

#### 4.0. OVERVIEW OF POTENTIALLY APPLICABLE CONTROL TECHNIQUES AND TECHNOLOGIES

Nitrogen oxides are formed by the oxidation of nitrogen during the fuel combustion process. The formation of thermal  $\text{NO}_x$  is a function of the flame temperature, flame turbulence, the amount of nitrogen and oxygen available for the thermal reaction, and the gas phase residence time at high temperature. To reduce the amount of thermal  $\text{NO}_x$  formed, one or more of these variables needs to be minimized. The formation of fuel and feed  $\text{NO}_x$  is not as well understood as the thermal  $\text{NO}_x$  formation. In general, however, the greater the concentration of nitrogen in the fuel and feed, the greater the fuel  $\text{NO}_x$  emissions. Therefore, reducing the amount of fuel and feed-bound nitrogen should reduce the contribution of the fuel and feed  $\text{NO}_x$ .

The typical  $\text{NO}_x$  emissions from a cement plant depend upon the type of the cement kiln as shown in Table 4-1. For any given type of kiln, the amount of  $\text{NO}_x$  formed is directly related to the amount of energy consumed in the cement-making process. Thus, measures that improve the energy efficiency of this process should reduce  $\text{NO}_x$  emissions in terms of lb of  $\text{NO}_x$  /ton of clinker. With the rising costs of energy and the very competitive cement market, greater attention is being paid to increasing overall energy efficiency, such as through reduction of overburning of clinker and improvement in gas-solids heat transfer. Continuous emissions monitoring of  $\text{CO}$ ,  $\text{NO}_x$ , and  $\text{O}_2$  provide an indication of kiln conditions and also provide inputs for process control. Newer cement kiln designs are generally based on preheater/precalciner systems which provide very efficient gas-solids contact and greater energy efficiency.  $\text{NO}_x$  control approaches are evaluated below under four categories:

High Temperature Emissions Controls,  
Combustion Optimization,  
Low Temperature Oxidation Emissions Controls, and  
Process Modifications.

This section of the report uses the EPA 2000 Report as the baseline for evaluating current control options for Ellis County kilns. The combustion and process optimization sections are included, with editing, from this report and describe the essential controls that have been considered and largely installed under the requirements of TAC Chapter 117. Additions to sections for process modifications to improve energy efficiency through calciner modifications and wet to dry conversions are discussed as site-specific options where applicable for Ellis

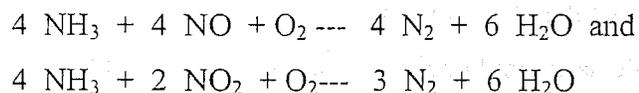
County Kilns. The section on oxidation controls is entirely new and was not considered in EPA 2000. The sections on SCR and SNCR consider EPA 2000 background information, but are written to reflect current status of these technologies and site-specific application to the Ellis County kiln.

## 4.1. High Temperature Emissions Controls

### 4.1.1. Selective Catalytic Reduction (SCR)

SCR is a process that uses ammonia in the presence of a catalyst to selectively reduce NO<sub>x</sub> emissions from exhaust gases. This technology is widely used for NO<sub>x</sub> abatement in other industries, such as coal-fired power stations and waste incinerators. The SCR process has been used extensively throughout the world to achieve a 90 percent reduction in NO<sub>x</sub> emissions from fossil fuel fired boilers. In the United States SCR technology has successfully been used for gas turbines, internal combustion engines, and utility boilers.

In SCR, anhydrous ammonia, usually diluted with air or steam, or urea, is injected through a grid system into hot flue gases that are then passed through a catalyst bed to carry out NO<sub>x</sub> reduction reactions. The two principal reactions are:



The first reaction represents the predominant reaction since 90 to 95 percent of NO<sub>x</sub> emissions in the flue gas are in the form of NO. A number of materials have been used for catalysts. Titanium dioxide (TiO<sub>2</sub>) and vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) mixtures are most commonly used as catalysts due to their resistance to SO<sub>x</sub> poisoning. Zeolite-based catalyst materials have also been developed capable of operating at higher temperatures than conventional metal-based catalysts. The catalyst is typically supported on ceramic materials, e.g., alumina in a honeycomb monolithic form. The active ingredients of the base metal (titania-vanadia) and zeolite catalysts often make up the bulk of the substrate material. The catalyst shape and reactor design vary depending upon the manufacturer.

The optimum temperature for the catalytic reactions depends upon the specific catalyst used and is usually in the range between 300 to 450°C (570 to 840°F). Without pre-heater and/or pre-calciner systems this temperature range may be higher than typical cement kiln flue gas temperatures, especially in plants using heat recovery systems or baghouses for particulate collection. But it may be possible to reheat the exhaust using heat recovery systems. Of particular relevance, then, is the ability to use SCR at wet kilns.

Ammonia is typically injected to produce a  $\text{NH}_3$ :  $\text{NO}_x$  molar ratio of 1.05-1.1:1 to achieve  $\text{NO}_x$  conversion of 80 to 90 percent with an ammonia "slip" of about 10 ppm of unreacted ammonia in the gases leaving the reactor. The  $\text{NO}_x$  destruction efficiency depends upon the temperature,  $\text{NH}_3$ :  $\text{NO}_x$  molar ratio, and the flue gas residence time (or the space velocity) used in the catalyst bed. The SCR reactor system can be designed for a desired  $\text{NO}_x$  reduction using appropriate reagent ratio, catalyst bed volume, and operating conditions. In general, the catalysts may be fouled or deactivated by the particulates present in the flue gas. In the case of cement plants, the presence of alkalis and lime, as well as sulfur dioxide, in the exhaust gases is also of concern. Recent developments, however, have led to sulfur tolerant SCR catalysts. In addition, soot blowers may be used to prevent dust accumulation on SCR catalysts.

In the cement industry, basically two SCR systems are being considered: low dust exhaust gas and high dust exhaust gas treatment. Low dust exhaust gas systems require reheating of the exhaust gases after de-dusting, resulting in additional cost. High dust systems are considered preferable for technical and economical reasons.

SCR may only be available as an applicable technology for dry kilns with preheat, as is described later herein. There are currently no installations of SCR units in any United States cement plants, however, a full-scale unit has been operating in Germany for over three years with SCR. As set forth in greater detail below, selective catalytic reduction has been installed and successfully operated at this one cement plant in Germany and SCR is now commonly used to control  $\text{NO}_x$  emissions from coal-fired power plants. This technology achieves  $\text{NO}_x$  emission reductions in the range of 80 to 90 percent or higher.

The experience of the German cement plant may be sufficient to demonstrate that the concerns regarding catalyst poisoning and fouling have been addressed with the development of a special catalyst specifically designed for the cement industry. In a typical design of a dry kiln with preheat, the SCR system could be located downstream of the pre-heater cyclones, prior to the roller mill. The process exhaust temperature at the outlet of the pre-heater cyclones would be approximately  $320^\circ\text{C}$  ( $608^\circ\text{F}$ ), which is ideal for a SCR system.

### **Potential Advantages of SCR.**

The potential advantages of SCR are as follows:

- **SCR can potentially provide a high degree of NO<sub>x</sub> removal.** Presently, guaranteed levels on SCR systems being provided in the power industry are in the 90% to 94% range. Even on difficult applications such as coal-fired power plants, which have very dusty flue gases, NO<sub>x</sub> control efficiencies of 90%+ are being guaranteed by vendors and being achieved.

**SCR is an add-on or end-of-pipe control technology.** For dry kilns with preheat, the SCR system would be located downstream of the cement kiln and pre-heater furnace and cyclones and hence it would not interfere with or affect the cement manufacturing process. This would be a big advantage over the Selective Non-Catalytic Reduction (SNCR) process, which must be carried out in process conditions.

- **SCR can use urea (CO(NH<sub>2</sub>)<sub>2</sub>) rather than ammonia as the reducing agent.** To use urea, a conversion system is required. In a typical conversion system, urea is mixed with water and then heated. The process converts the urea to gaseous ammonia, which is then injected into the flue gas. This system is commonly used where there are safety concerns arising from the transport and storage of ammonia.

