

# USE OF SNCR TO CONTROL EMISSIONS OF OXIDES OF NITROGEN FROM CEMENT PLANTS

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## **Abstract**

As air pollution environmental requirements for portland cement manufacturing facilities become ever more demanding, and opportunities for controlling emissions of oxides of nitrogen are restricted by other emission limitations (e.g., for carbon monoxide and sulfur oxides), the cement manufacturer is faced with the need to control  $\text{NO}_x$ , while continuing to control the other pollutants. There are a number of methods that may be adopted by plants to achieve these mutually competing goals. One of these is implementation of low- $\text{NO}_x$  calciners, which cause a portion of the calciner fuel to be burned under sub-stoichiometric (low oxygen) conditions – this method causes combustion under conditions which will suppress generation of fuel  $\text{NO}_x$  from the calciner, and may also cause decomposition of some of the  $\text{NO}_x$  (thermal and fuel) produced in the rotary kiln. Another method is selective non-catalytic reduction (SNCR) of  $\text{NO}_x$  using ammonia or urea. This latter method, when injected in the proper range of temperature, excess oxygen, and possibly carbon monoxide, has the advantage of compatibility with oxidizing conditions in the calciner, which will often minimize or avoid buildup difficulties associated with movement of sulfur as  $\text{SO}_2$  within the preheater. The most efficacious combination of one or both of these methods may be one of the best approaches available to control  $\text{NO}_x$  emissions for new and existing kiln systems, while simultaneously avoiding excessive emissions of CO or  $\text{SO}_2$  and reducing the process problems associated with sulfur cycles.

## **Introduction**

The cement industry is a vital industry for any modern society, because cement is an essential ingredient in concrete. One need only mention reinforced-concrete walls and girders, tunnels, dams, and roads to realize the dependence of our society upon cement products. In the cement-manufacturing process, the solid raw materials are heated to their clinkering temperature, typically 1400 to 1500°C (2550 to 2750°F), by burning various fuels such as coal. Portland cement has been defined as “hydraulic cement produced by pulverizing portland cement clinker and usually containing calcium sulfate.”<sup>1</sup> Portland cement clinker has been defined as “a clinker, partially fused by pyroprocessing, consisting predominantly of crystalline hydraulic calcium silicates.”<sup>1</sup> Burning an appropriately proportioned mixture of raw materials at a suitable temperature produces hard fused nodules called clinker, which are further ground to a desired fineness. Manufacture of all portland cements involves the same basic high temperature fusion and clinkering process responsible for the  $\text{NO}_x$  emissions from cement kilns. This is true because the principal reaction of concern in manufacturing viable cement is the formation of tricalcium silicate (“ $\text{C}_3\text{S}$ -alite”) from dicalcium silicate (“ $\text{C}_2\text{S}$ -belite”) and lime (“ $\text{CaO}$ ”). Alite is the ingredient chiefly responsible for early compressive strength, a property greatly desired by purchasers. If cement needed to contain no alite, it could be produced at much lower temperatures, generating much lower  $\text{NO}_x$  levels.

The purpose of this paper is to address how selective non-catalytic reduction using ammonia or urea may be used to help control  $\text{NO}_x$  emissions, given the above constraints.

## **Mechanisms of $\text{NO}_x$ Formation**

$\text{NO}_x$  is formed as a result of reactions occurring during combustion of fuels.  $\text{NO}_x$  is produced through three main mechanisms during combustion:

- Thermal NO<sub>x</sub>
- Fuel NO<sub>x</sub> and
- “Prompt” NO<sub>x</sub>

Thermal NO<sub>x</sub> is formed by the oxidation of molecular nitrogen at high temperatures in the presence of oxygen. Thermal NO<sub>x</sub> is affected by both excess O<sub>2</sub> in the flame and the temperature of the flame, and in general NO<sub>x</sub> levels increase with higher flame temperatures. Fuel NO<sub>x</sub> is the NO<sub>x</sub> that is formed by the oxidation of nitrogen present in the fuel. This is more a concern in calciner combustion than in the burning zone, since the burning zone will produce NO<sub>x</sub> rapidly, and will achieve near-equilibrium concentrations of NO almost irrespective of the fuel nitrogen. Calciner combustion occurs at a temperature too low for formation of appreciable thermal NO<sub>x</sub>, so that fuel NO<sub>x</sub> dominates in the calciner. “Prompt NO<sub>x</sub>” is a term applied to the formation of NO<sub>x</sub> which will form in reducing systems by oxidation of combustion intermediates such as HCN. This is generally not an important formation mechanism in cement kilns.

### **Process-related NO Formation and Primary Reductions**

In the cement manufacturing process, the formation of thermal NO is unavoidable, as the material temperatures needed to reach a level that will allow a portion of the kiln feed to become a molten liquid (which facilitates the formation of alite) are well above gas temperatures needed for the formation of thermal NO<sub>x</sub>. The material temperature required for this reaction can vary due to several factors but is typically in excess of 1425°C (2600°F).<sup>2</sup>

Therefore, the most direct way to avoid excessive concentrations of NO<sub>x</sub> is by modifications of the process to reduce the formation of the NO<sub>x</sub>.<sup>3</sup> Since NO<sub>x</sub> formation is dictated by high temperature and oxygen concentrations, one good way of avoiding NO formation is to lower the burning zone temperature. This temperature can be reduced if overburning is avoided, and/or if the burnability of the kiln feed can be improved. Burnability is largely a function of lime saturation factor, silica ratio, and coarse quartz or coarse calcite in the feed, etc. An equation used to describe the predicted free lime level in laboratory clinker burned for 30 minutes at 1400°C<sup>4</sup> is:

$$\%CaO_{1400} = 0.31(LSF-100) + 2.31SR + 0.73 Q_{45} + 0.33 C_{125} + 0.35 R_{45}, \text{ where}$$

LSF is the lime saturation factor, SR is the silica ratio, Q<sub>45</sub> is the % quartz coarser than 45 μm, C<sub>125</sub> is the % calcite coarser than 125 μm, and R<sub>45</sub> is the % certain acid insoluble grains coarser than 45 μm. In today’s world where every pound of cement that can be made is marketable, there is a trend toward grinding the mix coarser if the raw mill is a process limitation. Coarse feed is harder to burn, and it is harder to obtain the desired intermediate free lime level with a hard burning mix than with an easy burning mix. For this reason among others, there is a general tendency in North America to overburn the clinker, in order to ensure proper quality. Usually, it is satisfactory to burn the clinker to about 1.5% free lime, and very seldom will cement with this level of free lime fail the Autoclave Expansion (C 151) test, or suffer other quality-related problems. Burning to 0.2% free lime or so is not necessary or desirable, and will make it harder to cool or grind the resulting clinker.

It may be considered desirable to minimize the oxygen level in the kiln, in the interest of minimizing NO as well as maximizing production (if the ID fan is a production limitation). Reducing the excess O<sub>2</sub> can have negative effects on production, such as excessive CO emissions, increased SO<sub>2</sub> emissions, unduly light cement color, and quality effects such as water demand in concrete and cement setting behavior. For these reasons, excess air should not be reduced more than necessary.

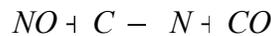
Beyond alterations in the chemical and physical properties of the feed, several technologies have been developed to help reduce the formation of NO<sub>x</sub> and subsequently convert remaining NO<sub>x</sub> into innocuous nitrogen gas. These are primarily accomplished through reductions in burning zone NO<sub>x</sub> formation while maintaining necessary temperatures via “low NO<sub>x</sub>” burners followed by reductions of NO<sub>x</sub> through a process described as staged combustion.

## Low NO<sub>x</sub> Burners

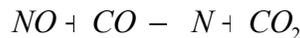
A 'low' NO<sub>x</sub> burner can be utilized for the main kiln burner of a preheater/precalciner kiln system and the only burner in preheater and long kilns. A low NO<sub>x</sub> burner is designed to create two distinct combustion zones while firing the fuel. The first zone is a high-temperature zone where combustion occurs in a fuel-rich environment in the presence of a less-than-stoichiometric oxygen level. The low level of oxygen minimizes NO<sub>x</sub> formation, and also creates CO which additionally reduces some of the NO<sub>x</sub> that is formed. This is then followed by an oxygen-rich environment to complete combustion, with reduced temperatures in which formation of thermal NO<sub>x</sub> is less favorable.

## Staging of Combustion via Calciner<sup>5</sup>

All major cement kiln suppliers offer new "low NO<sub>x</sub>" precalciner designs for new kilns. Fig. 1 shows two different designs from major manufacturers to achieve these conditions. These designs typically inject a portion of the fuel into the feed end of the kiln, countercurrent to the exhaust gas flow. This fuel is burned in a sub-stoichiometric O<sub>2</sub> environment to create a strongly reducing atmosphere (relatively high concentrations of CO) by following the reactions depicted in a simplified form here:

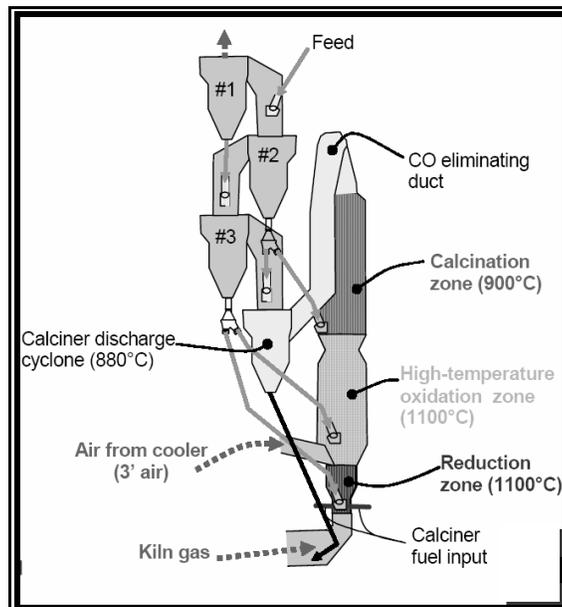


and

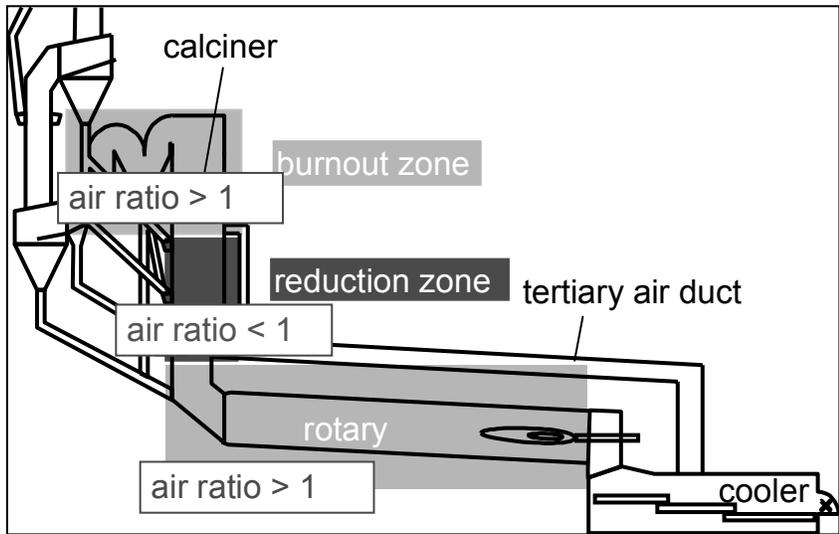


The following figures show two different designs from major equipment manufacturers to achieve these conditions.

**Fig. 1 –Staged Combustion Calciners**

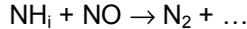
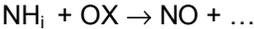


*Low-NO<sub>x</sub> ILC with high temperature Zone*



MSC-CC Calciner

Fuels introduced to the primary combustion zone undergo pyrolysis that liberates nitrogen originally bound in the fuel. Nitrogen-bearing products that are gaseous will again pyrolyze to form HCN and NH<sub>i</sub> radicals. With NO and oxygen radicals (OX) already present in the gas stream, the NH<sub>i</sub> will react as shown:



Because the primary stage of the combustion occurs in a high-temperature (1100° to 1200°C) reducing environment where CO is prevalent and oxygen radicals are relatively scarce, NH<sub>i</sub> radicals can scavenge oxygen from NO as shown in the second equation. This phenomenon is the basis for successful NO<sub>x</sub> reduction in staged combustion. Several precalciner kilns in the US have recently been retrofitted with these “low NO<sub>x</sub>” precalciner kilns and preliminary information indicates a noticeable reduction in NO<sub>x</sub> per ton of clinker. Up to 46 percent reduction of NO<sub>x</sub> emissions has been reported without causing excessive coating difficulties in the kiln.

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 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, or if alkalis, chlorine, and sulfur are abundant.

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 clearly 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.

Emissions reductions have also been found when tire-derived fuel was burned in a precalciner. In one case, when 47 percent of the coal fired in the calciner was substituted with tire-derived fuel, a reduction in NO<sub>x</sub> emissions of about 29 percent was observed.<sup>6</sup> This is primarily due to the combustion characteristics

of the tires themselves, which by virtue of the large size of the fuel particles create localized reducing zones during the combustion process similar to staged combustion.

