

## 6 – Cement Manufacturing Industry

### 1. The Cement Industry

#### Cement Production

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 EU-12 in 1995 was 172 million tonnes.

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. In 1995 there were 252 installations producing cement clinker and finished cement in the EU-15 and a total of 437 kilns. In recent years typical kiln size has come to be around 3000 tonnes clinker/day.

There is generally little import and export of cement, mainly as a result of the high cost of road transport. Road deliveries of cement generally do not exceed distances of 150 km. Consequently, the rate of consumption equals the rate of production for many EU member states, with the exception of Greece and Denmark. Their export accounts for approximately 50% of their cement production.

#### Technologies

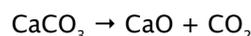
Cement is a finely ground, non-metallic, inorganic powder when mixed with water forms a paste that sets and hardens. This hydraulic hardening is primarily due to the formation of calcium silicate hydrates formed by mixing water and the cement components.

#### The Sources

The text is a summary of the IPPC (European Commission Integrated Pollution Prevention and Control) Reference Document on Best Available Techniques in the Cement and Lime Manufacturing Industries, December 2001.

See also Case Study 1 on Kunda Cement in Book 4 of this series.

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 residue 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:



The cement industry is thus main emitter of the greenhouse gas carbon dioxide, both because of its large energy use and the calcination reaction. About 5% of global CO<sub>2</sub> emissions is due to cement production.

In 1994 Europe's cement industry produced 44% Portland-composite cement 43%, Portland cement while Blastfurnace, Pozzolanic and other cements accounted for the rest. 78% of the production relied on dry process kilns, the rest is accounted for by semi-dry, semi-wet process and wet process kilns. The choice of manufacturing process is primarily motivated by the nature of the available raw materials.

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

The emissions from cement plants which cause greatest concern are nitrogen oxides (NO<sub>x</sub>), sulphur dioxide (SO<sub>2</sub>) and dust. Other emissions to be considered are carbon monoxides (CO), volatile organic compounds (VOCs), polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs), metals, and noise.

### 2. Production Technologies

#### The Basic Processes

The basic chemistry of the cement manufacturing process begins with the decomposition of calcium carbonate (CaCO<sub>3</sub>) at

about 900°C to leave calcium oxide (CaO, lime) and liberate gaseous carbon dioxide (CO<sub>2</sub>); this process is known as calcination. This is followed by the clinkering process in which the calcium oxide reacts at high temperature (typically 1400-1500°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 6.1 shows an overview of a dry process precalciner route.

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. 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.

### 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 residue can also be used as partial replacements for the natural raw materials as can fly ash,

