet silencers and lagging of ducting are used to achieve the required reduction.

2.3.6 Legislation

An overview of current legislation in the EU is given in Annex A.

2.3.7 Monitoring

According to the European Lime Association, EuLA, the reliability of continuous monitoring for the lime industry has not been established and is not justified. EuLA is of the opinion that due to plant size, the stability of the lime manufacturing process and for cost considerations continuous monitoring is not practical, nor necessary.

It could be appropriate to monitor large rotary lime kilns continuously. There is not much information available but at least one rotary lime kiln in Germany is monitoring the emissions of dust and NO_x continuously.

2.4 Techniques to consider in the determination of BAT

The main factors influencing the choice of kiln design are the characteristics of the available limestone, the lime quality demands, the price of available fuels, and the capacity of the kiln. Most modern designs of kilns produce reactive lime. Where lime of low reactivity is required, mixed-feed kilns are often used.

For most new installations, parallel-flow regenerative, annular shaft and other shaft kilns are preferred. Rotary kilns are used for calcining limestones with smaller particle sizes. Certain designs of kilns have special characteristics, for example, the travelling grate kiln is particularly suitable for the production of small batches of different qualities of quicklime.

Table 2.12 gives an overview of techniques that have a positive effect on, that is reduce, the emissions from the manufacture of lime. The techniques listed are described in more detail below. A short description, general emission levels (or reduction potential), applicability and cost information are given when available/appropriate. In addition to these emission-reduction techniques, the consumption of limestone and the use of energy are discussed in this chapter.

	Technique	NO _x	SO ₂	Dust	CO
Shaft kilns	Process control				X
	Cyclones			X	
	Fabric filters			X	
	EPs			X	
	Wet scrubbers			X	
	Fugitive abatement			X	
Rotary kilns	Process control	X	X	X	X
	Fuel selection	X	X	X	
	Cyclones			X	
	Fabric filters			X	
	EPs			X	
	Wet scrubbers			X	
	Fugitive abatement			X	
Milling plants	Fabric filters			X	
Hydrating plants	Fabric filters			X	
	Wet scrubbers			X	

Table 2.12: Overview of techniques applicable to the lime industry

2.4.1 Consumption of limestone

Minimum consumption of limestone results from maximising the yields of kilnstone from the quarry and of saleable quicklime from the kilnstone. This can be achieved by:

- installing kilns which can be operated with different sizes of limestone,
- installing two or more types of kiln, which are able to calcine different sizes of limestone (see Figure 2.10),
- specific quarrying and well-directed use of limestone (quality, grain size) according to available kiln types,
- reducing the production of wastes (for example, dust removed from exhaust gases and out-of-specification quicklime), and/or
- developing outlets for such wastes.

