CEMENT TECHNOLOGY

REPORT ON TRAINING VISIT

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Preface

I Mehrabuddin Shahabi, am a professor in Inorganic Materials Technology Department of Chemical Technology Faculty of Kabul Polytechnic University. I attended a 75 day training stay, from 1.10.2011 to 14.12.2011 in Slovak University of Technology in Bratislava, Slovakia.

Main purpose of this training stay was to recognize new pedagogic methods, and collecting new scientific articles and books on chemical technology topics.

Activities I have done during this training stay are listed below:

- Visiting and recognize with inorganic technology, inorganic materials and inorganic substances technology laboratories.
- Participating in some lectures, seminars, and laboratory works.
- Visiting faculty, bookstore, and library.

I want to appreciate and thank to prof. Dr. Jan Hives, Asist. prof. Dr. Vladimir Kovar, Assoc. prof. Dr. Juma Haydary, and to other teachers of the faculty of Chemical Technology of the Slovak University of Technology in Bratislava for their excellent cooperation and collaboration.

Some parts of collected materials are inserted in continuation of this report.

With respect

Mehrabuddin Shahabi, MSc.
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Introduction

Cement used in construction is characterized as **hydraulic** or **non-hydraulic**. Hydraulic cements (e.g., Portland cement) harden because of hydration, chemical reactions that occur independently of the mixture's water content; they can harden even underwater or when constantly exposed to wet weather. The chemical reaction that results when the anhydrous cement powder is mixed with water produces hydrates that are not water-soluble. Non-hydraulic cements (e.g., lime and gypsum plaster) must be kept dry in order to retain their strength.

The most important use of cement is the production of mortar and concrete—the bonding of natural or artificial aggregates to form a strong building material that is durable in the face of normal environmental effects.

Our country has a lot of rich natural mines, to educts and uses these mines.

Is needed modern technology, of course this might have improve the national economy stage and prepare good situation for the life of human being.

Afghanistan's national economy growth and development is not possible without developing the industrial section, one of important factors for reaching that goal is production of cement which’s raw materials are available inside Afghanistan.

In this report different steps of cement production is written and mentioned. The materials are taken from different valid and a new scientific sources.
1. Portland cement

Portland cement is the most common type of cement in general use around the world because it is a basic ingredient of concrete, mortar, stucco and most non-specialty grout. It is a fine powder produced by grinding Portland cement clinker (more than 90%), a limited amount of calcium sulfate (which controls the set time) and up to 5% minor constituents as allowed by various standards such as the European Standard EN197-1:

Portland cement clinker is a hydraulic material which shall consist of at least two-thirds by mass of calcium silicates (3CaO·SiO₂ and 2CaO·SiO₂), the remainder consisting of aluminium- and iron-containing clinker phases and other compounds. The ratio of CaO to SiO₂ shall not be less than 2.0. The magnesium oxide content (MgO) shall not exceed 5.0% by mass.

ASTM C 150 defines portland cement as "hydraulic cement (cement that not only hardens by reacting with water but also forms a water-resistant product) produced by pulverizing clinkers consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate as an inter ground addition." Clinkers are nodules (diameters, 0.2-1.0 inch [5–25 mm]) of a sintered material that is produced when a raw mixture of predetermined composition is heated to high temperature. The low cost and widespread availability of the limestone, shales, and other naturally occurring materials make portland cement one of the lowest-cost materials widely used over the last century throughout the world. Concrete becomes one of the most versatile construction materials available in the world.

Portland cement clinker is made by heating, in a kiln, a homogeneous mixture of raw materials to a sintering temperature, which is about 1450 °C for modern cements. The aluminium oxide and iron oxide are present as a flux and contribute little to the strength. For special cements, such as Low Heat (LH) and Sulfate Resistant (SR) types, it is necessary to limit the amount of tricalcium aluminate (3CaO·Al₂O₃) formed. The major raw material for the clinker-making is usually limestone (CaCO₃) mixed with a second material containing clay as source of alumino-silicate. Normally, an impure limestone which contains clay or SiO₂ is used. The CaCO₃ content of these limestones can be as low as 80%. Second raw materials (materials in the rawmix other than limestone) depend on the purity of the limestone. Some of the second raw materials used are clay, shale, sand, iron ore, bauxite, fly ash and slag. When a cement kiln is fired by coal, the ash of the coal acts as a secondary raw material.
1-1. History

Portland cement was developed from natural cements made in Britain in the early part of the nineteenth century, and its name is derived from its similarity to Portland stone, a type of building stone that was quarried on the Isle of Portland in Dorset, England.¹

The Portland cement is considered to originate from Joseph Aspdin, a British bricklayer from Leeds. It was one of his employees (Isaac Johnson), however, who developed the production technique, which resulted in a more fast-hardening cement with a higher compressive strength. This process was patented in 1824.¹ His cement was an artificial cement similar in properties to the material known as "Roman cement" (patented in 1796 by James Parker) and his process was similar to that patented in 1822 and used since 1811 by James Frost who called his cement "British Cement". The name "Portland cement" is also recorded in a directory published in 1823 being associated with a William Lockwood, Dave Stewart, and possibly others.

Aspdin's son William, in 1843, made an improved version of this cement and he initially called it "Patent Portland cement" although he had no patent. In 1848 William Aspdin further improved his cement and in 1853 he moved to Germany where he was involved in cement making. Many people have claimed to have made the first Portland cement in the modern sense, but it is generally accepted that it was first manufactured by William Aspdin at Northfleet, England in about 1842. The German Government issued a standard on Portland cement in 1878.
1-2. Production

Schematic explanation of Portland cement production

There are three fundamental stages in the production of Portland cement:

1. Preparation of the raw mixture
2. Production of the clinker
3. Preparation of the cement

To simplify the complex chemical formulae which describe the compounds present in cement, a cement chemist notation was invented. This notation reflects the fact that most of the elements are present in their highest oxidation state, and chemical analyses of cement are expressed as mass percent of these notional oxides.
1-3. Rawmix preparation

A limestone prehomogenization pile being built by a boom stacker

A completed limestone prehomogenization pile

The raw materials for Portland cement production are a mixture of minerals containing calcium oxide, silicon oxide, aluminium oxide, ferric oxide, and magnesium oxide, as fine powder in the 'Dry process' or in the form of a slurry in the 'Wet process'. The raw materials are usually quarried from local rock, which in some places is already practically the desired composition and in other places requires the addition of clay and limestone, as well as iron ore, bauxite or recycled materials. The individual raw materials are first crushed, typically to below 50 mm. In many plants, some or all of the raw materials are then roughly blended in a "prehomogenization pile." The raw materials are next ground together in a rawmill. Silos of individual raw materials are arranged over the feed conveyor belt. Accurately controlled proportions of each material are delivered onto the belt by weigh-feeders. Passing into the rawmill, the mixture is ground to rawmix. The fineness of rawmix is specified in terms of the size of the largest particles, and is usually controlled so that there are less than 5%-15% by mass of particles exceeding 90 μm in diameter. It is important that the rawmix contain no large particles in order to complete the chemical reactions in the kiln, and to ensure the mix is chemically homogeneous. In the case of a dry process, the rawmill also dries the raw materials, usually by passing hot exhaust gases from the kiln through the mill, so that the rawmix emerges as a fine powder. This is conveyed to the blending system by conveyor belt or by a powder pump. In the case of wet process, water is added to the rawmill feed, and the mill product is slurry with moisture content usually in the range 25–45% by mass. This slurry is conveyed to the blending system by conventional liquid pumps.
1-4. Rawmix Blending

The rawmix is formulated to a very tight chemical specification. Typically, the content of individual components in the rawmix must be controlled within 0.1% or better. Calcium and silicon are present in order to form the strength-producing calcium silicates. Aluminium and iron are used in order to produce liquid ("flux") in the kiln burning zone. The liquid acts as a solvent for the silicate-forming reactions, and allows these to occur at an economically low temperature. Insufficient aluminium and iron lead to difficult burning of the clinker, while excessive amounts lead to low strength due to dilution of the silicates by aluminates and ferrites. Very small changes in calcium content lead to large changes in the ratio of alite to belite in the clinker, and to corresponding changes in the cement's strength-growth characteristics. The relative amounts of each oxide are therefore kept constant in order to maintain steady conditions in the kiln, and to maintain constant product properties. In practice, the rawmix is controlled by frequent chemical analysis (hourly by X-Ray fluorescence analysis, or every three minutes by prompt gamma neutron activation analysis). The analysis data is used to make automatic adjustments to raw material feed rates. Remaining chemical variation is minimized by passing the raw mix through a blending system that homogenizes up to a day's supply of rawmix (15,000 tonnes in the case of a large kiln).