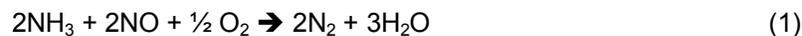
### **Secondary Control Technologies (End-of-pipe)**

Despite the advantages of low-NO<sub>x</sub> calciners for controlling NO<sub>x</sub> emissions, the reducing conditions necessary for effective decomposition of NO can lead to problems in operation, due in particular to the movement of sulfur in the riser duct and lower cyclones. Because of the foregoing, it is often necessary to adopt methods to decompose NO<sub>x</sub> that has already been formed. In addition to the methods already mentioned, there are several possibilities. One of these is the selective catalytic reduction (SCR) process, using a catalyst to promote the reaction of ammonia or urea with NO, and widely utilized in power plants. This process can be carried out at reduced temperatures, and is theoretically possible beyond the dust-collecting air pollution control device. Another method has surfaced from recent findings, suggesting that the NO or NO<sub>2</sub> present in the gas stream can be oxidized with materials such as ozone or hydrogen peroxide to produce materials that are highly water soluble. A scrubber could then remove the nitrates and nitrites formed, in a highly effective manner. While this technique may be effective, it requires the use of a scrubber, which is expensive and involves the generation of an additional waste stream (waste water) which must be managed. Because of the expense and technical difficulties associated with these two remediative methods, a third important end-of-pipe method has recently gained favor in the cement industry. This method is called Selective Non-Catalytic Reduction, or SNCR.<sup>7</sup> In SNCR, ammonia, urea, or other nitrogen compounds (such as cyanuric acid) are injected into a portion of the pyro-processing system with appropriate temperature and oxygen concentrations (and potentially also CO concentrations). The subject of the present paper is the practical application of SNCR to cement kilns.

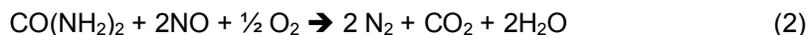
## **SNCR**

### **Theory of Reduction**

In SNCR<sup>7</sup>, the NO in the kiln (which typically represents at least 90% of the total NO<sub>x</sub>) reacts with ammonia as follows:



If urea is used, the reaction is:

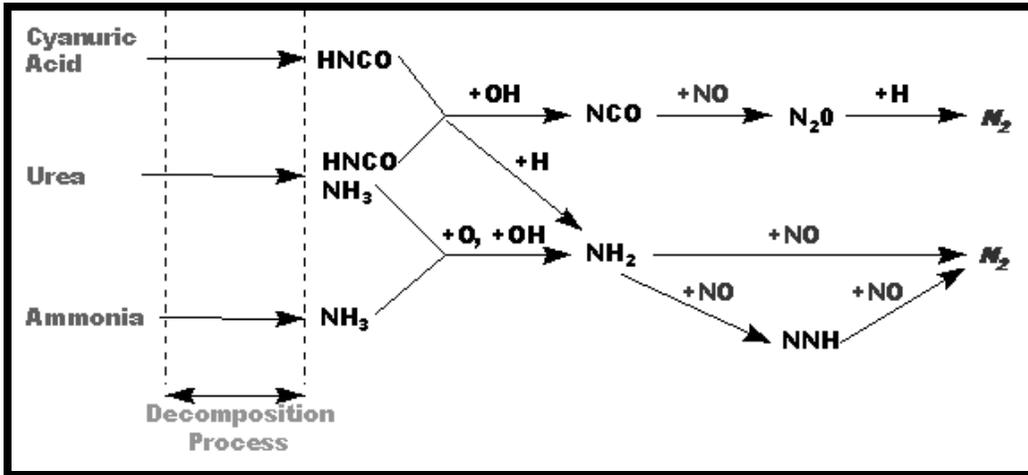


Either reaction in principle leads to the formation of innocuous nitrogen. The ammonia (and often the urea) is most conveniently introduced as a water solution.

### Reagents Used in the Process

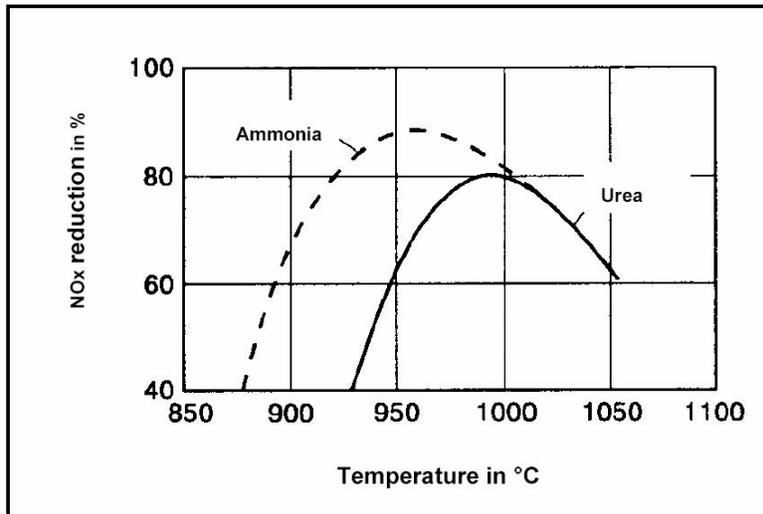
SNCR, as performed with ammonia and urea, may take several paths.

**Fig. 2 – Ammonia and Urea Dissociation and Reduction Pathways**



*Source: E3 (Engines Emissions, Energy) Research Laboratory, Department of Mechanical Engineering Texas A&M University*

With either reagent, if the temperature is too low, un-reacted reagent will result, typically referred to as “slip”. Alternatively, if the temperature is too high, some or all of the nitrogen present in the reagent may be oxidized to NO. The traditional optimum temperature range to avoid either of these undesirable outcomes for ammonia is about 1600-2100°F (870-1150°C); however several factors have been identified to shift this temperature window. For urea the temperature window is slightly higher, with optimal efficiency theoretically around 1000 °C.



**Fig. 3 – Relative Effectiveness of Ammonia and Urea in Reducing NO<sub>x</sub> in Cement Kilns**

With urea, the same problems exist with the temperature profile, along with a couple of new ones.<sup>8</sup> Urea decomposes under the proper conditions to give carbon dioxide, as shown in equation (2) above. If oxygen is present in sufficient concentration, carbon dioxide is formed, but if it is deficient, carbon

monoxide may be formed instead. We will discuss the dual roles of carbon monoxide later; suffice it to say that it can hinder the reaction to reduce NO in some circumstances, and hamper the efficiency of the process. Additionally, during dissociation of urea to NH<sub>2</sub>, the urea competes for the OH radicals present; these are needed for the SNCR-NO reduction reaction as well as for the burnout of CO to CO<sub>2</sub>. This leads to more un-reacted CO with these two competing reactions. In theory this problem should be equally vexing for ammonia as well, but appears much more prevalent with the use of urea. Additionally, the presence of the localized CO generation from the urea dissociation may further retard the consumption of NH<sub>2</sub> intermediate in the SNCR reaction, giving lower efficiency if sufficient oxygen is not present, which is typically the case in the kiln-calciner region. Also, a byproduct of the urea reaction, in particular, is nitrous oxide (N<sub>2</sub>O). While N<sub>2</sub>O is not a precursor to smog or acid rain, it is a serious greenhouse gas, with greenhouse effects more than 300 times as strong as those of carbon dioxide. (<http://yosemite.epa.gov/OAR/globalwarming.nsf/content/Emissions.html>).

The advantages of urea are primarily the handling and safety of the reagent. Urea has a much lower vapor pressure than ammonia, and can be easily handled with fewer concerns for leaks or spills. However, due to the reasons discussed, ammonia appears to be a much more effective reagent for use in the SNCR process, especially considering the minimal oxygen content and temperature windows present in the kiln-calciner regions.

### **Results of Full Scale Cement Plant SNCR Tests**

The following discussion outlines the test results of SNCR testing carried out at five cement plants. At one plant (Plant D), the testing included both urea and ammonia injection. In addition to the results previously discussed, work carried out by Rose, Alder and Erpelding<sup>9</sup> also suggests that ammonia is both more effective than urea, and is effective at a lower temperature, as was seen in Figure 3. Ammonia appears to have a maximum efficiency at about 950°C (1740°F), where about 90% of the NO<sub>x</sub> may be reacted if the oxygen and carbon monoxide concentrations are optimum. Urea, on the other hand, has a maximum efficiency of about 80% at 990°C (1814°F). It will be noted that the ammonia achieves a maximum efficiency of almost 70% at 900°C (1650°F); at this temperature, urea achieves almost no NO<sub>x</sub> reduction at all. For these reasons Plants A, D, and E were tested entirely with ammonia or a combination of both. Plants B and C tested with urea for the reasons noted - safety and ease of handling of urea. Based on the results and conclusions drawn from the testing, Plant A has installed a permanent SNCR system in March of 2005 and has been operating to date with ammonia only.

### **Burnability Effects**

The overall level of NO<sub>x</sub> from the burning zone will be a function of the composition of the clinker and the fineness of the kiln feed, particularly the quartz and calcite fractions. Table 1 shows the relative contributions of the feed chemistry to the kiln NO<sub>x</sub>; no data is currently available on the coarse quartz and coarse calcite contributions. As judged by LSF and silica ratio, Plant B is by far the hardest burning mix of those studied – a fact reflected in the high level of lbs NO<sub>2</sub>/ton clinker for this plant.

**Table 1: Plant Kiln Feed Chemical Composition**

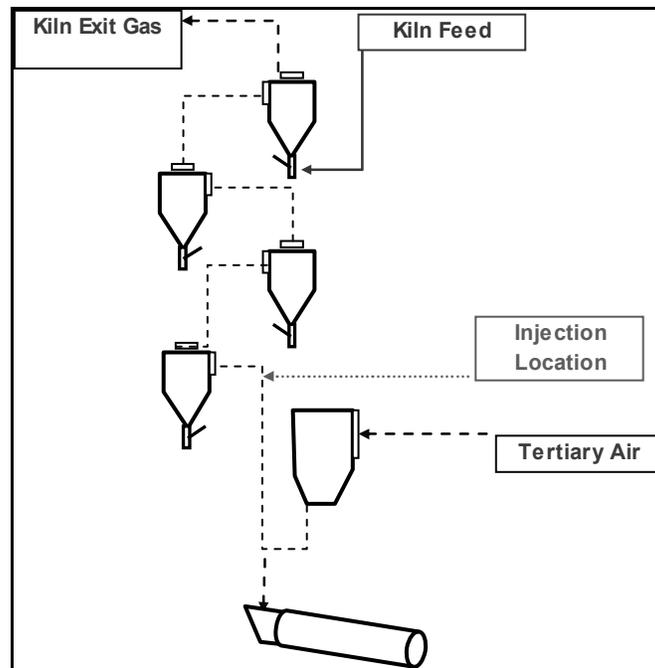
	CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	LSF	Silica Ratio
<b>Plant A</b>	43.56	12.45	2.24	3.43	0.12	0.31	0.31	107.9	2.20
<b>Plant B</b>	42.64	12.58	1.37	3.12	1.16	0.81	0.15	107.1	2.80
<b>Plant C</b>	42.52	13.53	1.72	3.86	0.66	0.82	0.23	97.6	2.42
<b>Plant (ignited) D</b>	63.60	21.43	3.06	5.36	1.27	0.62	0.36	93.1	2.54
<b>Plant (ignited) E</b>	64.22	20.66	4.70	3.05	0.74	2.05	0.20	99.6	2.67

## Plant A

Plant A is a 4-stage precalciner facility with no preheater bypass and a maximum production level of around 120 short tons per hour of clinker. The facility is designed with a separate line calciner and the ability to introduce tertiary air into three locations for the formation and control of staged combustion. Tertiary air can be introduced either into the calciner for combustion, the calciner burner as primary air for the fuel, or further along in the process in the ducting of the calciner for burnout of CO following the reducing zone of the staged combustion.

This plant also benefits from a low alkali and sulfur content in the feed, which facilitates operating the calciner under reducing conditions; despite this fact, it is preferable to operate the calciner under oxidizing conditions to avoid formation of buildups, with their attendant increases in pressure drop across the preheater and limited production due to ID fan inadequacies. For this reason, the plant has carried out SNCR testing without maximizing the low-NO<sub>x</sub> calciner capability of the system. Plant A was tested with ammonia, with injection after the calciner hopper, but before the bottom stage cyclone as shown in Figure 4. This location was then installed with a permanent SNCR system consisting of four nozzles at 90° degree intervals transecting the ducting. The retention time from the calciner to this location is on the order of nearly 3 seconds, giving sufficient time for the burnout of the coal currently used in the calciner.

