

# **SNCR NO<sub>x</sub> at U.S. Cement Plants. Is SCR Close Behind?**

**Paper # 638**

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## **ABSTRACT**

Many cement kilns recently constructed in the United States depend on staged combustion in the calciner (SCC) for nitrogen oxides (NO<sub>x</sub>) reduction. At the same time dozens of kilns have been retrofitted in Europe with selective non-catalytic reduction (SNCR) in addition to or in lieu of SCC. After great resistance to SNCR, a number of American operators have recently yielded and now propose SNCR. This paper examines the reasons for the shift. The theory, practice, and some unexpected problems are discussed with respect to SCC. Variations of SCC are compared and contrasted. The combination of SNCR and SCC is compared with SNCR alone. Finally the specter of selective catalytic reduction (SCR), which has been commercially demonstrated at one plant in Europe, is discussed, because it may be a viable alternative to SNCR when sulfur or ammonia are present in the raw materials. Some synergistic and counteractive effects of NO<sub>x</sub> control on other pollutants are reviewed and some possibilities for countering or exploiting these negative (counteractive) or positive synergies are suggested.

## **INTRODUCTION**

The requirements for very high temperatures and oxidizing conditions make cement manufacturing (pyroprocessing) an inherently large generator of NO<sub>x</sub> per unit of clinker produced. Fortunately the typical preheater/calciner (PH/C) kiln design includes some features that are compatible with lower NO<sub>x</sub> emissions. One is indirect firing, whereby the amount of air introduced through the primary burner into the kiln sintering zone is minimized. Another is the splitting of fuel between the very high temperature region near the kiln outlet and the more moderate temperatures that prevail in the calciner.

New projects in the United States incorporate combustion innovations in the calciner that destroy NO<sub>x</sub> produced in the kiln and minimize formation of additional NO<sub>x</sub>. All involve refinements of staged combustion principles and fall under the category of SCC. Operational problems ultimately limit the ability of SCC to achieve low emissions.

Operators in Europe usually opt for SNCR to meet progressively more stringent regulations. Generally U.S. applicants have claimed that SNCR and SCR are not technically, economically or environmentally feasible. The greatest fear claimed is possible cause or aggravation of visible plumes. They have been very reluctant to propose either technique as Best Available Control Technology (BACT).

Meanwhile large projects in Missouri and New York were delayed in part due to the long time that it took applicants to propose SNCR and negotiate the related permit conditions to meet the BACT NO<sub>x</sub> emission limits required by the state environmental agencies.

Recently, three applications for new cement kilns were received in Florida. All propose SNCR to meet  $\text{NO}_x$  emission limits lower than any project outside of the state. Two of the companies conducted tests on similar existing kilns to insure that SNCR can be implemented at their facilities without operational problems or high opacity. One permanently installed SNCR on its existing kiln in March 2005 even though it can meet its  $\text{NO}_x$  limit by SCC.

This paper examines the successes and limitations of SCC, the preliminary results of the SNCR testing, and the reasons for the shift to SNCR, in contrast to previous fears about this technology. This paper also examines the new concern that SCR may be required by state agencies following successful pilot testing and subsequent commercial installation at a German cement plant.

This review does not attempt to explain all the reasons for pollutant formation, all control options, or all the possible interactions and interferences between multi-pollutant control strategies. There are many excellent references that are readily available and more informative than attempted in this effort.

The interaction of  $\text{NO}_x$  control with internal (fuel) and external (raw materials) sulfur cycles must not be underestimated. Therefore reference will be made as necessary to sulfur cycles and transformations, control of  $\text{SO}_2$ , and to a lesser extent, carbon monoxide (CO) and total hydrocarbons (THC).

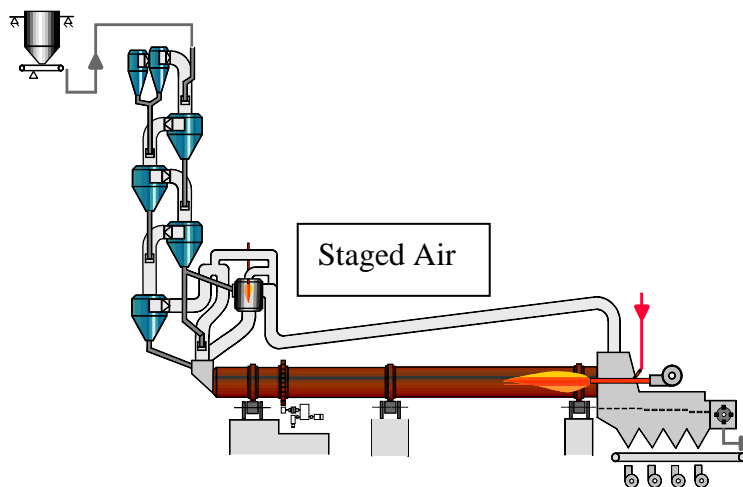
At a time of burgeoning global demand for cement and shortages in some key U.S. markets, it is important to disseminate the status of technology so that regulatory agencies and applicants are “on the same page”. This will expedite permitting, protect the environment, and insure that a healthy cement industry can meet demand in the U.S., in the face of expected and unexpected demand spikes in the world market.

## STAGED COMBUSTION IN THE CALCINER (SCC)

### Examples of SCC

One typical preheater/calciner (PH/C) design with a variation of SCC is shown in Figure 1.

**Figure 1.** Suwannee American Cement and Diagram of a PH/C Kiln with Combustion Chamber.



The design shown in the diagram is an example of *staged air* combustion practiced at Suwannee American Cement (SAC) in Branford, Florida. The calciner burner is vertically oriented in a separate combustion chamber of the type typically used for difficult to burn fuels such as petroleum coke. In this case it is used to burn calciner fuel (coal) in a reducing atmosphere to destroy NO<sub>x</sub> in the kiln exhaust as described below. The SAC kiln was supplied by Polysius. A similar calciner was promoted by Technip CLE as the Minox Low NO<sub>x</sub> calciner.

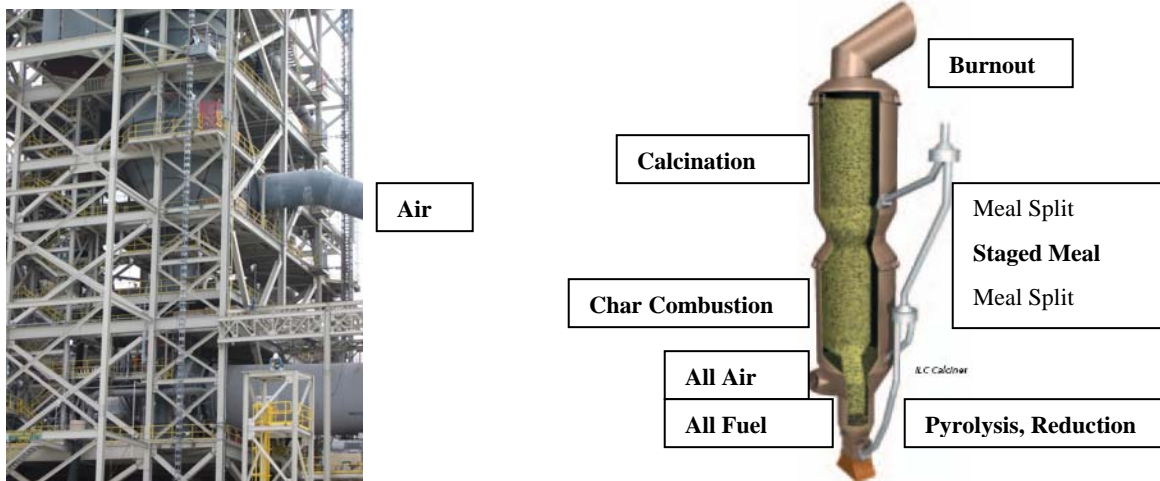
Figure 2 shows the Florida Rock Industries (FRI) plant in Newberry, Florida. It has a Polysius Multistage Combustion (MSC) in-line calciner. The calcination burner is mounted horizontally rather than in a separate combustion chamber, and provisions are included for a small burner in the kiln inlet housing. This version of SCC is an example of *air and fuel staging*. Instead of using the burner shown at the kiln inlet, FRI burns tires.

**Figure 2.** Florida Rock Industries PH/C Kiln and Diagram of Fuel and Air Staged Calciner



Figure 3 shows the Low NO<sub>x</sub> in line calciner at Titan America Pennsuco Kiln No. 5 in Medley, Florida. All fuel is fired in a reducing atmosphere near the kiln inlet and then all tertiary air is supplied in the lower part of the calciner. For lack of a better term, this design by F.L. Smidth will be referred to as *sequenced fuel and air introduction*.