1-5. Formation of Clinker

The raw mixture is heated in a cement kiln, a slowly rotating and sloped cylinder, with temperatures increasing over the length of the cylinder up to a peak temperature of 1400-1450 °C. A complex succession of chemical reactions takes place (see cement kiln) as the temperature rises. The peak temperature is regulated so that the product contains sintered but not fused lumps. Sintering consists of the melting of 25-30% of the mass of the material. The resulting liquid draws the remaining solid particles together by surface tension and acts as a solvent for the final chemical reaction in which alite is formed. Too low a temperature causes insufficient sintering and incomplete reaction, but too high a temperature results in a molten mass or glass, destruction of the kiln lining, and waste of fuel. When all goes according to plan, the resulting material is clinker. On cooling, it is conveyed to storage. Some effort is usually made to blend the clinker because, although the chemistry of the rawmix may have been tightly controlled, the kiln process potentially introduces new sources of chemical variability. The clinker can be stored for a number of years before use. Prolonged exposure to water decreases the reactivity of cement produced from weathered clinker.

The enthalpy of formation of clinker from calcium carbonate and clay minerals is about 1500 to 1700 kJ/kg. However, because of heat loss during production, actual values can be much higher. The high energy requirements and the release of significant amounts of carbon dioxide make cement production a concern for global warming. See "Environmental effects" below.
1-6. Cement grinding

A 10 MW cement mill, producing cement at 270 tonnes per hour

In order to achieve the desired setting qualities in the finished product, a quantity (2-8%, but typically 5%) of calcium sulfate (usually gypsum or anhydrite) is added to the clinker and the mixture is finely ground to form the finished cement powder. This is achieved in a cement mill. The grinding process is controlled to obtain a powder with a broad particle size range, in which typically 15% by mass consists of particles below 5 μm diameter, and 5% of particles above 45 μm. The measure of fineness usually used is the "specific surface area", which is the total particle surface area of a unit mass of cement. The rate of initial reaction (up to 24 hours) of the cement on addition of water is directly proportional to the specific surface area. Typical values are 320–380 m²·kg⁻¹ for general purpose cements, and 450–650 m²·kg⁻¹ for "rapid hardening" cements. The cement is conveyed by belt or powder pump to a silo for storage. Cement plants normally have sufficient silo space for 1–20 weeks production, depending upon local demand cycles. The cement is delivered to end-users either in bags or as bulk powder blown from a pressure vehicle into the customer's silo. In industrial countries, 80% or more of cement is delivered in bulk.

<table>
<thead>
<tr>
<th>Typical constituents of Portland clinker plus Gypsum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement chemists notation under CCN.</td>
</tr>
<tr>
<td><strong>Clinker</strong></td>
</tr>
<tr>
<td>Tricalcium silicate (CaO)₃ · SiO₂</td>
</tr>
<tr>
<td>Dicalcium silicate (CaO)₂ · SiO₂</td>
</tr>
<tr>
<td>Tricalcium aluminate (CaO)₃ · Al₂O₃</td>
</tr>
<tr>
<td>Tetracalcium aluminoferite (CaO)₄ · Al₂O₃ · Fe₂O₃</td>
</tr>
<tr>
<td>Gypsum CaSO₄ · 2 H₂O</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Typical constituents of Portland cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement chemists notation under CCN.</td>
</tr>
<tr>
<td><strong>Cement</strong></td>
</tr>
<tr>
<td>Calcium oxide, CaO</td>
</tr>
<tr>
<td>Silicon oxide, SiO₂</td>
</tr>
<tr>
<td>Aluminum oxide, Al₂O₃</td>
</tr>
</tbody>
</table>
An alternative fabrication technique EMC (Energetically modified cement) uses very finely ground cements that are made from mixtures of cement with sand or with slag or other pozzolan type minerals which are extremely finely ground together. Such cements can have the same physical characteristics as normal cement but with 50% less cement particularly due to their increased surface area for the chemical reaction. Even with intensive grinding they can use up to 50% less energy to fabricate than ordinary Portland cements.

<table>
<thead>
<tr>
<th>Compound</th>
<th>OPC %</th>
<th>FA %</th>
<th>EMC %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>62.4</td>
<td>15.0</td>
<td>40.9</td>
</tr>
<tr>
<td>SiO₂</td>
<td>17.8</td>
<td>49.4</td>
<td>33.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.0</td>
<td>19.6</td>
<td>6.3</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.9</td>
<td>5.2</td>
<td>4.1</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.2</td>
<td>0.8</td>
<td>1.6</td>
</tr>
<tr>
<td>Na₂O</td>
<td>&lt;0.1</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.3</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Insolubles</td>
<td>0.5</td>
<td>51.3</td>
<td>21.6</td>
</tr>
</tbody>
</table>

**1-7. Setting and hardening**

Cement sets when mixed with water by way of a complex series of chemical reactions still only partly understood. The different constituents slowly crystallise and the interlocking of their crystals gives cement its strength. Carbon dioxide is slowly absorbed to convert the portlandite (Ca(OH)₂) into insoluble calcium carbonate. After the initial setting, immersion in warm water will speed up setting. In Portland cement, gypsum is added as a compound preventing cement flash setting.

**1-8. Use**

The most common use for Portland cement is in the production of concrete. Concrete is a composite material consisting of aggregate (gravel and sand), cement, and water. As a construction material, concrete can be cast in almost any shape desired, and once hardened, can become a structural (load bearing) element. Users may be involved in the factory production of pre-cast units, such as panels, beams, road furniture, or may make cast-in-situ concrete such as building superstructures, roads, dams. These may be supplied with concrete mixed on site, or may be provided with "ready-mixed" concrete made at permanent mixing sites. Portland cement is also used in mortars (with sand and water only) for plasters and
screeds, and in grouts (cement/water mixes squeezed into gaps to consolidate foundations, road-beds, etc.).

When water is mixed with Portland cement, the product sets in a few hours and hardens over a period of weeks. These processes can vary widely depending upon the mix used and the conditions of curing of the product, but a typical concrete sets in about 6 hours and develops a compressive strength of 8 MPa in 24 hours. The strength rises to 15 MPa at 3 days, 23 MPa at 1 week, 35 MPa at 4 weeks and 41 MPa at 3 months. In principle, the strength continues to rise slowly as long as water is available for continued hydration, but concrete is usually allowed to dry out after a few weeks and this causes strength growth to stop.

1-9. Types of cement

1-9-1 Type I Portland cement is known as common or general purpose cement. It is generally assumed unless another type is specified. It is commonly used for general construction especially when making precast and prestressed concrete that is not to be in contact with soils or ground water. The typical compound compositions of this type are:

55% (C₃S), 19% (C₂S), 10% (C₃A), 7% (C₄AF), 2.8% MgO, 2.9% (SO₃), 1.0% Ignition loss, and 1.0% free CaO.

A limitation on the composition is that the (C₃A) shall not exceed fifteen percent.

1-9-2 Type II is intended to have moderate sulfate resistance with or without moderate heat of hydration. This type of cement costs about the same as Type I. Its typical compound composition is:

51% (C₃S), 24% (C₂S), 6% (C₃A), 11% (C₄AF), 2.9% MgO, 2.5% (SO₃), 0.8% Ignition loss, and 1.0% free CaO.

A limitation on the composition is that the (C₃A) shall not exceed eight percent which reduces its vulnerability to sulfates. This type is for general construction that is exposed to moderate sulfate attack and is meant for use when concrete is in contact with soils and ground water especially in the western United States due to the high sulfur content of the soil. Because of similar price to that of Type I, Type II is much used as a general purpose cement, and the majority of Portland cement sold in North America meets this specification.

Note: Cement meeting (among others) the specifications for Type I and II has become commonly available on the world market.