**Figure 4: SNCR Injection Location Plant A**



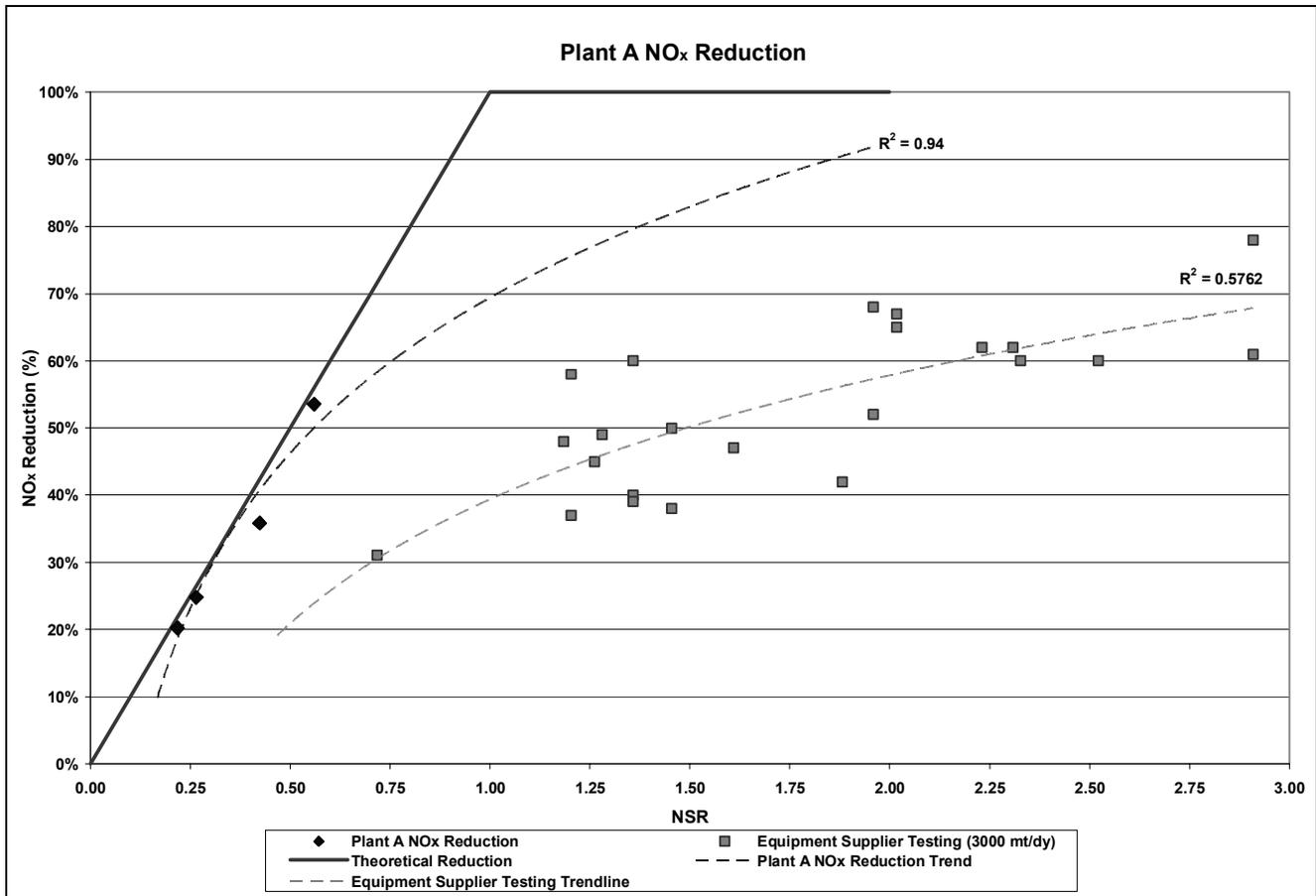
The results show typical reductions over a range of normalized stoichiometric ratios (NSR) for NH<sub>3</sub> to NO<sub>x</sub> expressed as NO<sub>x</sub> from the permanent system. The results appear in Table 2 below.

**Table 2. Results of SNCR Testing at Plant A**

Reagent Rate gph	NSR	Actual NO <sub>x</sub> Reduction %	Theoretical NO <sub>x</sub> Reduction lb/hr as NO <sub>2</sub>	SNCR Efficiency %
84.7	0.56	53.5%	267.2	96%
64.9	0.42	35.8%	353.3	85%
40.6	0.27	24.7%	450.6	94%
32.8	0.22	20.2%	471.7	93%
<b>Average</b>	<b>0.37</b>	<b>33.6%</b>		<b>92.0%</b>

Here, the theoretical NO<sub>x</sub> reduction is the number of lbs/hr of reduction of NO<sub>x</sub> at 100% efficiency, and the ratio of actual reduction to NSR is the efficiency of the SNCR process. Thus, 100% efficiency would mean complete reaction of every mole of NO with one mole of NH<sub>3</sub>, and an NSR of 1 would result in complete removal of all NO present at the injection location. In practice it is usually very difficult to achieve near theoretical reductions, but Plant A was able to achieve very high efficiencies of utilization of the ammonia. The results are also displayed graphically in the following figure, with the maximum theoretical reduction shown, as well as results obtained from an equipment supplier during testing conducted on a kiln system of similar size and design<sup>9</sup>.

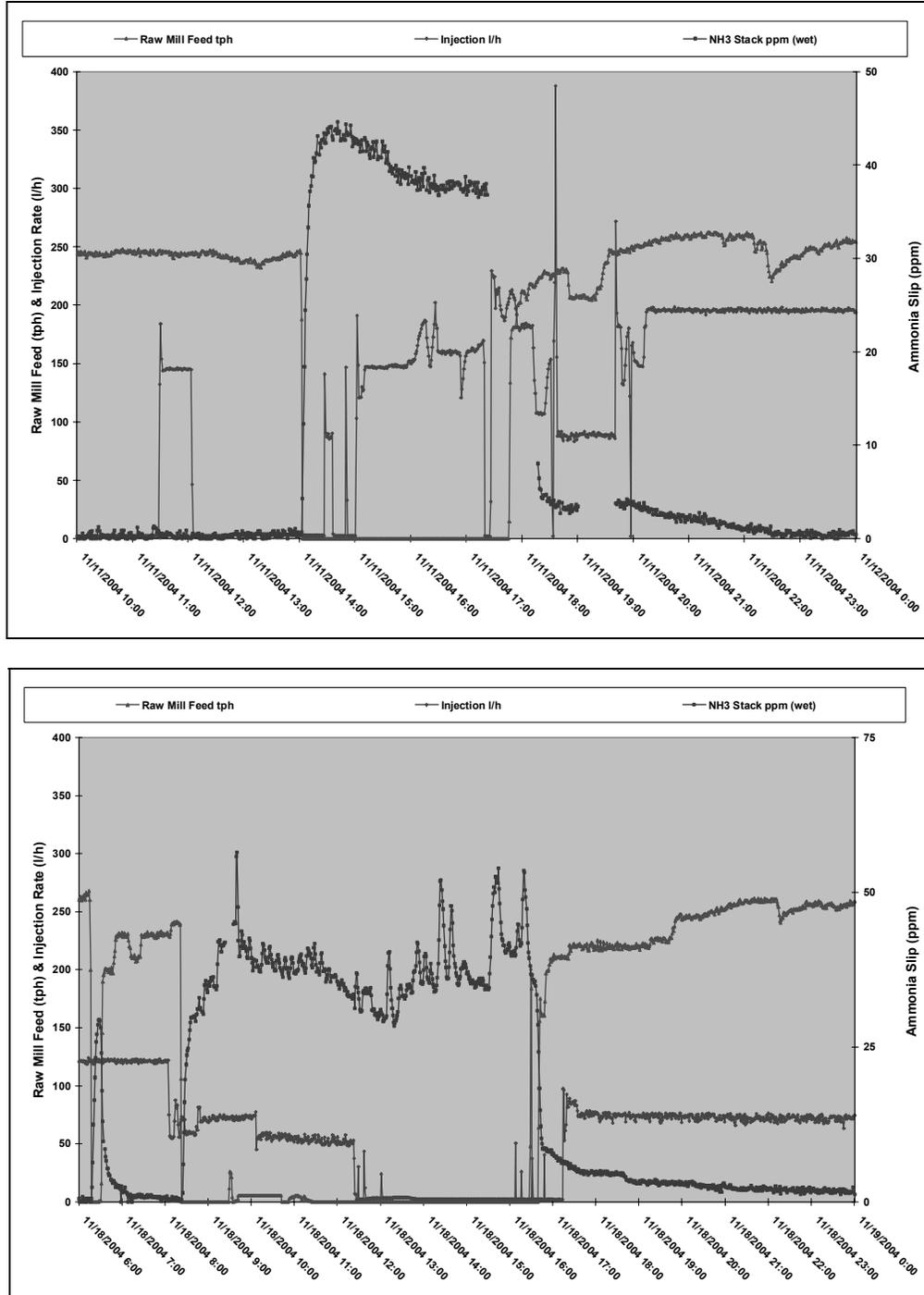
**Figure 5: SNCR Results Plant A**



From the reduction levels achieved in comparison to the theoretical limits and the results from previously established testing, this was a highly successful SNCR installation. The mechanisms responsible for this high efficiency of reduction will be discussed in more detail later in the paper.

One other outcome observed was the formation of an ammonia cycle within the roller mill system. Plant A does not have the ability to monitor ammonia continuously, but during a period of the testing an FTIR (Fourier Transform Infrared Analysis) gas analyzer unit was placed on the stack to observe NH<sub>3</sub> emissions. While the FTIR was monitoring, the raw mill was stopped on two occasions. During each of these occurrences ammonia was detected at the stack. Data from each of these is shown in Fig. 6:

**Figure 6: Plant A Ammonia Slip**



During the first instance with the raw mill down, no ammonia was injected into the kiln system through the SNCR system. On the second instance with the raw mill down, injection was occurring when the raw mill initially went down but was stopped part way through the outage. The injection rate did not appear to be correlated with the ammonia present in the stack. In both cases the concentration of ammonia in the stack gas peaked at about 50 ppm (v/v).

The ammonia seemed to be caught in an internal cycle in the kiln/raw mill system. When the raw mill was removed from the process during raw mill outages, the scrubbing offered by the raw meal was eliminated and the ammonia escaped through the stack. Plant A sent several kiln feed samples for evaluation for ammonia concentrations from varying periods during the testing, to evaluate the possible enrichment of the kiln feed with ammonia. The analytical results, when above the detection limit, did show an increase in ammonia concentrations in the kiln feed over baseline conditions prior to the injection of ammonia. However, due to the relatively low amounts of ammonia and the high detection limit for the method, it proved impossible to reach definitive conclusions. An ammonia cycle was present, in part due to the highly soluble nature of ammonia. The un-reacted ammonia condenses onto the moist particles in the raw mill (Plant A has 17% moisture in raw mill feed). As the volatile ammonia is introduced to the higher temperatures in the raw mill and/or preheater tower, it evaporates back into the gas stream to repeat the process. This process continues until the raw mill is down, removing the scrubbing effect, whereupon the ammonia escapes out the stack.

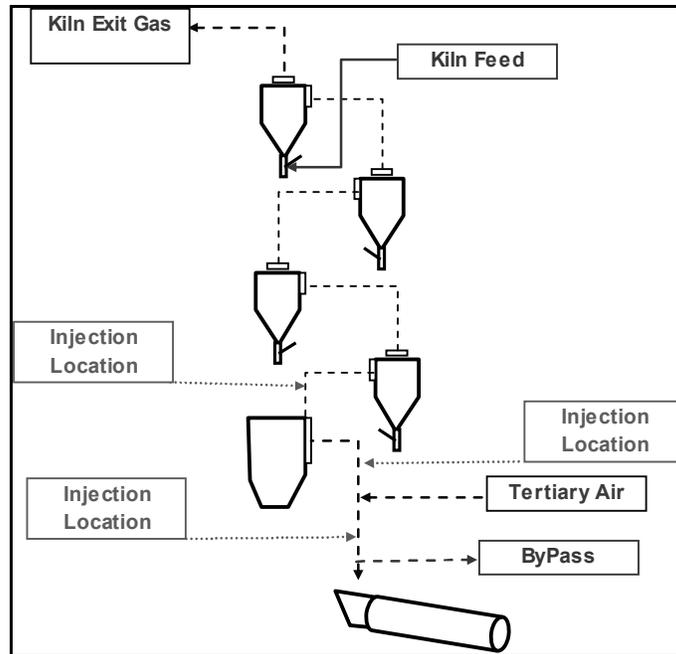
### **Plant B**

Plant B is a calciner kiln with a maximum production level of approximately 190 tons per hour of clinker. The plant is a 4-stage precalciner, recovering heat from the clinker cooler in tertiary air for use in combustion in the calciner. The plant has an alkali bypass which it utilizes both for sulfur and alkalis present in the raw materials and kiln fuel. During testing the plant was operating around 180 tons/hr. of clinker, with approximately 5% to 10% of the main stack flow bypassed through a separate bypass stack. After the bypass takeoff, the kiln exit gas travels through a riser duct before the tertiary air is introduced from the clinker cooler. Tertiary air is introduced in one location only; during testing the duct was fixed at 100% open. Following the tertiary air duct, the kiln riser abruptly stops and then is diverted tangentially into the calciner. Here fuel is fired from four locations. Following the calciner the exhaust gases are introduced immediately into the lowest cyclone. Retention time from the calciner to the lowest cyclone is on the order of 0.2 seconds to 0.8 seconds as a maximum.