### SCR at Coal-Fired Power Plants

Prior to 2001, there were approximately 12 coal-fired power plants in the United States utilizing SCR for NO<sub>x</sub> control. According to the Electric Power Research Institute, there are now about 200 coal-fired power plants (totaling 100,000 megawatts of generating capacity) on-line utilizing SCR control. Most of the plants on which SCR has been installed are designed for, and have been achieving, 80% to 90% control of NO<sub>x</sub>.

One possible problem mentioned with respect to utilizing SCR in cement plants is the technical feasibility of installing SCR in an environment where dust from the kiln could poison the catalyst, making SCR technically infeasible. On coal-fired power plants, the SCR catalyst is usually installed downstream of the boiler (between the economizer and the air pre-heater) prior to the particulate control device. As a result, the catalyst is subject to the full dust loading from coal combustion, just as it would be at a cement plant. Typically, coal contains 6% to 20% ash on a dry basis. The high dust, high temperature characteristics of coal plant emissions thus are similar to those of cement kiln exhaust gases. The experience of the power industry with SCR on coal-fired power plants suggests that the catalyst poisoning and fouling concerns may be manageable.

## SCR Experience in Cement Kilns.

Differences in the nature of the cement kiln and coal fired power plant processes, the chemical composition of the ash and other factors mean that the success of SCR in controlling NO<sub>x</sub> emissions from coal-fired power plants is not definitive evidence that the technology can be successfully applied at a cement plant. Among other things, dust from cement kilns is high in calcium, relative to coal dust, and calcium deactivates most conventional SCR catalysts. Also, the grain loading of cement kilns is likely to be different from that of coal-fired power plants, placing different stresses on the control device. As discussed in greater detail below, however, the recent successful use of SCR at a German cement plant demonstrates that these and other issues may have been resolved and that SCR is, under certain conditions, a technically feasible alternative for significantly reducing NO<sub>x</sub> emissions from cement kilns.

The Solnhofer Portland-Zementwerke AG cement plant in southern Germany located between Munich and Nuremberg has been in successful operation with SCR since 2001. Lurgi, the engineering company who supplied the SCR system, addressed the problem of catalyst deactivation discussed above (caused by the high calcium content of cement plant ash) by developing a catalyst specifically for the cement industry. The catalyst can use ammonia or urea as a reagent. If urea is used, a conversion unit is used to convert the urea to ammonia prior to injection in the SCR system. These units, which are quite common, avoid the need to store ammonia on-site for use as a reagent.

As of the beginning of 2005, there was no evidence of catalyst poisoning or deactivation. The problem of fouling from the heavy dust loading has proven to be quite manageable with regular maintenance (i.e., cleaning of the catalyst with a vacuum cleaning system).

The SCR system is achieving NO<sub>x</sub> emission reductions far in excess of those achievable using SNCR. Prior to installation of SCR, the Solnhofer plant, with SNCR, was achieving NO<sub>x</sub> emissions of 700 to 800 mg/ Nm<sup>3</sup> (equivalent to 2.8 to 3.2 lb/ton of clinker). With SCR, the plant has been achieving approximately 200 mg of NO<sub>x</sub>/Nm<sup>3</sup> (0.8 lb/ton of clinker). Based on an uncontrolled NO<sub>x</sub> emission rate of 1050 mg/Nm<sup>3</sup> (4.2 lb/ton of clinker), the emission rate corresponds to a NO<sub>x</sub> control efficiency of 80%. It has been indicated, however, that the SCR system was capable of achieving a lower NO<sub>x</sub> emission rate (they are not using all of their beds), but that they were operating at 200mg/Nm<sup>3</sup> since German law only required a NO<sub>x</sub> emission limit of 500mg/Nm<sup>3</sup>.

#### 4.1.1.1 Site Specific Application of SCR to Ellis County Cement Kilns

SCR offers the possibility of significant NO<sub>x</sub> reduction the plants in Ellis County. As an “add on” technology, which can achieve 90% or greater NO<sub>x</sub> reduction, with demonstrated performance at hundreds of coal fired power plants, SCR is a viable technology that is available to both for dry and wet kilns. The economics of SCR are greatly influenced by the temperature of the flue gas at the point of installation. [REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

The technology has been available at only one cement plant, the Solnhofer Portland - Zemetwerke AG dry kiln plant in Southern Germany, now in its fourth year of operation with SCR. While there are, at this time, no operating units in the U.S., the German experience leads one to assess the possibility that SCR can make a significant impact on NO<sub>x</sub> reduction in Ellis County. In fact, the Midwest Regional Planning Organization has recently concluded that SCR is a reasonably available technology for controlling NO<sub>x</sub> at cement plants (1), [REDACTED]

#### 4.1.1.2 Applicability of SCR to Cement Kilns and Areas of Concern

Before examining site-specific data, it is important to first examine the areas of concern with respect to SCR, many of which have been raised in the literature (see, for example, 2,3,4,5). This is necessary to see whether the data from the coal fired plants and from the one cement plant, is sufficient to attempt to make even qualified statements with respect to existing facilities, even though some analyses now suggest that the German data indicates that these problems will not exist for the cement industry in the U.S. (see, for example, reference 6). These concerns are delineated and discussed here. They include: catalyst deactivation due to catalyst poisoning; catalyst plugging and fouling due to high dust loading and deposits; reduction in NO<sub>x</sub> control efficiency due to high sulfur levels; temperature related factors leading to lower NO<sub>x</sub> removal

efficiencies;  $\text{NO}_x$  concentration variability and ammonia slip; and undesirable by-product formation in the SCR causing adverse affects on downstream equipment.

### Catalytic Deactivation Due to Catalyst Poisoning

Poisoning occurs when the contaminants in the gas being treated react with the catalyst, resulting in catalyst deactivation. It has been argued that the SCR catalyst in a cement plant will be subject to poisoning, principally from sodium (Na), potassium (K), and arsenic trioxide ( $\text{As}_2\text{O}_3$ ). Phosphorous, chromium and lead compounds can also poison an SCR catalyst, but since these are expected to be present in lower concentrations at cement kilns, they are of lesser concern. However, the typical concentration of sodium oxide ( $\text{Na}_2\text{O}$ ) in the particulate matter (PM) of certain coal-fired plants is greater than double the concentrations of  $\text{Na}_2\text{O}$  in the PM of the average cement plant, and the maximum concentration of  $\text{Na}_2\text{O}$  can be significantly greater than the maximum expected concentration of  $\text{Na}_2\text{O}$  in the PM of the average cement plant. Similarly, the concentration of  $\text{As}_2\text{O}_3$  in the flue gas of the typical coal fired plant is well above the concentration of  $\text{As}_2\text{O}_3$  in the expected flue gas from the average cement plant. Regarding the availability of catalyst poisons, an additional argument deals with the solubility of Na and K in the fly ash and the form of the fly-ash particles.

It is argued that in cement pre-heater pre-calciner kilns, materials such as sodium and potassium compounds may be present in relatively elevated concentrations on the surfaces of particles in “water soluble” form that can contact the surface of the SCR catalyst bed and thereby provide an opportunity to poison the  $\text{V}_2\text{O}_5$  “active ingredient” in the SCR bed. Conversely, it is argued, in coal-fired boilers, the sodium and potassium are, to a major extent, trapped within a glass-like fly-ash particle. It is widely known however that fly-ash particles from coal-fired boilers are in the form of tiny spheres (cenospheres) and that during the combustion of the coal, the particles are actually liquid and the spheres are formed as tiny bubbles by evolved gases trying to escape. Boilers are designed to cool the molten particles to a solid state such that they can be easily removed from boiler tubes. However, depending on the temperature of the fly ash and its chemical composition, some of the fly ash will deposit in various sections of the boiler. The deposits that form at the back-end of the boiler (on the economizer and air heater) are called “low-temperature deposits”. Low temperature deposits are usually characterized by low pH (highly acidic); many contain hydrated salts,

and for most bituminous coals are water-soluble. Therefore, coal-fired boilers do have fly-ash deposits in the economizer section of the boiler that are water-soluble. However, deactivation has not been found to occur. In addition, SCR systems have been installed on oil-fired boilers despite the relatively higher levels of water-soluble alkaline metals found in the fly ash from such boilers.