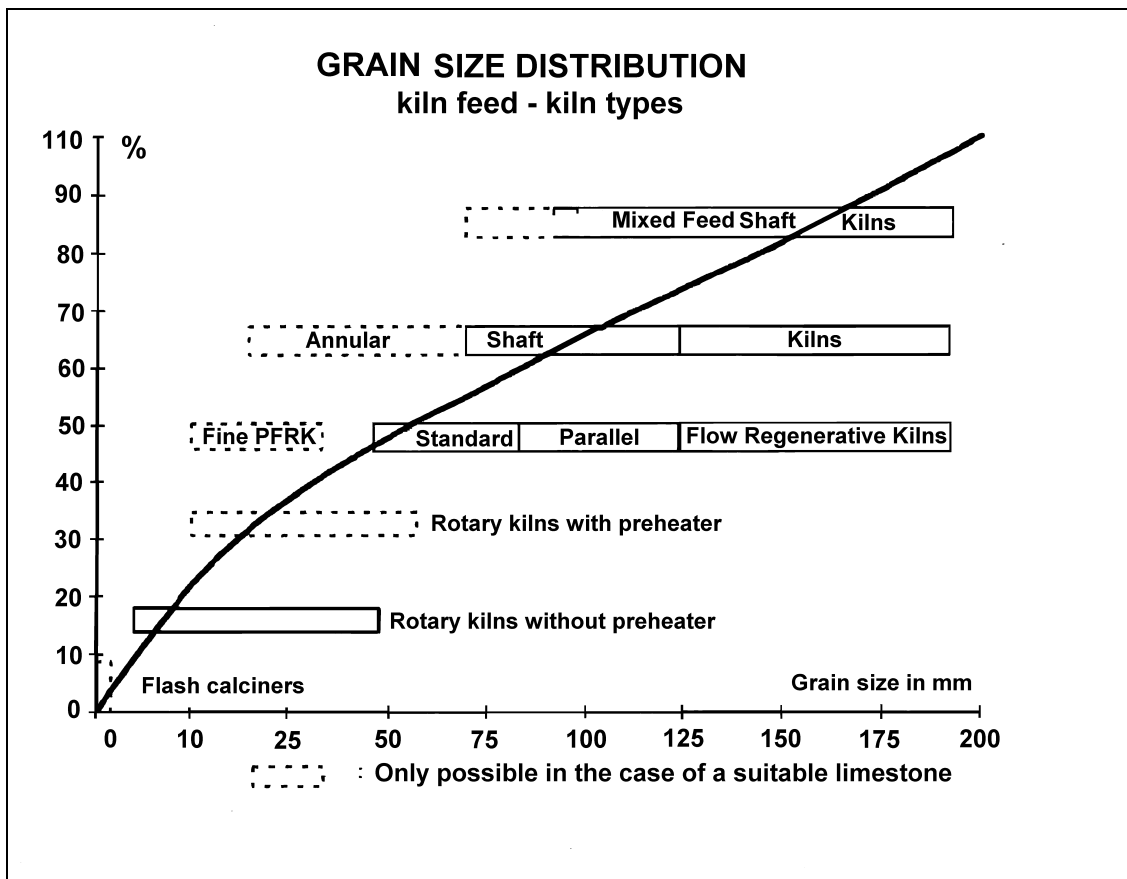


Figure 2.10: Grain size distribution – kiln feed – kiln types
[EuLA]

Keeping the consumption of limestone down also includes reducing wastes produced in hydrating plants (for example dust and, in some cases, removed CaCO_3 -rich fractions), and utilising wastes from hydrators and mills.

2.4.2 Use of energy

In most cases new kilns replace old kilns, but some existing kilns have been modified to reduce fuel energy use. Such modifications range from minor modifications -for example, the installation of heat exchangers to recover surplus heat in kiln gases or to permit the use of a wider range of fuels- to major changes in the configuration of the kiln. In some cases, where shaft kilns have ceased to be economically viable, it has been feasible to convert them to modern designs, for example converting a simple shaft kiln to the annular shaft design or linking a pair of shaft kilns to create a parallel-flow regenerative kiln. Conversion extends the life of expensive items of equipment, such as the kiln structure, the stone feed system and the lime handling/storage plant. In exceptional cases, it may be economic to shorten long rotary kilns and to fit a preheater, thus reducing the fuel use.

Heat recovery from the gaseous effluent which is produced by the exothermic reaction of the lime hydrating process, is used to preheat the water for the hydration of lime. Besides saving energy, this increase in the water temperature speeds the reaction process.

Electrical energy use can be minimised through the utilisation of energy efficient equipment, such as high-pressure roll mills.

Some of the reduction techniques described below, process control optimisation for example, also have a positive effect on energy use.

2.4.3 Process control optimisation

Maintaining kiln control parameters close to their optimum values has the effect of reducing all consumption/emission parameters in the lime burning process. This is due to, among other things, reduced numbers of shut downs and upset conditions. Management systems can be operated to ensure that good operating and maintenance practices are adopted and followed by all concerned, and that their observance is monitored.

2.4.4 Choice of fuel

The selection of fuel can influence the emissions from the kiln -especially SO₂ emissions from rotary kilns. Lime producers tend to avoid burning of wastes as fuel because of end use in for example food industry and water treatment plants. In some cases, where the lime products do not have too strict purity demands, it may be possible to use waste fuels. The use of suitable types of waste as fuels can reduce the input of natural resources, but should always be done with satisfactory control of the substances introduced into the kiln process.

2.4.5 Techniques for controlling NO_x emissions

NO_x emissions depend mainly on the quality of lime produced and the design of kiln. Low-NO_x burners have been fitted to a few rotary kilns. Other NO_x reduction technologies have not been applied.

The direct transfer of low-NO_x burner technology from cement kilns to lime kilns is not straightforward. In cement kilns, flame temperatures are higher and low-NO_x burners have been developed for reducing high initial levels of 'thermal NO_x'. In most lime kilns the levels of NO_x are lower and the 'thermal NO_x' is probably less important.

2.4.6 Techniques for controlling SO₂ emissions

SO₂ emissions, principally from rotary kilns, depend on the sulphur content of the fuel, the design of kiln and the required sulphur content of the lime produced. The selection of fuels with low sulphur content can therefore limit the SO₂ emissions, and so can production of lime with higher sulphur contents. There are absorbent addition techniques available, but they are currently not applied.

2.4.7 Techniques for controlling dust emissions

Rotary kilns are generally equipped with electrostatic precipitators, on account of the relatively high exhaust gas temperatures. Fabric filters are also used, particularly on preheater kilns, where exhaust gas temperatures are lower.

Shaft kilns are usually fitted with fabric filters. Wet scrubbers are sometimes used.

Lime grinding plants use fabric filters to collect the product and de-dust the conveying air.

Hydrating plants, with exhaust gases saturated with water vapour at about 90 °C, are generally fitted with wet scrubbers, although fabric filters are increasingly being used where the feed lime has a high reactivity.

Table 2.13 gives an overview of available data of dust emission control techniques in lime manufacturing.