**Figure 3.** Titan America PH/C Kiln and Diagram of Sequenced Fuel and Air Calciner

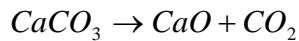


The tertiary air supply duct is readily visible in the photograph and the point where it enters the calciner is shown in the diagram. Another feature not fully appreciated is that raw meal is split to several sections of the calciner. Three meal splits are visible in the diagram. Effective SCC designs typically incorporate *meal staging* for numerous reasons. One key reason is to take advantage of the *catalytically* enhanced dissociation in the preheater of nitrogen oxide (NO) formed in the kiln.<sup>1</sup> Another important reason is as a temperature control stratagem.

## NO<sub>x</sub> Reduction by SCC

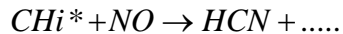
Exhaust gas leaving the kiln is characterized by excess air and high temperature that is less than required to sinter cement but greater than required to calcine raw meal.

**Equation 1.** Calcination of limestone occurs at approximately 900 degrees Celsius (°C) and liberates carbon dioxide to produce lime according to the following endothermic reaction:



This reaction tends to rapidly cool the kiln exhaust gas. The additional heat supplied by the calciner burner(s) and tertiary air sustains the reaction. This tends to limit the temperature of exhaust gases in and leaving the calciner to temperatures less than 900 °C. Combustion in the calciner proceeds as follows.

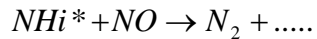
**Equation 2.** Fuel, such as a volatile coal, is heated and pyrolyzed releasing hydrocarbon radicals. These, in turn, catalytically react with NO to form hydrogen cyanide according to:<sup>2</sup>



Where:

$$i = 1, 2, 3$$

**Equation 3.** Ammonia-like radicals are also released during pyrolysis. Under reducing conditions and in the presence of raw meal they catalytically destroy NO according to:<sup>3</sup>



This mechanism suppresses formation of NO by the pyrolyzed fuel nitrogen and recruits that nitrogen to combat NO<sub>x</sub> in reactions that at first glance look much like SNCR or SCR.

Other reactions involving carbon monoxide (CO) or hydrogen (H<sub>2</sub>) are also catalytically driven and destroy NO<sub>x</sub> in this reducing atmosphere. In the subsequent burning of soot and char, the NO<sub>x</sub> reducing reactions proceed much more slowly and some of the remaining fuel nitrogen can form additional NO<sub>x</sub>.

The source cited for Equation 2 states, “the temperature is kept between 925-1050 °C or as high as possible without getting any encrustations in the kiln riser and the reduction zone”. The source of Equation 3 states, “to maximize the reduction potential, the temperature is maintained as high as possible in the reducing zones ..... the reducing atmosphere is initiated in the kiln inlet housing where the temperature is 1150 °C, or more”.

Thus it is not enough to specify SCC (or MSC, or Low NO<sub>x</sub> Calciner). What is actually sought is SCC with high temperature raw meal catalysis in a reducing atmosphere. Therefore SCC for NO<sub>x</sub> reduction must specify or qualify the conditions under which it will operate.

## Interactions Between SCC and the Internal Sulfur Cycle

Sulfur dioxide (SO<sub>2</sub>) formed by burning fuel in the main kiln burner can be efficiently scrubbed out by reactions with alkali species (Na and K) or with CaO in the kiln to form stable sulfate compounds that are incorporated into the clinker.

**Equation 4.** Kiln SO<sub>2</sub> reaching the calciner and all SO<sub>2</sub> from burning fuel in the calciner is completely scrubbed out at the temperatures prevailing in the calciner as follows:<sup>4</sup>

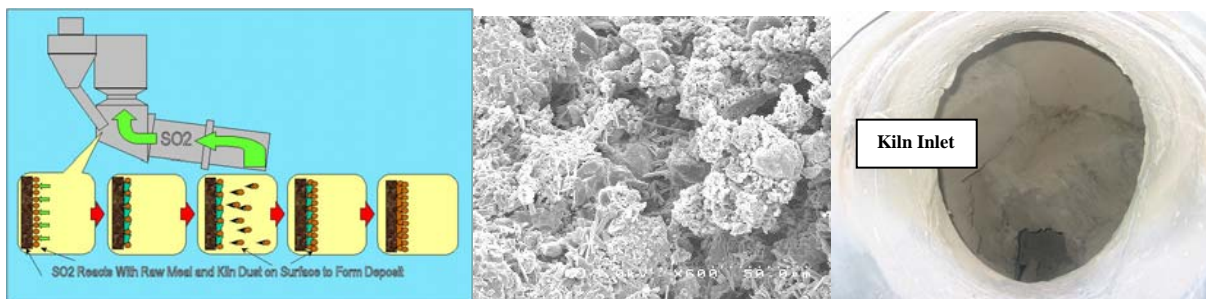


At 1,045°C, the formation and decomposition reactions for CaSO<sub>4</sub> are at equilibrium at normal excess oxygen levels. At higher temperatures, CaSO<sub>4</sub> will tend to decompose. As raw materials move through the high temperature regime in the kiln, the CaSO<sub>4</sub> can break down per the above reaction releasing the SO<sub>2</sub> or it can fuse/react with the alkali sulfates and other species to form stable compounds that depart with the clinker.

The concentrations and flows of SO<sub>2</sub> build up within the internal cycle of the kiln and calciner. One of the key design and operational objectives is to manage this cycle so that solid sulfur containing compounds do not form coatings and blockages. According to one author, “NO<sub>x</sub> abatement rates of up to 50 percent can generally be achieved with staged combustion. However the processes are critical with high circulating sulfur and alkali systems in conjunction with the reducing mode of operation and the operation can be seriously affected by the formation of coating”.<sup>5</sup>

If there is already insufficient alkali to balance the sulfur in the system, the recirculating flow of SO<sub>2</sub> is greater. The diagram and the microscopic photo in the following figure are from a Taiyeho Cement presentation and depict the formation of coating that might result under such circumstances even if reducing conditions are not encountered in the calciner.<sup>6</sup> The second photo is from an actual kiln inlet at a cement plant in Florida. Reducing conditions do not necessarily increase SO<sub>2</sub> emissions but can create considerable process problems due to sulfate deposits at the kiln inlet, in the riser duct, and cyclones.<sup>7</sup> Creating a higher temperature near the kiln inlet to promote NO<sub>x</sub> reduction would tend to release SO<sub>2</sub> per the above reactions or could cause sintering of the coatings. Also it could cause or aggravate coating tendencies in the riser and lower cyclones.

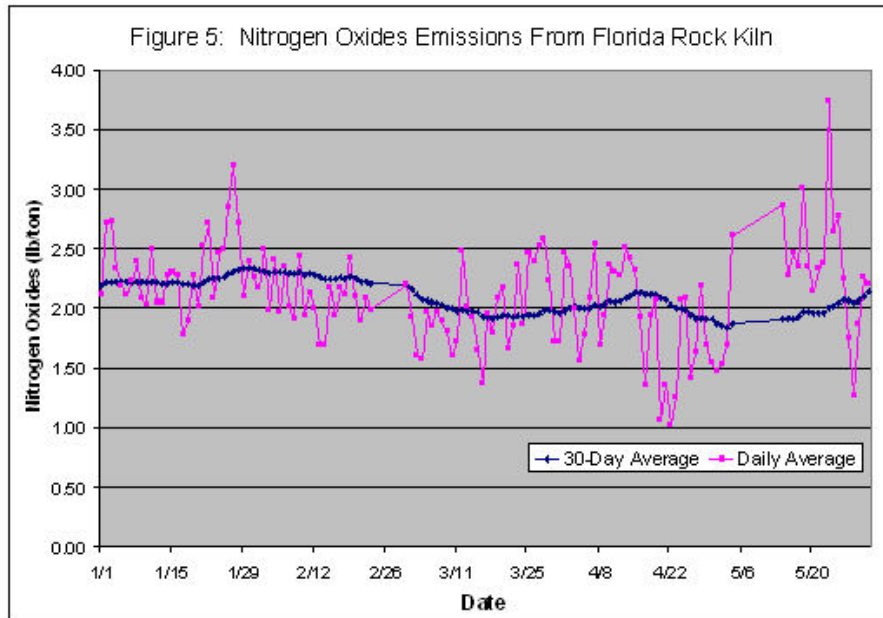
**Figure 4.** Coating Formation near Kiln Inlet and Microscope Photo. Nearly Choked Kiln Inlet.



Generally speaking, raw materials in Florida are low in both alkali and sulfur. Because of sulfur in the coal, there can easily be an imbalance between the two species. SAC and FRI partially cope with coating problems by use of air cannon and cardox charges, to free plugs and blockages caused by such coatings.