### Catalyst Plugging and Fouling Due To High Dust Loading and Depositing of "Sticky" Materials

Catalyst plugging and fouling involves the accumulation of dust that blocks access to the pores of the catalyst. It is argued that high dust loadings could plug or foul the SCR catalyst beds. However, the Solnhofen SCR system has operated at a dust loading of  $80 \text{ g/Nm}^3$ , a relatively high dust loading. The level of  $\text{NO}_x$  removal shows that high dust loading can be managed to avoid catalyst plugging and fouling while maintaining high levels of control. Related to the plugging and fouling issues, it is argued that "sticky deposits" in the pre-heater exhaust gas could foul and plug the SCR catalyst. Specifically, certain cement kiln operations could be prone to producing sticky deposits at exactly the temperature ranges in which SCR systems operate. Sticky deposits are a widespread problem occurring throughout the world on cement kiln induced draft (I.D.) fans. In many plants it is an extremely hard, layered, brick-like build-up that is associated with impingement of particulate at high velocity against the rotating parts of the fan impeller.

While the presence of alkali in the cement kiln system is a factor in the build-up, the mechanical aspect (namely, impact velocity) is more critical to the formation of build-up. The recommendation for avoiding build-up is to select a fan that minimizes the gas/dust velocity at the inlet of the fan rotor. Alternatives include using double inlet fans or using larger diameter, lower RPM (revolutions per minute) fans. Sticky deposits or build-up developing on other parts of the cement kiln system are not common. Thus, the sticky deposit problem appears to be related solely to the I.D. fan and is due to the high impact velocity of the dust particles mostly on the fan. This problem should not affect an SCR catalyst that is subject to comparatively low gas velocities in comparison to an I.D. fan.

For instance, gas velocities through an SCR system are typically less than 6.2 meters per second (1220 ft./min.), whereas peripheral gas speed at the kiln I.D. fan rotor inlet is approximately 15,000 ft./min. Possible problems relating to thermal sintering and catalyst

erosion have been addressed by advances in catalyst technology and proper system design. The problem of thermal sintering has been avoided by the incorporation of tungsten in the catalyst formulation and also by providing a bypass around the SCR system so that the catalyst is not exposed to high temperature excursions. Hardening the leading edge of the catalyst and also arranging the catalyst bed so that the airflow is parallel to the catalyst channels have addressed catalyst erosion.

### Reduction in NO<sub>x</sub> Control Efficiency Due to High Sulfur Levels

In general, operational histories of SCR installations at coal fired plants and the one cement plant indicates that NO<sub>x</sub> reductions are being achieved in a reliable manner. The reason that many of the older units are not achieving NO<sub>x</sub> removals greater than 80% is that the plants were not designed to achieve such high removal efficiencies. Great advances in the application of SCR technology have taken place. Present day SCR systems are typically achieving NO<sub>x</sub> reduction efficiencies of 90% or greater. It is argued that when only a low NO<sub>x</sub> reduction is required, the catalyst manufacturer can use a catalyst with a lower vanadium oxide content which will reduce the oxidation of SO<sub>2</sub> to SO<sub>3</sub> and thereby avoid the potential for CaSO<sub>4</sub> masking. However, the Solnhofen SCR system is achieving a high degree of NO<sub>x</sub> control.

It is argued that high SO<sub>3</sub> concentrations could lead to catalyst deactivation and other serious problems relating to SO<sub>2</sub> oxidation. A high SO<sub>3</sub> concentration (10 -20 ppmv) when coupled with the high calcium level in the cement kiln flue gas could purportedly cause deactivation of the SCR catalyst due to the masking effect of calcium sulfate (CaSO<sub>4</sub>). In addition, any SO<sub>3</sub> that does not react with the calcium could react with any unused NH<sub>3</sub> to form ammonium sulfate (AS) or ammonium bisulfate (ABS) that could cause fouling of downstream equipment. Sulfur in the raw mix can be in several forms, namely: calcium sulfate, magnesium sulfate, and sulfides such as pyrites or organically bound sulfur. Only the volatile sulfur compounds (namely: the sulfides and organically bound sulfur) are oxidized and released in the pre-heater as SO<sub>2</sub>. With respect to these concerns, the success of SCR systems at a number of coal-fired boilers show that SCR systems can be designed for high calcium and high sulfur flue gases and the SCR catalyst suppliers have indicated that CaSO<sub>4</sub> formation does not pose a major concern, as they assert that the SO<sub>3</sub> generated in the process is captured by the large amount of free lime in the gas stream. SO<sub>2</sub> oxidation by the catalyst will then have no negative impact on the amount of SO<sub>3</sub> formed

and subsequently captured. There is also concern regarding the possible formation of ammonium salts, which can form in SCR systems at temperatures below 580 to 590 F. However, this problem can be avoided by ensuring that the SCR inlet temperature is always 600F or greater.

#### Temperature Related Factors Leading to Lower NO<sub>x</sub> Removal Efficiencies

Several temperature-related factors have been identified as important to successful operation of an SCR system. These are: (1) an acceptable normal operating temperature; (2) an even temperature distribution; and (3) avoiding temperature extremes (which may lead to catalyst deactivation or sintering). Low temperatures can lead to lower NO<sub>x</sub> reduction efficiencies and/or higher catalyst activity (leading to possible SO<sub>2</sub> oxidation) and to possible ABS/AS formation in the catalyst pores. Concerns regarding a slightly lower than desirable inlet temperature, however, can be resolved by installing equipment to ensure a desired temperature of 600° F or greater going into the SCR system. Such control systems are commonly used on boiler air supply systems and economizer bypass ducts. Note that the SCR reactor should also have an automatically activated bypass duct around the SCR reactor, so that in the event of high temperature fluctuations (greater than approximately 800° F), automatically controlled dampers would send the hot flue gas to a reactor bypass duct, thus preventing any damage to the SCR catalyst. Therefore, temperature issues, whether involving normal operating temperatures or temperature fluctuations, should be correctable with simple process reconfigurations.

#### NO<sub>x</sub> Concentration Variability and NH<sub>3</sub> Slip

It has been argued that unlike a coal-boiler SCR application, an SCR system applied to a cement kiln will be faced with highly variable inlet NO<sub>x</sub> loadings and that elevated NH<sub>3</sub> slip levels are possible, which, coupled with possibly higher sulfur oxide levels, represent a serious risk. However, in an SCR system, the injected NH<sub>3</sub> is adsorbed onto the surface of the catalyst. Thus, there is a reservoir of unused NH<sub>3</sub> on the surface of the catalyst that is available to handle sudden peaks in inlet NO<sub>x</sub> concentrations and thereby enable SCR systems to control fluctuating levels of NO<sub>x</sub>. SCR systems do not have to overfeed ammonia to handle surges in inlet NO<sub>x</sub> concentration and so tend to have very low NH<sub>3</sub> slip levels.

Coal-fired boilers have been operating SCR systems successfully for years despite considerable NO<sub>x</sub> fluctuations in their flue gases. SCR suppliers typically guarantee a NH<sub>3</sub> slip of no more than 2 ppmv for any coal-fired boiler SCR application. In addition, the Solnhofen plant is a cement kiln with all of the inherent variability and has nevertheless been achieving a high degree of NO<sub>x</sub> control with a low ammonia slip level. Data at Solnhofen indicates that the SCR inlet NO<sub>x</sub> concentration varies considerably, from less than 1000 mg/Nm<sup>3</sup> to 2030 mg/Nm<sup>3</sup> while the outlet NO<sub>x</sub> concentration varies from approximately 300 to 726 mg/Nm<sup>3</sup>, but maintains an average outlet NO<sub>x</sub> concentration of less than 500 mg/Nm<sup>3</sup>. At these variable conditions, however, NH<sub>3</sub> slip has been maintained in the 1-2 ppmv range.