Technique	Applicability	Typical prod. rate (tpa)	Emission level		Cost ³	
			mg/m ³ ¹	kg/tonne ²	investment	operating
Cyclones	Mills, kilns, other processes	-	(~90 %)	-	-	-
EP or fabric filter	Rotary kiln	150000	<50	<0.2	1.4-3.0	1.0-2.0
Fabric filter	Parallel-flow regen. kiln	100000	<50	<0.2	0.3-1.0	0.5-1.0
Fabric filter	Annular shaft kiln	100000	<50	<0.2	0.3-1.0	0.5-1.0
Fabric filter	Other shaft kilns	50000	<50	<0.2	0.15-0.45	0.5-1.0
Fabric filter	Lime grinding systems	150000	<50	0.75 ⁴	0.08-0.45	0.1-1.0
Fabric filter	Lime hydrator	50000	<50	<0.04	0.05-0.13	0.1-0.3
Wet scrubber	Lime hydrator	50000	<50	<0.04	0.06-0.18	0.1-0.5
Fugitive dust abatement	All plants	-	-	-	-	-

1. normally referring to daily averages, dry gas, 273 K, 101.3 kPa and 10% O₂, except for hydrating plants for which conditions are as emitted.
2. kg/tonne lime: based on 4000 Nm³/tonne of lime for rotary kilns, 3500 Nm³/tonne of lime for shaft kilns and 800 Nm³/tonne of hydrated lime for lime hydrators
3. investment cost in 10⁶ euros and operating cost in euros/tonne lime
4. at 1500 m³/tonne and 50 mg/m³, exhaust gas volumes vary widely depending on installation.

Table 2.13: Overview of techniques to control dust emissions from the manufacturing of lime [EuLA, 1998], [Ecotechnici, 1986],

There is not much information available about achievable dust emission levels. Experiences have been reported from individual plants by members of the technical working group. These include a rotary lime kiln with an EP that is achieving below 20 mg/m³ in routine operation. Some experiences with fabric filters show that it is possible to achieve less than 5 mg/m³ on a daily basis, but in some of these cases this has required a change of bags 1-3 times a year.

Emission limit values for dust from lime plants within the European Union range from 25 to 250 mg dust/m³, see Annex A.

2.4.7.1 Cyclones

Cyclones are relatively inexpensive and easy to operate, but particles with small diameters are not captured effectively. Because of their inherently limited particle removal efficiency, they are mainly used to preclean the exhaust gases from mills, kilns and other processes. They relieve EPs and fabric filters from high dust loading, reduce erosion and abrasion problems and increase overall efficiency. [Ecotechnici, 1986]

Typically cyclones remove about 90% of the dust from lime kilns. [EuLA]

2.4.7.2 Electrostatic precipitators

Electrostatic precipitators are described in section 1.4.7.1.

Electrostatic precipitators are suitable for use at temperatures above the dew point and up to 370-400 °C (with mild steel construction). Rotary kilns with, and without, preheaters are often fitted with EPs. In some cases, this is because of the high exhaust gas temperature; in others it is because the kilns have large productive capacities and, consequently produce large volumes of gases (the cost of EPs relative to fabric filters fall with increasing size).

Electrostatic precipitators can reliably achieve dust loadings below 50 mg/Nm³. One rotary lime kiln fitted with an EP has been reported to achieve below 20 mg dust/m³ in routine operation.

When EPs are applied, especially at rotary kilns using coal or petcoke as fuel, it is important to avoid CO-trips. The number of CO-trips can be reduced by using modern control systems with fast measuring and control equipment which allow a higher switch-off criteria than the typically applied 0.5% CO by volume.

2.4.7.3 Fabric filters

Fabric filters are described in section 1.4.7.2.

Fabric filters are generally operated at temperatures above the dew point and up to 180-200 °C for “Nomex” cloth, and up to 250 °C for filter media such as fibreglass and “teflon”. However, they can be used at the dew point for treating emissions from hydrating plants. The fabric filter is then positioned directly above the hydrator, thereby minimising problems with condensation and return of collected solids to the process. Various types of filter media have been used, including moisture resistant fibre.

Well maintained fabric filters can reliably reduce dust concentrations to below 50 mg/Nm³. In some cases less than 5 mg dust/m³ have been achieved on a daily basis with fabric filters, but in some of these cases this has required a change of bags 1-3 times a year. The cause for the short life times of the bags is not known for certain in every case. Probable causes include variation in temperature of the gas due to the cyclic nature of the shaft kiln process, the lime dust behaviour and insufficient filter area. Insufficient filter area will cause too high filtration speed when cooling air is bleeding into the filter. The high velocity of the flue gases will reduce the effectiveness of the bag cleaning. Consequently the pressure of the cleaning air has to be increased to get the bags cleaned and this will shorten the duration of the bags. A filtration speed of 0.9-1.2 m/min has been recommended.

In one case the cause of the short life times of the bags was considered to be the insufficient size of the filter. The problem was solved by enlarging the filter and it is now achieving less than 5 mg/m³ with a 2 year life time guarantee on the bags [Junker].

Bags of “Gore-Tex” have also been used, and they also have had problems with short life times in some cases. At one plant the periodically excessive operating temperature was deemed to cause the problems [Junker].

The fabric filter should have multiple compartments which can be individually isolated in case of bag failure and it should be sufficient of these to allow adequate performance to be maintained if a compartment is taken off line. There should be ‘burst bag detectors’ on each compartment to indicate the need for maintenance when this happens.