## NO<sub>x</sub> Reduction by SCC in Florida Kilns

The FRI kiln has a BACT NO<sub>x</sub> limit of 2.45 lb/ton on a 30-day rolling average basis. Data from the first half of 2004 are summarized in Figure 5. Typical emissions from the FRI kiln are between 1.5 and 2.5 lb/ton, when tires are burned near the kiln inlet. Assuming “baseline” emissions of 3.5 lb/ton, the NO<sub>x</sub> reduction efficiency by SCC in a reducing atmosphere varies from 30 to 60 percent. According to FRI, the higher values near 3 lb/ton are observed on days when tires are not available. During such times, reducing conditions are maintained in the calciner, but a high temperature reducing zone near the kiln inlet is not achieved. The resulting reductions are less, all other factors being equal.



SAC has a BACT NO<sub>x</sub> emission limit of 2.9 lb/ton on a 24-hour rolling average basis. In contrast to the FRI operation, the kiln at SAC does not fire fuel at the kiln inlet although a burner was provided for that purpose. Therefore the version of SCC at SAC achieves a reducing atmosphere in the calciner, but not a high temperature reducing zone near the kiln inlet. Under this scenario, typical emissions varied between 2.2 and 2.6 lb/ton. Assuming a baseline of 3.5 lb/ton, this version of SCC achieves reductions of approximately 25 to 40 percent.

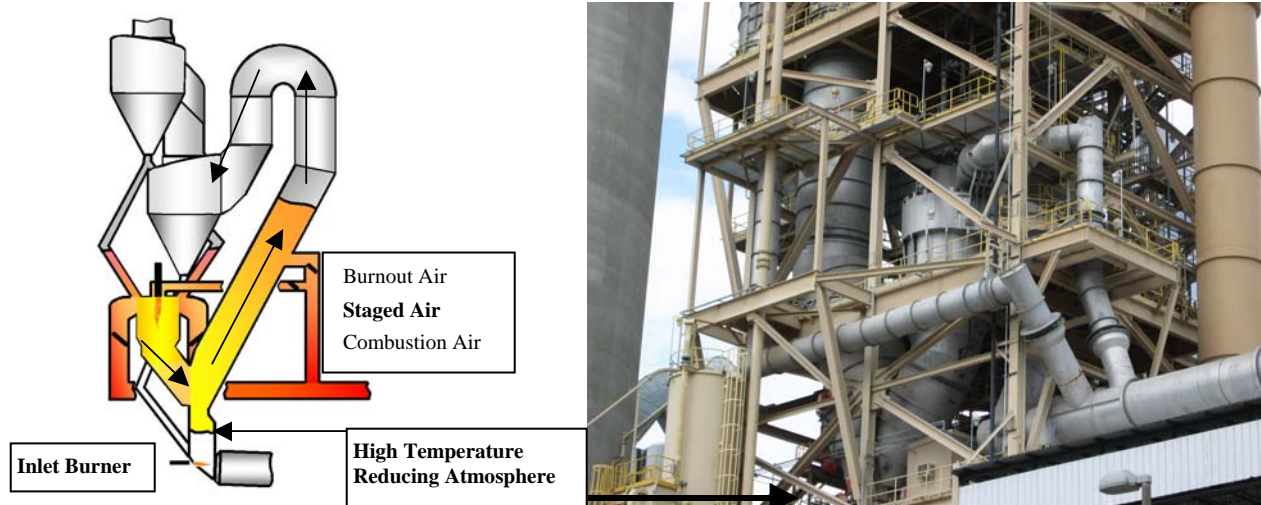
The permit issued to SAC provided the Florida Department of Environmental Protection (DEP) with the ability to further revise the NO<sub>x</sub> limit downward. SAC agreed to temporarily install and use the supplied kiln inlet burner with the fuel supply system to determine if creation of a high temperature reducing atmosphere could be achieved without unduly aggravating the coating tendencies. The principle of operation when using the two burners in the calciner is as follows:

“NO<sub>x</sub> from the sintering zone of the kiln is reduced by means of a burner in the kiln inlet. The fuel is injected against the direction of flow of the kiln gases and is pyrolysed in its gas phase. In the reducing atmosphere that is formed, the NO<sub>x</sub> is converted into nitrogen. In order to prevent new NO<sub>x</sub> from being generated in the calciner, the calcining fuel also has to be burned under reducing conditions. This is achieved by staggered introduction of the combustion air, so that the fuel is first burnt under reducing conditions and then under oxidizing conditions. Corresponding staggering of the raw meal also favorably influences the temperature in the reducing zone”.<sup>8</sup>



Figure 6 shows the SCC configuration used during the tests that were conducted in June 2004. In contrast to tire use at FRI, coal was burned at the inlet of the SAC kiln. The results are summarized in Table 1.<sup>9</sup>

**Figure 6.** Operation of Polysius MSC-CC with Kiln Inlet Burner. June 2004



**Table 1.** Summary of Emissions and Process Parameters During Testing of Kiln Inlet Burner.

Parameter	Baseline (Before)	KIB (6/9/04)	KIB (6/10/04)	Baseline (between)	KIB (6/15/04)
KIB Coal, ton/hr	0	1.12	1.16	0	1.28
Inlet NO <sub>x</sub> , ppm	253	159	263	229	280
Stack NO <sub>x</sub> , lb/ton	2.19	1.61	2.22	2.13	2.17
Inlet CO, ppm	292	5994	964	383	485
ID Fan CO, ppm	219	683	122	135	457
Clinker, tph	99	100	105	105	105
Raw Meal Feed, tph	177	183	184	172	180
Kiln feed, tph	152	155	162	161	161
Stage 1 exit T, °C	857	855	867	867	872
Stage 4 exit P, in. H <sub>2</sub> O	15.0	16.5	17.8	16.8	16.5
Stack THC, ppm	23.9	16.8	9.3	14.2	14.1

Use of the kiln inlet burner (KIB) resulted in decreased NO<sub>x</sub> concentration at the kiln inlet and decreased NO<sub>x</sub> emissions at the stack for the short term as well as increased CO concentrations at the kiln inlet and the induced draft fan. The pressure drop across the preheater increased but clinker quality was not affected. The KIB did not further affect clinker production rate, although subsequent tests show that production was already adversely affected by operating the calciner in a reducing atmosphere.

In the medium term, use of the KIB did not appear to reduce NO<sub>x</sub> but the pressure drop remained high and clinker quality was affected. The Stage 4 (top stages) exit pressure (and other stages as well) stayed relatively high, indicative of formation of partial blockage at the orifice. A high tonnage of coal with KIB operation showed an increase of Stage 1 (bottom stage) material temperature, probably indicative of coal burning in Stage 1 (due in part to very small kiln inlet).

The temporary reduction of NO<sub>x</sub> from 2.19 to 1.61 lb/ton verifies the capability of SCC in a high temperature reducing atmosphere to minimize NO<sub>x</sub> emissions. The inability to maintain the low emissions and the exacerbation of operational problems verifies the potential adverse effects when operating a high temperature reducing atmosphere at the kiln inlet. Obviously this conclusion is applicable for the combination of the raw materials and fuel used at this location.

SAC advised, “Of the nine MSC systems installed in the U.S., none is using the kiln inlet burner to achieve reducing conditions. Most facilities are able to meet their NO<sub>x</sub> limits (greater than those at SAC) without the use of this kiln inlet burner, possibly by creating reducing conditions in the same manner achieved by SAC”.<sup>10</sup>

This does not mean that lower emissions cannot possibly be achieved without unacceptable operational problems. The FRI kiln is similar to the SAC kiln but apparently operates SCC with a relatively high temperature reducing atmosphere using tires with fewer impacts than experienced by SAC when using coal.

It is conceivable that process, fuel, and raw material adjustments would permit the SAC plant to use the KIB continuously to reduce NO<sub>x</sub> emissions. For example, use of expensive natural gas in the calciner and kiln (where it would produce even more NO<sub>x</sub> than coal), would break the internal sulfur cycle and reduce the buildup problem. As discussed in the next section, SAC chose to test SNCR to determine if low emissions could be achieved while minimizing the operational problems that occur even without operating the KIB.

Compliance tests at the new 250 ton per hour Titan America kiln in Medley, Florida indicated NO<sub>x</sub> and CO emissions at 2.0 and 0.5 lb/ton, respectively.<sup>11</sup> Titan employs fewer air cannon and does not experience the level of coating problems and stoppages reported by SAC or FRI. The calciner design is shown in Figure 3. It depends on the introduction of all calciner fuel into a reducing atmosphere near the bottom of the calciner (not actually at the kiln inlet), followed by introduction of all tertiary air at a single level just above the fuel introduction point.

The manufacturer describes the design as follows: “The Low NO<sub>x</sub> ILC design is based on dividing the meal from the second lowest preheater cyclone to the kiln riser and the calciner, which are separated by an expanded riser duct that forms a reducing NO<sub>x</sub> zone. The calcining chamber is built (at least partially) into the kiln riser. 100 percent of the fuel is fired to the kiln riser duct. As a result, it is possible to obtain both reducing conditions and a high temperature zone in one simple system (without multiple firing points) for the lowest possible NO<sub>x</sub> emissions.