#### Undesirable Byproduct Formation in the SCR Causing Adverse Effects on Downstream Equipment

Concerns have been raised regarding the generation and release of SO<sub>3</sub> that could cause corrosion of downstream equipment, or that the SO<sub>3</sub> may react with unused NH<sub>3</sub> to form ammonium salts (ABS and AS), which could plug or corrode downstream equipment. In addition it is argued that ammonium salts could increase condensable particulate matter levels, making it difficult for a facility to meet its particulate matter emission limit. In SCR systems with SO<sub>2</sub>, NH<sub>3</sub> and moisture present, ammonium salts will form at temperatures below 580-590° F. The best way to prevent their formation is to continuously control the SCR inlet temperature such that it is always 600° F or greater. Regarding the possible release of SO<sub>3</sub>, catalyst manufacturers report that the SO<sub>3</sub> gas is totally captured by conversion to particulate calcium sulfates and sulfites as it is contacted by free lime upstream, within, and downstream of the SCR catalyst. Thus, the formation of undesirable byproducts should be inherently controlled by the free lime in the system and can be further controlled by controlling the SCR inlet temperature.

#### 4.1.1.3 General Conclusions

The experience of coal-fired power plants and the one cement plant with SCR offers the following lessons. First, the success of coal-fired power plants shows that catalyst deactivation from alkali poisoning is not expected to be a significant problem for cement kiln applications. Second, the success of SCR systems on a number of coal-fired boilers reveals that even when

[REDACTED]

#### 4.1.1.4 Site-Specific Analyses

The follow sub-sections are specific to TXI, Holcim, and Ash Grove. In what follows, the additional NO<sub>x</sub> associated with gas re-heat, if required, has not been added, as the level of additional NO<sub>x</sub> would be below 10 tons per year and 85% of that would be removed.

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]





#### 4.1.2 Selective Noncatalytic Reduction (SNCR)

This control technique relies on the reduction of NO<sub>x</sub> in exhaust gases by ammonia or urea, without using any catalyst, with the same reactions as in the case of the SCR process. Because of low capital and maintenance costs associated with this technology vis-à-vis other end-of-pipe technologies like SCR and oxidative methods, it is likely to command attention in the near future within the industry. This approach combines a low initial capital cost and avoids the problem related to catalyst fouling and replacement associated with SCR technology. SNCR requires injection of the reagents in the kiln at a temperature between 870 to 1,090°C (1,600 to 2,000°F). In principle, any of a number of nitrogen compounds may be used as SNCR reagents (e.g., cyanuric acid, pyridine, and ammonium acetate). However, for reasons of cost, safety, simplicity, and by-product formation, ammonia and urea have been used in most of the SNCR applications. The selection of reagents is process and temperature specific. At higher temperatures, urea decomposes to produce ammonia, which is responsible for NO<sub>x</sub> reduction. In cement kiln applications, ammonia typically has performed best as the reducing reagent.

Because no catalyst is used to increase the reaction rate, the temperature window is critical for conducting this reaction. At higher temperatures, the rate of a competing reaction for the direct oxidation of ammonia which actually forms additional NO<sub>x</sub> becomes significant. At lower temperatures, the rates of NO<sub>x</sub> reduction reactions become too slow resulting in too much unreacted ammonia being released to the atmosphere (i.e., ammonia slip). The effective temperature window range can be lowered to about 700°C (1,300°F) by the addition of hydrogen along with the reducing agent.<sup>51</sup> Addition of hydrogen can promote SCNR reactions (enhanced SNCR), but high levels of sulfur oxides may interfere with this reaction. Nalco Fuel Tech, the producer of the SNCR technology NO<sub>x</sub>OUT<sup>®</sup>, has also introduced NO<sub>x</sub>OUT<sup>®</sup> PLUS which is said to broaden the operating temperature window and to reduce ammonia slip and CO and NO<sub>2</sub> formation.

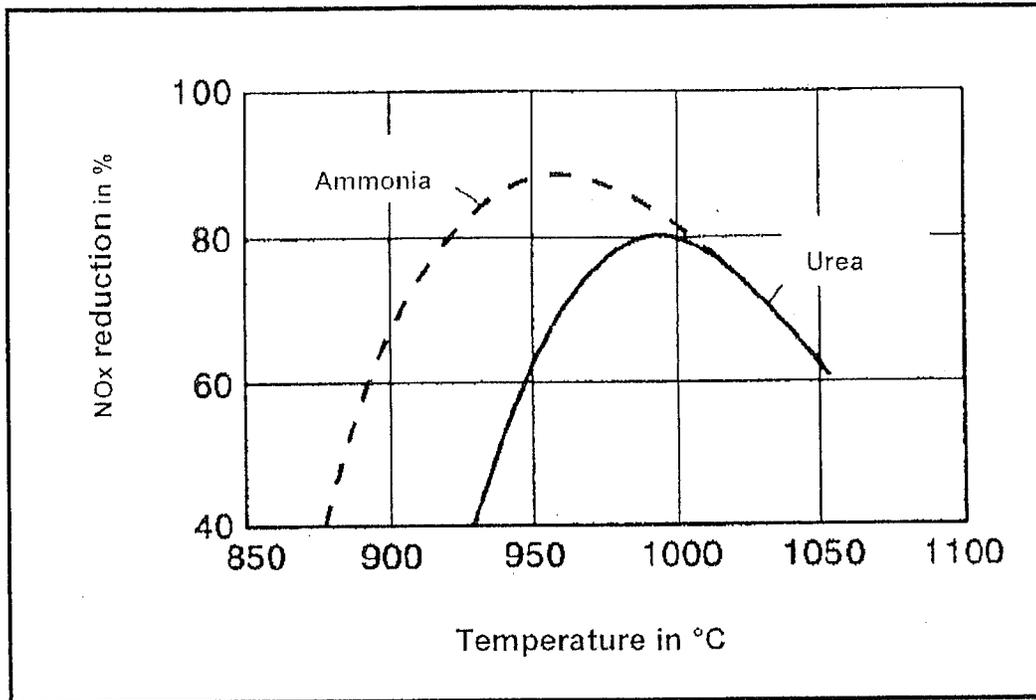
In a conventional long kiln, the appropriate temperature window is in the middle of a kiln. Because of the rotating nature of a long kiln, continuous injection of ammonia- or urea-based reagents has presently not been considered possible. The technology developed for mid-kiln firing of containerized solid fuels allows injection of a certain amount of material once during the kiln revolution. Injection of solid ammonium or urea salts in this manner has not been

used because of the rapid decomposition of such salts. Therefore, SNCR technology has not been applicable to date for long dry or wet kilns. However, Fuel Tech Inc. is currently evaluating dry dust or pellet injection methods for direct injection into kilns.<sup>52</sup> The possibility of injection of ammonia or solid urea inside automobile tires that are injected into the kiln has still to be evaluated. With the known ability of mixing air fans to induce turbulence in the system, mixing combustion gases containing NOx with ammonia, either generated from urea or from ammonium salts, may also offer possibilities. Chain gas temperatures generally are in the range of 1500-1600°F (815-871°C). The mid-kiln injection systems are usually down kiln somewhat from this point, which means that they will be higher than this in gas temperature. There is a good possibility that the correct temperature range can be achieved if mixing is induced and volatilization or decomposition of the urea can be delayed by inserting it in a solid form in a carrier such as a tire. This option needs to be explored. It will clearly be necessary to mix the NOx with the reagent before the latter has an opportunity for decomposition. Inducing turbulence is presently conceived as a key element in this strategy.

In preheater/precalciner type cement kilns, the temperatures at the cooler end of the rotating kiln, in the riser duct, and in the lower section of the cyclone preheater tower are likely to be in the temperature window appropriate for SNCR. Such kilns are therefore good candidates for application of SNCR technology.