The long term performance level of fabric filters depends on the maintenance of the filter and how often the bags are changed. The emission level can be very low, but it is costly. Approximate costs for filter bag replacement are 50 euros per bag including materials, labour and lost production. A 300 tonnes per day, gas-fired Maerz kiln requires approximately 640 filter bags (3.5 m x 0.15 m “Nomex”). The total cost for a complete change of filter bags could be estimated at 32000 euros. These figures do not include maintenance of the bag filter other than bag changes.

2.4.7.4 Wet scrubbers

There are many types of scrubbers, but the venturi scrubber is the most widely used in the lime industry. The gas is forced to pass through a throat, in which velocities reach 60 to 120 m/s. Water, added upstream of the throat, is shattered into fine drops by pneumatic forces, and is thus intimately mixed with the gas. Dust particles, trapped by the droplets, become heavier and are easily removed in an entrainment separator (usually cyclonic) attached to the venturi scrubber.

Wet scrubbers are generally chosen when the exhaust gas temperatures are close to, or below the dew point. They are sometimes used with higher temperature gases, in which case, the water cools the gases and reduces their volume. Wet scrubbers may also be chosen if space is limited.

2.4.7.5 Fugitive dust abatement

Good housekeeping can reduce the emission of fugitive dust. Techniques applied for the abatement of fugitive dust in the lime industry are the same as in the cement industry; these are described in section 1.4.7.3.

2.4.8 Waste

In most cases, the collected dust is principally calcium carbonate, with varying amounts of calcium oxide, fuel ash and clay. Disposal techniques for the collected dust ranges from incorporation into commercial products (for example, building lime, lime for soil stabilisation, hydrated lime and pelletised products) to landfill.

Where wet scrubbers are used, the collected suspension is settled, the liquor is generally recycled and the wet solids are in most cases landfilled.

2.5 Best available techniques for the lime industry

In understanding this chapter and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector; for the manufacture of lime these are emissions to air and energy use. The emissions to air from lime plants include nitrogen oxides (NO_x), sulphur dioxide (SO₂), carbon monoxide (CO) and dust;
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this chapter that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous chapter. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this chapter could be used to judge the current performance of an existing installation or to judge a proposal for a new installation and thereby assist in the determination of appropriate "BAT-based" conditions for that installation. It is foreseen that new installations could be designed to perform at or even better than the general "BAT" levels presented here. It is also considered that many existing installations could reasonably be expected, over time, to move towards the general "BAT" levels or do better.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

Emission levels given below are expressed on a daily average basis and standard conditions of 273 K, 101.3 kPa, 10% oxygen and dry gas, except for hydrating plants for which conditions are as emitted.

General primary measures

Best available techniques for the manufacturing of lime includes the following general primary measures:

- A smooth and stable kiln process, operating close to the process parameter set points, is beneficial for all kiln emissions as well as the energy use. This can be obtained by applying:
 - Process control optimisation.
- Minimising fuel energy use by means of:
 - Heat recovery from exhaust gases.
- Minimising electrical energy use by means of:
 - Utilisation of mills and other electricity based equipment with high energy efficiency.
- Minimising limestone consumption by means of:
 - Kiln selection to make optimum use of quarried limestone;
 - Specific quarrying and well-directed use of limestone (quality, grain size).
- Careful selection and control of substances entering the kiln can reduce/avoid emissions:
 - Selection of fuels with low contents of sulphur (rotary kilns in particular), nitrogen and chlorine.

Dust

Best available techniques for reducing dust emissions are the combination of the above described general primary measures and:

- Minimisation/prevention of dust emissions from fugitive sources as described in section 1.4.7.3.
- Efficient removal of particulate matter from point sources by application of:
 - Fabric filters with multiple compartments and ‘burst bag detectors’
 - Electrostatic precipitators
 - Wet scrubbers

The BAT emission level associated with these techniques is 50 mg/m³. This emission level can be achieved by fabric filters and/or electrostatic precipitators and/or wet scrubbers at the various types of installations in the lime industry.

Waste

The utilisation of dust, out-of-specification quicklime and hydrated lime in selected commercial products is considered to constitute BAT.

2.6 Emerging techniques in the lime industry

2.6.1 Fluidised bed calcination

The calcination of finely divided limestone in a fluidised bed has been practiced on a relatively small scale for many years. It has several potential advantages, including:

- the use of surplus grades of fine limestone,
- low NO_x emissions, and
- low SO₂ emissions, when using high sulphur fuels.

However, the technique does not have a particularly low specific heat use, the finely divided products are not suitable for many applications and the residual calcium carbonate level is relatively high. Initial problems with using the technique for kilns with productive capacities in excess of 150 tonnes per day appear to have been resolved.

Figure 2.11 shows a schematic diagram of a fluidised bed kiln. Fine limestone is fed to a preheater vessel using air heated by the kiln exhaust gas via a heat exchanger. The preheated limestone then enters the first fluidised bed vessel where the temperature is increased and limestone starts to be calcined. As the limestone is calcined, the lighter quicklime flows over the weir wall into the next fluidised bed vessel where calcination is completed. The quicklime then passes through the cooler where it is cooled by ambient air.