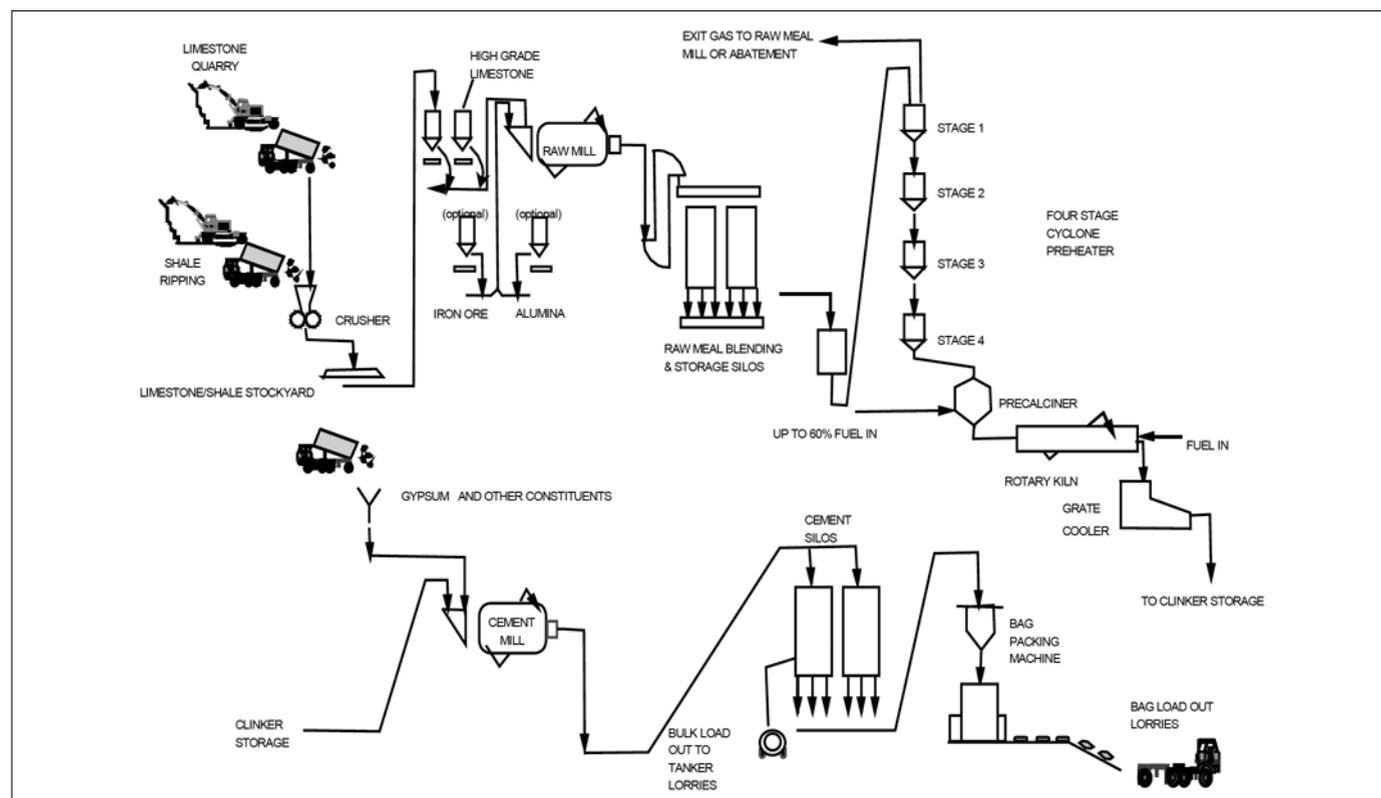


Figure 6.1 A typical precalciner dry process.

blast furnace slag, silica fume, iron slag, paper sludge, pyrite ash and phosphogypsum (from flue gas desulphurisation and phosphoric acid production).

The natural raw materials are most often obtained from open surface quarries, by rock drilling, blasting, excavation, hauling and crushing. In most cases the quarry is close to the plant. 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.

The raw materials 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. The fineness and particle size distribution of the product leaving a raw grinding system is of great importance for the subsequent burning process.

### Fuels

Three different types of fuels are mainly used in cement kiln firing; in decreasing order of importance these are pulverised coal and pet coke; (heavy) fuel oil; and natural gas. The main ash constituents of these fuels, silica and alumina compounds, combine with the raw materials to become part of the clinker.

The high temperatures and long residence times in the kiln system destroys completely all organic substances, which makes a wide variety of alternative fuel options possible, in particular different types of wastes. Wastes, that are fed through the main burner, will be decomposed in the primary burning zone, at temperatures up to 2000°C. The types of waste most frequently used as fuels in Europe today are used tyres, waste oils, sewage sludge, rubber, waste woods, plastics, paper waste, paper sludge, and spent solvents.

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 allowing easy

and complete combustion. This is possible with all liquid and gaseous fuels. For pulverised solid fuels, good design of hoppers, conveyors and feeders is essential. Solid fuel preparation (crushing, grinding and drying) is usually carried out on site.

### Clinker Burning

This part of the process is the most important in terms of emissions and of product quality and cost. In clinker burning, the raw meal is fed to the rotary kiln system where it is dried, preheated, 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. The clinker needs to be burned under oxidising conditions, why an excess of air is required in the sintering zone. Since the rotary kiln was introduced around 1895 it has become the central part of all modern clinker producing installations.