“The combustion air is drawn either through the kiln or through a separate tertiary air duct. Because the kiln combustion gases are drawn through the calciner, the calciner size is necessarily larger to attain the required gas velocity and retention time. Following the reduction zone, the calciner’s cylindrical section is sequentially tapered. The resultant rapid changes in cross-sectional areas create strong vortexes ensuring effective mixing of fuel, raw meal, and gas. The top of the calciner is most often provided with a loop duct to ensure optimum gas retention time, mixing and complete combustion of the fuel”.<sup>12</sup>



It appears that all calciner fuel participates in the creation of the high temperature reducing condition. The maximum amount of kiln exhaust gas is acted upon in the shortest amount of time and at the highest possible temperature. This rapidly drives the catalytic NO<sub>x</sub> destruction reactions and then quenches the atmosphere with lower temperature tertiary air before the NO<sub>x</sub> forming reactions predominate. In the subsequent oxidizing atmosphere there are competing NO<sub>x</sub> formation and destruction reactions. The duration of conditions in the calciner favorable to formation of coating (e.g. SO<sub>2</sub> evolution) is minimized.

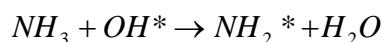
The Titan America experience shows that low NO<sub>x</sub> and CO can be attained by SCC with a high temperature reducing atmosphere without excessive coating formation. Titan applied to increase annual hours of operation and limit NO<sub>x</sub> emissions to 2.1 lb/ton clinker on a 30-day basis.<sup>13</sup>

## SELECTIVE NON-CATALYTIC REDUCTION (SNCR)

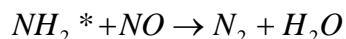
There are numerous references on the efficacy of SNCR for the control of NO<sub>x</sub>. The technology has been widely practiced in the power industry, at waste-to-energy facilities and at numerous miscellaneous applications.

It suffices to state that ammonia (NH<sub>3</sub>) is injected at a point in the process characterized by a suitable temperature window between 850 and 1050 °C depending on residence time, turbulence, oxygen content, and a number of other factors specific to the given gas stream. SNCR destroys NO<sub>x</sub> by a two-step process as follows:

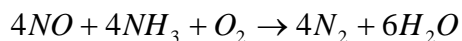
**Equation 5.** Ammonia reacts with available hydroxyl radicals to form amine radicals and water per the following theoretical equation:



**Equation 6.** Amine radicals combine with nitrogen oxides to form nitrogen and water.



**Equation 7.** The two steps are typically expressed as a single “global reaction”.



The simplified equation does not convey the kinetics. But it suggests that, theoretically, SNCR will function best in an oxidizing atmosphere.

**Equation 8.** In a reducing atmosphere, CO competes with ammonia for available OH radicals

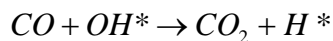
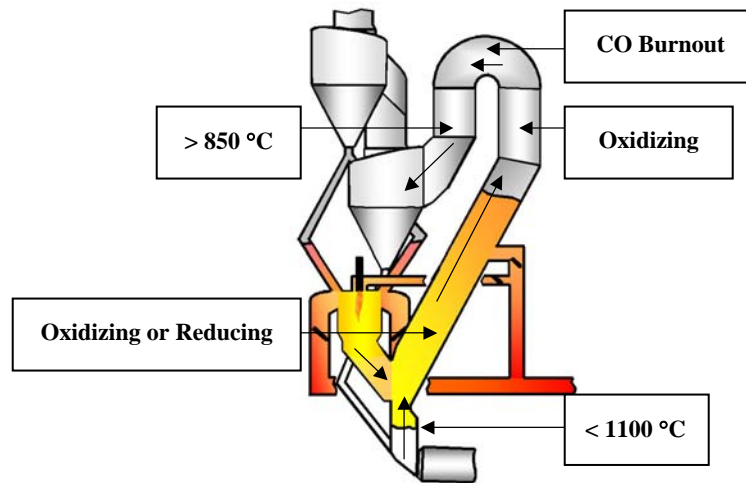


Figure 7 shows that the necessary temperature window exists at least between the kiln inlet and the bottom cyclone that receives the exhaust from the calcination section. The physical extent of the window for oxidizing conditions depends on the damper positions for the tertiary air branches for the shown calciner design. In selecting a level (or levels) for ammonia injection there must be some optimization of temperature and oxygen.

Based on the foregoing, ammonia should be injected after introduction of tertiary air and preferably after completion of CO burnout. There may also be favorable injection points closer to the kiln inlet if oxidizing conditions exist in the calciner.

**Figure 7.** Temperature and Oxidizing Windows for SNCR in a Staged Combustion Calciner.



## Examples of SNCR

Fueltech and Ash Grove conducted a successful short-term demonstration of SNCR in the early 1990's on a 100 tons per hour PH/C kiln.  $\text{NO}_x$  was efficiently reduced from the range of 3.5 – 6 pounds per ton of clinker to less than 1 lb/ton.<sup>14</sup> No significant adverse comments were made in the paper describing the experience. The fact that the authors included the SNCR supplier as well as respected company personnel lends credence to this effort.

As of 2000, there were at least 18 kilns in Europe that had installed SNCR.<sup>15</sup> Most of these SNCR installations were designed and operated for  $\text{NO}_x$  reduction rates of 10 – 50 percent with  $\text{NH}_3/\text{NO}_2$  molar ratios of 0.5-0.9 and emissions of 500-800  $\text{mg NO}_x/\text{m}^3$  (~2.3 to 3.6 lb/ton). By contrast with the other European countries, the Swedish EPA limits  $\text{NO}_x$  emissions from *existing* cement plants to 200  $\text{mg}/\text{m}^3$  (~0.9 lb/ton).

An SCC system similar to SAC's calciner was installed in 1997 at the Scancem Slite Plant on Gotland Island, Sweden. Scancem no longer operates the calciner in SCC and reducing atmosphere because of clogging of the kiln inlet due to the increased sulfur content in the hot meal when trying to achieve low  $\text{NO}_x$  emissions. The Environmental Director of Gotland County presented a paper at the famous Paris  $\text{NO}_x$  Conference of March 2001 on the subsequent SNCR experience at Slite.<sup>16</sup> Following is a description of the project taken from the paper:

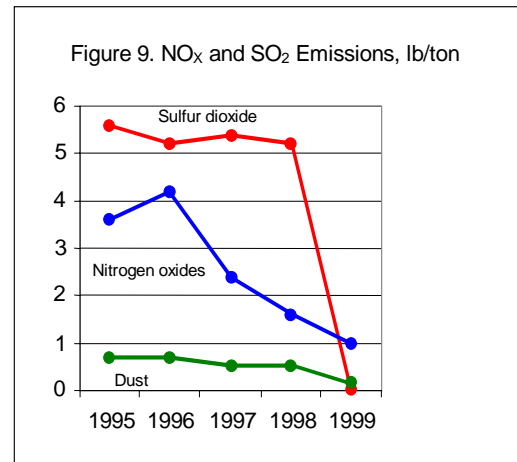
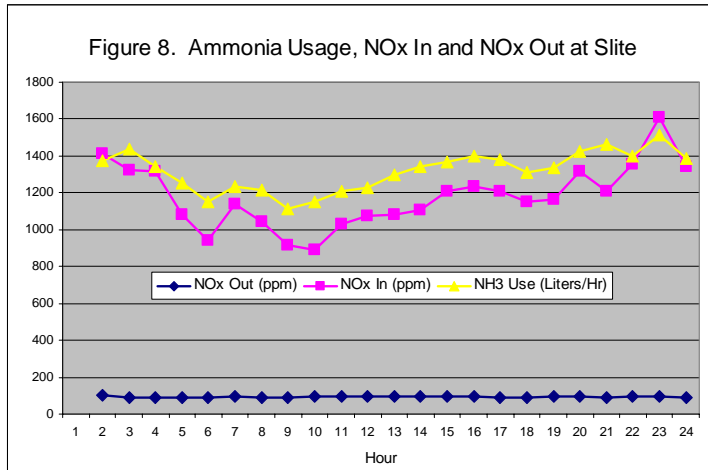
“Petro Miljö erected the unit during the autumn of 1996. The unit consists of a tank for storing 25 percent ammonia solution, pumping gear for ammonia and water, mixing modules to achieve the correct ammonia solution, and injection equipment for atomising and distributing the agent into the gas flow. All equipment is controlled by an automatic control and management system.

“The unit was designed to achieve at least 80 % reduction of  $\text{NO}_x$ . The investment cost was about 1.1 million euros (0.55 million euros for the SNCR installation and another 0.55 million euros for the ammonia water storage) and the operating cost is about 0.55 euros/tonne of clinker. The total cost (investment + operating costs) is less than 0.6 euros/tonne of clinker.” The kiln has a production capacity of 5,800 metric tons per day. The conclusions are:

“After more than three years of operation, the initial  $\text{NO}_x$  emission level of approximately 1200  $\text{mg}/\text{m}^3$  has been reduced to approximately 200  $\text{mg}/\text{m}^3$  with a molar ratio of 1.1-1.2. At an  $\text{NH}_3/\text{NO}$  molar ratio of around 1.0 the  $\text{NO}_x$  level has been reduced by about 80 percent.