1-9-3 Type III has relatively high early strength. Its typical compound composition is:

57% (C₃S), 19% (C₂S), 10% (C₃A), 7% (C₄AF), 3.0% MgO, 3.1% (SO₃), 0.9% Ignition loss, and 1.3% free CaO.

This cement is similar to Type I, but ground finer. Some manufacturers make a separate clinker with higher C₃S and/or C₃A content, but this is increasingly rare, and the general
purpose clinker is usually used, ground to a specific surface typically 50-80% higher. The gypsum level may also be increased a small amount. This gives the concrete using this type of cement a three day compressive strength equal to the seven day compressive strength of types I and II. Its seven day compressive strength is almost equal to types I and II 28 day compressive strengths. The only downside is that the six month strength of type III is the same or slightly less than that of types I and II. Therefore the long-term strength is sacrificed a little. It is usually used for precast concrete manufacture, where high 1-day strength allows fast turnover of molds. It may also be used in emergency construction and repairs and construction of machine bases and gate installations.

1-9-4 Type IV Portland cement is generally known for its low heat of hydration. Its typical compound composition is:

28% (C\textsubscript{3}S), 49% (C\textsubscript{2}S), 4% (C\textsubscript{3}A), 12% (C\textsubscript{4}AF), 1.8% MgO, 1.9% (SO\textsubscript{3}), 0.9% Ignition loss, and 0.8% free CaO.

The percentages of (C\textsubscript{2}S) and (C\textsubscript{4}AF) are relatively high and (C\textsubscript{3}S) and (C\textsubscript{3}A) are relatively low. A limitation on this type is that the maximum percentage of (C\textsubscript{3}A) is seven, and the maximum percentage of (C\textsubscript{3}S) is thirty-five. This causes the heat given off by the hydration reaction to develop at a slower rate. However, as a consequence the strength of the concrete develops slowly. After one or two years the strength is higher than the other types after full curing. This cement is used for very large concrete structures, such as dams, which have a low surface to volume ratio. This type of cement is generally not stocked by manufacturers but some might consider a large special order. This type of cement has not been made for many years, because Portland-pozzolan cements and ground granulated blast furnace slag addition offer a cheaper and more reliable alternative.

1-9-5 Type V is used where sulfate resistance is important. Its typical compound composition is:

38% (C\textsubscript{3}S), 43% (C\textsubscript{2}S), 4% (C\textsubscript{3}A), 9% (C\textsubscript{4}AF), 1.9% MgO, 1.8% (SO\textsubscript{3}), 0.9% Ignition loss, and 0.8% free CaO.

This cement has a very low (C\textsubscript{3}A) composition which accounts for its high sulfate resistance. The maximum content of (C\textsubscript{3}A) allowed is five percent for Type V Portland cement. Another limitation is that the (C\textsubscript{4}AF) + 2(C\textsubscript{3}A) composition cannot exceed twenty percent. This type is used in concrete that is to be exposed to alkali soil and ground water sulfates which react with (C\textsubscript{3}A) causing disruptive expansion. It is unavailable in many places although its use is common in the western United States and Canada. As with Type IV, Type V Portland cement has mainly been supplanted by the use of ordinary cement with added ground granulated blast furnace slag or tertiary blended cements containing slag and fly ash.

Types Ia, Ila, and IIIa have the same composition as types I, II, and III. The only difference is that in Ia, IIa, and IIIa an air-entraining agent is ground into the mix. The air-entrainment must meet the minimum and maximum optional specification found in the ASTM manual. These types are only available in the eastern United States and Canada but can only be found on a limited basis. They are a poor approach to air-entrainment which improves resistance to freezing under low temperatures.
Types II(MH) and II(MH)a have recently been added with a similar composition as types II and IIa but with a mild heat.

Constituents that are permitted in Portland-composite cements are artificial pozzolans (blastfurnace slag, silica fume, and fly ashes) or natural pozzolans (siliceous or siliceous aluminous materials such as volcanic ash glasses, calcined clays and shale).

1-9-6 White Portland cement

White Portland cement or white ordinary Portland cement (WOPC) is similar to ordinary, gray Portland cement in all respects except for its high degree of whiteness. Obtaining this color requires substantial modification to the method of manufacture and, because of this, it is somewhat more expensive than the gray product.

1-10. Safety issues

Bags of cement routinely have health and safety warnings printed on them because not only is cement highly alkaline, but the setting process is exothermic. As a result, wet cement is strongly caustic and can easily cause severe skin burns if not promptly washed off with water. Similarly, dry cement powder in contact with mucous membranes can cause severe eye or respiratory irritation. Cement users should wear protective clothing.

When traditional Portland cement is mixed with water the dissolution of calcium, sodium and potassium hydroxides produces a highly alkaline solution (pH ~13): gloves, goggles and a filter mask should be used for protection, and hands should be washed after contact as most cement can cause acute ulcerative damage 8–12 hours after contact if skin is not washed promptly. The reaction of cement dust with moisture in the sinuses and lungs can also cause a chemical burn as well as headaches, fatigue, and lung cancer. The development of formulations of cement that include fast-reacting pozzolans such as silica fume as well as some slow-reacting products such as fly ash have allowed for the production of comparatively low-alkalinity cements (pH<11) that are much less toxic and which have become widely commercially available, largely replacing high-pH formulations in much of the United States. Once any cement sets, the hardened mass loses chemical reactivity and can be safely touched without gloves.

1-11. Environmental effects

Portland cement manufacture can cause environmental impacts at all stages of the process. These include emissions of airborne pollution in the form of dust, gases, noise and vibration when operating machinery and during blasting in quarries, consumption of large quantities of fuel during manufacture, release of CO₂ from the raw materials during manufacture, and damage to countryside from quarrying. Equipment to reduce dust emissions during quarrying and manufacture of cement is widely used, and equipment to trap and separate exhaust gases are coming into increased use. Environmental protection also includes
the re-integration of quarries into the countryside after they have been closed down by returning them to nature or re-cultivating them.

Epidemiologic Notes and Reports Sulfur Dioxide Exposure in Portland Cement Plants, from the Centers for Disease Control, states "Workers at Portland cement facilities, particularly those burning fuel containing sulfur, should be aware of the acute and chronic effects of exposure to SO$_2$ [sulfur dioxide], and peak and full-shift concentrations of SO$_2$ should be periodically measured."

"The Arizona Department of Environmental Quality was informed this week that the Arizona Portland Cement Co. failed a second round of testing for emissions of hazardous air pollutants at the company's Rillito plant near Tucson. The latest round of testing, performed in January 2003 by the company, is designed to ensure that the facility complies with federal standards governing the emissions of dioxins and furans, which are byproducts of the manufacturing process." Cement Reviews' "Environmental News" web page details case after case of environmental problems with cement manufacturing. An independent research effort of AEA Technology to identify critical issues for the cement industry today concluded the most important environment, health and safety performance issues facing the cement industry are atmospheric releases (including greenhouse gas emissions, dioxin, NO$_x$, SO$_2$, and particulates), accidents and worker exposure to dust.

The CO$_2$ associated with Portland cement manufacture falls into 3 categories:

Source 1. CO$_2$ derived from decarbonation of limestone,

Source 2. CO$_2$ from kiln fuel combustion,

Source 3. CO$_2$ produced by vehicles in cement plants and distribution.

Source 1 is fairly constant: minimum around 0.47 kg CO$_2$ per kg of cement, maximum 0.54, typical value around 0.50 worldwide. Source 2 varies with plant efficiency: efficient precalciner plant 0.24 kg CO$_2$ per kg cement, low-efficiency wet process as high as 0.65, typical modern practices (e.g. UK) averaging around 0.30. Source 3 is almost insignificant at 0.002-0.005. So typical total CO$_2$ is around 0.80 kg CO$_2$ per kg of finished cement. This leaves aside the CO$_2$ associated with electric power consumption, since this varies according to the local generation type and efficiency. Typical electrical energy consumption is of the order of 90-150 kWh per tonne cement, equivalent to 0.09-0.15 kg CO$_2$ per kg finished cement if the electricity is coal-generated.