The first rotary kilns were long wet kilns, where the whole heat consuming thermal process takes place in the kiln itself. The introduction of the dry process allowed drying, preheating and calcination 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.

The fuel introduced via the main burner produces the main flame with flame temperatures around 2000°C. For process-optimisation the flame has to be adjustable within certain limits. In a modern indirectly fired burner, the flame is shaped

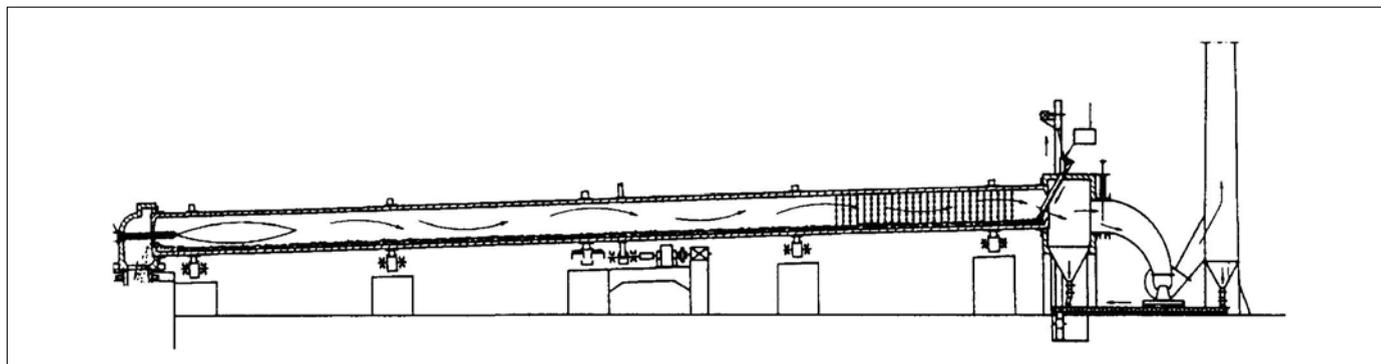
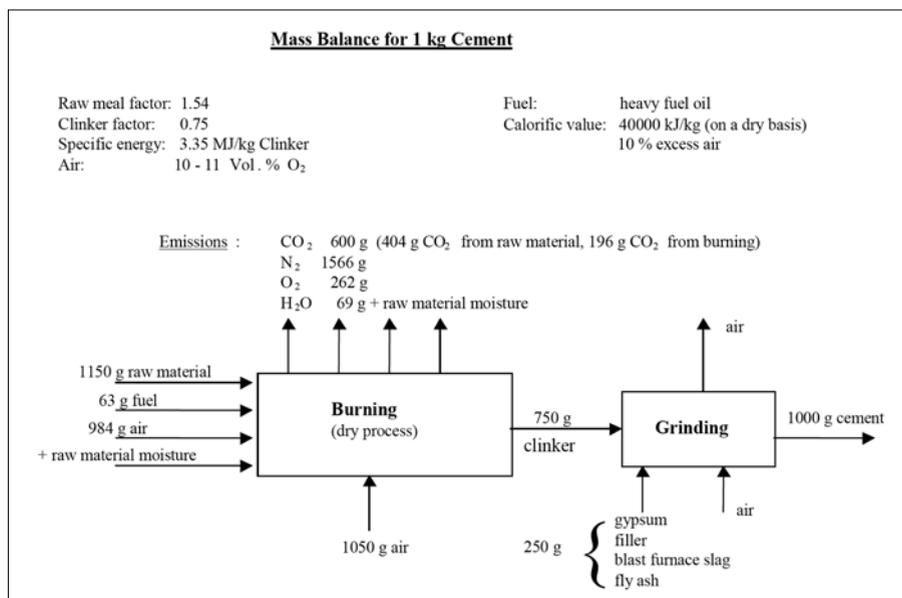


Figure 6.2 Long wet rotary kiln with chains.

