Retrofitting in Cement Plants for Emissions Reduction

Gaseous emission — nitrogen oxides and sulphur oxides — can be reduced by making some changes to the existing installation.

The cement manufacturing process has undergone a lot of technological advancements with respect to product types, raw material and fuel types and improved automation and energy efficiency. Most of the emissions to the environment are in the form of particulates, carbon dioxide, nitrogen oxides and sulphur oxides in exhaust gases. In some countries, mercury emissions are monitored and controlled. In cases where fuel or raw material quality lead to higher emissions, end of pipe control technology can be applied to meet emission norms.

NO_x formation in kiln flames is generally by both thermal and fuel routes (for coal, oil and petroleum coke). NO, formation takes place in the high temperature clinker burning process and the amount is directly related to the main flame temperature which is typically 1800 -2000 °C. Thermal NO_v is formed by the combination of atmospheric nitrogen and oxygen at very high temperatures. The reaction takes place between oxygen radicals, nitrogen radicals and molecular nitrogen. Apart from temperature, the in-flame oxygen concentration and the residence time in the high temperature zones influence the final thermal NO_v emissions. Most fuels, other than gas, contain nitrogen bound as an organic compound in the structure. When the fuel is burnt this organic nitrogen becomes converted into a range of cyanide and amine species some of which are subsequently oxidised to NO_x, depending on the local oxygen

availability, but this mechanism is less dependent on temperature.

Typical NO_x emission values in older technologies can be as high as $1800-2000 \text{ mg/Nm}^3$, while average emission values are around 1200 mg/Nm^3 (based on $10\% O_2$).

Sulphur is input into the clinker burning process via raw materials and fuels. Higher SO₂ emissions by rotary kiln systems in the cement industry are due to sulphides contained in the raw material which become oxidised to form SO₂ at the temperatures between 370 to 420 °C prevailing in the kiln preheater. In some cases sulphur in fuel can also affect the emission of SO₂. High values in the range of 600 to 800 mg/Nm³ have been observed.

Recently the norms for gaseous emissions from cement plants have undergone revision in India and the Ministry of Environment and Forests (MoEF) has amended the Environment (protection) Rules of 1986. The limits for NO_x emissions for new plants are set at 600 mg/ Nm^3 at $10\%O_2$ (800 for older plants), and that for SO_2 are set at 100 mg/ Nm^3 at $10\%O_2$, dry basis. It will therefore be essential for producers to review their current operations to meet these new requirements, which are now quite stringent.

 NO_{X} emissions are dependent on certain process related factors such as

- · Feed mix composition
- Kiln fuel type
- Increased thermal efficiency
- Burner Type

There are certain limits to which these factors can be optimised to

reduce emissions while ensuring product quality and operational efficiency. As a result it becomes necessary to look at other solutions like retrofitting existing preheater, calciner or Tertiary Air TA duct to reduce the emissions.

For controlling NO_x emissions the following retrofitting options can be incorporated in existing Preheater Precalciner type Dry cement Kilns.

Installing low NOX burners (LNB) in the kiln.

Two distinct combustion zones are created using LNBs. Flame turbulence and air and fuel mixing are suppressed during the first stage of combustion. A fuel-rich, oxygen-lean, high temperature combustion zone is created first by reducing the amount of primary air in the primary combustion zone and delaying the combustion of all of the fuel. A portion of the flue gas can be recycled into the primary combustion zone to reduce the oxygen content of the primary air.

At the high temperatures required to complete clinkering reactions, thermal NO_x formation is suppressed in the primary combustion zone because less oxygen is available.

A secondary, oxygen-rich combustion zone follows, where fuel combustion is completed. Cooler secondary combustion air is mixed into the secondary combustion zone, lowering the temperature. Although excess oxygen is available, NO_X formation is suppressed in the secondary combustion zone because of lower temperature.

FEATURE: RETROFITTING

This method can secure to 10%–15% NO $_{\rm X}$ reduction. However, the exact values will depend on the existing level of emissions.

