

Gas Emissions from Cement Kilns

The Procal 2000 is a state of the art continuous emissions monitoring (CEM) system that measures many of the gases emitted during cement production such as carbon dioxide (CO₂), carbon monoxide (CO), nitric oxides (NO_x) and sulphur dioxide (SO₂). Approximately 5% of global CO₂ emissions originate from the heating of raw materials in cement manufacture. At the heart of the cement production process is the decarbonisation of limestone which results in the emission of large quantities of carbon dioxide.

Using infra red absorption spectroscopy and gas filter correlation technology a Procal 2000 instrument can provide in-stack analysis of up to six gases including carbon dioxide with a typical accuracy of ±2% of full scale concentration. In addition, the Procal 2000 can be configured to provide an individual measurement channel for each gas (NO_x, CO, SO₂ and hydrocarbons) released from the kiln.

The mechanisms that produce gas emissions in the manufacture of cement

The cement kiln is a harsh high alkaline environment where the combustion of fuel and the breakdown of raw materials occur at high temperatures. The robust design and high quality material construction of the Procal 2000 provides for a low maintenance analyser that is able to deliver reliable performance when suitably located in the cement kiln stack.

The cement kiln is designed for the purpose of calcination by which limestone undergoes a transformation to calcium carbonate with the simultaneous release of carbon dioxide on the application of heat. At elevated temperatures decomposition of the CO₂ can occur resulting in the release of carbon monoxide and oxygen (O₂). Levels of CO can be elevated by the presence of metallic catalysts or the partial oxidation of hydrocarbons in the raw material fed into the kiln. Naturally occurring hydrocarbons in the raw feed are also vapourised and pyrolyzed at high temperature resulting in the release of organic hydrocarbons which are swept out of the kiln.

Figure 1. The high temperature flame inside a cement kiln



The kiln is heated by a high temperature flame (see figure 1) and NO_x gases are emitted by thermal fixation of nitrogen in the combustion air and by the oxidation of chemically bound nitrogen in the fuel during combustion. As the flame temperature

increases, the amount of thermally generated NO_x also increases. Further NO_x gases are also released from nitrogen compounds in the kiln feed as it is heated.

Process variations are normal in cement kiln operations and can produce significant variations in NO_x emissions as discussed below. The Procal 2000 is an in-situ analyser that is flange mounted at a pre-determined measurement location on the stack. The Procal 2000 consists of a probe, which resides inside the stack, patented sintered panels on the probe allow gases to pass into the probe whilst preventing the ingress of dust. Unlike higher maintenance extractive systems, gas filtering or sample conditioning is not required. The insertion of the sampling probe directly into the gas environment results in the Procal 2000 having a fast response time (120seconds to T90) capable of measuring rapid changes in NO_x levels.

Cement is produced from a material known as “Clinker” that is formed in the kiln. For “clinkering” reactions to take place a very high temperature is required and if a minimum temperature is not achieved the clinker formation reactions can stop. The clinker reactions are exothermic (produce heat) and if the reaction stops the temperature decreases even further. Further heating must then be applied by burning more fuel and once the reaction re-starts there is a further temperature increase due to the exothermic nature of the reaction that requires a further adjustment to the amount of fuel being burnt. NO_x emissions also depend on the type of fuel used with higher nitrogen content fuels having more nitrogen available for NO_x formation. Higher thermal NO_x formation also results from higher flame temperatures which are higher for gas burners than for coal burners. The Procal 2000 with its fast response time can monitor these process variations and the changing NO_x levels.

SO₂ emissions depend on the content of the volatile sulphur in the raw materials and the type of fuel used. As cement kilns have highly alkaline internal environments most of the potential SO₂ emissions are absorbed and kilns that use raw materials with little or no volatile sulphur have relatively low SO₂ emission levels. However, in systems that have sulphide sulphur (Pyrites) in the kiln feed, the sulphur absorption rate may be reduced leading to higher emissions. Sulphur present in the fuel is largely incorporated into the clinker itself and is not normally emitted to the atmosphere. SO₂ emissions can be controlled using dry or wet scrubbers with wet scrubbers generally reducing SO₂ emissions by about 90 percent.