The NOx reduction efficiency of SNCR depends upon the temperature, oxygen, carbon monoxide, and residence time, as well as the ammonia and NOx concentrations in the flue gas. Injection of ammonia at a  $\text{NH}_3:3\text{NOx}$  proportion of 1 to 1.5 will reduce NOx emissions between 60 to 80 percent. Using a molar ratio of 0.5 will give NOx reductions of approximately 40 percent.<sup>47</sup> Work done by the German equipment supplier Polysius<sup>48</sup> has shown that the optimum temperature for reduction of NOx by ammonia is about 950°C (1,740°F), while for urea, the temperature increases to about 1,000°C (1,830°F). Ammonia is also somewhat more efficient, as shown in Figure 4-1.1. below.

Figure 4-1.1. Dependence of NO<sub>x</sub> reduction on temperature for ammonia and urea.



Actual SNCR results with ammonia (19% aqueous solution) at one US plant employing a calciner are given in Table 4-1.3. It can be seen that the reduction was remarkably good, considering that ammonia was never added at greater than a stoichiometric equivalent to NO<sub>x</sub>. Due in part to the fact that no excess ammonia was introduced into the system, no ammonia slip was demonstrated. The ammonia emissions were undetectable.

Table 4-1.3. Summary of Test Results for SNCR Test

Run #	Molar Ratio	NO <sub>x</sub> Reduction	Average NO <sub>x</sub> Before	Average NO <sub>x</sub> During SNCR
	NH <sub>3</sub> :NO	%	lb/hr	lb/hr
1	0.918	65.49%	325.47	112.31
2	0.533	36.71%	322.90	204.35
3	0.425	44.93%	345.52	190.27
4	0.331	16.90%	282.70	234.91
5	0.465	15.49%	290.18	245.25
6	0.286	12.95%	269.35	234.47
7	0.534	45.06%	269.35	147.97
8	0.552	31.91%	281.71	191.81
Long term	0.368	47.78%	329.83	172.24

These results were very good. The temperature and oxygen concentrations were nearly optimum for the SNCR system. The carbon monoxide levels were somewhat higher than has been considered optimum, but according to Brouwer et al.<sup>49</sup>, CO may promote the reaction at the lower end of the temperature range, because of the temperature increase due to the heat given off by the reaction of CO with OH radicals. Among other SNCR tests recently performed, tests have been carried out at a preheater plant and four calciner plants. Some of these tests were carried out using ammonia, and others using urea. At the preheater plant, both ammonia and urea were tested, injecting the reagents into the kiln riser duct. Ammonia proved to be considerably more effective than urea, in keeping with the Polysius plot given above.

Despite these successes, the reagent consumption can be significantly higher with greater ammonia slip in SNCR systems as compared to SCR systems. Operating experience has identified several concerns with both ammonia and urea-based SNCR processes. The most frequently reported is the buildup of ammonium bisulfite or bisulfate scale which is significant for sulfur-containing fuels. SNCR processes also appear to convert some NO<sub>x</sub> to N<sub>2</sub>O.<sup>53</sup> The rate of N<sub>2</sub>O formation is a weak function of both the reactant and the NO concentration. However, N<sub>2</sub>O formation seems to be inherently more prevalent in systems using urea than those using ammonia.<sup>54</sup>

The NO<sub>x</sub> destruction efficiency also depends upon the flue gas residence time in the appropriate temperature window. Unlike an SCR system where the reaction temperature is controlled in a dedicated reactor, an SNCR system relies on the existing gas temperature profile to provide an adequate residence time for a desired NO<sub>x</sub> destruction. Maximum achievable NO<sub>x</sub> reduction in a cement kiln may thus depend upon the gas temperature profile.

The SNCR process was demonstrated in Europe in a preheater type kiln. Both ammonia- and urea-based reagents were investigated. The reagents were injected in the gas duct as shown in Figure 4-1.2.<sup>55</sup> With a molar ratio of reagent to NO<sub>2</sub> of 1:1, about 70 percent reduction in NO<sub>x</sub> emissions was observed with ammonia-based reagent and about 35 percent NO<sub>x</sub> reduction was obtained with urea.<sup>55</sup> With this reagent ratio, there was no major increase in ammonia emissions in exhaust gases over the background level of ammonia emissions generated by kiln feed material. Greater NO<sub>x</sub> reductions were observed with more than stoichiometric amount of reagent, although there was increasing ammonia 'slip' in the exhaust gases.



Albert Scheuer, of the Research Institute of the Cement Industry in Düsseldorf, Germany, reported on 148 SNCR trials carried out on five different kilns. Three kiln systems had cyclone preheaters and two had grate preheaters. A 25% molar concentration of  $\text{NH}_3$  in water was the main reagent tested, with some additional testing done with ammonium sulfate solutions and with urea solutions. Scheuer reported that NO reductions with the  $\text{NH}_3$ /water solution ranged from 15% to 75% and that temperature appeared to be one of the main determinants of the effectiveness of the reagent. Maximum NO reduction occurred at  $980^\circ\text{C}$  ( $1796^\circ\text{F}$ ).  $\text{NH}_3$  escape occurred when temperatures were less than  $900^\circ\text{C}$  ( $1652^\circ\text{F}$ ) and when the NO concentration fluctuated.  $\text{NH}_3$  utilization decreased significantly with increasing  $\text{NH}_3$ :NO molar ratio and with decreasing NO concentration in the exhaust gases, indicating that SNCR appears to be a less promising methodology at low NO emissions rates.<sup>13,56</sup>

SNCR is presently being used in 18 cement kilns in Europe. Fifteen kilns are in Germany, two are in Sweden, and one is in Switzerland. These kilns are either suspension preheater kilns or precalciner kilns. The most common reagent used is 25% ammonia water.<sup>1</sup> NOx reduction rates vary from 10 to 50 percent with  $\text{NH}_3$ /NO<sub>2</sub> molar ratio of 0.5 to 0.9, NOx emissions at these reductions are 2.4 to 3.8 lb/ton of clinker. Two dry process cyclone preheater/precalciner kilns in Sweden achieve 80 to 85 percent reduction (1.0 lb/ton of clinker) at a  $\text{NH}_3$ /NO<sub>2</sub> molar ratio of 1.0 to 1.1.<sup>1</sup> One reason for the remarkable results in these kilns is the use of multiple injection points (12 in all) that ensure long enough retention time for the reaction to take place. The optimum temperature is said to be  $900$ - $1,100^\circ\text{C}$  ( $1,650$ - $2,010^\circ\text{F}$ ) in good agreement with other authors. These results suggest that some SNCR tests may have been carried out under lower-than-optimum temperatures.

F. L. Smidth and Company tested SNCR on a preheater/precalciner kiln.<sup>3</sup> Ammonia was injected into the lower cyclone of the preheater tower where temperatures are favorable for the

a  $\text{NH}_3/\text{NO}_2$  molar ratio of 1.0 to 1.1.<sup>1</sup> One reason for the remarkable results in these kilns is the use of multiple injection points (12 in all) that ensure long enough retention time for the reaction to take place. The optimum temperature is said to be 900-1,100°C (1,650-2,010°F) in good agreement with other authors. These results suggest that some SNCR tests may have been carried out under lower-than-optimum temperatures.

F. L. Smidth and Company tested SNCR on a preheater/precalciner kiln.<sup>3</sup> Ammonia was injected into the lower cyclone of the preheater tower where temperatures are favorable for the reduction reactions to occur. NOx emissions reductions during this experiment averaged 40 percent, but NOx reductions of over 90 percent were obtained when the ammonia injection rate was 10 to 20 percent in excess of stoichiometric.