Staged combustion in Calciner (SCC)

SCC works by staging the introduction of fuel, combustion air, and feed material in a manner to minimise NOx formation and reduce NO_v to nitrogen. NO_v formed in the kiln's combustion zone is chemically reduced by maintaining a reducing atmosphere at the kiln feed end by firing fuel in this region. The reducing atmosphere is maintained in the calciner region by controlling combustion air such that the calcining fuel is first burned under reducing conditions to reduce NOx and then burned under oxidising conditions to complete the combustion reaction. However, the overall process parameters during kiln operation under such reducing conditions must be carefully watched to limit the CO emission, especially where ESP is being used instead of bag house.

Controlling the introduction of raw meal allows for control of the calciner temperature. Through these mechanisms, both fuel NO_X and thermal NO_X are controlled. The combustion chamber allows for improved control over the introduction of tertiary air in the calciner region, which helps to promote the proper reducing environment for NO_X control.

The various technology providers achieve this staged combustion by different methods:

- Staged air combustion in which along with delivery of the tertiary air to the calciner inlet, a portion of the tertiary air is delivered close to calciner outlet. Modification to the TA duct and calciner is required.
- Staged air and fuel: Fuel is fired both in kiln riser and calciner and

- TA is delivered both at inlet of calciner and in the combustion zone close to the calciner outlet.
- Sequenced Fuel and Air: This is the case of a typical Low NO_x ILC system, where all fuel is fired in a reducing atmosphere near the kiln inlet, and tertiary air is supplied in the lower part of the calciner. Raw meal is split and introduced at different sections of the calciner. This type of calciner does not stage fuel or air, but instead injects all calciner fuel at the bottom of the calciner, before the kiln inlet. All tertiary air is introduced at a single point just above the fuel. A hightemperature reducing zone is created in the kiln riser duct, and the calciner is partially built into the kiln riser.

This method can secure to 25%–30% NO_x reduction. However the exact values will depend on the existing level of emissions.

Selective Non-Catalytic Reduction

The SNCR process is basically the injection of ammonia in the form of ammonia water or urea in the flue-gas at a suitable temperature. An aqueous ammonia solution is the reagent that has been most often used for cement kilns, and experience indicates that an ammonia solution is most effective for PH/PC cement kiln applications. Other reagent alternatives include anhydrous ammonia (injected as a gas), urea solutions, and ammonium sulfate solutions. This reagent is called a reductant.

An SNCR system's performance depends on

- Residence time available in optimum temperature range
- Degree of mixing between injected reagent and combustion gases
- Uncontrolled NO_x concentration level and Oxygen level

• Molar ratio of injected reagent to uncontrolled NO_v.

The SNCR system can be easily installed as retrofit in an existing pyroprocessing system. The following are the main additions

- Reductant receipt and storage section. Adequate safety measures have to be taken for the handling of Ammonia solution or Ammonia.
- The reductant pumping and delivery section
- The reductant distribution system
- The ammonia injection lances at calciner and/or kiln riser duct.
 The exact location and number of injection points will differ from one system to the next and are optimised through testing.
- Measurement equipment is necessary to maintain the appropriate ammonia feed rate and additional monitoring equipment is required to record the amount of NOx and ammonia slip in the gases exiting the SNCR system to adjust the amount of ammonia entering the system.
- Temperature monitors are also required to make sure that the ammonia is delivered to the correct location.

Sometimes it may be necessary to use multiple reduction techniques so that the emission standards can be met. Due to the high operational cost of the system, SNCR should be used to the extent necessary only after achieving NOx reduction based on Process Optimisation and other retrofitting avenues described earlier in this paper.

Similarly the SO₂ emission from kilns are dependent on multiple factors, some of which can be optimised to reduce emissions. The following factors can be evaluated to optimise the SO₂ emissions from cement kiln:

· Inherent SO, removal efficiency

- of the kiln system,
- Limit raw material sulphur concentration and form of sulphur,
- Raw mix design: The molecular ratio between sulphur (and chloride) and alkalis (sodium and potassium),
- Whether oxidising or reducing conditions exist in the kiln system and where these conditions exist,
- The temperature profile in the kiln system,
- If an in-line raw mill is available and operating.