SNCR testing was carried out utilizing urea reagent, with injection at four locations:

1. Riser duct, after the alkali bypass takeoff, but before the tertiary air duct (2 nozzles)
2. Gas exit of the lowest stage cyclone (2 nozzles)
3. The same location as (1), but with 4 nozzles
4. In the riser duct, after the tertiary air duct, but before the calciner.

Fig. 7 shows the layout of the kiln gas exit and riser duct with bypass takeoff and tertiary air introduction before entering the calciner and lowest stage cyclone.



**Figure 7. Plant B Calciner Configuration**

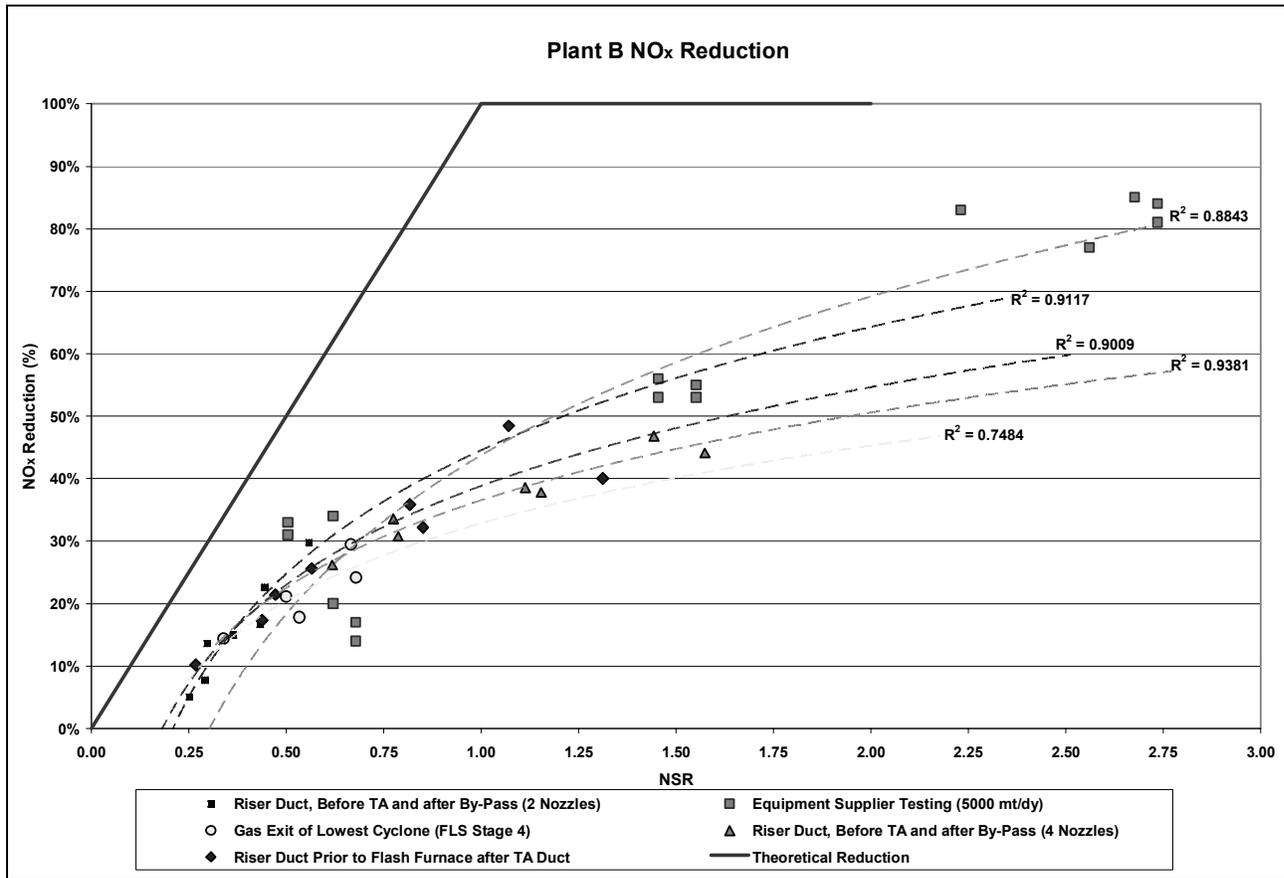
The average results for the four locations and a graph of the results are given in Table 3 and Fig. 8 below.

**Table 3: SNCR Testing at Plant B**

LOCATION	Reagent Rate	NSR	Actual NO <sub>x</sub> Reduction	Theoretical NO <sub>x</sub> Reduction	SNCR Efficiency
	gph			lb/hr as NO <sub>2</sub>	
Riser Duct prior to TA Duct (2 Nozzles)	145.0	0.38	15.8%	1360.9	39.4%
Gas Exit of lowest Cyclone	180.5	0.54	21.4%	874.0	39.6%
Riser Duct prior to TA Duct (4 Nozzles)	314.2	1.07	36.8%	-125.9*	36.1%
Riser Duct after TA Duct	282.0	0.72	28.9%	639.5	40.7%

\* A negative theoretical NO<sub>x</sub> reduction implies that there is more than enough ammonia to reduce all NO<sub>x</sub> present.

Figure 8: SNCR Results Plant B



The results did not vary greatly from the reduction levels achieved in testing from an equipment supplier on a similar sized calciner (5000 metric tons per day)<sup>9</sup>. The ideal location was identified to be in the lower portion of the riser duct prior to the tertiary air introduction. This was due to several factors.

The selection of urea reagent forced higher temperature profiles for increased reduction efficiency. Location 2, the gas exit after the lowest cyclone, had conditions very similar to those used at Plant A: temperature around 1550°F, sufficient oxygen (1% to 2%), CO at 1000 to 2000 ppm, and sufficient retention time for the reaction. However, with urea the reaction did not achieve comparable efficiency. As previously discussed the dissociation and reaction of urea is improved by a higher temperature profile with the presence of sufficient oxygen and perhaps longer retention time. In Plant B, the temperature was the most significant factor affecting the efficiency. This led to the highest temperature injection location (riser duct location prior to the introduction of the “colder” tertiary air) being selected as the most efficient injection location, which still resulted in much lower efficiency than in Plant A.

Additionally, Plant B’s calciner cross section was much larger in size than that of Plant A. As noted from Rose, Alder and Erpelding<sup>9</sup> a measurable reduction in efficiency of the SNCR process is observed as the cross sectional size of the injection location increases. This is partially attributed to a reduction in mixing capabilities at the injection location from both the reagent and the NO present in the gas stream. It may also be due in part to mixing occurring as a result of wall effects. However, with the nozzles selected and tested, little difference was noted between the uses of one, two, three, or four nozzles at the same flow rates, calling into question the hypothesis of a lack of mixing between reagent and gas stream. Fluid dynamic mixing effects may be more effective with ammonia reagent. .

One other noticeable difference between the results at Plants A and B was the observed increase in CO from Plant B, especially when injection of the reagent was in locations with lower oxygen content. As

previously discussed, urea can create CO in its dissociation into  $\text{NH}_3$ , but may also interfere with the OH radical and retard the burnout of CO to  $\text{CO}_2$  more rapidly than with ammonia. Perhaps the creation of the  $\text{NH}_3$  from urea results in the dissociation of the urea and creates denser localized areas of CO, which can interfere with the oxygen-enhanced  $\text{NH}_2/\text{NO}$  interaction.

Ammonia slip was not monitored for at Plant B, but during testing a pronounced detached plume was noted, despite low levels of  $\text{SO}_2$  present in the main stack. This, coupled with the overall low level of efficiency for  $\text{NO}_x$  removal, suggests that Plant B would achieve only limited  $\text{NO}_x$  reduction with the SNCR system as tested; however some improvements learned from other tests may be possible.

There is an interesting explanation for the relatively inefficient removal of NO from Plant B (and Plant C) relative to the other plants. Plants B and C are calciner kilns, where the most efficient location for reagent injection is in the riser duct. This would be expected to deal efficiently with the NO generated in the burning zone, but cannot address fuel  $\text{NO}_x$  generated in the calciner, as the injection point is upstream. No direct measurements of  $\text{NO}_x$  and flow combined were taken upstream of the injection site, so no direct measurement of the efficiency can be offered in terms of NSR. For comparison purposes the NSR given assumes all NO is generated from the kiln burning zone, none of the NO from the kiln is reduced in the calciner, and that the calciner generates no further NO. Of course these are not valid assumptions, as fuel  $\text{NO}_x$  is contributed from the calciner for most fuels, so the SNCR efficiency determined at the stack is most likely artificially low, since at the injection location the reagent did not have the opportunity to react with NO generated further back in the process, in the calciner.

Since the riser duct location was optimum for these kilns despite the fact that the fuel  $\text{NO}_x$  from the calciner was not treated, it appears that the location after the calciner was too low a temperature, or at too high a CO level, to be effective with the selected reagent of urea. Again, this shows the distinct advantages associated with the use of ammonia rather than urea, as the optimum temperature for ammonia is lower.

### **Plant C**

Plant C is a two string preheater tower with one string equipped with a calciner and the other a simple preheater. The calciner string is much larger in throughput, receiving approximately 80 to 85% of the gas and material flow. Maximum production level is approximately 215 tons per hour of clinker. The plant has an alkali bypass which it utilizes both for sulfur and alkalis present in the fuel and raw materials. Tertiary air from the cooler is introduced prior to the calciner in the calciner string of the tower. During testing the plant was operating around 206 tons of clinker. The fuel utilized in the main burner and calciner during testing was petroleum coke, and as a result of low volatile matter content and limited retention time available in the calciner resulted in elevated CO levels after the calciner and through the lower stage. In addition, residual carbonaceous material in the raw meal is believed to contribute to elevated CO levels throughout the preheater and calciner strings.

SNCR testing was carried out utilizing urea, with injection to each of the strings. For the calciner the injection locations were as follows:

1. Lower portion of the calciner (2 nozzles)
2. Upper portion of the calciner (2 nozzles)
3. Gas exit of the lowest cyclone after calciner (2 nozzles)

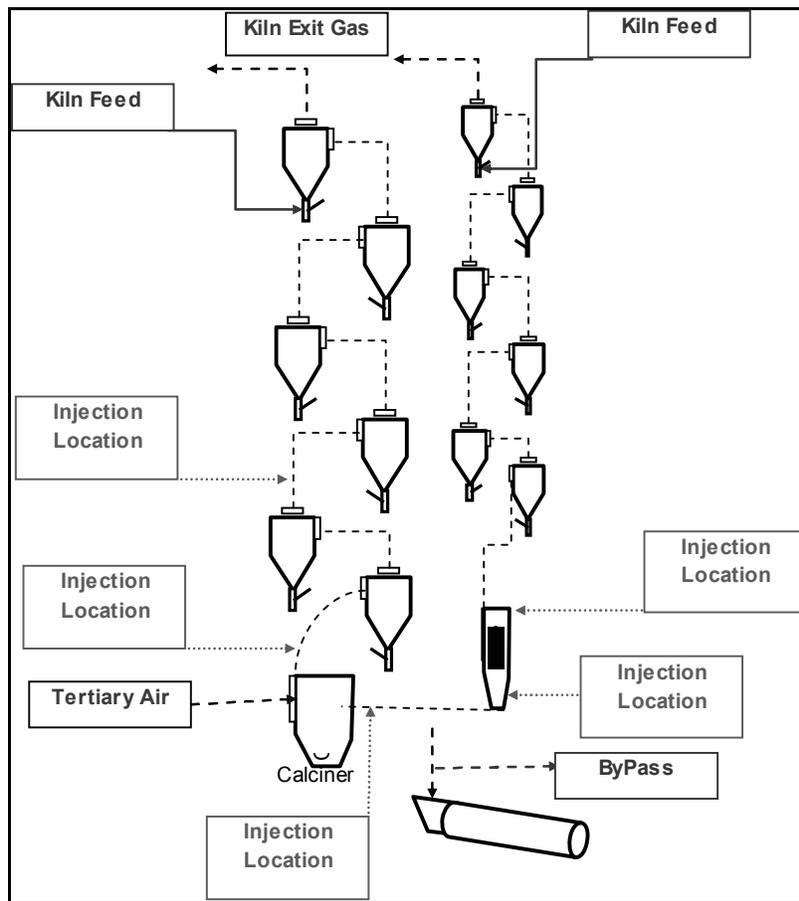
SNCR testing was additionally carried out on the preheater string of the system in the following locations:

1. Lower portion of the riser duct (2 nozzles)
2. Upper portion of the riser duct (2 nozzles)

A combination of locations was also tested with the upper portion of the riser on the preheater string and the upper portion of the calciner.