Overall, with nuclear- or hydroelectric power and efficient manufacturing, CO$_2$ generation can be as little as 0.7 kg per kg cement, but can be as high as twice this amount. The thrust of innovation for the future is to reduce sources 1 and 2 by modification of the chemistry of cement, by the use of wastes, and by adopting more efficient processes. Although cement manufacturing is clearly a very large CO$_2$ emitter, concrete (of which cement makes up about 15%) compares quite favorably with other building systems in this regard.
1-12. Cement plants used for waste disposal or processing

Used tires being fed to a pair of cement kilns

Due to the high temperatures inside cement kilns, combined with the oxidizing (oxygen-rich) atmosphere and long residence times, cement kilns are used as a processing option for various types of waste streams: indeed, they efficiently destroy many hazardous organic compounds. The waste streams also often contain combustible materials which allow the substitution of part of the fossil fuel normally used in the process.
2. Cement kiln

Cement kilns are used for the pyroprocessing stage of manufacture of Portland and other types of hydraulic cement, in which calcium carbonate reacts with silica-bearing minerals to form a mixture of calcium silicates. Over a billion tonnes of cement are made per year, and cement kilns are the heart of this production process: their capacity usually define the capacity of the cement plant. As the main energy-consuming and greenhouse-gas–emitting stage of cement manufacture, improvement of kiln efficiency has been the central concern of cement manufacturing technology.

2-1. The manufacture of cement clinker

A preheater tower, rawmix silo and exhaust stack. Bottom left: rawmill. Bottom right: rotary kiln with tertiary air duct above. The U-shaped duct leading from the kiln inlet is an "alkali bleed".

A typical process of manufacture consists of three stages:

- grinding a mixture of limestone and clay or shale to make a fine "rawmix" (see Rawmill);
- heating the rawmix to sintering temperature (up to 1450 °C) in a cement kiln;
- grinding the resulting clinker to make cement (see Cement mill).

In the second stage, the rawmix is fed into the kiln and gradually heated by contact with the hot gases from combustion of the kiln fuel. Successive chemical reactions take place as the temperature of the rawmix rises:

- 70 to 110 °C - Free water is evaporated.
- 400 to 600 °C - clay-like minerals are decomposed into their constituent oxides; principally SiO₂ and Al₂O₃. Dolomite (CaMg(CO₃)₂) decomposes to calcium carbonate, MgO and CO₂.
- 650 to 900 °C - calcium carbonate reacts with SiO₂ to form belite (Ca₂SiO₄).
- 900 to 1050 °C - the remaining calcium carbonate decomposes to calcium oxide and CO₂.
- 1300 to 1450 °C - partial (20–30%) melting takes place, and belite reacts with calcium oxide to form alite (Ca$_3$O·SiO$_4$).

Typical clinker nodules

Alite is the characteristic constituent of Portland cement. Typically, a peak temperature of 1400–1450 °C is required to complete the reaction. The partial melting causes the material to aggregate into lumps or nodules, typically of diameter 1–10 mm. This is called clinker. The hot clinker next falls into a cooler which recovers most of its heat, and cools the clinker to around 100 °C, at which temperature it can be conveniently conveyed to storage. The cement kiln system is designed to accomplish these processes.

2-2. The rotary kiln

General layout of a rotary kiln

The rotary kiln consists of a tube made from steel plate, and lined with firebrick. The tube slopes slightly (1–4°) and slowly rotates on its axis at between 30 and 250 revolutions per hour. Rawmix is fed in at the upper end, and the rotation of the kiln causes it gradually to move downhill to the other end of the kiln. At the other end fuel, in the form of gas, oil, or pulverized solid fuel, is blown in through the "burner pipe", producing a large concentric flame in the lower part of the kiln tube. As material moves under the flame, it reaches its peak temperature, before dropping out of the kiln tube into the cooler. Air is drawn first through the cooler and then through the kiln for combustion of the fuel. In the cooler the air is heated.
by the cooling clinker, so that it may be 400 to 800 °C before it enters the kiln, thus causing intense and rapid combustion of the fuel.

The earliest successful rotary kilns were developed in Pennsylvania around 1890, and were about 1.5 m in diameter and 15 m in length. Such a kiln made about 20 tonnes of clinker per day. The fuel, initially, was oil, which was readily available in Pennsylvania at the time. It was particularly easy to get a good flame with this fuel. Within the next 10 years, the technique of firing by blowing in pulverized coal was developed, allowing the use of the cheapest available fuel. By 1905, the largest kilns were 2.7 x 60 m in size, and made 190 tonnes per day. At that date, after only 15 years of development, rotary kilns accounted for half of world production. Since then, the capacity of kilns has increased steadily, and the largest kilns today produce around 10,000 tonnes per day. In contrast to static kilns, the material passes through quickly: it takes from 3 hours (in some old wet process kilns) to as little as 10 minutes (in short precalciner kilns). Rotary kilns run 24 hours a day, and are typically stopped only for a few days once or twice a year for essential maintenance. This is an important discipline, because heating up and cooling down are long, wasteful and damaging processes. Uninterrupted runs as long as 18 months have been achieved.

2-3. The wet process and the dry process

From the earliest times, two different methods of rawmix preparation were used: the mineral components were either dry-ground to form a flour-like powder, or were wet-ground with added water to produce a fine slurry with the consistency of paint, and with a typical water content of 40–45%.

The wet process suffered the obvious disadvantage that, when the slurry was introduced into the kiln, a large amount of extra fuel was used in evaporating the water. Furthermore, a larger kiln was needed for a given clinker output, because much of the kiln's length was used up for the drying process. On the other hand, the wet process had a number of advantages. Wet grinding of hard minerals is usually much more efficient than dry grinding. When slurry is dried in the kiln, it forms a granular crumble that is ideal for subsequent heating in the kiln. In the dry process, it is very difficult to keep the fine powder rawmix in the kiln, because the fast-flowing combustion gases tend to blow it back out again. It became a practice to spray water into dry kilns in order to "damp down" the dry mix, and thus, for many years there was little difference in efficiency between the two processes, and the overwhelming majority of kilns used the wet process. By 1950, a typical large, wet process kiln, fitted with drying-zone heat exchangers, was 3.3 x 120 m in size, made 680 tonnes per day, and used about 0.25–0.30 tonnes of coal fuel for every tonne of clinker produced. Before the energy crisis of the 1970s put an end to new wet-process installations, kilns as large as 5.8 x 225 m in size were making 3000 tonnes per day.

An interesting footnote on the wet process history is that some manufacturers have in fact made very old wet process facilities profitable through the use of waste fuels. Plants that burn waste fuels enjoy a negative fuel cost (they are paid by industries needing to dispose of materials that have energy content and can be safely disposed of in the cement kiln thanks to its high temperatures and longer retention times). As a result the inefficiency of the wet process is an advantage—to the manufacturer. By locating waste burning operations at older
wet process locations, higher fuel consumption actually equates to higher profits for the manufacturer, although it produces correspondingly greater emission of CO₂. Manufacturers who think such emissions should be reduced are abandoning the use of wet process.

2-4. Preheaters

In the 1930s, significantly, in Germany, the first attempts were made to redesign the kiln system to minimize waste of fuel. This led to two significant developments:

- the grate preheater
- the gas-suspension preheater.

2-4-1. Grate preheaters

The grate preheater consists of a chamber containing a chain-like high-temperature steel moving grate, attached to the cold end of the rotary kiln. A dry-powder rawmix is turned into hard pellets of 10–20 mm diameter in a nodulizing pan, with the addition of 10-15% water. The pellets are loaded onto the moving grate, and the hot combustion gases from the rear of the kiln are passed through the bed of pellets from beneath. This dries and partially calcines the rawmix very efficiently. The pellets then drop into the kiln. Very little powdery material is blown out of the kiln. Because the rawmix is damped in order to make pellets, this is referred to as a "semi-dry" process. The grate preheater is also applicable to the "semi-wet" process, in which the rawmix is made as a slurry, which is first de-watered with a high-pressure filter, and the resulting "filter-cake" is extruded into pellets, which are fed to the grate. In this case, the water content of the pellets is 17-20%. Grate preheaters were most popular in the 1950s and 60s, when a typical system would have a grate 28 m long and 4 m wide, and a rotary kiln of 3.9 x 60 m, making 1050 tonnes per day, using about 0.11-0.13 tonnes of coal fuel for every tonne of clinker produced. Systems up to 3000 tonnes per day were installed.