**Figure 6.3** Mass balance for the production of 1 kg cement.



and adjusted by the primary air (10-15% of total combustion air).

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 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.

Grate preheater technology, 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 reduced the heat losses and increased energy efficiency. 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 leaves the drying chamber at 90-150°C.

The invention of the suspension preheater in the early 1930s was a significant development. Preheating and even partial calcination of the dry raw meal 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.

The four-stage cyclone preheater kiln system 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. Almost all four-stage suspension preheaters operate with rotary kilns with three supports.

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.

### Clinker Coolers

The clinker cooler is an integral part of the kiln system and has a decisive influence on performance and economy. 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.

There are two main types of coolers, rotary and grate. 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. Cooling in grate coolers is achieved by passing a current of air upwards through a layer of clinker lying on an air-permeable grate. Introduction and development of modern technology reciprocating grate coolers started around 1983. The design was a step closer to optimum heat exchange and also more compact coolers using less cooling air and smaller dedusting systems.

### Cement Grinding and Storage

Clinker and other cement components are stored in silos or in closed sheds until further processed. Portland cement is produced by intergrinding cement clinker and sulphates such as gypsum and anhydrite. In blended cements (composite cements)

**Table 6.1 Consumption of raw materials in cement production.**  
*A typical cement plant has an annual production of about 1 Mt (1 million tonnes) clinker.*

Materials (dry basis)	per tonne clinker	per tonne cement	per Mt clinker
Limestone, clay, shale, marl, other	1.57 t	1.27 t	1,568,000 t
Gypsum, anhydrite	-	0.05 t	61,000 t
Mineral additions	-	0.14 t	172,000 t

there are other constituents, such as granulated blast furnace slag, natural or artificial pozzolanas, limestone, or inert fillers.

Grinding plants may be at separate locations from clinker production plants. Commonly used finish grinding systems are tube mill, closed circuit, vertical roller mill, and roller press. The crushed material leaving the mill is transported to a separator, the oversize fraction being returned to the mill. Mineral additions are usually ground together with the clinker and gypsum. The particle size distribution of the product leaving the cement grinding system is of great importance for the cement quality. The ready product is stored in silos until shipped.

### 3. Consumption and Emission Levels

#### Consumption of Raw Materials and Energy

For cement on average, energy costs in the form of fuel and electricity represent 50% of the total production cost. 80% of this is used in the burning process. The chemical reaction takes in a modern process about 60% of the burning energy use and becomes part of the product. The theoretical energy use for the burning process (chemical reactions) is about 1700 to 1800 MJ/tonne clinker. Total burning energy requirement is in 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, and 5000-6000 for wet process long kilns.

Electrical energy represents approximately 20% of the overall energy requirement or 90-130 kWh/tonne cement. The main use is for the mills for finish grinding and raw grinding and the exhaust fans from kiln/raw mill and cement mill, which together account for more than 80% of electrical energy usage.

#### Emissions

The main environmental issues associated with cement production are emissions to air and energy use. Waste water dis-

charge 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 ground water.

The releases to air from the kiln system derive from the physical and chemical reactions of the raw materials and the combustion of fuels. The main constituents are nitrogen from the combustion air; CO<sub>2</sub> from calcination 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 acts as a built-in circulating fluidised bed. Thus many components that result from the combustion of the fuel or from the transformation of the raw material remain in the gas phase only until they are absorbed by, or condensed on, the raw material flowing counter currently.

Typical kiln exhaust gas volumes expressed as m<sup>3</sup>/tonne of clinker (dry gas, 101.3 kPa, 273°K) are between 1700 and 2500 for all types of kilns. 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 outside storage of raw materials and solid fuels as well as from materials transport systems, including cement product loading.