Figure 9 shows the layout of the kiln gas exit, calciner and riser duct with bypass takeoff and tertiary air.

**Figure 9: Plant C Configuration**

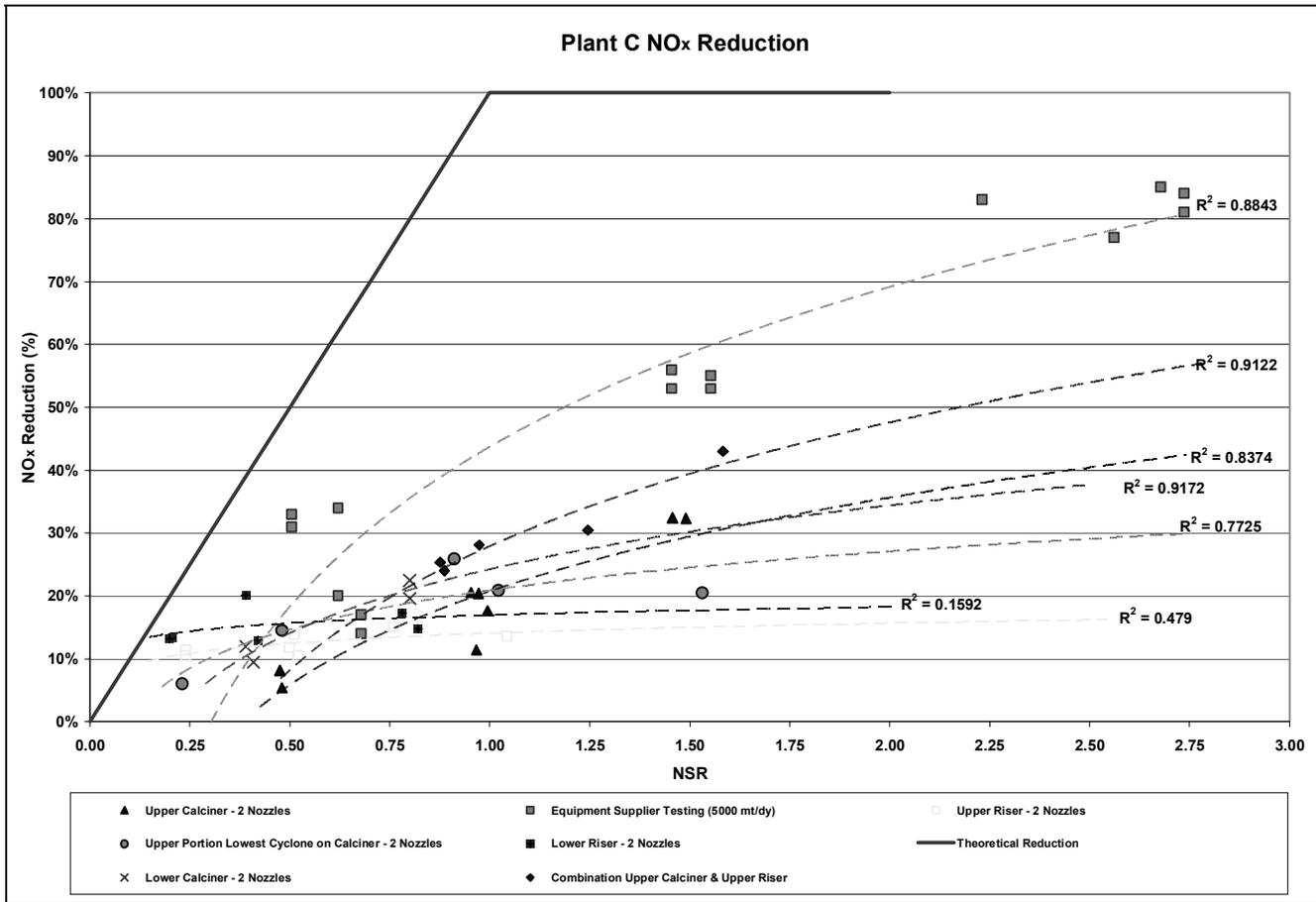


The average results for the locations and a graph of the results are given in Table 4 and Fig. 10 below.

**Table 4: SNCR Testing at Plant C**

LOCATION	Reagent Rate	NSR	Actual NO <sub>x</sub> Reduction	Theoretical NO <sub>x</sub> Reduction	SNCR Efficiency
	gph		%	lb/hr as NO <sub>2</sub>	%
Upper Calciner - 2 Nozzles	226.1	0.97	18.6%	50.9	18.1%
Upper Riser - 2 Nozzles	120.8	0.54	12.4%	756.4	27.9%
Upper Portion Lowest Cyclone on Calciner - 2 Nozzles	190.7	0.81	16.8%	338.7	23.3%
Lower Riser - 2 Nozzles	131.8	0.47	15.3%	1082.9	42.4%
Lower Calciner - 2 Nozzles	169.5	0.60	15.9%	825.6	26.7%
Combination Upper Calciner & Upper Riser	310.8	1.11	30.2%	-213.7	27.3%

Figure 10: SNCR Results Plant C



In general the reduction efficiencies for Plant C were very low, resulting in minimal decrease in NO<sub>x</sub> emissions despite high NSR. As discussed, the choice of urea as the reagent probably hurt in the efficiency of the NSR. As stated earlier, independent measurements have shown that a great deal of the NO<sub>x</sub> at this plant is generated in the tower, (fuel and feed NO<sub>x</sub>) subsequent to the injection site. As previously discussed this makes the ability to calculate the overall NSR and efficiency difficult, since injection locations prior to the calciner do not reduce the NO<sub>x</sub> generation within the calciner and the molar rate of NO from the kiln is not easily known. In the case of Plant C, the operation of the kiln and the calciner do quite an effective job at reducing the thermal generation of NO from the burning zone so injection zones prior to the calciner will have two disadvantages. First they will have only limited amounts of NO present to reduce. When compared to the overall rates of NO reduction, it will appear to have very limited efficiency, but in reality the SNCR may be effectively reducing the limited NO present at the location of injection. Secondly, the NO reduced by the SNCR prior to the calciner would have been greatly reduced by the calciner with its inherent reducing zone as operated during the testing. Since these principles of staged combustion are present in the calciner and quite effective with Plant C for reducing kiln NO, the effectiveness of the low-NO<sub>x</sub> calciner should be maximized, with subsequent reduction from SNCR. The choice and location of testing should most likely have focused on post calciner injection, since low NO is present entering the calciner and there is significant generation of NO from the fuel in the calciner. The size of Plant C may have contributed some inefficiency, as Plant C is the largest of the plants tested.

In the preheater string the reduction was more effective in the upper portions of the riser, which was unusual given the reagent selection. With urea it was identified in Plant B that temperature was the predominant factor in controlling the efficiency. However, temperatures in the riser duct of Plant C may

not increase in the upper portions but it is presumed that the CO present in the kiln inlet from uncombusted fuel decreases in the upper portion of the riser. This may contribute to the increased efficiency at the upper portion of the riser.

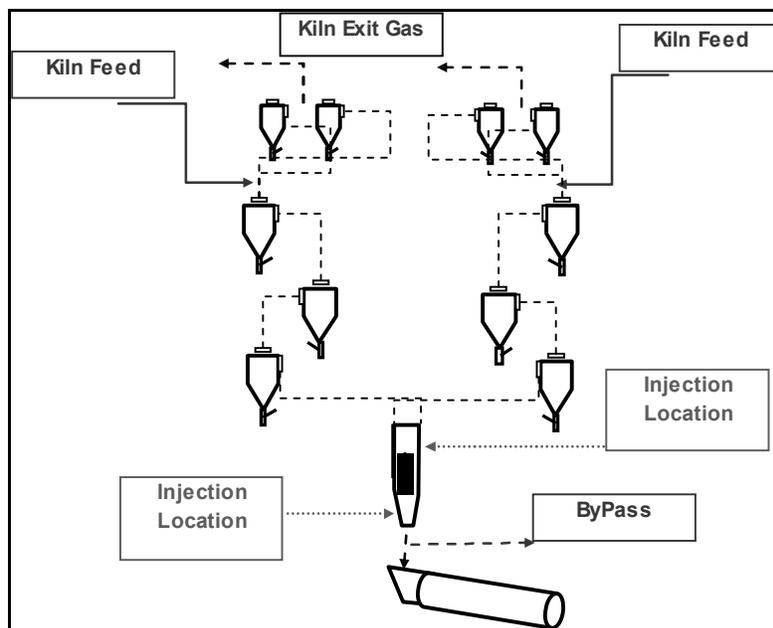
### Plant D

Plant D is a two string preheater kiln without calciner, with a maximum production level of approximately 110 tons per hour of clinker. The plant has an alkali bypass which it utilizes both for sulfur and alkalis present in the raw materials and fuel. During testing, the plant was operating with an hourly production of around 105 tons of clinker. Fuel utilized during testing was Pet Coke. SNCR testing was carried out utilizing both urea and ammonia. The injection locations were selected in to be in the upper and lower portions of the common riser duct. (In kilns without calciners, the optimum temperature will usually be found in the riser duct).

1. Lower portion of the riser with urea (4 nozzles)
2. Upper portion of the riser with urea (3 nozzles)
3. Upper portion of the riser with ammonia (3 nozzles)

Fig 11 shows the layout of the kiln gas exit and riser duct with bypass takeoff.

**Figure 11: Plant D Configuration**

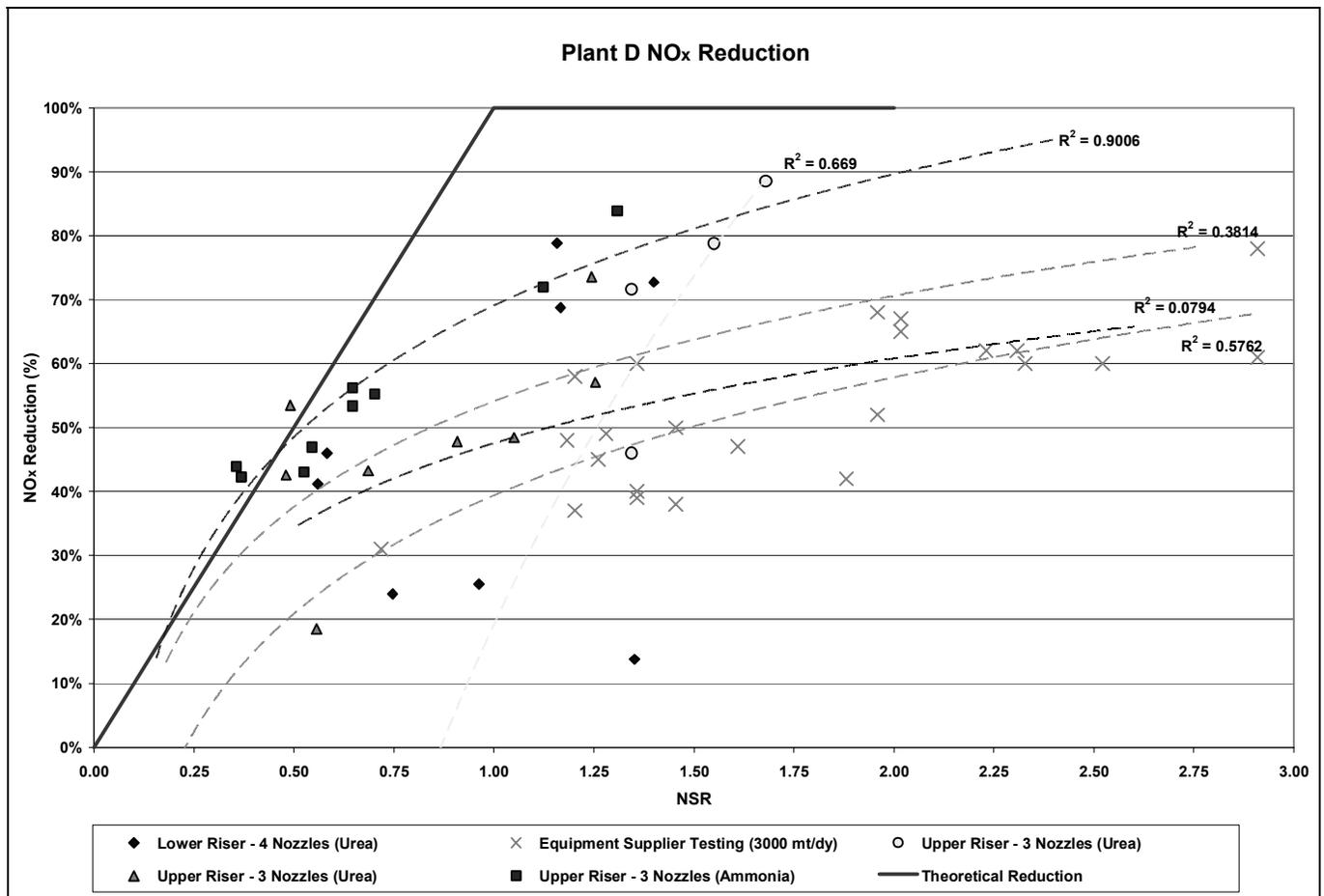


The average results for the locations and a graph of the results are given in Table 5 and Fig. 12 below.