2-4-2. Gas-suspension preheaters

Cutaway view of cyclone showing air path
The key component of the gas-suspension preheater is the cyclone. A cyclone is a conical vessel into which a dust-bearing gas-stream is passed tangentially. This produces a vortex within the vessel. The gas leaves the vessel through a co-axial "vortex-finder". The solids are thrown to the outside edge of the vessel by centrifugal action, and leave through a valve in the vertex of the cone. Cyclones were originally used to clean up the dust-laden gases leaving simple dry process kilns. If, instead, the entire feed of rawmix is encouraged to pass through the cyclone, it is found that a very efficient heat exchange takes place: the gas is efficiently cooled, hence producing less waste of heat to the atmosphere, and the rawmix is efficiently heated. This efficiency is further increased if a number of cyclones are connected in series.

![4-Stage preheater, showing path of feed](image)

The number of cyclones stages used in practice varies from 1 to 6. Energy, in the form of fan-power, is required to draw the gases through the string of cyclones, and at a string of 6 cyclones, the cost of the added fan-power needed for an extra cyclone exceeds the efficiency advantage gained. It is normal to use the warm exhaust gas to dry the raw materials in the rawmill, and if the raw materials are wet, hot gas from a less efficient preheater is desirable. For this reason, the most commonly encountered suspension preheaters have 4 cyclones. The hot feed that leaves the base of the preheater string is typically 20% calcined, so the kiln has less subsequent processing to do, and can therefore achieve a higher specific output. Typical large systems installed in the early 1970s had cyclones 6 m in diameter, a rotary kiln of 5 x 75 m, making 2500 tonnes per day, using about 0.11-0.12 tonnes of coal fuel for every tonne of clinker produced.

A penalty paid for the efficiency of suspension preheaters is their tendency to block up. Salts, such as the sulfate and chloride of sodium and potassium, tend to evaporate in the burning zone of the kiln. They are carried back in vapor form, and re-condense when a sufficiently low temperature is encountered. Because these salts re-circulate back into the rawmix and re-enter the burning zone, a recirculation cycle establishes itself. A kiln with 0.1% chloride in the rawmix and clinker may have 5% chloride in the mid-kiln material. Condensation usually occurs in the preheater, and a sticky deposit of liquid salts glues dusty rawmix into a hard deposit, typically on surfaces against which the gas-flow is impacting. This can choke the preheater to the point that air-flow can no longer be maintained in the kiln. It then becomes necessary to manually break the build-up away. Modern installations often have automatic devices installed at vulnerable points to knock out build-up regularly. An alternative approach is to "bleed off" some of the kiln exhaust at the kiln inlet where the salts are still in the vapor phase, and remove and discard the solids in this. This is usually termed an "alkali
bleed” and it breaks the recirculation cycle. It can also be of advantage for cement quality reasons, since it reduces the alkali content of the clinker. However, hot gas is run to waste so the process is inefficient and increases kiln fuel consumption.

2-5. Precalciner

In the 1970s the precalciner was pioneered in Japan, and has subsequently become the equipment of choice for new large installations worldwide. The precalciner is a development of the suspension preheater. The philosophy is this: the amount of fuel that can be burned in the kiln is directly related to the size of the kiln. If part of the fuel necessary to burn the rawmix is burned outside the kiln, the output of the system can be increased for a given kiln size. Users of suspension preheaters found that output could be increased by injecting extra fuel into the base of the preheater. The logical development was to install a specially designed combustion chamber at the base of the preheater, into which pulverized coal is injected. This is referred to as an "air-through" precalciner, because the combustion air for both the kiln fuel and the calciner fuel all passes through the kiln. This kind of precalciner can burn up to 30% (typically 20%) of its fuel in the calciner. If more fuel were injected in the calciner, the extra amount of air drawn through the kiln would cool the kiln flame excessively. The feed is 40-60% calcined before it enters the rotary kiln.

The ultimate development is the "air-separate" precalciner, in which the hot combustion air for the calciner arrives in a duct directly from the cooler, bypassing the kiln. Typically, 60-75% of the fuel is burned in the precalciner. In these systems, the feed entering the rotary kiln is 100% calcined. The kiln has only to raise the feed to sintering temperature. In theory the maximum efficiency would be achieved if all the fuel were burned in the preheater, but the sintering operation involves partial melting and nodulization to make clinker, and the rolling action of the rotary kiln remains the most efficient way of doing this. Large modern installations typically have two parallel strings of 4 or 5 cyclones, with one attached to the kiln and the other attached to the precalciner chamber. A rotary kiln of 6 x 100 m makes 8,000–10,000 tonnes per day, using about 0.10-0.11 tonnes of coal fuel for every tonne of clinker produced. The kiln is dwarfed by the massive preheater tower and cooler in these installations. Such a kiln produces 3 million tonnes of clinker per year, and consumes 300,000 tonnes of coal. A diameter of 6 m appears to be the limit of size of rotary kilns, because the flexibility of the steel shell becomes unmanageable at or above this size, and the firebrick lining tends to fail when the kiln flexes.

A particular advantage of the air-separate precalciner is that a large proportion, or even 100%, of the alkali-laden kiln exhaust gas can be taken off as alkali bleed (see above). Because this accounts for only 40% of the system heat input, it can be done with lower heat wastage than in a simple suspension preheater bleed. Because of this, air-separate precalciners are now always prescribed when only high-alkali raw materials are available at a cement plant.

The accompanying figures show the movement towards the use of the more efficient processes in North America (for which data is readily available). But the average output per kiln in, for example, Thailand is twice that in North America.
2-6. Ancillary equipment

Essential equipment in addition to the kiln tube and the preheater are:

- Cooler
- Fuel mills
- Fans
- Exhaust gas cleaning equipment.

2-6-1. Coolers

A pair of kilns with satellite coolers in Ashaka, Nigeria Sysy

Early systems used rotary coolers, which were rotating cylinders similar to the kiln, into which the hot clinker dropped. The combustion air was drawn up through the cooler as the clinker moved down, cascading through the air stream. In the 1920s, satellite coolers became common and remained in use until recently. These consist of a set (typically 7–9) of tubes attached to the kiln tube. They have the advantage that they are sealed to the kiln, and require no separate drive. From about 1930, the grate cooler was developed. This consists of a perforated grate through which cold air is blown, enclosed in a rectangular chamber. A bed of clinker up to 0.5 m deep moves along the grate. These coolers have two main advantages: they cool the clinker rapidly, which is desirable from a quality point of view (to avoid that alite, thermodynamically unstable below 1250°C, revert to belite and free CaO on slow cooling), and, because they do not rotate, hot air can be ducted out of them for use in fuel drying, or for use as precalciner combustion air. The latter advantage means that they have become the only type used in modern systems.

2-6-2. Fuel mills

Fuel systems are divided into two categories:

- Direct firing
- Indirect firing

In direct firing, the fuel is fed at a controlled rate to the fuel mill, and the fine product is immediately blown into the kiln. The advantage of this system is that it is not necessary to
store the hazardous ground fuel: it is used as soon as it is made. For this reason it was the system of choice for older kilns. A disadvantage is that the fuel mill has to run all the time: if it breaks down, the kiln has to stop if no backup system is available.

In indirect firing, the fuel is ground by an intermittently run mill, and the fine product is stored in a silo of sufficient size to supply the kiln through fuel mill stoppage periods. The fine fuel is metered out of the silo at a controlled rate and blown into the kiln. This method is now favoured for precalciner systems, because both the kiln and the precalciner can be fed with fuel from the same system. Special techniques are required to store the fine fuel safely, and coals with high volatiles are normally milled in an inert atmosphere (e.g. CO₂).

2-6-3. Fans

A large volume of gases has to be moved through the kiln system. Particularly in suspension preheater systems a high degree of suction has to be developed at the exit of the system to drive this. Fans are also used to force air through the cooler bed, and to propel the fuel into the kiln. Fans account for most of the electric power consumed in the system, typically amounting to 10–15 kW·h per tonne of clinker.