In North America, SNCR has been tested on at least nine kilns. In some of the earlier work, NOxOUT<sup>®</sup> technology was tested under ten different operating conditions at a preheater/precalciner kiln in Seattle, Washington during October 1993. NOx emissions were effectively reduced from 3.5 to 6.0 lb NOx/ton of clinker to less than 1 lb NOx/ton of clinker.<sup>57</sup> Another test of NOxOUT<sup>®</sup> technology was conducted during October 1998 in Davenport, Iowa. This test found NOx reductions of 10 to 20 percent from a baseline of approximately 350 pounds NOx/hour, although higher levels of reduction are thought to be achievable when the baseline is higher.<sup>58</sup> An evaluation of NOxOUT<sup>®</sup> technology was conducted in 1994 for a long dry kiln in Southern California, but the study concluded that application of the NOxOUT<sup>®</sup> technology at the subject kiln was technically infeasible.<sup>60</sup> The details of this testing are not known.

**Biosolids Injection (BSI).** The Mitsubishi Cement Corporation's Cushenbury plant in Lucerne Valley, CA, uses biosolids injection technology (BSI) to achieve SNCR of NOx. The BSI process was developed by the Cement Industry Environmental Consortium (CIEC). The founding participants in the CIEC are Southdown, Inc., Riverside Cement Company, Mitsubishi Cement Corporation, California Department of Commerce (now Trade & Commerce Agency), and the San Bernardino County Air Pollution Control District (now Mojave Desert Air Quality Management District). This technology is covered under U.S. Patent No. 5,586,510 issued December 24, 1996.<sup>13</sup>

The basic principle is to utilize the naturally occurring ammonia content of dewatered biosolids as the reagent. The dewatered biosolids are obtained from wastewater treatment plants.

Since the biosolids are mechanically dewatered without heat input, the solids content varies between 16 and 30 percent (moisture content of 84 to 70%). Depending on the moisture content, the net Btu content (after evaporating the moisture) of the biosolids varies between -750 and +2200 Btu/lb. Since the biosolids heating value is relatively small, the net effect on kiln fuel combustion is expected to be small.<sup>61</sup>

The same conditions that affect NO<sub>x</sub> reduction performance in SNCR affect BSI performance: temperature (927°C / 1,700°F is optimal), residence time (> 0.5 seconds is desirable), inlet NO<sub>x</sub> concentration, inlet CO concentration, and NH<sub>3</sub>/NO<sub>x</sub> molar ratio. Another key issue is mixing effectiveness, which affects the extent of contact and, hence, reaction between NH<sub>3</sub> and NO<sub>x</sub>. The BSI technology is applicable to preheater/precalciner kilns because the temperature window for BSI (927°C / 1700°F) occurs in a location where it is feasible to inject biosolids.<sup>61</sup>

The biosolids are injected into the mixing chamber where the flue gas stream leaving the kiln and precalciner mix. The mixing chamber offers the benefits of good residence time in the appropriate temperature window (927°C / 1700°F) and high mixing effectiveness.<sup>61</sup>

At the Cushenbury plant, BSI underwent long-term testing and eventual adoption in 1994 and 1995. The kiln is fueled with coal (85 percent) and tires (15 percent). The plant began using tire-derived fuel (TDF) in mid-1993, so it is difficult to isolate the effects of TDF or BSI on NO<sub>x</sub> emissions. The company estimates that the use of TDF reduces NO<sub>x</sub> emissions from the kiln by 30 to 40 percent.<sup>62</sup> Before the SNCR technology was adopted, the company estimated NO<sub>x</sub> emissions averaged 2.4 pounds/ton of clinker; afterwards, the average fell to 1.2 lb/ton of clinker, a 50 percent reduction. The effects of BSI on CO emissions varies between a large increase and no change at all, but in all cases it has remained below 500 ppm. BSI has not caused any significant changes in either metal HAP or organic HAP emissions. Using the SNCR biosolids technology, the kiln also reduced its fuel consumption by 5 percent.<sup>61</sup>

**NO<sub>x</sub>OUT<sup>®</sup>**. An SNCR process using aqueous urea was developed by Electric Power Research Institute (EPRI) and is now marketed by Nalco Fuel Tech, Inc., under the trade name of NO<sub>x</sub>OUT<sup>®</sup>. In the urea reaction with NO, one mole of urea reacts with two moles of NO to complete the reaction to nitrogen, carbon dioxide and water. Normalized Stoichiometric Ratio (NSR) is used to express the reagent feed rate relative to the reaction stoichiometry. The NSR takes into account the 2:1 mole ratio of the NO:urea reaction as the “normalized” ratio. If 50% of the urea reacts to reduce NO to nitrogen, reduction of 100% NO<sub>x</sub> occurs at NSR=2; 80%

window.<sup>63</sup> One modification of the urea-based SNCR system is the addition of methanol injection downstream of the urea injection point to improve overall NOx removal. Nalco also introduced an improved NOxOUT<sup>®</sup> PLUS, which is said to further broaden the operating temperature window and to reduce ammonia slip and CO and NO<sub>2</sub> formation.

[REDACTED]

NOxOUT<sup>®</sup> was tested for one week in October of 1998 on the preheater/precalciner kiln at the Lafarge-Davenport Plant. Operating conditions were unstable most of that week and only five hours of testing produced results that could provide a reasonable indication of what may be achievable with NOxOUT<sup>®</sup>. The baseline NOx rate was approximately 350 lbs NOx/hour. Using NOxOUT<sup>®</sup>, emission reductions of 10 to 20 percent were achieved.<sup>59</sup> Operating conditions such as residence time, temperature, and the use of coal at this kiln were contrasted to conditions at the Ash Grove kiln that achieved greater reductions to explain why NOxOUT<sup>®</sup> may achieve better results on some kilns than others.

Nalco also has conducted a number of demonstrations and commercial projects in preheater/precalciner cement kilns. The fuels have included coal, and coal in combination with No. 6 heavy fuel oil, waste oil, and/or tire chips. The clinker capacity on these kilns ranged from approximately 1000 metric tons to 3200 metric tons per day. The results of two tests with average NOx reductions of approximately 50%, were featured in a recent report (see Table 4-1.4).<sup>52</sup>

**Table 4-1.4. Emissions Reductions From Two Kilns Using NOxOUT<sup>®</sup>**

	<b>Baseline NOx Emissions (ppm)</b>	<b>NOx Emissions with NOxOUT<sup>®</sup> (ppm)</b>	<b>Percent Reduction (%)</b>
Kiln A, Test 1	412	203	51

approximately 1000 metric tons to 3200 metric tons per day. The results of two tests with average NOx reductions of approximately 50%, were featured in a recent report (see Table 4-1.4).<sup>52</sup>

**Table 4-1.4. Emissions Reductions From Two Kilns Using NOxOUT®**

	<b>Baseline NOx Emissions (ppm)</b>	<b>NOx Emissions with NOxOUT® (ppm)</b>	<b>Percent Reduction (%)</b>
Kiln A, Test 1	412	203	51
Kiln A, Test 2	389	185	53
Kiln B	525	284	46



[REDACTED]



## **4.2 Combustion Optimization**

This section of the report is taken from the EPA 2000 Report and is included, with minor editing by the ERG Team. This information is included to provide the Texas environmental communities with the comprehensive background information necessary to understand the parameters that dictate NO<sub>x</sub> control options at cement kilns. Combustion optimization is largely in place in the Ellis County kilns, with the exception of the TXI wet kilns that are awaiting permits for mid-kiln firing to comply with the requirements of TAC Chapter 117.

Combustion optimization is generally applicable to all types of kilns and is an efficient way to reduce the formation of thermal NO<sub>x</sub>. The combustion modifications discussed in this section focus on staging the combustion to minimize combustion at the maximum temperatures. This can be accomplished by modifying the way oxygen or fuel is provided for combustion. For the purposes of this report, the level of emissions reduction contained in TAC Chapter 117 is the level associated with combustion and process optimization. As such, the techniques below have largely been already required and implemented at the Ellis County cement plants. However, the differing performance of the kilns may indicate that more combustion and process optimization could be implemented as part of the effort to reach higher NO<sub>x</sub> emissions reductions levels.

### **4.2.1 Staged Combustion of Air**

Staging of combustion air allows combustion of fuel to proceed in two distinct zones. In the first zone, the initial combustion is conducted in a fuel-rich, oxygen-poor flame zone. This zone provides the high temperatures necessary for completion of the clinkering reactions, but the lack of available oxygen minimizes the formation of thermal and fuel NO<sub>x</sub>. The lack of sufficient oxygen leads to only partial combustion of the fuel.