#### Oxides of Nitrogen

Nitrogen oxides (NO<sub>x</sub>) are of major significance with respect to air pollution from cement manufacturing plants. NO<sub>x</sub> emission measurements revealed a mean value of 2.1 g NO<sub>2</sub>/kg of clinker, which corresponds to 1050 mg NO<sub>2</sub>/m<sup>3</sup>. The mean values varied from 371-964 mg NO<sub>x</sub>/m<sup>3</sup>. NO and NO<sub>2</sub> are the dominant nitrogen oxides in cement kiln exhaust gases (NO >90% of the nitrogen oxides).

There are two main sources for production of NO<sub>x</sub>:

- Thermal NO<sub>x</sub> when part of the nitrogen in the combustion air reacts with oxygen to form oxides of nitrogen in the kiln burning zone, where it is hot enough, above 1200°C. The reaction increases with temperature and oxygen content (air excess factor). Hard-to-burn mixes which require hotter burning zones will tend to generate more thermal NO<sub>x</sub> than kilns with easier-burning mixes.
- Fuel NO<sub>x</sub> when nitrogen chemically bound in the fuel either form N<sub>2</sub> gas, or react with oxygen in the air to form various oxides of nitrogen. In a precalciner the prevailing temperature of 850-950°C is too low to form significant thermal NO<sub>x</sub>, but fuel NO<sub>x</sub> will occur.

## Sulphur Dioxide

Sulphur dioxide 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<sub>2</sub> emissions.

## Dust

Traditionally the emission of dust, particularly from kiln stacks, has been the main environmental concern in 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 reduce dust emissions to levels, often below 10 mg/m<sup>3</sup>, where they cease to be significant.

## Carbon Dioxides CO<sub>2</sub>

The emission of CO<sub>2</sub> 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. Mineral additions reduce CO<sub>2</sub> emission as counted per tonnes of cement. Approximately 60% originates in the calcination process and the remaining 40% is related to fuel combustion. As an 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 CO<sub>2</sub> emission of 0.32 tonne per tonne of clinker, when regarding fuel part only. Using natural gas instead reduces this level by

approximately 25%. Emissions of combustion CO<sub>2</sub> have been progressively reduced about 30% in the last 25 years mainly by more fuel efficient kiln processes.

## Other Emissions

The emission of *carbon monoxide 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. Control of CO levels is critical in cement kilns when EPs are used for particulate abatement. 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.

In combustion processes in general, the occurrence of *volatile organic compounds* is often associated with incomplete combustion and CO formation. 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.

Any chlorine input in the presence of organic material may potentially cause the formation of *polychlorinated dibenzodioxins (PCDDs)* and *polychlorinated dibenzofurans (PCDFs)* in the combustion processes. Their formation is known to oc-

**Table 6.2** Emission ranges data from European cement kilns.

Parameter	mg/Nm <sup>3</sup>	kg/tonne clinker	tonnes/year
NO <sub>x</sub> (as NO <sub>2</sub> )	<200–3000	<0.4-6	400-6000
SO <sub>2</sub>	<10–3500	<0.02-7	<20-7000
Dust	5–200	0.01-0.4	10-400
CO	500–2000	1-4	1000-4000
CO <sub>2</sub>	400-520 g/Nm <sup>3</sup>	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 <sup>3</sup>	<200-1000 ng/t	<0.2-1 g/year
<b>Metals:</b>			
Σ (Hg, Cd, Tl)	0.01-0.3 (mainly Hg)	20-600 mg/t	20-600 kg/year
Σ (As, Co, Ni, Se, Te)	0.001-0.1	2-200 mg/t	2-200 kg/year
Σ (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 m<sup>3</sup>/tonne clinker and 1 million tonnes clinker/year. Emission ranges are one-year averages and are indicative values based on various measurement techniques. O<sub>2</sub>-content is normally 10%.

cur 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. Emissions of PCDDs and PCDFs is generally low during steady kiln conditions.