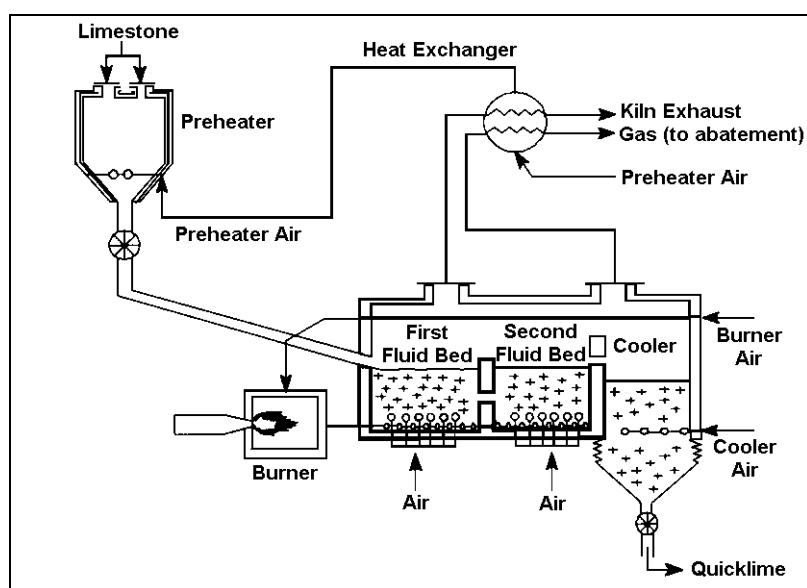


Figure 2.11: Fluidised bed kiln.
[UK IPC Note, 1996]

Although fluidised bed technology may offer lower pollutant releases than other lime kiln technologies, it is not well proven and can only produce fine lime with a high reactivity.

2.6.2 Flash calciner/suspension preheater

The technique of feeding finely divided limestone via a suspension preheater into a flash calciner was developed in the cement industry. However, it is only suitable for a limited range of limestone qualities and has been used in a very small number of installations. Two kilns have recently been installed in Australia using this technique. In one the product from the flash

calciner is passed through a short rotary kiln. The rotary section is designed to control the % CaCO_3 and the reactivity of the lime within customer specifications.

The technique is particularly suitable for “sandy” limestones as the flash calciner kiln accepts feedstone in the 0-2 mm range. It is understood to have high capital costs, which are likely to restrict its use to relatively large output levels (for example, about 500 tonnes/day).

2.6.3 Absorbent addition to reduce SO_2 emissions

The use of absorbents to reduce SO_2 emissions is well established in other industries. It has not, however, been applied to rotary lime kilns. The following techniques may merit further investigation:

- Use of fine limestone: At a straight rotary kiln fed with dolomite it has been observed that significant reductions in SO_2 emissions can occur with feedstones which either contain high levels of finely divided limestone or are prone to break up on heating. The finely divided limestone calcines, is entrained in the kiln gases and removes SO_2 en route to, and in, the dust collector.
- Lime injection into the combustion air: A patented technique (EP 0 734 755 A1) describes the reduction of SO_2 emissions from rotary kilns by injecting finely divided quick- or hydrated lime into the air fed into the firing hood of the kiln.
- Injection of an absorbent into the exhaust gases: A recognised technique for reducing SO_2 concentrations in gaseous emissions is to:
 - a) inject an absorbent (e.g., hydrated lime or sodium bicarbonate) into the gas stream, and
 - b) provide sufficient gas residence time between the injection point and the dust collector (preferably a fabric filter) to obtain efficient absorption.It would seem feasible to adapt this technique to rotary lime kilns.

2.6.4 CO-peak management

The CO-peak management technique being developed for cement kilns fitted with electrostatic precipitators (EPs) may be applicable in some circumstances to rotary lime kilns equipped with EPs. However, the rate of dust emission (kg/tonne of product) following the deactivation of the EP is generally very much lower in the case of lime kilns than in that of cement kilns, owing to the relatively coarse size of the limestone and the absence of any dust recycle.

2.6.5 Ceramic filters

Ceramic filters are not currently used on lime kilns. However, they are able to remove dust efficiently from gases at very high temperatures, and it is possible that, with kilns such as rotary kilns producing dead-burned dolomite, de-dusting high temperature gases might enable certain heat recovery systems to become viable.

2.7 Conclusions and recommendations

The experts nominated to the Technical Working Group by Member States, Norway, European Environmental Bureau and European Industry (EuLA - The European Lime Association) have all taken part in this exchange of information.

There is not much information easily available about lime industry and the information sources are few. EuLA has been helpful in collecting and providing information, but it is not a big industry association and did not have a lot of information available when this information exchange exercise started.

There is not much economic information available.

Before an update of this reference document is carried out, it could be useful to make a survey of current abatement techniques, emissions and consumptions and of monitoring in the lime industry.