Legislation

The Procal 2000 analyser has been in service for over 25 years with continual product improvement to match ever-tightening legislative requirements. To date, over 2,400 Procal 2000 units are in operation worldwide.

Emissions from cement manufacturing in Europe are covered by the EU Directive on Integrated Pollution Prevention and Control (IPPC) (2008/1/EC). Under this directive installations are required to have a permit containing emission limit values and to operate under conditions based on the application of Best Available Techniques (BAT). The aim of the IPPC is to minimise emissions of pollutants. Permit conditions also have to address energy efficiency, waste minimisation, prevention of accidental emissions and site restoration. The Environment Agency monitors current legislation

in the UK and operation restrictions are outlined in the Integrated Pollution Control (IPC) Guidance Notes series 2 for the Mineral Industry Sector and Waste Disposal and Recycling Sector (Environment Agency, 1997). For example, NO_x emissions on cement manufacturing plants must be less than 900 mg/Nm³ at the standard reference conditions (276K, 101.3 kPa, 11% oxygen and dry gas). Since the sector produces large scale combustion products, it is subject to tightening legislation and must conform to new controls that are introduced.

Pollution Control Methods

The cement industry has a number of well established pollution control methods. In certain cases NO_x emission limits can be maintained within permit levels using a combination of low NO_x burners and alternative/waste fuels. NO_x emissions can be reduced further by the addition of either a Selective Non-Catalytic reactor (SNCR) or a Selective Catalytic Reactor (SCR).

Process modifications in combination with close control of the combustion process (e.g. operating at the minimum necessary temperature and controlling the level of excess air) improve fuel efficiency and lead to a lower NO_x level as less fuel is required. As combustion temperature increases the NO_x emission level also increases and therefore operating at the minimum temperature for the clinker reaction to take place reduces NO_x emissions. Excess air is required to provide an oxidising atmosphere within the burning zone of the kiln and this must be optimised to yield clinker of good quality. Optimum oxidising conditions are obtained when the oxygen level is between 1-2%.

In order to determine the excess air level in the kiln both carbon monoxide and oxygen monitoring of the kiln exhaust gas are required. The in-situ PROCAL 2000 continuous emission monitoring system (CEM) used in conjunction with an oxygen monitor can be used for this purpose. A feedback control system that incorporates measurement data acquired from a Procal 2000 analyser system can accurately control the excess air and maintain a level that promotes both optimum combustion and oxidising conditions. The close control of excess air has been shown to lead to a reduction of NO_x levels by up to 15%.

In cases where NO_x levels are not sufficiently reduced by process modifications and process control then NO_x reduction technologies must be implemented. Nitric Oxide can be converted to hydrogen cyanide (HCN) in re-burning reactions in a post burner flame. Fuels with a high volatile content are used to provide the flame and NO_x gas passing through the flame is converted to HCN. Car tyres, in a chipped form, have a high volatile content and can be substituted for coal in the combustion. The tyre material is ideal for the re-burn effect and can lead to a 30-45% reduction in NO_x levels. A Selective Catalytic Reactor (SCR) can also be introduced at the exit of the kiln to reduce the NO_x gases. A Procal 2000 can continuously measure the NO_x entering and exiting the SCR system and can be used to optimise the SCR control preventing ammonia slip. For a SNCR, ammonia is injected into the pre-heater at a location where the gas temperature is sufficiently high (900-1000 ° C or 1,650 – 1,830°F) such that the ammonia does not require the presence of a catalyst in order to reduce the NO_x concentrations to Nitrogen (N₂).

History of Cement and Kiln Development

Cement in the form of calcined gypsum was used by the Egyptians and developed further by the Greeks and Romans who added sand to lime to make mortar and coarse stone for concrete. Roman ingenuity allowed the construction of harbours with the discovery of a cement known as 'pozzolana' that set under water. The Pozzolana cement was created by adding crushed volcanic ash to lime. The modern manufacture of cement dates back to 1824 when Joseph Aspin took out a patent for 'Portland Cement' a material he produced by firing finely-ground clay and limestone until the limestone calcinated. In 1845, Isaac Johnson made the first modern Portland Cement by firing a mixture of chalk and clay at much higher temperatures, similar to those used today. At the temperatures (1400C-1500C), clinkering occurs and minerals form which are very reactive and more strongly cementitious.