“The results show that it is possible to reach a degree of purification of over 80% without having any slip of ammonia or higher levels of N<sub>2</sub>O. No increase in CO emissions have been measured and no traces of any NH<sub>3</sub> have been found in the cement”.

Based on Figure 8, it takes 1,200 to 1,400 liters per hour (L/hr) of 25 percent ammonia to reduce NO<sub>x</sub> from 1,200 to 200 mg/m<sup>3</sup> (~0.9 lb/ton, 100 ppm). Figure 9 shows the annual improvement in NO<sub>x</sub> and SO<sub>2</sub>.



One important point is that the reduction in NO<sub>x</sub> occurred concurrently with reductions in previously high SO<sub>2</sub> (over 5 lb/ton) by the installation of a scrubber. Without the scrubber and at the target NO<sub>x</sub> removal efficiencies, there would be a potential for a visible detached plume because of the high NH<sub>3</sub>/NO molar ratio and the high SO<sub>2</sub> emissions (when not controlled).

According to the Gotland Environmental Director, “the Slite plant has a big stake in showing the highest possible reduction because there is a discussion going on in the Environmental Court if they should decide that the plant has to install SCR technology to further reduce the emission of NO<sub>x</sub>”. The findings are corroborated in Scancem’s 1998 Environmental Report as follows:

“A flue gas desulfurization system was commissioned at the Slite plant at the end of 1998. The system is designed to reduce sulfur dioxide emissions by 90 percent. Systems for reducing nitrogen oxide emissions were placed in operation in Slite and Skövde earlier during the year. The goal to reduce emissions by 80 percent was reached”.<sup>17</sup>

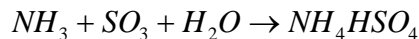
Recently Polysius conducted SNCR tests at three European plants ranging from 1,900 to 5,000 metric tons per day of capacity.<sup>18</sup> The three plants were equipped with SCC for operation in a reducing atmosphere (i.e. Polysius MSC). The drawings in the article show kiln inlet burners suggesting the fully described MSC technology was in operation. According to the paper:

“The base emissions without the addition of NH<sub>3</sub> were scattered very widely between 400 and 800 mg/m<sup>3</sup> (~1.8 and 3.6 lb/ton). The emission values were lowered from the initial value of 500 mg/m<sup>3</sup> (~2.3 lb/ton) in steps to 250 mg/m<sup>3</sup> (~1.2 lb/ton) by adding ammonia, which corresponded to abatement rates of 38 to 68 percent”. Examination of the time series shows that emissions were further reduced to less than 100 mg/m<sup>3</sup> (~0.5 lb/ton) by using 250 L/hr of 25 percent ammonia solution but at a high NH<sub>3</sub>/NO ratio and slip potential. Presumably this occurred on the smallest (1,900 metric TPD) kiln. The greatest NO<sub>x</sub> reduction occurred when ammonia was injected after the final air stage and after full mixing in a subsequent deflection chamber. Introduction of ammonia prior to the chamber or in the reducing atmosphere was less effective.

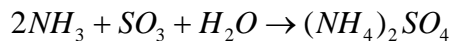
## Interactions Between SNCR and the External Cycle

Sulfide or elemental sulfur contained in raw materials may be “roasted” or oxidized to SO<sub>2</sub> in areas of the pyroprocessing system where sufficient oxygen is present and the material temperature is in the range of 300-600°C.<sup>19,20</sup> Uncontrolled SO<sub>2</sub> emissions are only about 0.10 lb/ton and less than 100 tons per year at the Florida PH/C kilns because there are only minute amounts of sulfur in most of the available limestone. Uncontrolled SO<sub>2</sub> emissions can be as much as two orders of magnitude greater where pyritic sulfur is present in the raw materials. Unreacted ammonia from the SNCR process or from raw materials reacts with SO<sub>2</sub> and SO<sub>3</sub> at temperatures prevalent in the upper preheater, pollution control equipment, and outside the stack.

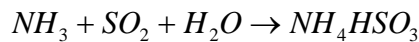
**Equation 9.** Ammonium bisulfate is formed in accordance with the following reaction.



**Equation 10.** Ammonium sulfate is formed per the following reaction.



**Equation 11.** Finally, ammonium bisulfite is formed as follows.



When a PH/C kiln is operated with the raw mill on line, these compounds condense. They go back into the feed system and to the preheater, where they vaporize again. They subsequently condense again in the raw mill. When the raw mill is taken off line, the volatile salts are no longer captured in the raw mill, and go to the dust collector. Since the dust collector cannot capture the new, high concentrations efficiently, the plume becomes highly visible. When the raw mill is put back into operation, the plume ceases again. This cycle continues indefinitely, unless something is done to break it.<sup>21</sup> Qualitatively, it would seem that the filter cake in a baghouse would even out the emissions of these compounds more so than an electrostatic precipitator, so it is not a foregone conclusion that the plume will be highly visible.

If a plant has a persistent detached plume that is attributable to (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> it is necessary to get rid of one of the two reactants that ultimately form (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> - either the NH<sub>3</sub> or the SO<sub>2</sub>.<sup>22</sup> The obvious method of avoiding the feared plumes when using SNCR is by minimizing ammonia use when SO<sub>2</sub> emissions are likely.

Operating the raw mill promotes SO<sub>2</sub> removal by limestone scrubbing under humid conditions, due in part to freshly generated limestone surface produced by grinding. Some of the SO<sub>2</sub> generated in the top preheater stages is also scrubbed out by small amounts of free CaO that are carried back from hotter zones by combustion flue gases.

Another SO<sub>2</sub> removal technique is to extend the inherent self-scrubbing (by CaO) that occurs in the calciner to the upper sections of the preheater where pyrite-derived SO<sub>2</sub> is evolved. This involves conveyance of lime from the calciner (by differential pressure) to the upper stages of the preheater. The system consists of a cyclone and some ductwork and involves no moving parts.<sup>23</sup>

A very fine suspension of slaked lime can be introduced into the gas-conditioning tower to remove SO<sub>2</sub>, particularly when the raw mill does not operate. The droplets react, dry, and are captured by the particulate control equipment where excess lime (from the dried droplets) continues to remove remaining SO<sub>2</sub>.<sup>24</sup>

If the three SO<sub>2</sub> measures are insufficient to achieve permitted SO<sub>2</sub> requirements, then conventional wet or dry scrubbers can be considered. The TXI Midlothian scrubber system was estimated to cost \$13,000,000. Emissions of SO<sub>2</sub> from the new kiln were permitted at over 1,300 tons per year and 1.33 lb/ton of clinker.<sup>25</sup> It is not certain whether SO<sub>2</sub> emissions are actually as high as permitted. If they are that high and an SNCR system were installed at such a plant for additional NO<sub>x</sub> control, then it might be necessary to limit ammonia slip or to further enhance SO<sub>2</sub> removal to avoid a detached plume.

### SNCR Experience in Florida Kilns

Following the poor results of the kiln inlet burner tests, SAC elected to conduct SNCR tests in conjunction with SCC in a reducing atmosphere similar to the tests on the three European kilns. SAC also decided to test SNCR with the SCC calciner operating in an oxidizing atmosphere. The tests were conducted by the kiln supplier in November 2004. Some of the equipment used is shown in the following figure:

**Figure 10.** Aqueous Ammonia Supply Truck, Compressed Air, One of Four Ports, An Injector

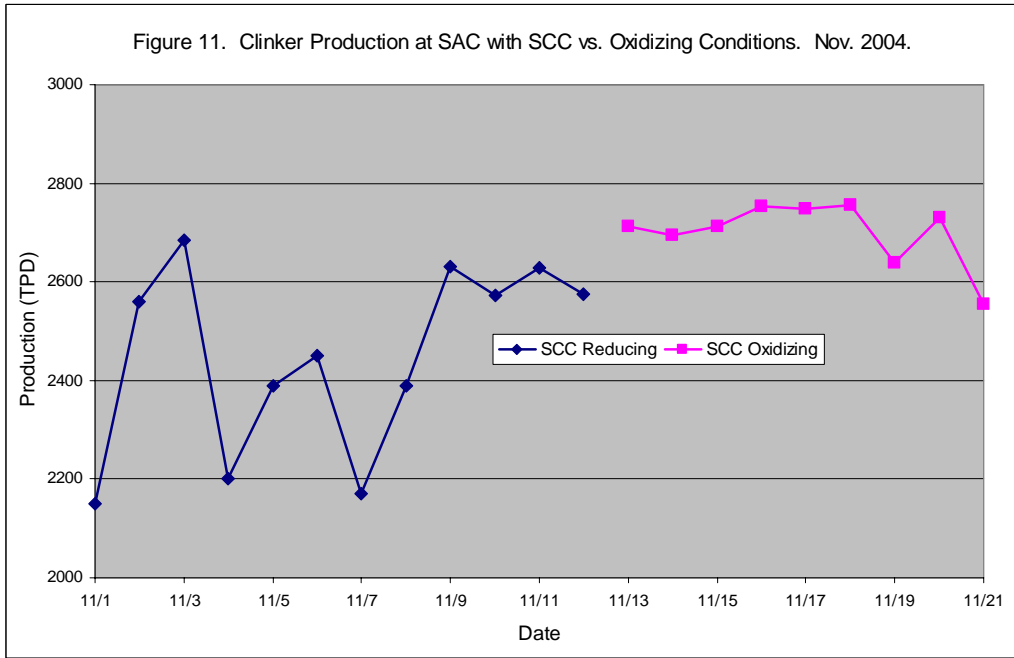


Not shown is the metering system or the additional continuous emission monitoring equipment. Referring back to Figure 6, four ports were installed after the bend in the duct work following the top air injection branch for tertiary air. This setup is relatively simple. It is noteworthy that it suffices for treatment of all of the exhaust gas from the calciner and not just a slip stream. In fact at times a single injector sufficed for adequate NO<sub>x</sub> control.