2-6-4. Gas cleaning

The exhaust gases from a modern kiln typically amount to 2 tonnes (or 1500 cubic metres at STP) per tonne of clinker made. The gases carry a large amount of dust—typically 30 grams per cubic metre. Environmental regulations specific to different countries require that this be reduced to (typically) 0.1 gram per cubic metre, so dust capture needs to be at least 99.7% efficient. Methods of capture include electrostatic precipitators and bag-filters. See also cement kiln emissions.
2-7. Kiln fuels

Fuels that have been used for primary firing include coal, petroleum coke, heavy fuel oil, natural gas, landfill off-gas and oil refinery flare gas. High carbon fuels such as coal are preferred for kiln firing, because they yield a luminous flame. The clinker is brought to its peak temperature mainly by radiant heat transfer, and a bright (i.e. high emissivity) and hot flame is essential for this. In favorable circumstances, high-rank bituminous coal can produce a flame at 2050 °C. Natural gas can only produce a flame of, at best 1950 °C, and this is also less luminous, so it tends to result in lower kiln output.

In addition to these primary fuels, various combustible waste materials have been fed to kilns, notably used tires, which are very difficult to dispose of by other means. In theory, cement kilns are an attractive way of disposing of hazardous materials, because of:

- the temperatures in the kiln, which are much higher than in other combustion systems (e.g. incinerators),
- the alkaline conditions in the kiln, afforded by the high-calcium rawmix, which can absorb acidic combustion products,
- the ability of the clinker to absorb heavy metals into its structure.

Whole tires are commonly introduced in the kiln, by rolling them into the upper end of a preheater kiln, or by dropping them through a slot midway along a long wet kiln. In either case, the high gas temperatures (1000–1200 °C) cause almost instantaneous, complete and smokeless combustion of the tire. Alternatively, tires are chopped into 5–10 mm chips, in which form they can be injected into a precalceriner combustion chamber. The steel and zinc in the tires become chemically incorporated into the clinker.
Other wastes have included solvents and clinical wastes. A very high level of monitoring of both the fuel and its combustion products is necessary to maintain safe operation.

For maximum kiln efficiency, high quality conventional fuels are the best choice. When using waste materials, in order to avoid prohibited emissions (e.g. of dioxins) it is necessary to control the kiln system in a manner that is non-optimal for efficiency and output, and coarse combustibles such as tires can cause major product quality problems.

2-8. Kiln control

Online X-ray diffraction with automatic sample feed for free calcium oxide measurement

The objective of kiln operation is to make clinker with the required chemical and physical properties, at the maximum rate that the size of kiln will allow, while meeting environmental standards, at the lowest possible operating costs. The kiln is very sensitive to control strategies, and a poorly run kiln can easily double cement plant operating costs.

Formation of the desired clinker minerals involves heating the rawmix through the temperature stages mentioned above. The finishing transformation that takes place in the hottest part of the kiln, under the flame, is the reaction of belite \((\text{Ca}_2\text{SiO}_4)\) with calcium oxide to form alite \((\text{Ca}_3\text{O} \cdot \text{SiO}_4)\):

\[
\text{Ca}_2\text{SiO}_4 + \text{CaO} \rightarrow \text{Ca}_3\text{SiO}_5
\]

Also abbreviated in the cement chemist notation (CCN) as:

\[
\text{C}_2\text{S} + \text{C} \rightarrow \text{C}_3\text{S}
\]

Tricalcium silicate is thermodynamically unstable below 1250°C, but can be preserved in a metastable state at room temperature by fast cooling: on slow cooling it tends to revert to belite \((\text{Ca}_2\text{SiO}_4)\) and CaO.

If the reaction is incomplete, excessive amounts of free calcium oxide remain in the clinker. Regular measurement of the free CaO content is used as a means of tracking the clinker quality. As a parameter in kiln control, free CaO data is somewhat ineffective because, even with fast automated sampling and analysis, the data, when it arrives, may be 10 minutes "out of date", and more immediate data must be used for minute-to-minute control.

Conversion of belite to alite requires partial melting, the resulting liquid being the solvent in which the reaction takes place. The amount of liquid, and hence the speed of the finishing reaction, is related to temperature. To meet the clinker quality objective, the most obvious control is that the clinker should reach a peak temperature such that the finishing reaction takes place to the required degree. A further reason to maintain constant liquid formation in the hot end of the kiln is that the sintering material forms a dam that prevents the cooler upstream feed from flooding out of the kiln. The feed in the calcining zone, because it is a powder evolving carbon dioxide, is extremely fluid. Cooling of the burning zone, and loss of
unburned material into the cooler, is called "flushing", and in addition to causing lost production can cause massive damage.

However, for efficient operation, steady conditions need to be maintained throughout the whole kiln system. The feed at each stage must be at a temperature such that it is "ready" for processing in the next stage. To ensure this, the temperature of both feed and gas must be optimized and maintained at every point. The external controls available to achieve this are few:

- Feed rate: this defines the kiln output
- Rotary kiln speed: this controls the rate at which the feed moves through the kiln tube
- Fuel injection rate: this controls the rate at which the "hot end" of the system is heated
- Exhaust fan speed or power: this controls gas flow, and the rate at which heat is drawn from the "hot end" of the system to the "cold end"

In the case of precalciner kilns, further controls are available:

- Independent control of fuel to kiln and calciner
- Independent fan controls where there are multiple preheater strings.

The independent use of fan speed and fuel rate is constrained by the fact that there must always be sufficient oxygen available to burn the fuel, and in particular, to burn carbon to carbon dioxide. If carbon monoxide is formed, this represents a waste of fuel, and also indicates reducing conditions within the kiln which must be avoided at all costs since it causes destruction of the clinker mineral structure. For this reason, the exhaust gas is continually analyzed for $\text{O}_2$, $\text{CO}$, $\text{NO}$ and $\text{SO}_2$.

The assessment of the clinker peak temperature has always been problematic. Contact temperature measurement is impossible because of the chemically aggressive and abrasive nature of the hot clinker, and optical methods such as infrared pyrometry are difficult because of the dust and fume-laden atmosphere in the burning zone. The traditional method of assessment was to view the bed of clinker and deduce the amount of liquid formation by experience. As more liquid forms, the clinker becomes stickier, and the bed of material climbs higher up the rising side of the kiln. It is usually also possible to assess the length of the zone of liquid formation, beyond which powdery "fresh" feed can be seen. Cameras, with or without infrared measurement capability, are mounted on the kiln hood to facilitate this. On many kilns, the same information can be inferred from the kiln motor power drawn, since sticky feed riding high on the kiln wall increases the eccentric turning load of the kiln.

Further information can be obtained from the exhaust gas analyzers. The formation of NO from nitrogen and oxygen takes place only at high temperatures, and so the NO level gives an indication of the combined feed and flame temperature. SO$_2$ is formed by thermal decomposition of calcium sulfate in the clinker, and so also gives an indication of clinker temperature. Modern computer control systems usually make a "calculated" temperature, using contributions from all these information sources, and then set about controlling it.

As an exercise in process control, kiln control is extremely challenging, because of multiple inter-related variables, non-linear responses, and variable process lags. Computer control systems were first tried in the early 1960s, initially with poor results due mainly to poor process measurements. Since 1990, complex high level supervisory control systems have been standard on new installations. These operate using expert system strategies that
maintain a "just sufficient" burning zone temperature, below which the kiln's operating condition will deteriorate catastrophically, thus requiring rapid-response, "knife-edge" control.

2-9. Cement kiln emissions

Emissions from cement works are determined both by continuous and discontinuous measuring methods, which are described in corresponding national guidelines and standards. Continuous measurement is primarily used for dust, NOx and SO2, while the remaining parameters relevant pursuant to ambient pollution legislation are usually determined discontinuously by individual measurements.

The following descriptions of emissions refer to modern kiln plants based on dry process technology.

2-9-1. Carbon dioxide

During the clinker burning process CO2 is emitted. CO2 accounts for the main share of these gases. CO2 emissions are both raw material-related and energy-related. Raw material-related emissions are produced during limestone decarbonation (CaCO3) and account for about 60 % of total CO2 emissions.

2-9-2. Dust

To manufacture 1 t of Portland cement, about 1.5 to 1.7 t raw materials, 0.1 t coal and 1 t clinker (besides other cement constituents and sulfate agents) must be ground to dust fineness during production. In this process, the steps of raw material processing, fuel preparation, clinker burning and cement grinding constitute major emission sources for particulate components. While particulate emissions of up to 3,000 mg/m³ were measured leaving the stack of cement rotary kiln plants as recently as in the 1950s, legal limits are typically 30 mg/m³ today, and much lower levels are achievable.