Important developments in the manufacturing process soon followed with the development of the rotary kiln for making lime. Rotary kilns heat the clinker mainly by radiant heat transfer and this is more efficient at higher temperatures. The rotary kiln allows high burning temperatures to be achieved and as the clinker is constantly moving within the kiln, a fairly uniform clinkering temperature is achieved in the hottest part of the kiln known as the burning zone. The addition of gypsum to control the setting of the cement and the use of ball mills to grind the clinker were also introduced around the end of the 19th Century.

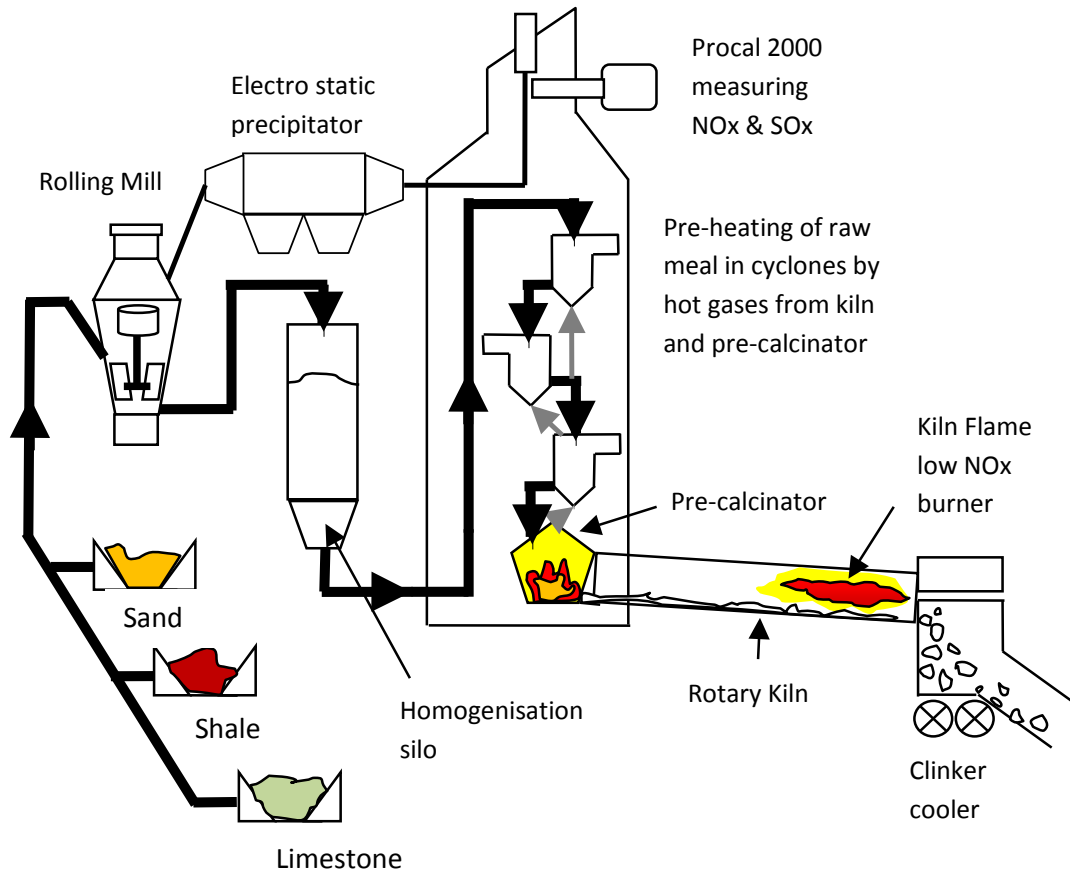
Figure 2. A modern rotary kiln



The Procal 2000 CEM system on a modern cement plant

A schematic of a modern cement manufacturing plant is shown in Figure 3. Cement is typically made from limestone and clay or shale and many cement plants are normally situated near limestone quarries to insure a constant supply of lime for use in the kiln. Portland cement is formed from a mixture of lime (CaO) and silica (SiO₂) with a small proportion of alumina (Al₂O₃) and iron oxide (Fe₂O₃).