One would expect the NO<sub>x</sub> at the stack outlet to be the parameter of greatest interest. Those results were actually expected by the author per the discussions of previous trials and commercial installations. In fact the most interesting parameter is clinker production.

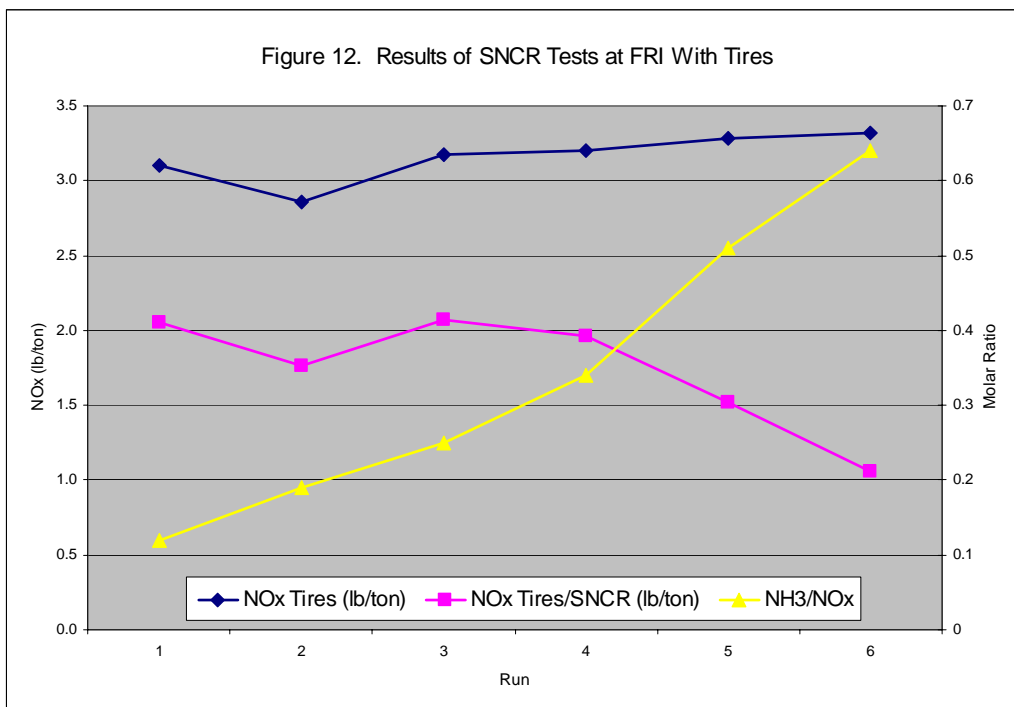
Figure 11 is a graph of the clinker production time series. The series on the left hand side reflects operation of the kiln under SCC with a reducing atmosphere. Ammonia injection began on November 8 with a less aggressive reducing atmosphere. The one on the right hand side reflects operation of SCC with an oxidizing atmosphere. As anticipated, operating the calciner in an oxidizing atmosphere rather than a reducing atmosphere caused less coating formation, plugging and stoppages. Daily production was sustained at a higher level by operating the calciner in a less reducing atmosphere and then at an even higher level in an oxidizing atmosphere. While not unexpected, it is a real eye-opener and incentive to find means other than SCC with a reducing atmosphere to control NO<sub>x</sub> at this kiln.

The permitted emission rates were easily achieved by SNCR whether or not the calciner was operated in an oxidizing or reducing atmosphere. SAC received a permit to: permanently increase production from 105 to 120 tons of clinker per hour; meet an additional NO<sub>x</sub> limit of 2.4 lb/ton on a 30-day basis; keep the daily 2.9 lb/ton limit; install an SNCR system; and inject fly ash directly into the calciner.<sup>26</sup> Operation under the terms of the new permit began on April 1, 2005.



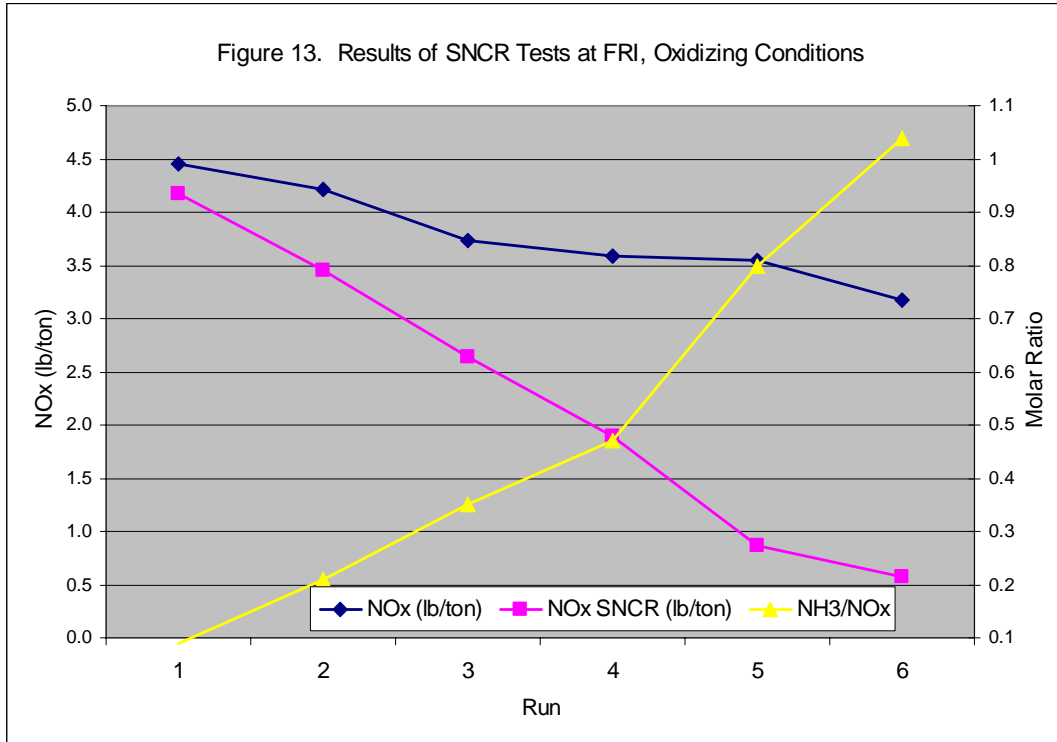
The requested  $\text{NO}_x$  limits can be achieved using SCC with a high temperature reducing atmosphere without SNCR. However, SAC will typically operate the calciner in an oxidizing atmosphere and use SNCR to maintain higher production capacity. The will also allow SAC to use the combustion chamber to burn petroleum coke blends as already allowed while meeting permitted  $\text{NO}_x$  limits.

Following the testing at SAC, the kiln supplier performed similar testing at the nearby Florida Rock Industries (FRI), but of shorter duration. FRI conducted SNCR tests while burning tires and maintaining a reducing atmosphere in the calciner. The following chart summarizes the testing while burning tires.





The results indicate very substantial NO<sub>x</sub> reductions by SNCR compared with NO<sub>x</sub> emissions burning tires alone (representative of SCC in a mildly reducing atmosphere) even with molar ratios much less than 1.0. The following chart summarizes results of tests conducted while the calciner was operated in an oxidizing atmosphere.



Under oxidizing conditions, baseline emissions were greater than they were when tires were used. Very low emissions were achieved at molar ratios approaching 1.0. The baseline emissions also tended to decline probably due to recirculating NH<sub>3</sub> from previous runs.