2-9-3. Nitrogen oxides (NOx)

The clinker burning process is a high-temperature process resulting in the formation of nitrogen oxides (NOx). The amount formed is directly related to the main flame temperature (typically 1850–2000 °C). Nitrogen monoxide (NO) accounts for about 95 %, and nitrogen dioxide (NO2) for about 5 % of this compound present in the exhaust gas of rotary kiln plants. As most of the NO is converted to NO2 in the atmosphere, emissions are given as NO2 per cubic metre exhaust gas.

Without reduction measures, process-related NOx contents in the exhaust gas of rotary kiln plants would in most cases considerably exceed the specifications of e.g. European legislation for waste burning plants (0.50 g/m³ for new plants and 0.80 g/m³ for existing plants).

Reduction measures are aimed at smoothing and optimising plant operation. Technically, staged combustion and Selective Non-Catalytic NO Reduction (SNCR) are applied to cope with the emission limit values.
High process temperatures are required to convert the raw material mix to Portland cement clinker. Kiln charge temperatures in the sintering zone of rotary kilns range at around 1450 °C. To reach these, flame temperatures of about 2000 °C are necessary. For reasons of clinker quality the burning process takes place under oxidising conditions, under which the partial oxidation of the molecular nitrogen in the combustion air resulting in the formation of nitrogen monoxide (NO) dominates. This reaction is also called thermal NO formation. At the lower temperatures prevailing in a precalciner, however, thermal NO formation is negligible: here, the nitrogen bound in the fuel can result in the formation of what is known as fuel-related NO. Staged combustion is used to reduce NO: calciner fuel is added with insufficient combustion air. This causes CO to form. The CO then reduces the NO into molecular nitrogen:

\[ 2 \text{CO} + 2 \text{NO} \rightarrow 2 \text{CO}_2 + \text{N}_2. \]

Hot tertiary air is then added to oxidize the remaining CO.

2-9-4. **Sulfur dioxide (SO₂)**

Sulfur is input into the clinker burning process via raw materials and fuels. Depending on their origin, the raw materials may contain sulfur bound as sulfide or sulfate. Higher SO₂ emissions by rotary kiln systems in the cement industry are often attributable to the sulfides contained in the raw material, which become oxidised to form SO₂ at the temperatures between 370 °C and 420 °C prevailing in the kiln preheater. Most of the sulfides are pyrite or marcasite contained in the raw materials. Given the sulfide concentrations found e.g. in German raw material deposits, SO₂ emission concentrations can total up to 1.2 g/m³ depending on the site location. In some cases, injected calcium hydroxide is used to lower SO₂ emissions.

The sulfur input with the fuels is completely converted to SO₂ during combustion in the rotary kiln. In the preheater and the kiln, this SO₂ reacts to form alkali sulfates, which are bound in the clinker, provided that oxidizing conditions are maintained in the kiln.

2-9-5. **Carbon monoxide (CO) and total carbon**

The exhaust gas concentrations of CO and organically bound carbon are a yardstick for the burn-out rate of the fuels utilised in energy conversion plants, such as power stations. By contrast, the clinker burning process is a material conversion process that must always be operated with excess air for reasons of clinker quality. In concert with long residence times in the high-temperature range, this leads to complete fuel burn-up.

The emissions of CO and organically bound carbon during the clinker burning process are caused by the small quantities of organic constituents input via the natural raw materials (remnants of organisms and plants incorporated in the rock in the course of geological history). These are converted during kiln feed preheating and become oxidized to form CO and CO₂. In this process, small portions of organic trace gases (total organic carbon) are formed as well. In case of the clinker burning process, the content of CO and organic trace gases in the clean gas therefore may not be directly related to combustion conditions.
2-9-6. Gaseous inorganic chlorine compounds (HCl)

Chlorides are minor additional constituents contained in the raw materials and fuels of the clinker burning process. They are released when the fuels are burnt or the kiln feed is heated, and primarily react with the alkalis from the kiln feed to form alkali chlorides. These compounds, which are initially vaporous, condense on the kiln feed or the kiln dust, at temperatures between 700 °C and 900 °C, subsequently re-enter the rotary kiln system and evaporate again. This cycle in the area between the rotary kiln and the preheater can result in coating formation. A bypass at the kiln inlet allows effective reduction of alkali chloride cycles and to diminish coating build-up problems. During the clinker burning process, gaseous inorganic chlorine compounds are either not emitted at all or in very small quantities only.

2-9-7. Gaseous inorganic fluorine compounds (HF)

Of the fluorine present in rotary kilns, 90 to 95 % is bound in the clinker, and the remainder is bound with dust in the form of calcium fluoride stable under the conditions of the burning process. Ultra-fine dust fractions that pass through the measuring gas filter may give the impression of low contents of gaseous fluorine compounds in rotary kiln systems of the cement industry.

2-9-8. Trace elements

The emission behaviour of the individual elements in the clinker burning process is determined by the input scenario, the behaviour in the plant and the precipitation efficiency of the dust collection device. The trace elements introduced into the burning process via the raw materials and fuels may evaporate completely or partially in the hot zones of the preheater and/or rotary kiln depending on their volatility, react with the constituents present in the gas phase, and condense on the kiln feed in the cooler sections of the kiln system. Depending on the volatility and the operating conditions, this may result in the formation of cycles that are either restricted to the kiln and the preheater or include the combined drying and grinding plant as well. Trace elements from the fuels initially enter the combustion gases, but are emitted to an extremely small extent only owing to the retention capacity of the kiln and the preheater.

Under the conditions prevailing in the clinker burning process, non-volatile elements (e.g. arsenic, vanadium, nickel) are completely bound in the clinker.

Elements such as lead and cadmium preferentially react with the excess chlorides and sulfates in the section between the rotary kiln and the preheater, forming volatile compounds. Owing to the large surface area available, these compounds condense on the kiln feed particles at temperatures between 700 °C and 900 °C. In this way, the volatile elements accumulated in the kiln-preheater system are precipitated again in the cyclone preheater, remaining almost completely in the clinker.

Thallium (as the chloride) condenses in the upper zone of the cyclone preheater at temperatures between 450 °C and 500 °C. As a consequence, a cycle can be formed between preheater, raw material drying and exhaust gas purification.
Mercury and its compounds are not precipitated in the kiln and the preheater. They condense on the exhaust gas route due to the cooling of the gas and are partially adsorbed by the raw material particles. This portion is precipitated in the kiln exhaust gas filter.

Owing to trace element behaviour during the clinker burning process and the high precipitation efficiency of the dust collection devices trace element

Emission concentrations are on a low overall level.
3. Cement mill

3-1. Materials ground

Portland clinker is the main constituent of most cements. In Portland cement, a little calcium sulfate (typically 3-10%) is added in order to retard the hydration of tricalcium aluminate. The calcium sulfate may consist of natural gypsum, anhydrite, or synthetic wastes such as flue gas desulfurization gypsum. In addition, up to 5% calcium carbonate and up to 1% of other minerals may be added. It is normal to add a certain amount of water, and small quantities of organic grinding aids and performance enhancers. "Blended cements" and Masonry cements may include large additions (up to 40%) of natural pozzolans, fly ash, limestone, silica fume or metakaolin. Blast furnace slag cement may include up to 70% ground granulated blast furnace slag. See cement. Gypsum and calcium carbonate are relatively soft minerals, and rapidly grind to ultra-fine particles. Grinding aids are typically chemicals added at a rate of 0.01-0.03% that coat the newly-formed surfaces of broken mineral particles and prevent re-agglomeration. They include 1,2-propanediol, acetic acid, triethanolamine and lignosulfonates.

3-2. Temperature control

Heat generated in the grinding process causes gypsum (CaSO₄·2H₂O) to lose water, forming bassanite (CaSO₄·0.2-0.7H₂O) or γ-anhydrite (CaSO₄·~0.05H₂O). The latter minerals are rapidly soluble, and about 2% of these in cement is needed to control tricalcium aluminate hydration. If more than this amount forms, crystallization of gypsum on their re-hydration causes "false set" - a sudden thickening of the cement mix a few minutes after mixing, which thins out on re-mixing. High milling temperature causes this. On the other hand, if milling temperature is too low, insufficient rapidly-soluble sulfate is available and this causes "flash set" - an irreversible stiffening of the mix. Obtaining the optimum amount of rapidly-soluble sulfate requires milling with a mill exit temperature within a few degrees of 115°C. Where the milling system is too hot, some manufacturers use 2.5% gypsum and the
remaining calcium sulfate as natural $\alpha$-anhydrite ($\text{CaSO}_4$). Complete dehydration of this mixture yields the optimum 2% $\gamma$-anhydrite. In the case of some efficient modern mills, insufficient heat is generated. This is corrected by recirculating part of the hot exhaust air to the mill inlet.