In the second, fuel-lean zone, additional (secondary) combustion air is added to complete the combustion process. However, the temperature in this second zone is much lower than the first zone because of mixing with the cooler secondary air, so the formation of NO<sub>x</sub> is minimized in spite of the excess available oxygen. This staged approach can be used for combustion of all fossil fuels. Staged combustion is typically achieved by using only a part of the combustion air (primary air) for fuel injection in the flame zone, with remaining secondary air being injected in the subsequent cooler zone.

For effective staging of combustion air to reduce NO<sub>x</sub> emissions, cement plants must have indirect-fired kilns. In a direct-fired cement kiln, air used for conveying pulverized coal from a coal mill, i.e., primary air, is typically 17 to 20 percent of the total combustion air. The amount of primary air may be reduced by separating the coal mill air from coal. A cement kiln using less than 10 percent of primary air is an indirect-fired kiln. Conversion of a direct-fired kiln to an indirect-fired kiln involves adding particle separation equipment such as a cyclone or a baghouse and a fan to provide the primary air used to transport the powdered coal from storage to the kiln. An indirect-firing system increases overall energy efficiency by allowing a greater proportion of hot clinker cooler air to be used as secondary combustion air.

#### **4.2.2 Flue Gas Recirculation**

In addition to changing the combustion air distribution, the oxygen content of the primary air may be reduced to produce a fuel-rich combustion zone by recycling a portion of the flue gas into the primary combustion zone.<sup>15</sup> The recycled flue gas may be premixed with the primary combustion air or may be injected directly into the flame zone. Direct injection allows more precise control of the amount and location of the flue gas recirculation (FGR). In order for FGR to reduce NO<sub>x</sub> formation, recycled flue gas must enter the flame zone. The FGR also reduces the peak flame temperature by heating the inert combustion products contained in the recycled flue gas.

The use of FGR may not be a viable method of reducing NO<sub>x</sub> in a full-size cement kiln burning zone. FGR's effectiveness relies on cooling the flame and generating an oxygen-deficient (reducing) atmosphere for combustion to reduce NO<sub>x</sub> formation, conditions that may not be compatible with cement kiln operation. High flame temperature and an oxidizing atmosphere are process requirements to produce a quality clinker product. A cement kiln differs from a utility boiler and other combustion devices because minimum temperatures and an oxidizing atmosphere are required to initiate chemical reactions in a cement kiln in addition to the providing the required heat (Btu/ton of clinker). Reduced flame temperatures and reducing conditions in the burning zone of a cement kiln may not be compatible with the production of cement clinker.<sup>13</sup>

Coupling a low-NO<sub>x</sub> step burner with flue gas recirculation has been shown to reduce NO<sub>x</sub> emissions further in a cement kiln.<sup>16</sup> The additional NO<sub>x</sub> reduction attributable to FGR was

estimated to be about 15 to 38 percent depending upon the proportion of FGR used.<sup>16</sup>

Incorporation of FGR in a cement kiln also results in somewhat increased power consumption and reduced kiln output.

#### 4.2.3 Low-NOx Burners

Some cement kiln burners, specifically marketed as low-NOx, burners, typically use 5 to 7 percent primary air<sup>17,18</sup> and thus can be used only on indirect-fired kiln systems. Low-NOx burners can be installed on any type of kiln. Low-NOx burners are designed to reduce flame turbulence, delay fuel/air mixing, and establish fuel-rich zones for initial combustion. The longer, less intense flames resulting from the staged combustion lower flame temperatures and reduce thermal NOx formation. Some of the burner designs produce a low pressure zone at the burner center by injecting fuel at high velocities along the burner edges. Such a low pressure zone, as shown in Figure 4-2,<sup>17</sup> tends to recirculate hot combustion gas which is retrieved through an internal reverse flow zone around the extension of the burner centerline. The recirculated combustion gas is deficient in oxygen, thus producing a similar effect as FGR. Combustion of the fuel in the first stage thus takes place in an oxygen-deficient zone before the fuel is diluted in the secondary air. Installing such a burner reduces NOx emissions from the kiln-burning zone by up to 30 percent.<sup>17,19,20</sup>

Low-NOx burners have been used by the cement industry for twenty years.<sup>21</sup> Many suppliers offer low-NOx burners and most of these systems focus on lowering the NOx formation in the calciner by air or fuel staging, by reburning, or by high temperature combustion.<sup>22</sup> Test data from several different low-NOx burners are now available. Thomsen Jensen, and Schomburg reported on tests of a F.L. Smidth in-line calciner low-NOx system in a preheater/precalciner kiln where different percentages of coal were added to the reduction zone of the precalciner (the remaining coal was added to the oxidizing zone).<sup>22</sup> When 100 percent of the coal was added to the reduction zone of the precalciner, the NOx content at the preheater exit was reduced by 44 percent relative to when zero coal was added (see Table 4-4.1).

**Table 4-4.1. NOx emissions from a precalciner equipped  
With a low-NOx burner**

Percent coal added to reduction zone <sup>a</sup> (lb nox/ton of clinker)	Nox emissions <sup>b</sup> lb nox/ton of clinker)	Percent reduction <sup>b</sup> (%)
0	2.8	-
50	1.9	31
100	1.6	44

<sup>A</sup> the remaining percentage of the coal was added to the oxidizing zone.

<sup>B</sup> emission measurements were taken at the preheater exit.

<sup>C</sup> percent reductions are relative to emissions when zero percent of the coal was added; the original measurements were in kg nox/ton of clinker to the hundredth place - the percent reductions were calculated using the original measurements, which results in slightly different values than when lb nox/ton of clinker are used.

Steinbiß, Bauer, and Breidenstein reported emissions changes for five kilns before and after the installation of Pyro-Jet low-NOx burners (see Table 4-4.2.).<sup>21</sup> The emission reductions ranged from 15 to 33 percent. Information on kiln-type was not provided.

**Table 4-4.2. NOx Emissions Before And After Installation  
Of Pyro-Jet Low-NOx Burners**

Kiln	Before Installation (ppm)	After Installation (ppm)	Percent Reduction (%)
A	970	650	33
B	not given	not given	30
C	650	460	29
D	900	730	19
E	not given	not given	15

There are two new data sources on emissions reductions from the use of Rotaflam<sup>®</sup> low-NOx burners. The Pillard Combustion Equipment and Control Systems published data on four kilns, comparing NOx emissions with a 3 channel burner to emissions when a Rotaflam<sup>®</sup> burner was used (see Table 4-4.3.)<sup>23</sup> The emission reductions ranged from 23 to 47 percent. Information on kiln-type was not provided.

**Table 4-4.3. NOx Emissions With 3 Channel And Rotaflam<sup>®</sup> Low-NOx Burners**

Kiln	With 3 Channel Burner (ppm)	With Rotaflam <sup>®</sup> Burner (ppm)	Percent Reduction (%)
A	774	409	47
B	865	664	23
C	484	350	28
D	487	336	31

Emissions data are also available before and after a Rotaflam<sup>®</sup> low-NOx burner was installed on a long-wet kiln (see Table 4-4.4.).<sup>24</sup> The average emissions decreased 14 percent.

**Table 4-4.4. Emissions Before And After Installation Of A Rotaflam<sup>®</sup> Burner On A Wet Kiln**

Year	Average Emissions(lb NOx/ton of clinker)	Percent Reduction <sup>a</sup> (%)
1990	277	-
1992 <sup>b</sup>	288	-
1993	269	-
1994	275	-
1995 (Rotaflam <sup>®</sup> installed)	239	14

<sup>a</sup> Percent reduction is relative to the 1990, 1992-1994 average NOx emissions, 277.25 lb NOx/h.

<sup>b</sup> 1991 data were not provided.