Raw materials and fuels will always contain *metals*, but concentrations vary widely from one location to another. In particular, the use of coal and waste fuels may increase the input of metals into the process. The behaviour of the metals in the burning process depends on their volatility. Nonvolatile 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. Thallium and mercury and their compounds are particularly easily volatilised and to a lesser extent so are cadmium, lead, selenium and their compounds. The dusts from the production of cement contain small amounts of compounds of metals.

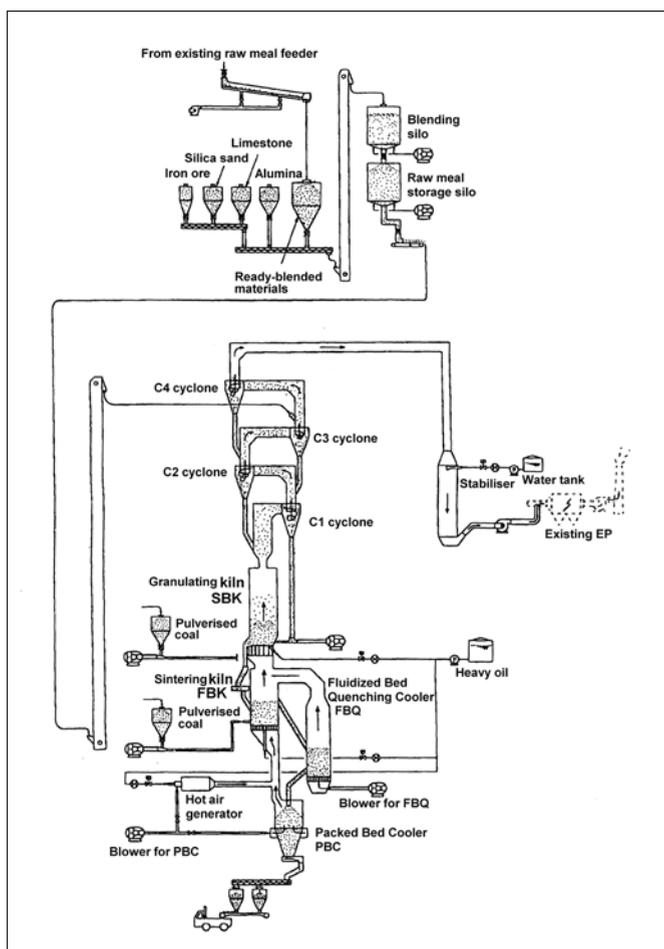


Figure 6.4 Fluidised bed cement kiln.

## 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.

## 4. Technology Development and Cleaner Production Opportunities

### Reducing Material Input

The environmental impact of cement manufacturing is largely caused by clinker production. In Europe the average clinker content in cement is 80-85%. Many manufacturers work to further lower the clinker content, e.g. by adding fillers, such as sand, slag, limestone, fly-ash and pozzolana, in the grinding step. 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.

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 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. Cement production offers one possibility to burn hazardous waste, that otherwise is a problem.

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 SO<sub>2</sub>. The same is valid for raw materials and fuels containing other substances, for example nitrogen, metals and organic compounds.

### Selection of Process

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 today state of the art. The wet process kilns operating in Europe are generally expected to convert to the dry process when renewed, and so are semi-dry and semi-wet processes. Thus kiln systems with 5 cyclone preheater stages and precalciner are considered standard technology for new plants. Such a configuration will use 2900-3200 MJ/tonne clinker. Reduced energy input in other kiln systems requires short dry process kiln with multi stage preheating and precalcination. 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.

Any kiln system should be run under optimal conditions. Optimisation includes 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. Optimisation 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. Reduction of emissions, such as NO<sub>x</sub>, SO<sub>2</sub> and dust, are secondary effects of the optimisation of the clinker burning process.

### Fluidised Bed Technology

A technology using fluidised bed cement kiln system is a project subsidised by the Ministry of International Trade and Industry in Japan since 1986. A 200 tonnes clinker/day large scale pilot plant was constructed in the end of 1995.