Figure 3. A modern cement plant with a Procal 2000 CEMs measuring NO_x and SO₂



The raw materials are crushed through a milling process and additional materials are added to obtain the correct chemical proportions. After the milling, the fine powder material known as raw meal is stored in a homogenisation silo. Kiln development has been aimed at reducing the water content and on newer plants this is achieved using a pre-heater system and a dry kiln. The pre-heater tower contains 4-6 cyclone separation vessels that remove the water prior to calcination. Hot gases from the kiln pass upwards at the same time as the raw meal travels downwards and the tower acts as a counter current heat exchanger with heat passing from the rising gases to the descending raw meal. The fast moving hot gases keep the meal suspended in the air and the process allows 30-40% of the meal to be de-carbonated before entering the kiln.

The construction of the kiln is in the form of a long tube that is tilted by a small angle to the horizontal. At one end of the kiln is a long flame with a temperature of 2000°C that is produced by burning either fossil fuels or waste derived fuels. Several types of kiln exist. In a dry-process kiln water is driven off before the kiln mix enters the kiln. In a wet-kiln the water is removed inside the kiln tube and kiln is normally longer to allow this process to take place.

Inside the kiln the feed is heated to 800-900°C at which temperature calcination of the limestone occurs and carbon dioxide is released. Heat transfer occurs through a large mass of material and the CO₂ gas has to escape outwards as the heat moves inwards.

The Procal 2000 analyser is normally located near the top of the cement kiln stack as shown in figure 3. In the example shown NO_x and SO₂ emissions from the kiln are measured. The Procal 2000 system comprises the Procal 2000 analyser and a Procal 1000 analyser control and data logging unit. The latter is capable of controlling up to six Procal analysers and is designed to accept signal I/O from other instruments in the process such as an oxygen monitoring device. The Procal 1000 provides a single CEMS data hub capable of displaying gas concentrations and third party analyser I/O along with information on sample conditions, diagnostic data and trends. The information can also be made available to external components in a variety of industry standard data protocols. The Procal 1000 allows emission readings to be transmitted to the control room allowing operators to adjust the temperature or flow of the material in the kiln and to optimise the cement production.

The heated material moves down the kiln as it rotates and enters the burning zone where the temperature reaches 1450°C. At this temperature sintering occurs and the CaO reacts with the other components in a liquid state to form calcium silicates, aluminates and alumina-ferrite, the main components of cement. A product described as clinker is formed containing rounded nodules between 1-25mm across. The reaction of the calcium silicates in the clinker material with water defines the strength of the concrete when it is finally used.

After passing through the burning zone the clinker starts to cool, slowly at first, then more rapidly as it passes over the 'nose ring' at the end of the kiln and drops out into the clinker cooler. The clinker material is cooled to prevent not only damage to the clinker handling equipment such as conveyer belts but also to prevent excessive temperatures being reached in the finishing mill. The grinding of the clinker requires large amounts of energy and rapid cooling of the clinker can reduce the amount of grinding required. The heat can be extracted from the clinker in an energy efficient mill and used to heat raw materials. Faster cooling of the clinker also enhances silicate reactivity. A small amount of gypsum (3-5%) is added to the clinker to control the setting properties of the cement when it is used. The cooled clinker then enters the finishing mill where it is finely ground to obtain pure cement. The finishing mill consists of ball mills with two or more separate chambers containing different sizes of grinding media (steel balls).

During this phase, different mineral materials, called 'additions', may be added alongside the gypsum. Used in varying proportions, these additions, which are of natural or industrial origin, give the cement specific properties such as reduced permeability, greater resistance to sulphates and aggressive environments, improved workability, or higher-quality finishes.

Finally, the cement is stored in silos before being shipped in bulk or in bags to the sites where it will be used.

To date twenty five Procal 2000s have been installed world-wide in various cement plants operated by Lafarge Cement. The Procal 2000 is normally configured on these plants to measure SO₂ in the range 0-1000ppm, NO in the range 0-2500ppm, CO in the range 0-500ppm and H₂O in the range 0-20%.