3-3. Ball Mills

Ball Mill Layout

A ball mill is a horizontal cylinder partly filled with steel balls (or occasionally other shapes) that rotates on its axis, imparting a tumbling and cascading action to the balls. Material fed through the mill is crushed by impact and ground by attrition between the balls. The grinding media are usually made of high-chromium steel. The smaller grades are occasionally cylindrical ("pebs") rather than spherical. There exists a speed of rotation (the "critical speed") at which the contents of the mill would simply ride over the roof of the mill due to centrifugal action. The critical speed (rpm) is given by: $n_C = \frac{42.29}{\sqrt{d}}$, where $d$ is the internal diameter in metres. Ball mills are normally operated at around 75% of critical speed, so a mill with diameter 5 metres will turn at around 14 rpm.

The mill is usually divided into at least two chambers, (Depends upon feed input size presently mill installed with Roller Press are mostly single chambered), allowing the use of different sizes of grinding media. Large balls are used at the inlet, to crush clinker nodules (which can be over 25 mm in diameter). Ball diameter here is in the range 60-80 mm. In a two-chamber mill, the media in the second chamber are typically in the range 15-40 mm, although media down to 5 mm are sometimes encountered. As a general rule, the size of media has to match the size of material being ground: large media can't produce the ultra-fine particles required in the finished cement, but small media can't break large clinker particles. Mills with as many as four chambers, allowing a tight segregation of media sizes, were once used, but this is now becoming rare. Alternatives to multi-chamber mills are:

- pairs of mills, run in tandem, charged with different-sized media.
- use of alternative technology (see Roll-presses below) to crush the clinker prior to fine-grinding in a ball mill.
A current of air is passed through the mill. This helps keep the mill cool, and sweeps out evaporated moisture which would otherwise cause hydration and disrupt material flow. The dusty exhaust air is cleaned, usually with bag filters.

Typical mill/separator circuit

3-4. Closed-circuit systems

The efficiency of the early stages of grinding in a ball mill is much greater than that for formation of ultra-fine particles, so ball mills operate most efficiently by making a coarse product, the fine fractions of this is then separated, and the coarse part being returned to the mill inlet. The proportion of the mill-exit material returned to the inlet may vary from 10-30% when ordinary cement is being ground, to 85-95% for extremely fine cement products. It is important for system efficiency that the minimum amount of material of finished-product fineness is returned to the inlet. Modern separators are capable of making a very precise size "cut" and contribute significantly to the reduction of energy consumption, and have the additional advantage that they cool both the product and the returned material, thus minimizing over-heating.

Efficient closed-circuit systems, because of their tight particle size control, lead to cements with relatively narrow particle size distributions (i.e. for a given mean particle size, they have fewer large and small particles). This is of advantage in that it maximizes the strength-production potential the clinker, because large particles are inert. As a rule of thumb, only the outer 7 μm "skin" of each particle hydrates in concrete, so any particle over 14 μm diameter always leaves an un-reacted core. However, the lack of ultra-fine particles can be a disadvantage. These particles normally pack the spaces between the larger particles in a cement paste, and if absent the deficit is made up with extra water, leading to lower strength. This can be remedied by including 5% calcium carbonate in the cement: this soft mineral produces adequate ultra-fines on the first pass through the mill.
3-5. **Energy consumption and output**

3-5-1. **Clinker hardness**

The hardness of clinker is important for the energy cost of the grinding process. It depends both on the clinker's mineral composition and its thermal history. The easiest-ground clinker mineral is alite, so high-alite clinkers reduce grinding costs, although they are more expensive to make in the kiln. The toughest mineral is belite, because it is harder, and is somewhat plastic, so that crystals tend to flatten rather than shatter when impacted in the mill. The mode of burning of the clinker is also important. Clinker rapidly burned at the minimum temperature for combination, then rapidly cooled, contains small, defective crystals that grind easily. These crystals are usually also optimal for reactivity. On the other hand, long burning at excess temperature, and slow cooling, lead to large, well-formed crystals that are hard to grind and un-reactive. The effect of such a clinker can be to double milling costs.

3-6. **Roller mills**

These have been used for many years for the less exacting raw-milling process, but recently roller mills, in combination with high-efficiency separators, have been used for cement grinding. The grinding action employs much greater stress on the material than in a ball mill, and is therefore more efficient. Energy consumption is typically half that of a ball mill. However, the narrowness of the particle size distribution of the cement is problematic, and the process has yet to receive wide acceptance.

3-6-1. **High pressure roll presses**

These consist of a pair of rollers set 8-30 mm apart and counter-rotating with surface speed around 0.9 - 1.8 m.s⁻¹. The bearings of the rollers are designed to deliver a pressure of 50 MPa or more. The bed of material drawn between the rollers emerges as a slab-like agglomeration of highly-fractured particles. The energy efficiency of this process is
comparatively high. Systems have been designed, including a de-agglomerator and separator, that will deliver material of cement fineness. However, particle size distribution is again a problem, and roll presses are now increasingly popular as a "pre-grind" process, with the cement finished in a single chamber ball mill. This gives good cement performance, and reduces energy consumption by 20-40% compared with a standard ball mill system.

3-7. Capacity of cement mills

The cement mills on a cement plant are usually sized for a clinker consumption considerably greater than the output of the plant's kilns. This is for two reasons:

- The mills are sized to cope with peaks in market demand for cement. In temperate countries, the summer demand for cement is usually much higher than that in winter. Excess clinker produced in winter goes into storage in readiness for summer demand peaks. For this reason, plants with highly seasonal demand usually have very large clinker stores.
- Cement milling is the largest user of electric power on a cement plant, and because they can easily be started and stopped, it often pays to operate cement mills only during "off-peak" periods when cheaper power is available. This is also favourable for electricity producers, who can negotiate power prices with major users in order to balance their generating capacity over 24 hours. More sophisticated arrangements such as "power shedding" are often employed. This consists of the cement manufacturer shutting down the plant at short notice when the power supplier expects a critical demand peak, in return for favourable prices. Clearly, plenty of excess cement milling capacity is needed in order to "catch up" after such interruptions.

3-8. Control of product quality

In addition to control of temperature (mentioned above), the main requirement is to obtain a consistent fineness of the product. From the earliest times, fineness was measured by sieving the cement. As cements have become finer, the use of sieves is less applicable, but the amount retained on a 45 μm sieve is still measured, usually by air-jet sieving or wet-sieving. The amount passing this sieve (typically 95% in modern general-purpose cements) is related to the overall strength-development potential of the cement, because the larger particles are essentially unreactive.

The main measure of fineness today is specific surface. Because cement particles react with water at their surface, the specific surface area is directly related to the cement's initial reactivity. By adjusting the fineness of grind, the manufacture can produce a range of products from a single clinker. Tight control of fineness is necessary in order to obtain cement with the desired consistent day-to-day performance, so round-the-clock measurements are made on the cement as it is produced, and mill feed-rates and separator settings are adjusted to maintain constant specific surface.
A more comprehensive picture of fineness is given by particle size analysis, yielding a measure of the amount of each size range present, from sub-micrometer upwards. This used to be mainly a research tool, but with the advent of cheap, industrialized laser-diffraction analyzers, its use for routine control is becoming more frequent. This may take the form of a desk-top analyzer fed with automatically gathered samples in a robotized laboratory, or, increasingly commonly, instruments attached directly to the output ducts of the mill. In either case, the results can be fed directly into the mill control system, allowing complete automation of fineness control.

In addition to fineness, added materials in the cement must be controlled. In the case of gypsum addition, the material used is gypsum feed rate. Again, this process is often completely automated. Similar measurement and control protocols are applied to other materials added, such as limestone, slag and fly-ash, frequently of variable quality, and it is normal practise to measure the sulfate content of the cement regularly, typically by x-ray fluorescence, using the results to adjust the.
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