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<sub>x</sub> emission is 115-190 mg/m<sup>3</sup> when heavy oil is used and 440-515 mg/m<sup>3</sup> when pulverised coal is used as fuel. 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 CO<sub>2</sub> emission can be reduced by 10-12%.

The final target of the technical development of the fluidised bed cement kiln system based in the feasibility study on a 3000 tonne clinker/day plant is: reduction of heat use by 10-12%; reduction of CO<sub>2</sub> emission by 10-12%; a NO<sub>x</sub> emission level of 380 mg/m<sup>3</sup> or less; current SO<sub>x</sub> emission levels; reduction of the construction cost by 30%; reduction of the installation area by 30%.

### Techniques for Controlling NO<sub>x</sub> Emissions

Reduced emissions of NO<sub>x</sub> is achieved by reduced flame and burning temperatures and the consumption of fuel, as well as by zones with a reducing atmosphere in the kiln system. Control of oxygen content (excess air) is critical to NO<sub>x</sub> control. Generally the lower the oxygen content (excess air) at for instance a cement kiln back end, the less NO<sub>x</sub> is produced. NO<sub>x</sub> reductions of up to 30% have been reported.

**Table 6.3** Overview of techniques for controlling NO<sub>x</sub>.

Technique	Kiln systems applicability	Reduction efficiency	Reported emissions		Reported costs <sup>3</sup>	
			mg/m <sup>3</sup> <sup>1</sup>	kg/tonne <sup>2</sup>	investment	operating
Flame cooling	All	0-50%	400-	0.8-	0.0 -0.2	0.0-0.5
Low-NO <sub>x</sub> 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 <sup>4</sup>	0.2-0.4 <sup>4</sup>
					3.5-4.5 <sup>5</sup>	No info. <sup>5</sup>

1) Normally referring to daily averages, dry gas, 273 K, 101.3 kPa and 10% O<sub>2</sub>.

2) Kg/tonne clinker: based on 2000 m<sup>3</sup>/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<sub>x</sub>/m<sup>3</sup>.

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<sub>x</sub>/m<sup>3</sup>), operating costs ca. 25% lower than for SNCR.

5) Costs estimated by Cembureau for a full scale installation.

*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  $\text{NO}_x$  reduction in the burning zone. Reduction efficiency from 0-50% has been reported.

Designs of *low- $\text{NO}_x$  burners* vary in detail but essentially the coal 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). 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.  $\text{NO}_x$  reductions of up to 30% are achievable in successful installations.

*Selective catalytic reduction (SCR)* reduces  $\text{NO}$  and  $\text{NO}_2$  to  $\text{N}_2$  with the help of  $\text{NH}_3$  and a catalyst at a temperature range of about 300-400°C. This technology is widely used for  $\text{NO}_x$  abatement in other industries (coal-fired power stations, waste incinerators). Large  $\text{NO}_x$  emission reductions are potentially achievable by SCR high dust systems (85-95%). As the catalysts remove hydrocarbons as well, SCR will in general also reduce VOC and PCDD/Fs.

*Selective non-catalytic reduction (SNCR)* involves injecting  $\text{NH}_2\text{X}$  compounds into the exhaust gas to reduce  $\text{NO}$  to  $\text{N}_2$ . The reaction has an optimum in a temperature window of about 800 to 1000°C; sufficient retention time must be provided for the injected agents to react with  $\text{NO}$ . The right temperature window is easy to obtain in suspension preheater kilns, precalciner kilns and possibly in some Lepol kilns. The most common  $\text{NH}_2\text{X}$  agent is about 25% ammonia in water. The achievable  $\text{NO}_x$  emission level can in the best of cases be less than 200  $\text{mg}/\text{m}^3$  if the initial level is not higher than about 1000-1300  $\text{mg}/\text{m}^3$  (80-85% reduction), although the majority of installations are today operated to achieve an emission level of 500-800  $\text{mg}/\text{m}^3$  (10-50% reduction). The first full scale plant with SNCR technology has been in operation in Germany in the end of 1999. 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. The driving force for these plants to invest in high-performing SNCR installations was the Swedish policy to reduce  $\text{NO}_x$  emissions.