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GLOSSARY OF TERMS AND ABBREVIATIONS

atm	normal atmosphere (1 atm = 101325 N/m ²)
Ag	silver
Al	aluminium
Al ₂ O ₃	aluminium oxide
As	arsenic
bar	(1.013 bar = 1 atm)
Ba	barium
Be	beryllium
cSt	centistoke
°C	degree Celsius
Ca	calcium
CaCO ₃	calcium carbonate
CaO	calcium oxide
Ca(OH) ₂	calcium hydroxide
Cd	cadmium
Co	cobalt
Cr	chromium
Cu	copper
CH ₄	methane
CN	cyanide
CO	carbon monoxide
CO ₂	carbon dioxide
dolomite	type of limestone the carbonate fraction of which is dominated by the mineral dolomite, calcium magnesium carbonate [CaMg(CO ₃)].
e.g.	for example (exempli gratia, latin)
EP	electrostatic precipitator
F	fluorine
Fe	iron
Fe ₂ O ₃	iron oxide
Hg	mercury
HCl	hydrochloric acid
HF	hydrofluoric acid
H ₂ O	water
H ₂ S	hydrogen sulphide
i.e.	that is (id est, latin)
kcal	kilocalorie (1 kcal = 4.19 kJ)
kg	kilogramme (1 kg = 1000 g)
kJ	kilojoule (1 kJ = 0.24 kcal)
kWh	kilowatt-hour (1 kWh = 3600 kJ = 3.6 MJ)
K	1) potassium; 2) degree Kelvin (0 °C = 273.15 K)
m	metre
m/min	metre/minute
m ²	squaremetre
m ³	cubicmetre
µm	micrometre (1 µm = 10 ⁻⁶ m)
mg	milligramme (1 mg = 10 ⁻³ gramme)
mm	millimetre (1 mm = 10 ⁻³ m)
mmWG	millimetre water gauge
MgCO ₃	magnesium carbonate
MgO	magnesium oxide
Mn	manganese
Mt	megatonne (1 Mt = 10 ⁶ tonne)

MJ	megajoule (1 MJ = 1000 kJ = 10 ⁶ joule)
ng	nanogramme (1 ng = 10 ⁻⁹ gramme)
N ₂	nitrogen
Na	sodium
Ni	nickel
Nm ³	normal cubic metre (101,3 kPa, 273 K)
NH ₃	ammonia
NH ₄	ammonium
Ω cm	ohm centimetre, unit of specific resistance
NO	nitrogen monoxide
NO ₂	nitrogen dioxide
NO _x	nitrogen oxides
O ₂	oxygen
Pb	lead
Pd	palladium
Pozzolana	Pozzolanas are materials that, though not cementitious in themselves, contain silica (and alumina) in a reactive form able to combine with lime in the presence of water to form compounds with cementitious properties. Natural pozzolana is composed mainly of a fine, chocolate-red volcanic earth. An artificial pozzolana has been developed that combines a fly ash and water-quenched boiler slag.
Pozzolanic cement	Pozzolanic cements are mixtures of portland cement and a pozzolanic material that may be either natural or artificial. The natural pozzolanas are mainly materials of volcanic origin but include some diatomaceous earths. Artificial materials include fly ash, burned clays, and shales.
Pt	platinum
PCDDs	polychlorinated dibenzodioxins
PCDFs	polychlorinated dibenzofurans
Rh	rhodium
Sb	antimony
Se	selenium
siliceous limestone	limestone that contains silicon dioxide (SiO ₂)
SiO ₂	silicium dioxide
Sn	tin
SCR	selective catalytic reduction
SNCR	selective non-catalytic reduction
SO ₂	sulphur dioxide
SO ₃	sulphur trioxide
SO _x	sulphur oxides
t	tonne (metric)
Te	tellurium
Ti	titanium
Tl	thallium
tpa	tonnes per annum (year)
TCDD	tetrachlorodibenzodioxin
TE	toxicity equivalents (dioxins and furans)
TEQ	international toxicity equivalents (dioxins and furans)
TOC	total organic carbon
V	vanadium
VOC	volatile organic compounds
Zn	zinc
% v/v	percentage by volume

ANNEX A: EXISTING NATIONAL AND INTERNATIONAL LEGISLATION

National emission limits for the production of CEMENT within the European Union

The tables below provides national ELV's. The applications of the figures are different from one country to another (averaging time, reference conditions, measurements techniques, compliance criteria, etc.).

Dust mg/Nm ³	Data based on	new/modified or existing plant	kiln stack	clinker cooling	cement grinding	other point sources
Austria	Na (a)	new/modified existing	50 50	50 50	50 50	50 50
Belgium	P	new/modified existing	50 50-150	50 50-400	50 50-150	50-300
Denmark	P	existing	50 (b)	50 (b)	50 (b)	50 (b)
Finland	P	new/modified existing	50 50 (c)	50 50	30-50 30-50	30-50 30-50
France	Na	new/modified existing	50 50 (d)	100 100 (d)	50 50 (e)	30 30
Germany	Na	new/modified existing	50 50	50 50	50 50	50 50
Greece	Na/R	new/modified existing	100 150	100 150	100 150	
Ireland	Na	new/modified existing	50 50	100 100	75 75	50 50
Italy	Na/P	existing	50	50	50	50
Luxembourg	P	existing	30 (f)			
Netherlands	P	existing	15 (f)	10 (f)	10 (f)	10 (f)
Portugal	Na	new/modified existing	50 100	100 100	75 75	50 50
Spain	Na	new/modified existing	 400/250 (g) 100 (h)	170/100 (g) 100 (h) 170/100 (g) 100 (h)	300/250 (g) 75 (h) 300/250 (g) 75 (h)	300/250 (g) 50 (h) 300/250 (g) 50 (h)
Sweden	P	existing	50 (i)	50	50	20
United Kingdom	Na (j)	new/modified existing	40 (k) (l)	50 (k) (l)	40 (k) (l)	50 (k) (l)