Table 5. SNCR Testing at Plant D

LOCATION	Reagent Rate	NSR	Actual NO <sub>x</sub> Reduction	Theoretical NO <sub>x</sub> Reduction	SNCR Efficiency
	gph		%	lb/hr as NO <sub>2</sub>	
Lower Riser - 4 Nozzles (Urea)	80.4	0.99	46.3%	19.5	50.0%
Upper Riser - 3 Nozzles (Urea)	77.6	1.48	71.2%	-190.6	47.7%
Upper Riser - 3 Nozzles (Urea)	47.6	0.83	48.1%	69.9	62.2%
Upper Riser - 3 Nozzles (Ammonia)	58.8	0.66	53.9%	119.3	89.7%

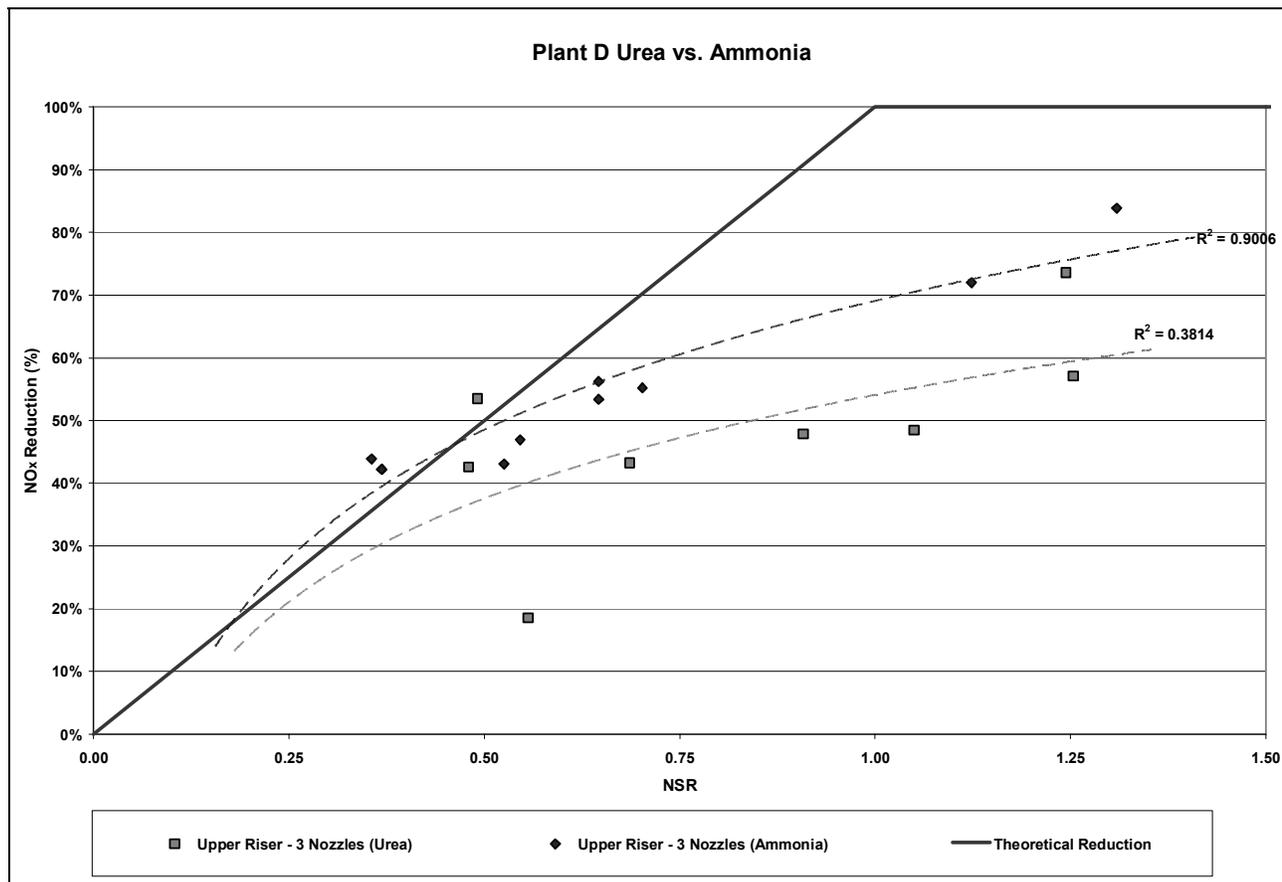
Figure12. SNCR Results Plant D



Plant D experienced the most efficient reductions of any plant tested with urea. This plant has low CO in the riser duct and sufficient temperature for the highly temperature sensitive urea reaction. Also, no fuel

is burned subsequent to the injection location, so no chance of additional fuel NO<sub>x</sub> formation exists. Feed NO<sub>x</sub>, of course, could still form. Plant D was also the only plant to test both with urea and with ammonia. Results in the same location showed marked improvement with the use of ammonia and almost theoretical reductions in NO resulted from the use of ammonia. Fig. 13 shows the same injection location with the same number of nozzles with the use of urea versus ammonia.

**Figure 13: Plant D Urea versus Ammonia**



Results at Plant D have shown the efficiency advantages of ammonia over urea, as well as the possible influence of size and wall effects that could be present in smaller cross-sectional injection locations.

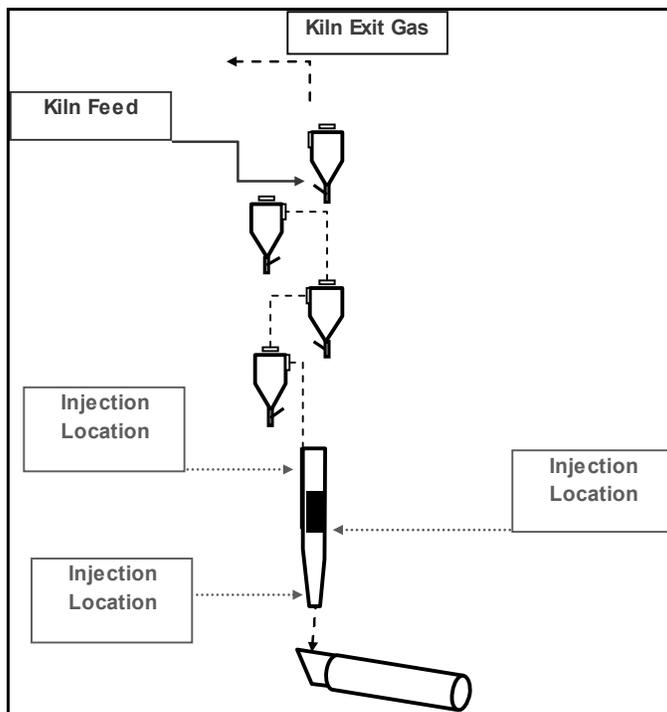
**Plant E**

Plant E is a small preheater kiln with a maximum production of approximately 30 tons per hour of clinker. The plant does not have an alkali bypass despite the fact that during testing it was firing 100% pet coke and has high SO<sub>3</sub> concentrations in the clinker (2.52% SO<sub>3</sub>). SNCR testing was carried out utilizing ammonia with injection locations throughout the riser duct as follows:

1. Lower portion of the riser (2 nozzles)
2. Lower portion of the riser (1 nozzles)
3. Middle portion of the riser (2 nozzles)
4. Middle portion of the riser (1 nozzles)
5. Upper portion of the riser (2 nozzles)
6. Upper portion of the riser (1 nozzles)

Fig. 14 shows the layout of the kiln gas exit and riser duct with bypass takeoff.

**Figure 14: Plant E Configuration**

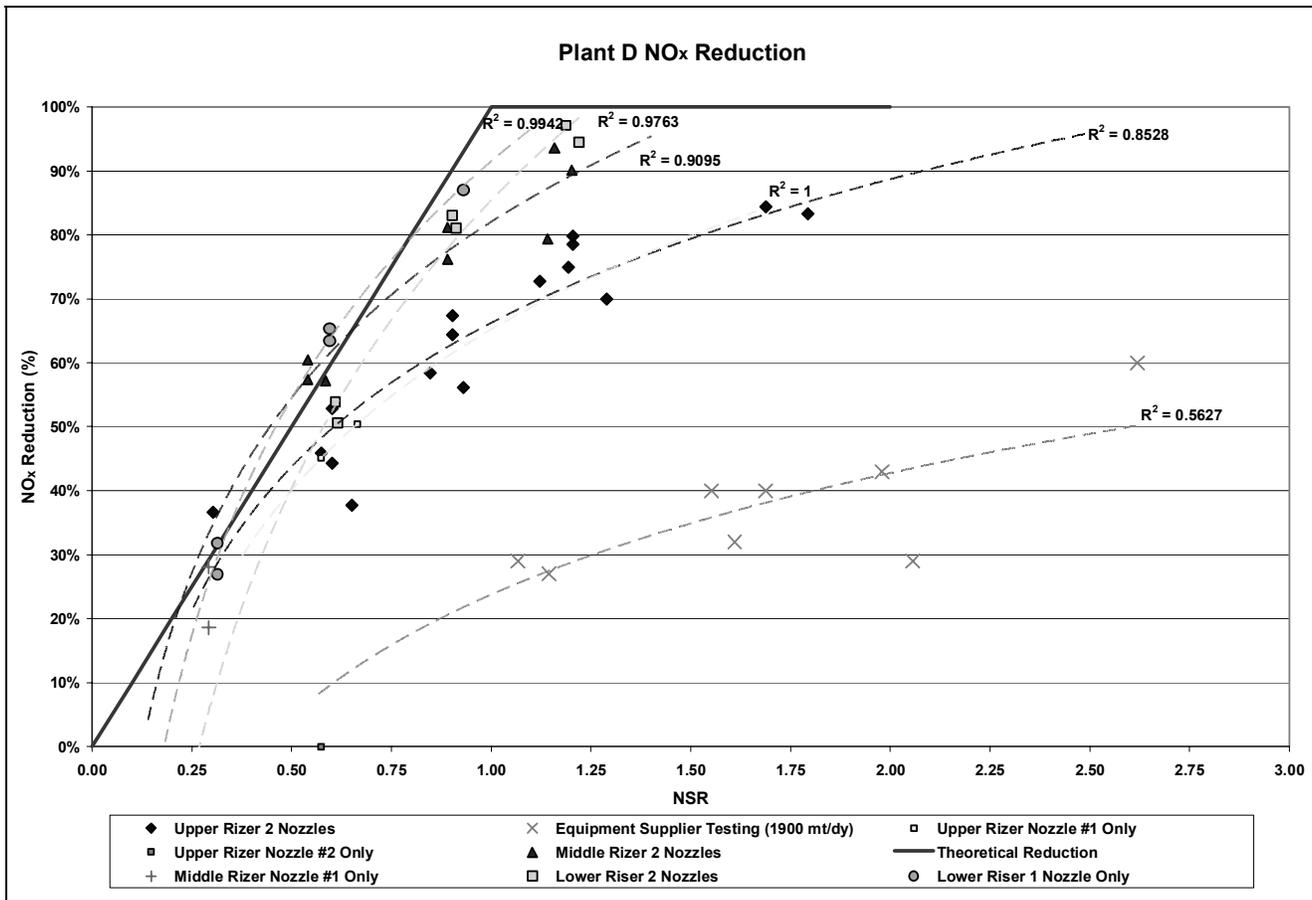


The average results for the locations and a graph of the results are given in Table 6 and Fig. 15 below.

**Table 6. SNCR Testing at Plant E**

LOCATION	Reagent Rate	NSR	Actual NO <sub>x</sub> Reduction	Theoretical NO <sub>x</sub> Reduction	SNCR Efficiency
	gph		%	lb/hr as NO <sub>2</sub>	%
Lower Riser - 2 Nozzles	46.4	0.91	76.7%	18.7	85.1%
Lower Riser - 1 Nozzle	28.0	0.55	54.9%	91.2	99.3%
Middle Riser - 2 Nozzles	46.4	0.87	74.4%	30.1	89.7%
Middle Riser - 1 Nozzle	15.6	0.29	26.0%	154.5	90.5%
Upper Riser - 2 Nozzles	51.3	0.99	63.0%	2.0	69.1%
Upper Riser - 1 Nozzles	31.2	0.62	44.2%	77.8	71.9%

Figure 15: SNCR Results Plant E



Plant E, with low CO and high oxygen throughout the kiln inlet and the riser duct, experienced very efficient reduction of NO. The lower portions of the riser duct with higher temperature were the most efficient of the reduction locations. CO and oxygen are fairly uniform throughout the riser so the higher temperature provided higher reductions, but even at the lower temperatures exiting the riser duct, reduction efficiencies were quite high. As with Plant D the absence of a calciner or post kiln burner NO source made the evaluation of the NSR and SNCR efficiency accurate and reliable.