When the emission values cannot be improved by process optimisation alone, it becomes necessary to adopt suitable secondary measures. Some of the retrofit solutions are described below.

Lime Addition to Kiln Feed

Lime Addition to Kiln Feed consists of mixing lime (CaO) with the raw Kiln feed. The CaO would react with SO, driven off in the kiln to form calcium sulfite (CaSO₂) and calcium sulfate (CaSO). The reactions can occur in the calciner, throughout the rotary kiln, and in the lower stages of the flash calciner (i.e., at any location in the system at which CaO and SO, are present simultaneously and are mixed adequately). The amount of SO, absorbed through this mechanism at any location in the pyroprocess is dependent on the site-specific temperature and other factors such as the time of contact between the reactants. Once sulfur is absorbed as CaSO, in the materials in the pyroprocess, it is unlikely to be released again as SO₂. CaSO, would be retained in the raw mix and ultimately be converted into clinker.

Installation of SOX reduction cyclone

SO₂ formed in the upper cyclone stages of the preheater can be reduced by reaction with the naturally

occurring CaO present in the pyro system. CaO is formed in the calciner, and gas and dust containing high amounts of CaO can be directed to the upper stages for SO₂ reduction by a minor calciner modification.

This SO, removal system consists of a low pressure cyclone, with inlet outlet ducts, a material feed pipe, sluice flap and distribution box. The inlet duct conveys gas from the inline calciner to the SO, collecting cyclone. The outlet duct conveys gas to the Stage two or three inlet duct. A material feed pipe is provided for the SO, collecting cyclone and will terminate at stage below top stage or top stage distribution box. This system uses the differential pressure across the preheater tower to provide the driving force to convey the calcined material from the bottom

Upto 35% control of SO₂ is possible depending on existing situation in the kiln.

Dry Sorbent Injection

Dry Sorbent Injection (DSI) utilises finely ground sorbent which is injected in the gas stream of the kiln. The sorbent typically used is a hydrated lime, sodium bicarbonate or Trona (soda ash). Water may be injected separately from the sorbent either downstream or upstream of the dry sorbent injection point to humidify the flue gas.

The relative position of the dry sorbent and water injection is optimised to promote maximum droplet scavenging or impacts between sorbent particles and water droplets, both suspended in the gas stream. Fly ash, reaction products, and any unreacted sorbent are collected in the particulate control device. Some extent of dry scrubbing is inherent in the preheater tower.

Upto 60% control of SO_2 is possible depending on the amount of lime that is fed into the kiln.

Wet Lime Scrubbing

This is based on the reaction between Ca(OH)₂ and SO₂ with a lime slurry is introduced as a mist into a gas stream containing SO₂. The mole ration of Ca(OH)₂ to SO₂ is usually 2:1. This slurry can be introduced in the existing Gas Conditioning tower located between preheater and in-line raw mills. The lime spray can be modulated depending on kiln operating conditions such as when raw mill is not in operation.

Upto 90% control of SO₂ is possible depending on the existing system and improvement required. However the handling of such systems with the cement plant entails higher operation and maintenance costs. Hence the wet and semi-dry processes are not deployed unless the emissions are exceptionally high.

Engineering consultants like ERCOM, who have a global experience, have already assisted their customers abroad in achieving stringent emission limits. A quick and efficient technical audit can be carried for existing cement plants to check the likely compliance levels with respect to the new MoEF Notification. By assisting plants in carrying out process optimisation, we can help reduce the emissions with primary measures. In order to achieve further reductions, we can help clients in selecting the appropriate cost effective retrofit solution. Plant modifications for reduction of emission can be evaluated by us and we can aid in timely implementation with minimum disturbance to plant operation. Together with technology providers and cement plant owners, we can go a long way in paving the path for sustainable and environment friendly cement production.

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