### SELECTIVE CATALYTIC REDUCTION (SCR)

There are hundreds of examples of SCR for the control of NO<sub>x</sub>. Numerous installations exist in the United States, Europe and Japan. Most of the projects have been conducted in the electric power industry for a wide selection of fuels, energy cycles, and operating conditions.

SCR relies on the same principle as SNCR. The reactions occur at lower temperatures and require a catalyst, typically containing vanadium, titanium, or zeolite. Based on the design of the catalyst and operating conditions, the temperature window is between 200 and 600 °C. The high range of the SCR temperature window exists in the upper stages of the preheater, while the lower range prevails at the preheater exit, then through the downcomer, through the gas conditioning tower and to the induced draft fan prior to the raw mill.

Some applications of SCR are for low dust environments, such as natural gas fired combustion turbines. High dust applications have been developed, particularly for the coal fired plants. In a cement plant a low dust application would require expensive reheat of exhaust gas so the high dust option is much more attractive.

A very important pilot scale demonstration was conducted in 1997 to 1999 at the Solnhofer Portland Cement Plant in Germany. The pilot scale system was installed after the preheater in a temperature range between 300 and 340 °C. The reactor had four chambers to allow simultaneous testing of four different catalyst formulations.

The SCR system supplier, respected company personnel, and the director of the section within the German Federal Environmental Office (FEO) responsible for regulating the cement industry prepared a paper which was presented at the 2001 Paris NO<sub>x</sub> Conference.<sup>27</sup> Among the findings were:

- Catalyst pitch should be greater than 8 mm for easier cleaning;
- NO<sub>x</sub> in the exhaust gas is reduced by 30 percent with no ammonia use, relying on its presence in local raw materials; and
- NO<sub>x</sub> reduction rates above 90 percent, with NH<sub>3</sub> slip less than 5 ppm, can be achieved.

A paper was presented at the same conference by a representative of the Austrian FEO regarding an SCR demonstration at a cement plant in Kirchdorf, Austria. The findings were consistent with those of the Solnhofer pilot plant.<sup>28</sup>

The pilot plant testing at Solnhofer was followed up in 2000 by a commercial installation of SCR under the sponsorship of the German FEO. Following are pictures from the ground up and a bird's eye view of the installation. Presuming that the plant was operating and running the SCR system when the aerial picture was taken, SCR does not cause a high opacity plume there.

**Figure 14.** SCR System Adjacent to Preheater Tower at Solnhofer Portland Cement Plant.



The three coauthors of the paper on the pilot plant demonstration collaborated on a follow-up paper for the commercial demonstration that was published as a Lecture by the Association of German Engineers.<sup>29</sup> Key findings are:

- The system reduced raw material NH<sub>3</sub> that might otherwise have been converted to “raw material NO<sub>x</sub>”;
- Slip was contained to less than 1 mg/m<sup>3</sup>; and
- Reductions of hydrocarbons and SO<sub>2</sub> on the order of 50 to 70 percent were also attained.

The NH<sub>3</sub> (25% aqueous solution) consumption rates needed to reduce NO<sub>x</sub> concentration from 1200 mg/m<sup>3</sup> to 800, 500, and 200 mg/m<sup>3</sup> were 46, 64, and 85 liters L/hr respectively. By comparison, the Slite kiln consumes around 1200 L/hr to achieve 200 mg/m<sup>3</sup> on a kiln about four times the size of the Solnhofer installation. Correcting for size, it *appears* to take less than one-third as much ammonia to achieve 200 mg/m<sup>3</sup> by SCR at Solnhofer compared to SNCR at Slite. The difference must be accounted by raw material ammonia and more efficient reactions at Solnhofer.

The authors made cost comparisons between SCR and SNCR to reduce NO<sub>x</sub> from 1,200 to 800, 500, and 200 mg/m<sup>3</sup>. In doing so, they made the following assumptions: clinker production is 480,000 metric tons per year; the facility operates 7,500 hours per year; the SCR system costs 2.5 million Euros; an SNCR system costs 1.0 million Euros; and the catalyst will last 3-4 years.

The costs for control by SNCR varied from approximately 0.40 to 1.40 Euros per ton of clinker for NO<sub>x</sub> reduction to values between 800 and 200 mg/m<sup>3</sup>. The costs for control by SCR varied from approximately 0.80 to 1.00 Euros per ton of clinker for NO<sub>x</sub> reductions to values between 800 and 200 mg/m<sup>3</sup>. For reference, the author of the Slite paper estimated only 0.60 Euros per ton of clinker to achieve 200 mg/m<sup>3</sup> at the much larger Swedish installation.

According to the German analysis, the crossover point is at approximately 550 mg NO<sub>x</sub>/m<sup>3</sup>. This means that for objectives less than 550 mg/m<sup>3</sup> (roughly 2.5 lb/ton of clinker), SCR is the more economic option. The reductions in THC, SO<sub>2</sub>, and NH<sub>3</sub> emissions as well as the reduction of the potential for plume opacity emissions make the SCR option even more attractive where significant amounts of sulfur, organic matter or ammonia are present in the raw materials.

Early on during the commercial demonstration, the German official advised this author, “with SCR you can meet NO<sub>x</sub> standards of 200 mg/m<sup>3</sup>”.<sup>30</sup> More recently he advised the author, “the SCR in Solnhofen works in an excellent manner”.<sup>31</sup> It is noteworthy that the plant had an SNCR system prior to installing the SCR unit. They can achieve their permitted emission limit with either technology but continue to use SCR.

According to the Cement Industry Research Institute of the German Cement Works Association the status of SCR is as follows: “As with the SNCR process, a suitable reducing agent, such as ammonia, is injected into the exhaust gas flow. Owing to the catalyst, however, the reduction reaction takes place at a lower temperature range of 300 to 400 °C and results in a higher yield and lower NH<sub>3</sub> slip.

“In the year 2000, the first industrial scale SCR plant world-wide was installed in a German cement works. The plant operates on the basis of the so-called “High Dust Method”, i.e. the entire dust-loaded gas leaving the preheater is channelled through the SCR reactor after emerging from the preheater tower. This reactor may be equipped with up to six layers of a honeycomb catalyst.

“During the first months after commissioning, the main focus of activities was placed on optimizing catalyst geometry and the filter system in order to ensure reliable operation of the SCR system at high dust concentrations (up to 100 g/m<sup>3</sup>). The works had assumed direct control of a substantial part of this development work.

“The economic efficiency of the SCR process will have major influence on the extent to which the process will be applied for NO<sub>x</sub> abatement at cement works in the future. Apart from capital costs as well as the consumption of reducing agent and power, the service life of the catalyst will substantially determine overall costs. After one year of operation, the catalyst’s loss of activity was fairly low. The operator therefore reckons with a service life of 3 to 4 years”.<sup>32</sup>

The Austrian FEO sent experts to visit the Solnhofer Portland Cement Plant to find how the facility was doing in July 2003. They posted a short version of the second Solnhofer paper on their website.<sup>33</sup> They also added the following update based on their visit:

“The reactor in the plant can be equipped with six catalyst sections of which three layers are in use. With these three, 500 mg NO<sub>x</sub>/m<sup>3</sup> and less than 1 mg NH<sub>3</sub>/Nm<sup>3</sup> are emitted. A reduction to 200 mg/m<sup>3</sup> is possible by variation of the NH<sub>3</sub> use. The actual working time of the catalyst is at present at approximately 18,000 hours with an expectation of another further 3-4 years.” These experts included their findings on SCR technology in a more comprehensive report published in 2004 by the Austrian FEO on waste use and emissions reductions in the cement industry.<sup>34</sup> During 2003, the plant emitted less than 500 mg NO<sub>x</sub>/m<sup>3</sup> on 95.6 percent of operating days.<sup>35</sup>

Some in this country believe it is not possible to get firm bids or that the only technically feasible option is a low dust design and expensive reheat. However, this author believes that a well-developed request for a quote, that provides time after startup for catalyst suppliers to select the optimum catalyst formulation and pitch for the given project, will result in favorable bids.

In view of the documented success at Solnhofer and the technical underpinning, the author hereby updates his conclusion of 2001 that SCR is an “exotic technology” when applied to cement plants. He now considers it to be a viable technical and economic option when very low emissions are required and ammonia use must be limited. SCR is favored especially when SNCR and raw material ammonia or sulfur can cause or aggravate visible plumes.

The author believes that the possibility of combining SNCR with a small or “trim” SCR system should be assessed when very low emissions are required. Under such a scenario, this would reduce the NH<sub>3</sub> use required by an SNCR system while avoiding the capital costs and footprint of a large SCR system. Such options are sometimes used for power plant control equipment retrofits, especially when space is at a premium.

## **CONCLUSION**

SCC with a reducing atmosphere is an excellent NO<sub>x</sub> control option when moderate levels of control are required and there is a good balance between fuel sulfur, alkali, chlorides, etc.