The Fuller Company low NOx In-Line Calciner was installed in an RMC Lonestar kiln which reported 30-40 percent reductions in the amount of thermally formed NOx after installation.<sup>25</sup>

In January 2000, the PCA and PCA provided results of a survey of cement facilities where the respondents indicated 14% of the operating U.S. kilns (22 kilns) have already installed a low-NOx burner (81% of the facilities representing 81% of the operating U.S. kilns responded to the survey). The remaining 139 kilns that are represented by the survey have not installed low-NOx burners.<sup>26,27</sup>

#### 4.2.4 Staged Combustion of Fuel

In conventional long (wet or dry) rotary kilns, all heat required for the cement-making process is supplied in the primary kiln burning zone, where the combustion occurs at the hottest temperature in the kiln. In the cement-making process, the preheating and calcination of the raw materials requires a large amount of heat but are typically at a temperature of 600 to 900 °C (1,100 to 1,650 °F) which is much lower than the kiln's clinker-burning temperature of 1,200 to 1480 °C (2,200 to 2,700 °F).<sup>28</sup> In the secondary combustion method, part of the fuel is burned at a much lower temperature in a secondary firing zone to complete the preheating and calcination of the raw materials.

#### 4.2.5 Preheater/Precalciner and Tire Derived Fuel

This concept of a secondary firing zone is the basis of the preheater/precalciner cement kiln design. Almost all new cement kilns have a preheater/precalciner-type designs. In the preheater kilns, the primary emphasis is on efficient heat recovery from kiln exhaust gases (see Figure 4-4.1).<sup>29</sup> However, up to 15 to 20 percent of the fuel may be fired in the riser duct in preheater designs.<sup>29</sup>

Precalciner systems typically employ a tower of four-stage cyclones for efficient gas-solids contact which improves the energy efficiency of the overall process (see Figure 4-4.2).<sup>29</sup> In a typical precalciner kiln almost 40 to 50 percent of the fuel is burned at a lower (calcination) temperature which reduces the thermal NO<sub>x</sub> formation considerably.

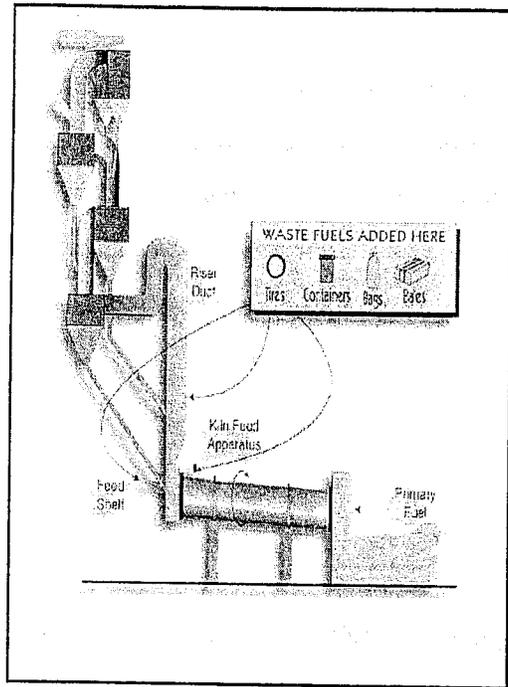


Figure 5-2. Schematic of preheater.<sup>28</sup>

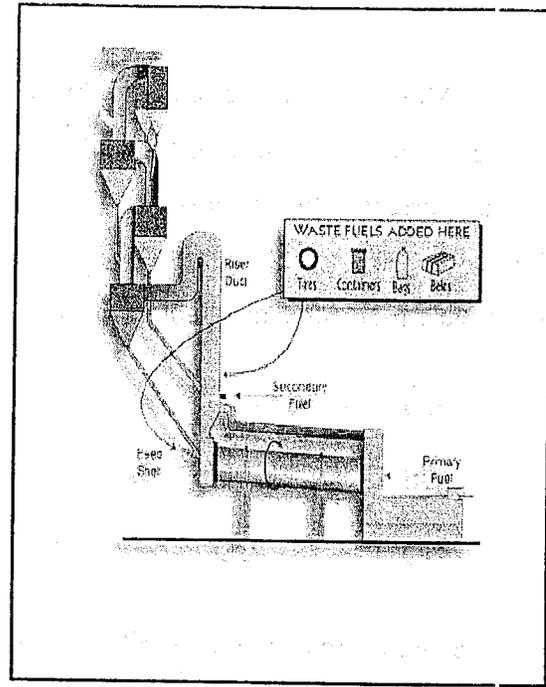


Figure 5-3. Schematic of precalciner.<sup>29</sup>

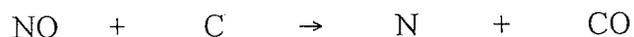
Figure 4-4.1.. Schematic of Preheater.<sup>29</sup> Figure 4-4.2. Schematic of precalciner<sup>29</sup>

Tire-derived fuel can also be added to the feed end of a preheater or precalciner kiln. The Mitsubishi Cement Company's Cushenbury Plant in Lucerne Valley, CA began using whole waste tires as a fuel supplement in 1993. The waste tires are delivered in enclosed container trucks and dumped into the plant's automated handling system. A live bottom hopper and singulator place the waste tires on a conveyor system. This conveyor system transports the tires to the feed end of the kiln and drops the tire into an airlock system that allows the waste tire to fall onto the feed plate inside the kiln at a rate of five to six tires per minute.

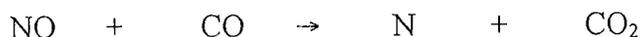
Currently, 8,000 to 9,000 tires are burned per day, totaling about 13 percent of the fuel. Tires have a fuel content of approximately 14,000 Btu/lb and a sulfur content that is roughly the same as the coal that would be used. The steel belting in the waste tires supplements the iron requirements and approximately 2 percent of the iron in the final product comes from the tires. The addition of waste tires reduces NO<sub>x</sub> emissions from the kiln by 30 to 40 percent, and there is no significant change in toxic, hydrocarbon, or metal emissions.<sup>30,31,32</sup>

#### 4.2.6 Low- NO<sub>x</sub> Precalciners

Most of the major cement kiln suppliers are now offering “low NO<sub>x</sub>” precalciner designs for new kilns. These designs typically inject a portion of the fuel into the feed end of the kiln, countercurrent to the exhaust gas flow, as illustrated in Figure 5-4 (*where is this?*).<sup>33</sup> This fuel is burned in a substoichiometric O<sub>2</sub> environment to create a strongly reducing atmosphere (relatively high concentrations of CO) by following the simplified reactions:



and



This reducing atmosphere inhibits the formation of fuel NO<sub>x</sub> and destroys a portion of the NO<sub>x</sub> formed in the kiln burning zone. In some designs, additional fuel is then added, again with insufficient O<sub>2</sub> for complete combustion, to create another reducing zone. Several precalciner kilns in the US have recently been retrofitted with these “low NO<sub>x</sub>” precalciners and preliminary information indicates a noticeable reduction in NO<sub>x</sub> per ton of clinker.<sup>13</sup> Up to 46 percent reduction of NO<sub>x</sub> emissions have been reported without causing excessive coating difficulties in the kiln.<sup>33</sup>

Nitrogen present in the fuel may also participate in the reduction of NO<sub>x</sub>. The primary NO<sub>x</sub> formation mechanism in the secondary firing is the fuel NO<sub>x</sub> formation which depends upon the nitrogen content of the fuel used. In order for the above reactions to proceed at reasonable rates the temperature in the reduction zone should be maintained between 1000 and 1200°C (1830 to 2190°F). These temperatures may lead to coating difficulties, particularly if the fuel used is coal with high ash content.<sup>34</sup>

It is not possible to use “staged combustion” on preheater kilns that are firing fuel in the riser since in staged combustion it is necessary to add the fuel in an oxygen deficient atmosphere and then supply additional combustion air to fully combust the fuel. Preheater kilns do not have tertiary air ducts to supply the additional combustion air. The air for combustion of the secondary fuel must come through the kiln, which precludes introducing the secondary fuel into an atmosphere with insufficient oxygen for complete combustion.<sup>13</sup>