Na=National law; R=Regional law; P=Typical permit

- Daily averages and reference condition of 273 K, 101.3 kPa, dry gas and 10% O₂.
- Limits under discussion. Reference condition of 273 K, 101.3 kPa, dry gas and 10% O₂.
- Existing plant must meet 50 mg/Nm³ by January 1, 2001. Monthly averages and reference condition of 10% O₂ and dry gas.
- Existing plant with emission <150 mg/Nm³ must meet limit for new plant by 2001.
- Existing plant must meet limit for new plant by 2001.
- Daily average values.
- Current limits.
- Limits under discussion.
- Daily average value. A limit value of 90 mg/Nm³, including start/stop and CO-trips, applies for monthly averages.
- IPC Guidance Note S2 3.01.
- 'Benchmark releases'
- Benchmark releases are, in particular, not applicable to existing plant but are a factor in considering appropriate limits.

[Based on [Cembureau report, 1997] and information provided by TWG experts]

SO ₂ , NO _x mg/Nm ³ PCDD/Fs	Data based on	new/modified or existing plant	SO ₂ normal situation	SO ₂ S-rich raw materials	NO _x	PCDD/Fs ng TEQ/Nm ³
Austria	Na (a)	new/modified existing	200 200	400 400	500 1000	
Belgium	P	new/modified existing	1000 1000		1800 1800	
Denmark	P (a)	existing	5/250/450 (b)	no limit	1200/2500/850 (c)	no limit
Finland	P (d)	existing	150-400		1200-1800	
France	Na	new/modified existing	500 500(e)	1200/1800 (f) 1200/1800 (e,f)	1200/1500/1800 (g) 1200/1500/1800 (g)	
Germany	Na	new/modified existing	400 400	400 400	500 800	
Greece						
Ireland	Na	new/modified existing	400 400	700 700	1300 1300	n.a. n.a.
Italy	Na/P	new/modified existing	600		1800	10000 (h) 10000 (h)
Luxemburg	P	existing	100 (i)		800 (j)	0.1 (k)
Netherlands	P	existing	(l)		1300 (j)	0.1
Portugal	Na	new/modified existing	400		1300	0.1 0.1
Spain	Na	new/modified existing	2400/6000 (m) 600 (n) 2400/6000 (m) 600 (n)	2400/6000 (m) 1800 (n) 2400/6000 (m) 1800 (n)	1300-1800 (n)	
Sweden	P	existing	-	<200	<200	0.1
UK	Na (o)	new/modified existing	200 (p) (q)	600-2500 (r)	900 (p) 500-1200 (q)(s)	

Na=National law; R=Regional law; P=Typical permit

- a) Daily averages and reference condition of 273 K, 101.3 kPa, dry gas and 10% O₂.
- b) 5 for semi-dry process, 250 for wet process and 450 for wet process with wet scrubber and heat recovery. Limits under discussion.
- c) 1200 for semi-dry process, 2500 for wet process and 850 for wet process with wet scrubber and heat recovery. Limits under discussion.
- d) Monthly averages, reference condition of 10% O₂ and dry gas
- e) Existing plant must meet limit for new plant by 2001.
- f) 1200 mg/Nm³ if ≥ 200 kg/h; 1800 mg/Nm³ if < 200 kg/h.
- g) 1200 mg/Nm³ for dry process with heat recuperation, 1500 mg/Nm³ for semi dry and semi wet processes, and 1800 mg/Nm³ for wet and dry processes without heat recuperation.
- h) General rule for any kind of industrial emission.
- i) Half hour average.
- j) Daily average value.
- k) 6 hour average.
- l) 90 kg/h as daily average, maximum 375 tonne/year.
- m) Current limits.
- n) Limits under discussion.
- o) IPC Guidance Note S2 3.01.
- p) 'Benchmark releases'
- q) Benchmark releases are, in particular, not applicable to existing plant but are a factor in considering appropriate limits.
- r) Limit values reflect the actual levels of releases. Daily averages and reference condition of dry gas and actual O₂ content.
- s) Actual releases, daily averages, not all plants currently have limits.

[Based on [Cembureau report, 1997] and information provided by TWG experts]

The table below provides national ELV's for metals and other emissions from the kiln stack. As for the previous tables the applications of the figures are different from one country to another (averaging time, reference conditions, measurements techniques, compliance criteria, etc.).