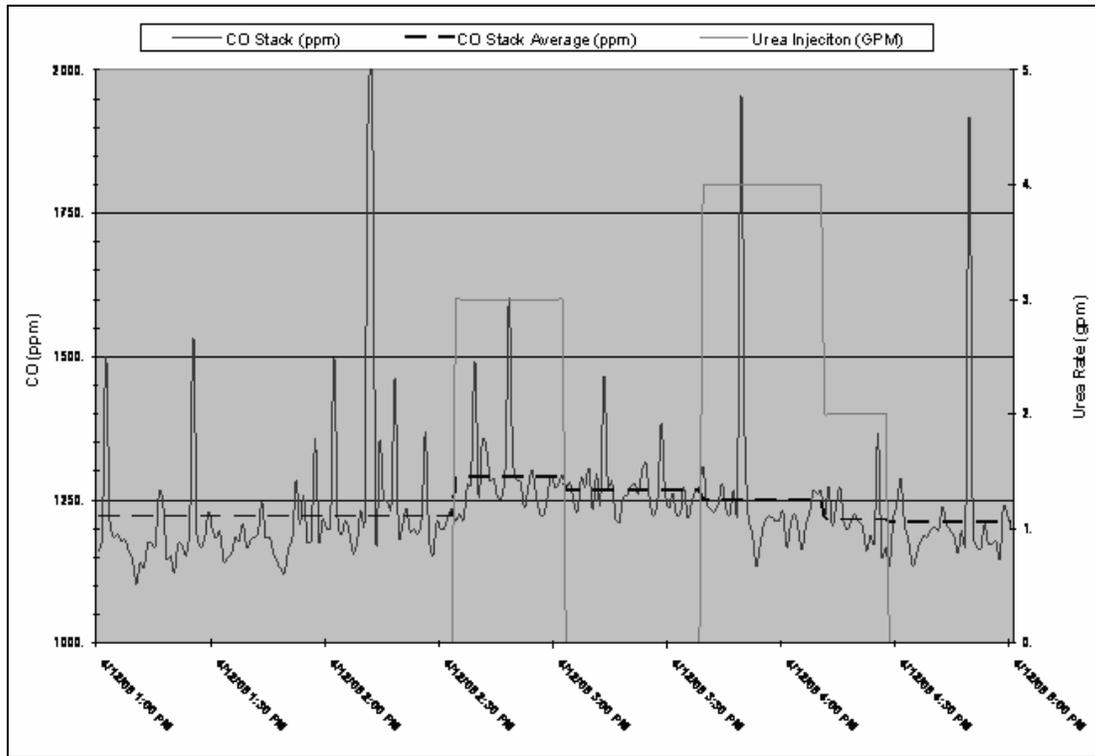
Plant D was also by far the smallest kiln to be tested and exhibited very high efficiencies for the reduction of NO. These results suggest that considering the possible influence of mixing and wall effects on SNCR efficiency may have some validity after all.

## Conclusions

### Reagent

With regard to the selection of reagent, ammonia solution is seemingly always favored in the cement manufacturing process for efficiencies in reduction. In research by D. Kupper and L. Brentrup<sup>7</sup>, it was noted that ammonia water was much more effective at reducing NO<sub>x</sub> emissions than urea solution. In particular, ammonia has greater reaction efficiency through the normal temperature window present in the preheater or calciner. Additionally the increase of CO is much more prevalent with the use of urea, especially when used in injection locations with low oxygen or high CO. It appears the dissociation of the urea results in additional CO that then may compete for the OH radical pool for the oxidation to CO<sub>2</sub>. Fig. 16 shows the marked increase in CO from injection of urea in Plant B in the high CO region after the calciner.

Figure 16: CO Increase in Plant B

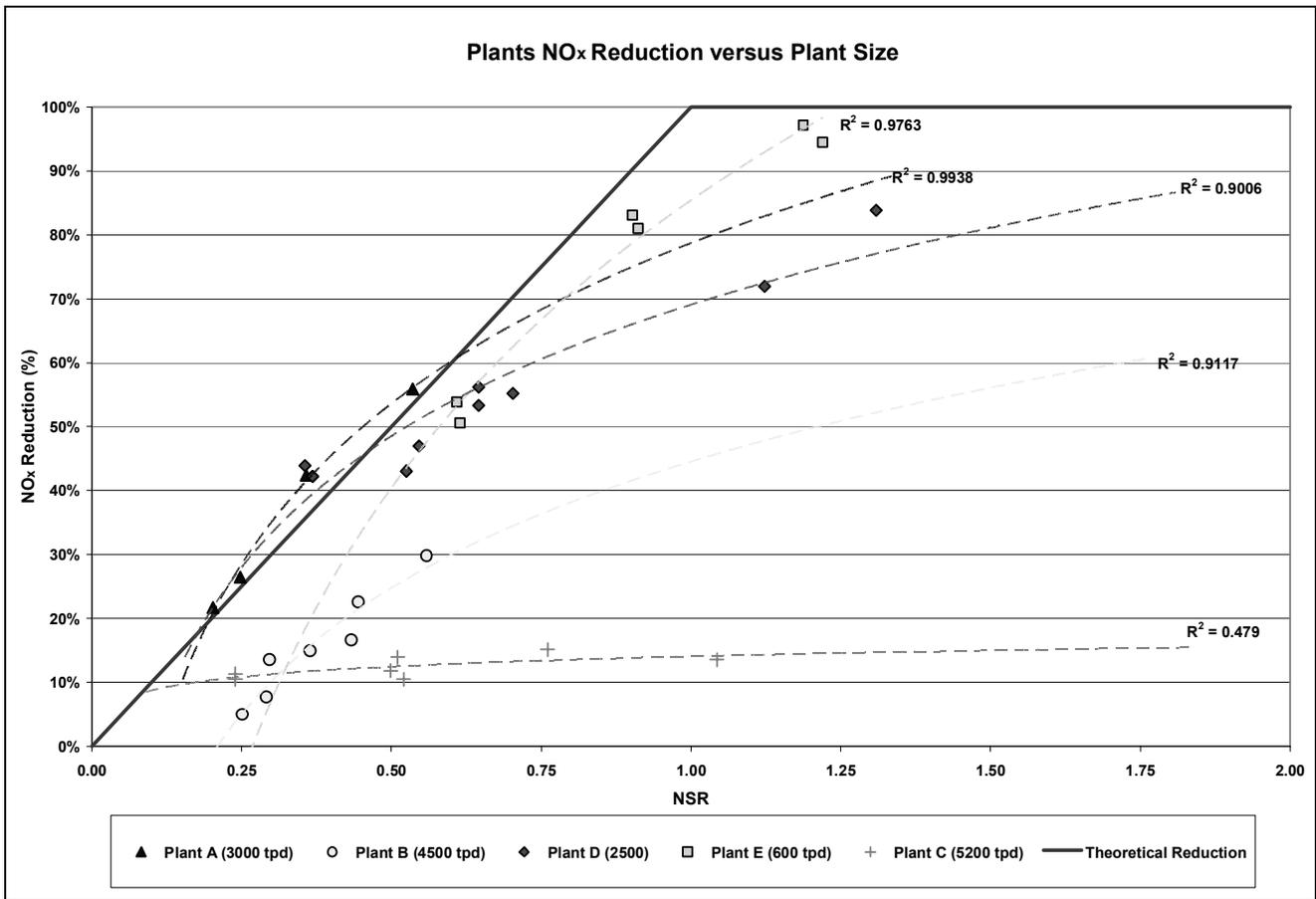


This localized increase in CO with the dissociation of urea to  $\text{NH}_3$  may be one reason why urea achieves lower efficiency in the applications tested. This increase in CO competes for the limited OH radicals, and not only for burnout of the CO; these same radicals are needed for the  $\text{NH}_3$ -to- $\text{NH}_2\text{OH}$  intermediate, fundamental for reduction of the NO to  $\text{N}_2$ . In the low oxygen environment of preheater and calciner regions the presence of oxygen to generate these OH radicals is limited. This was also noted in research by Steuch<sup>8</sup> which showed increased concentrations of CO at the stack. The CO increase was minimized with oxygen concentrations greater than 2.4% and at NSR injection ratio of less than 0.7. Additionally, urea indicated a strong dependence on temperatures in the range of 1600 to 1700°F for effective reduction. Ammonia was shown to react with NO with high efficiencies at temperatures as low as 1500°F, giving many more useful potential injection locations than urea.

### Plant Size versus Reduction

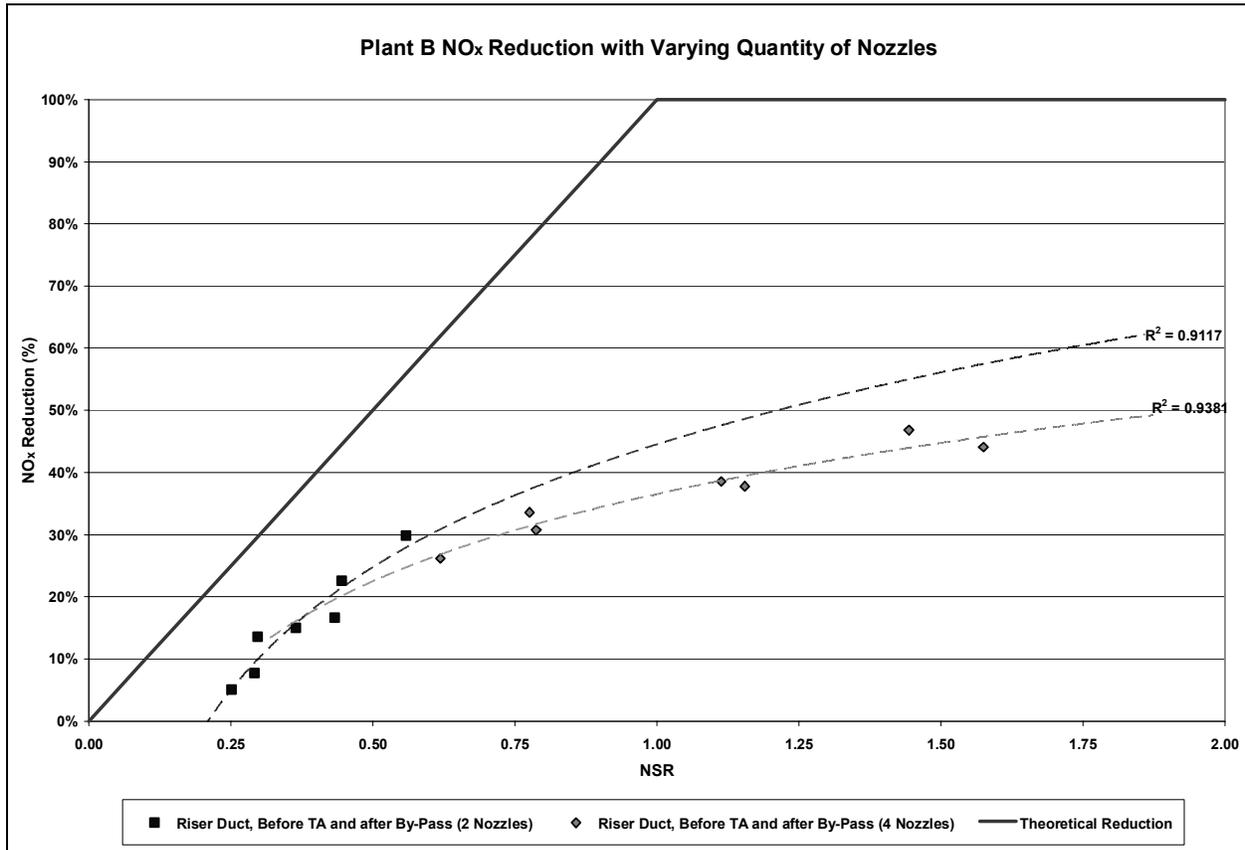
A correlation between plant size and reduction efficiency was noted during the testing conducted. This correlated with previous findings<sup>9,10</sup> that larger plants had lower efficiencies than smaller sized plants. The following figure shows the best results achieved from all five plants and the three plants with sizes from 600 to 3000 tons per day have much higher efficiencies than the two larger facilities.

Figure 17: All Plants NO<sub>x</sub> Reduction and Plant Size



Intuitively it seems to make sense that large gas flows with larger cross sectional areas would result in less mixing and direct contact between the NH<sub>3</sub> and NO. However testing conducted at several of the plants shows that the addition of more injector nozzles in the same location traversing the ducting did not increase efficiency. Under the first assumption the increase in injection locations with the same flow should have overcome the presumed lack of mixing and increased efficiency noted. Fig. 18 shows testing conducted at the same location with varying number of nozzles for Plant B.

**Figure 18: Plant B Results with Different Nozzle Configurations**



As can be seen, no change was noted with four versus two nozzles. However, the correlation between size and reduction efficiency is evident and may instead rely on the fluid dynamic mixing differences experienced or stratification present as size increases. Additionally the influence of wall effects which exert a slowing effect on the terminal velocity of particles, may increase the laminar character of flow, and could impact the efficiency of the reaction with the reagent and the NO present in the gas stream. Catalytic effects of iron compounds have also been shown to aid decomposition of NO; wall effects may enhance interaction between such potential catalysts and gas stream components; this will be discussed subsequently. Complex conceptual fluid dynamic modeling of injection locations would be required to further examine the influence of wall effects and is beyond the scope of this paper.