There are considerable unaccounted costs for SCC not apparent during design. These become more evident with the realities of available fuels and raw materials, particularly when low NO<sub>x</sub> emissions are required. SCC requires larger calciners and long ducts with costly structural impacts on the entire preheater structure. The costs associated with possible operational difficulties and lower production must be considered when compared with SNCR.

SNCR is a technical and economic alternative to SCC with a reducing atmosphere, particularly when there are imbalances between sulfur and alkali or other phenomena that cause coating formations. SCR is a technical and economic alternative to SNCR particularly when sulfur or organic matter or ammonia are present in the raw materials or when very low NO<sub>x</sub> emissions are required.

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## DISCLAIMER

The author acquired most of the references and prepared this paper on his own time to partially fulfill the continuing educational requirements of the Florida Board of Professional Engineers. While additional references were drawn from the public records of his employer, the conclusions are those of the author alone based on the information he had when he prepared the paper.

## KEY WORDS

Cement, BACT, SNCR, SCR, Staged Combustion, Calciner, Nitrogen Oxides, Sulfur Dioxide

## REFERENCES

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- <sup>1</sup> Sprung, Siegbert. Technological Problems in Pyroprocessing Cement Clinker: Cause and Solution. Beton Verlag. 1982.
- <sup>2</sup> Thomsen, K.; Jensen, L.S.; Schomberg, F. "FLS-Fuller ILC-Low NO<sub>x</sub> Calciner Commissioning and Operation at Lone Star in St. Cruz in California," *Zement Kalk Gips International*, **1998**, 10, 542-550.
- <sup>3</sup> Terry, Mark S. "BACT: What is available with Today's Technology," *Krupp Polysius Technical Seminar*. 1999.
- <sup>4</sup> Miller, F. M.; Hawkins, G. J. "Formation and Emission of Sulfur Dioxide from the Portland Cement Industry" in *Proceedings of the 93<sup>rd</sup> Air and Waste Management Association Conference*. 2000. San Diego, CA.
- <sup>5</sup> Xeller, H. "New Developments in NO<sub>x</sub> Abatement in the Cement Industry, Part 2", *Zement Kalk Gips International*, **1998**, 4, 208-218.
- <sup>6</sup> Presentation. Waste Management Technologies in Japanese Cement Industry. Taiyeho Cement, Taiyeho Engineering, CTI/Industry Joint Seminar, February 2004.
- <sup>7</sup> Reference 4.
- <sup>8</sup> Brochure. DOPOL<sup>R</sup> '90 Preheater and PREPOL<sup>R</sup> Calcining System. Krupp Polysius.
- <sup>9</sup> Electronic mail transmission from F. MacGregor Miller, PhD., Cement Etc., to A. A. Linero, Florida DEP. Inquiry regarding Paris 2001 Presentation. May 13, 2002.
- <sup>10</sup> Electronic mail transmission from Joe Horton, Suwannee American Cement, to A. A. Linero, Florida DEP. Response to Control Technology Information Request. February 25, 2004.

- 
- <sup>11</sup> Source Test Report. Pennsuco Cement Kiln PK5 – Titan America, Medley, Florida. October 20-22 and November 4-5, 2004.
- <sup>12</sup> Brochure. Dry Process Kilns. F.L. Smidth.
- <sup>13</sup> Application. Titan America Cement. Hours of Operation Increase and Emission Limit Adjustments. Pennsuco Cement Plant, Medley, Florida. April 2005.
- <sup>14</sup> Sun, W.H.; Bisnett, M.J.; Kirk, D.W.; Steuch, H.E.; Hille, J. "Reduction of NO<sub>x</sub> Emissions from Cement Kiln/Calcliner through the Use of the NO<sub>x</sub>OUT<sup>R</sup> Process," In *Proceedings of the AWMA International Specialty Conference on Waste Combustion in Boiler and Industrial Furnaces*, April 21, 1994.
- <sup>15</sup> Institute for Prospective Technological Studies, *Reference Document on Best Available Techniques in the Cement and Lime Manufacturing Industries*; European Integrated Pollution Prevention and Control Bureau: Seville, Spain, March 2000.
- <sup>16</sup> Junker, P., Director of Environmental Protection for Gotland County, Swedish EPA. "Reduction with SNCR Technology at Slite Cement Plant", In *Proceedings of the Paris NO<sub>x</sub>/N<sub>2</sub>O-conference*, March 21-22, 2001.
- <sup>17</sup> *Scancem 1998 Environmental Report*, Scancem: Malmo, Sweden, 1999.
- <sup>18</sup> D. Rose, K. Adler, R. Erpelding, "NO<sub>x</sub> abatement with the SNCR process in kiln plants with staged combustion," In *Polysius Teilt Mit 218, 35th Polysius Cement Day*, Hannover, Germany, April 2001.
- <sup>19</sup> Miller, F. M.; Young, G. L.; von Seebach, M., *Formation and Techniques for Control of Sulfur Dioxide and Other Sulfur Compounds in Portland Cement Kiln Systems*; Portland Cement Association: Skokie, Illinois, 2001.
- <sup>20</sup> Greer, W. L., *Interactions Among Gaseous Pollutants from Cement Manufacture and Their Control Technologies*; Portland Cement Association: Skokie, Illinois, 2003.
- <sup>21</sup> Reference 4.
- <sup>22</sup> Miller, F. M. "Management of Detached Plumes in Cement Plants" in *Proceedings of the 2001 IEEE-IAS/PCA Cement Industry Technical Conference*.
- <sup>23</sup> Letter and attachments from Walter Greer, Ash Grove Cement, to John Ramsey, Kansas Department of Health and Environment, re: Sulfur Absorbing Enhancements at the Chanute Plant, dated May 14, 1999.
- <sup>24</sup> SO<sub>2</sub> Removal and Secondary Plume Abatement – MicroMist Micro-fine Lime<sup>TM</sup> Semi-dry Injection Systems. Product Information Brochure. EnviroCare International: Novato, CA, 1998.
- <sup>25</sup> Texas Natural Resources Conservation Commission. Technical Review – New Kiln and Modification of Existing Plant at Texas Industries, L.P. Midlothian Cement Plant. Permit No. 1360a. August 1998
- <sup>26</sup> Florida Department of Environmental Protection. Production Increase, Fly ash Injection, and SNCR at Suwannee American Cement Plant. Final Permit Modification. March 15, 2005.



- 
- <sup>27</sup> Haug, N., Dr. Ing.; Sauter, G., Dipl. Ing.; Samant, G., Dr. Ing., “New developments of High Dust–SCR Technology in the Cement Industry Results of Pilot Tests in Solnhofen and Development State of a Full Scale SCR Unit”, in Proceedings of the *Paris NO<sub>x</sub>/N<sub>2</sub>O Conference*, March 21-22, 2001.
- <sup>28</sup> Kossina, I., Dipl. Ing., “Reduction of NO<sub>x</sub> Emissions from Exhaust Gases of Cement Kilns by Selective Catalytic Reduction”, In Proceedings of the *Paris NO<sub>x</sub>/N<sub>2</sub>O Conference*, March 21-22, 2001.
- <sup>29</sup> Haug, N., Dr. Ing.; Sauter, G., Dipl. Ing.; Samant, G., Dr. Ing., “Einsatz der High-Dust-SCR Technologie in der Zementindustrie”, in VDI Vortrag 2002.
- <sup>30</sup> Electronic mail transmission from Norbert Haug, Dr. Ing., German Umweltbundesamt, to A. A. Linero, Florida DEP. Inquiry regarding Paris 2001 Presentation. May 13, 2002.
- <sup>31</sup> Electronic mail transmission from Norbert Haug, Dr. Ing., German Umweltbundesamt, to A. A. Linero, Florida DEP. Cement NO<sub>x</sub> Emission Standards. August 31, 2000.
- <sup>32</sup> Forschungsinstitut der Zementindustrie. *Environmental Protection in Cement Manufacture*; Verein Deutscher Zementwerke: Düsseldorf, Germany, 2004.
- <sup>33</sup> Austria Umweltbundesamt. Web Report - Erste Anlage zur Katalytischen Entstickung (SCR) in Einem Zementwerk. [www.umweltbundesamt.at/umwelt/industrie/branche/mineral/zement](http://www.umweltbundesamt.at/umwelt/industrie/branche/mineral/zement) accessed on January 16, 2005.
- <sup>34</sup> Szednyj, I., Dipl. Ing., Schindler, I., Dipl. Ing.; Berichte 237 - Aktuelle Entwicklungen Hinsichtlich Abfalleinsatz und Emissionsminderungstechniken in der Zementindustrie. Umweltbundesamt GmbH. Wien. 2004. 107 pages.
- <sup>35</sup> Solnhofen Holding AG. Web Report Summary Table. Unterrichtung der Öffentlichkeit gemäß der 17. BImSchV über den Betrieb des Zementwerkes. [www.spz-solnhofen.de](http://www.spz-solnhofen.de) accessed on March 29, 2005.