*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

$\text{NO}_x$  to elementary nitrogen. Some modern well optimised plants achieve emission levels below 500  $\text{mg NO}_x/\text{Nm}^3$  with multi-staged combustion.

The addition of mineralisers, e.g. calcium fluoride, to the raw material to adjust the clinker quality allows the sintering zone temperature to be reduced, which leads to less  $\text{NO}_x$  formation. The  $\text{NO}_x$  reduction might be between 10 and 15%, but reductions of up to 50% has been reported.

### Techniques for Controlling $\text{SO}_2$ Emissions

The first step with respect to  $\text{SO}_2$  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  $\text{SO}_2$  level and increasing the  $\text{NO}_x$  level. A balance to protect the environment should be sought by optimising  $\text{NO}_x/\text{SO}_2/\text{CO}$  by adjusting the back end oxygen content.  $\text{SO}_2$  reductions of up to 50% have been reported. The *addition of absorbents* such as slaked lime ( $\text{Ca}(\text{OH})_2$ ), quicklime ( $\text{CaO}$ ) or activated fly ash with high  $\text{CaO}$  content to the exhaust gas of the kiln can absorb some of the  $\text{SO}_2$ . The  $\text{SO}_2$  will react with the lime to  $\text{CaSO}_3$  and  $\text{CaSO}_4$ , which becomes incorporated into the clinker.  $\text{SO}_2$  reductions of 60 to 80% can be achieved by absorbent injection in suspension preheater kiln systems.

To reduce very high  $\text{SO}_2$  emissions (more than 1500  $\text{mg}/\text{Nm}^3$ ) 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 allow efficient absorption of  $\text{SO}_2$ . The gas leaving the venturi is loaded with absorbent which is collected in an electrostatic precipitator. An  $\text{SO}_2$  reduction of 90% may be achieved, that corresponds to a clean gas content of 300  $\text{mg SO}_2/\text{m}^3$  when the initial  $\text{SO}_2$  concentration is 3000  $\text{mg}/\text{m}^3$ . A dry scrubber will also reduce emissions of  $\text{HCl}$  and  $\text{HF}$ .

The *wet scrubber* is the most commonly used technique for flue gas desulphurisation in coal fired power plants. The  $\text{SO}_x$  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. The wet scrubbers currently in use in the European cement industry are all 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. The  $\text{SO}_2$  reduction achieved can be more than 90%.

Pollutants such as SO<sub>2</sub>, organic compounds, metals, NH<sub>3</sub>, NH<sub>4</sub> 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<sub>3</sub> is present, or added, the filter will remove NO<sub>x</sub> as well.

### Techniques for Controlling Dust Emissions

The three main point sources of dust emissions from cement plants 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 standard. Both types have a very high dedusting efficiency during normal operation. A disadvantage of fabric filters is that used filter bags are waste and have to be disposed of according to national regulations. Dust releases from handling and storage of materials and the crushing and grinding of raw materials and fuels, called fugitive dust, can also be significant.

*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, so the material falls into collection hoppers below. EPs are able to operate under conditions of high temperatures, up to approximately 400°C, and high humidity. Under best conditions EPs can reduce levels down to 5-15 mg/m<sup>3</sup> as monthly average.

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. The use of modern fabric filters can reduce dust emissions to below 5 mg/m<sup>3</sup>. Besides dust, the fabric filter also removes substances that adsorb to the dust particles, such as dioxins and metals if present.

*Fugitive emission* sources mainly arise from storage and handling of raw materials, fuels and clinker and from vehicle traffic at the manufacturing site. Proper and complete maintenance of the installation always has the indirect result of reducing fugitive dust by reducing air leakage and spillage points. Outdoor storage piles of dusty materials should be avoided. Point sources of dust can be controlled by a water spray injection system. Areas used by lorries should be paved when possible, clean and watered, especially during dry weather.