Metals, others mg/Nm ³	Measuring interval	Σ (Cd, Tl, Hg)	Σ (Se, Te, As, Co, Ni)	Σ (Sb, Pb, Cr, Cu, Mn, V, Sn)	TOC	HCL	HF	NH ₃	CO
Austria	3 years (a)	0.1/0.2 (b)	1.0 (c)						
Belgium	6 months	0.2	1 (d)	5	75 (e)	30	5		
Denmark									
Finland									
France	1 year	0.2	1.0	5.0 (f)					
Germany	3 year	0.2	1.0	5.0 (g)	(h)	30 (i)	5 (i)		
Greece									
Ireland									
Italy	varies	0.2	1.0 (j) 1.0 (k)	5.0 (l) 5.0 (m)	(n)	30	5	250	
Luxemburg (o)	1 year	0.2	1	5 (p)	30	30	5		
Netherlands	1 year	0.15	1.0 (q)	1.0 (q)	40	10	1		
Portugal	6 months	0.2	1.0	5.0	50	250	50		1000
Spain	varies	0.2 (r)	1.0 (r)	5.0 (r)					
Sweden	1 year	(s)	(s)	(s)					
UK									

- a) Half hourly averages and reference condition of 273 K, 101.3 kPa, dry gas and 10% O₂.
- b) Group comprises Cd, Tl, Be. The limit 0.1 applies individually, 0.2 applies for the sum
- c) As, Co, Ni, Pb.
- d) As, Co, Ni.
- e) CH₄ excepted.
- f) Zn also included.
- g) Cyanides (soluble) given as CN, fluorides (soluble) given as F, Pt, Pd and Rh are also included.
- h) Limits are required for organic compounds divided into three classes of danger: (from TA-Luft)
CLASS I: 20, CLASS II: 100, CLASS III: 150.
- i) Emission limit applies for sum of this and other compounds.
- j) Se, Te only.
- k) As, Cr(VI), Co, Ni.
- l) Sb, Cr(III), Mn, Pd, Pb, Pt, Cu, Rh, Sn, V.
- m) Σ(Cd, Tl, Hg, Se, Te, Sb, Cr(III), Mn, Pd, Pb, Pt, Cu, Rh, Sn, V)
- n) Limits are required for specific organic compounds (ca. 200) divided into five classes of danger:
CLASS I: 5, CLASS II: 20, CLASS III: 150, CLASS IV: 300, CLASS V: 600.
- o) Half hour average.
- p) Σ(Cd, Hg, Tl, As, Co, Ni, Se, Te, Sb, Cu, Pb, Cr, V, Fluorures)
- q) Σ(Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Sn, Se, Te)
- r) Limits under discussion.
- s) No limit specified in the permit. Actual levels are reported initially and are taken into account in the issuing of the permit. Selected elements are reported annually.

[Based on [Cembureau report, 1997] and information provided by TWG experts]

National emission limits for releases into air from LIME kilns within the European Union

The tables below provides national ELV's. The applications of the figures are different from one country to another (averaging time, reference conditions, measurements techniques, compliance criteria, etc.).

Dust, SO ₂ , NO _x , HCl mg/m ³	Data based on	Mass flow kg/h	Dust	SO ₂	NO _x	HCl
Austria	P		50			
Belgium		>0.5 <0.5	50 150			
Denmark	P		20-40	500	500	100
Finland	P		50-150	250	150-200	
France	Na	>1 <1 >25	40 100	300	500	50
Germany	Na, R	>0.5 >5	50	500	500 (a)	30
Greece	Na		100/150 (b)			
Ireland	Na		50	750	1800	
Italy	Na	>5	50	500	1800	
Luxemburg						
Netherlands						
Portugal	Na		150	2700	1500	
Spain	Na		250			
Sweden	P		25-50 (c)			
United Kingdom	Na (d)		40/50 (e)	200 (e)	900 (e)	

Na=National law; R=Regional law; P=Typical permit

a) case by case consideration of emission limit for rotary kilns

b) 100 for new/modified plants, 150 for existing plants

c) for older lime kilns up to 250 mg/m³.

d) IPC Guidance Note S2 3.01.

e) 'Benchmark releases'. Benchmark release levels are not emission limits but are subject to consideration of site specific emission limits.

[Based on and information provided by TWG experts]

EC legislation applicable to the production of cement and lime

- Council Directive 94/67/EC on the incineration of hazardous waste
- Proposal for a Directive on the incineration of waste adopted by the Commission October 7, 1998 (O.J. C372 of December 2, 1998, pp 11-26).

ANNEX B: NO_x AND SO₂ ABATEMENT IN THE CEMENT INDUSTRY

The tables below present the (currently known) number of full scale installations in the EU and EFTA countries with NO_x and SO₂ abatement techniques.

NO _x	Flame cooling	Mineralised clinker	Staged combustion	SNCR	SCR
Austria	3	1	1		
Denmark		1			
France	10	1			
Germany		4	7	15	1 ¹
Italy			3		
Sweden			1	2	
Switzerland				1	
Total	13	7	12	18	1

1) Will be in operation in the end of 1999

[Based on a Cembureau survey carried out in April 1999 and information provided by TWG experts]

SO ₂	Absorbent addition	Wet scrubber	Dry scrubber	Activated carbon
Austria		1		
Belgium	2			
Denmark		2		
Germany	11			
Italy	1			
Sweden		1		
Switzerland			1	1
United Kingdom		1		
Total	14	5	1	1

[Based on a Cembureau survey carried out in April 1999 and information provided by TWG experts]