### **Sulfur Cycle Effects on SNCR Reaction**

The presence of sulfur and chlorine were originally thought to be potentially troublesome to the SNCR reaction due to the propensity of ammonia to interact with sulfates and chlorides. However, in the high temperature profile of the injection locations the stability of ammonium salts was known to be low and with the volatility of the ammonia, it was expected to readily volatilize even if transiently combined with sulfate or chloride. It was not known if this would develop a cycle<sup>11, 12</sup> that might impair the reaction of the NH<sub>3</sub> with the NO as it circulated with sulfur or even chlorine. It appears that the presence of sulfur has little effect on the use of ammonia as a reagent. Plant E, which fired 100% pet coke, had high SO<sub>2</sub> in the area of injection, high clinker SO<sub>3</sub> and yet Plant E experienced some of the highest efficiencies in reduction. This has led to the perhaps intuitive conclusion that the presence of sulfur, all other things equal, has no apparent detrimental impact on the SNCR reaction.

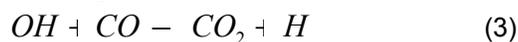
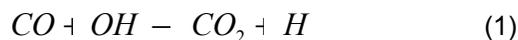
### **Catalytic Reactions from Kiln Feed**

The correlation between the content of iron in the kiln feed and an increase in the reduction efficiency of the SNCR reaction has been noted by researchers.<sup>13,14</sup> It was observed that Plant A, D and E, which had higher iron percentage in the kiln feed than Plant B and C, had much higher SNCR efficiencies. It should also be noted that these plants also utilized ammonia instead of urea and are smaller sized of the five plants. The presence of some catalytic reduction with ammonia either in the injection location or at higher portions of the tower at lower temperatures cannot be discounted. The Selective Catalytic Reduction (SCR) reaction can occur at temperatures from 570°F and 840°F. This temperature profile is present at the top of preheater towers, so retention time in the area of greater than ten seconds at this temperature are experienced in all of the preheater towers. Despite the lack of presence of a traditional catalyst such as oxides of titanium and vanadium, the influence of increased NO reduction by catalytic mechanisms cannot be discounted from the testing conducted.

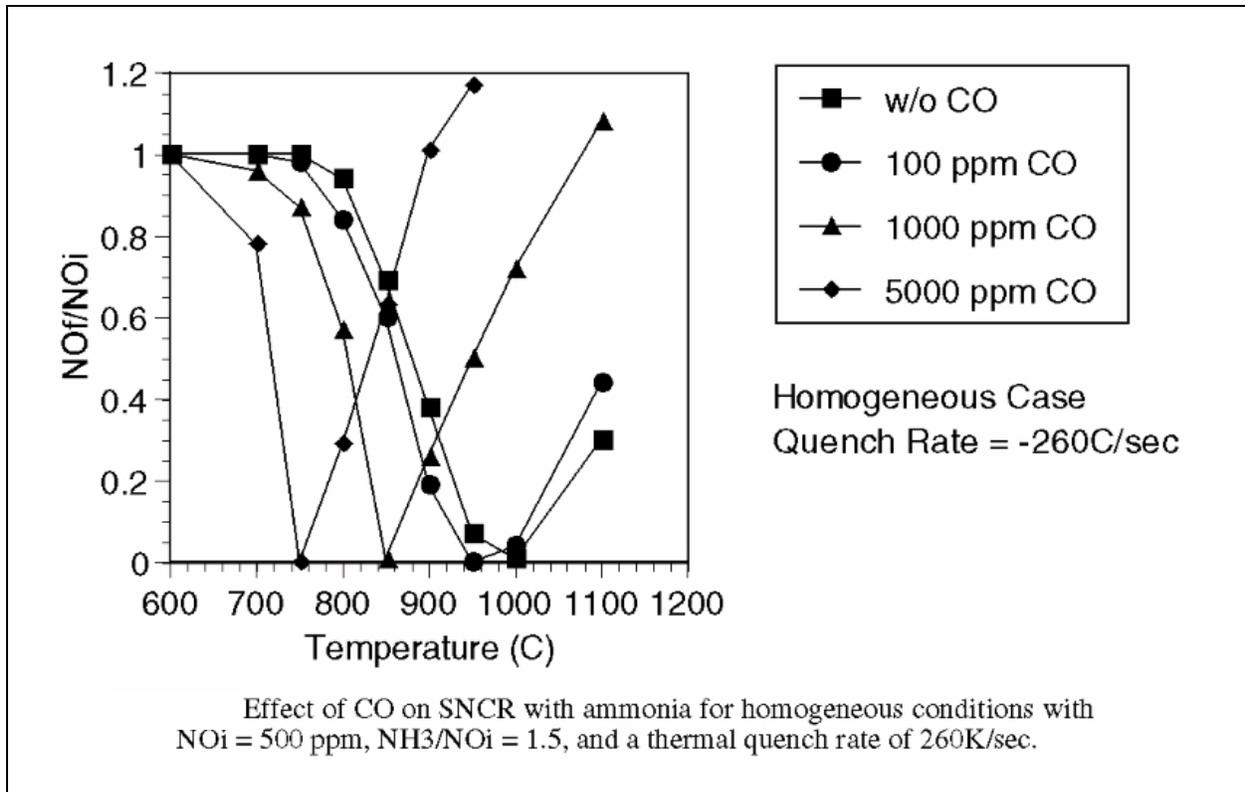
### **CO Effect on SNCR Reaction**

CO was show to have both a positive and negative impact on the reduction of NO with the NH<sub>2</sub> radical. In high concentrations, CO inhibited the reaction from occurring by consuming some of the OH radical present. With the use of urea, this was compounded even more by the localized creation of CO during the urea dissociation. However, in Plant A the CO, in the presence of one to two percent oxygen, was shown to act as a catalyst and drive the NO reduction reaction at lower temperatures and with increased efficiency, as reported by Brouwer and co-workers.<sup>15</sup>

In Plant A the injection location varied, but typically operated within a range of 1000 to 1500 ppm CO, one to two percent oxygen, and temperature profile of 1550 to 1650°F. In the presence of sufficient oxygen, the radical pool can be sufficient to promote both the CO-to-CO<sub>2</sub> reaction and the NH<sub>3</sub>/NO<sub>x</sub> reactions. The burnout of CO to CO<sub>2</sub> may actually promote the reaction of the NH<sub>3</sub> with NO<sub>x</sub> if the radical pool is sufficient, by creating localized areas of high temperature due to the release of heat from CO<sub>2</sub> formation. By contrast, a high CO atmosphere with little oxygen or insufficient mixing of the oxygen creates a competing reaction for the limited radical supply. The following equations show the chain reaction of burnout of CO and the continuing creation of radicals when both oxygen and CO are present in approximately stoichiometric ratios:



These processes create localized elevated temperatures and the continual creation of more radicals during the time retained in these conditions. This reaction and interaction between both oxygen and CO appears to be needed at injection locations other than those at the riser duct to achieve a high level of efficiency of reduction. Perhaps the increase of size in ducting in the larger plants, which was observed to adversely affect the efficiency of the SNCR reaction, can contribute to an increased distance in stratification of the oxygen and CO needed for the reactions 1 through 4 to continue while in the limited temperature windows favorable for SNCR. Fig. 19 below illustrates this relationship.



**Figure 19: Effect of CO on SNCR**

## Overall Recommendations

As has been emphasized throughout this paper, certain inherent conditions can improve or reduce the efficiency with which SNCR can reduce the NO. Several of these factors cannot be changed or modified significantly, due to limitations on the design and construction of the preheater tower, available raw materials, or fuels. However it does appear that three key approaches for reduction of NO have been identified and the use of one or both should be achievable at most locations so as to approach the desired efficiency.

The first approach to reduction of kiln NO in the riser duct relies on the traditional reduction techniques, requiring high temperature, sufficient oxygen, and low CO. In most cases this should be available in calciner systems, and for preheater kilns it is the only option. However, if sufficient oxygen is not present in the riser or kiln exit, due to carryover of unburned fuel or insufficient oxygen from the kiln itself, then the efficiency for this reduction will suffer. Additionally this location upstream of the calciner will only reduce the kiln NO, which is presumed to be the majority of the NO formed, but will not reduce the amount of NO generated in the calciner from fuel nitrogen. Thus this location will have no effect on calciner  $\text{NO}_x$  or subsequent NO generated from feed nitrogen in the calciner.

The second approach for reduction via SNCR has shown to be a post calciner location. In most situations temperatures are lower in these regions than in the riser duct, and locating a spot with adequate oxygen and small amounts of CO will lead to the greatest efficiencies. In calciners with limited retention time for burnout of CO, such a location may not exist or even be at the exit of the lowest cyclone. However for most new designs of calciners, a location in the burnout zone should be located with sufficient oxygen, CO and temperatures. Depending on fuel usage and its associated volatility a location prior to the lowest cyclone should be sufficient.

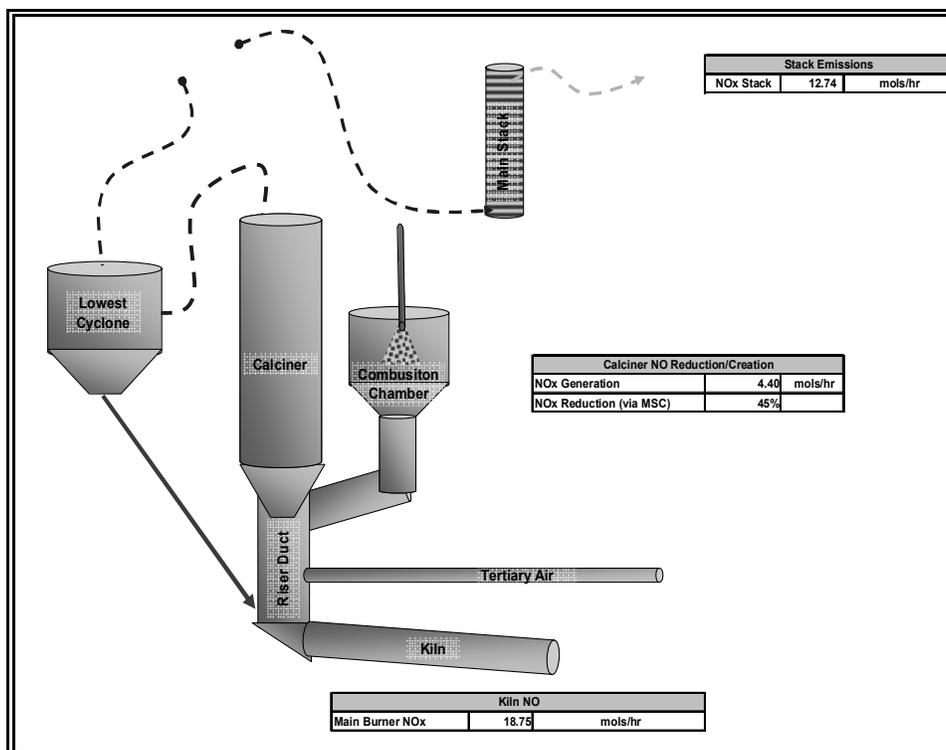
The other distinct advantage of a post-calciner injection location in a calciner system is the reduction of

total NO<sub>x</sub> output from both combustion sources. While it is assumed that most of the NO<sub>x</sub> at the stack is produced via the thermal NO mechanism in the kiln, calculations at Plant A showed approximately twenty percent NO<sub>x</sub> generation in the calciner. From studies conducted at Plant C, the majority of NO<sub>x</sub> generation occurs in the calciner as well. This generation of NO<sub>x</sub> was also noted by Tokheim<sup>5</sup> in his studies of the impact of staged combustion on the reduction of NO<sub>x</sub>, where it was noted that thirty to forty percent of the total NO<sub>x</sub> was generated in the calciner. With an injection location in the riser duct, the ability to reduce this source of NO<sub>x</sub> would be sacrificed.

Another benefit of the post-calciner location is the utilization of inherent staged combustion for initial reduction of NO from the kiln via the design and operation of the staged combustion in the calciner. This mechanism for reduction will be present integral to the operation of the calciner and should be utilized to reduce as much kiln-generated NO as possible, with SNCR treating the unreduced kiln NO or newly created NO<sub>x</sub> from the calciner. This allows for accurate NSR calculations and reduction efficiencies from SNCR to be calculated. With SNCR injection locations prior to the calciner, no reliable means of determining molar ratios of NO<sub>x</sub> exists, due to the difficulty in calculating gas flows through the kiln inlet.

To illustrate this point, a total NO<sub>x</sub> balance for Plant A has been calculated and shown in the following figure. Concentrations of NO at the kiln inlet are known, as well as estimated flows from CO<sub>2</sub> balances. Molar rates of NO as NO<sub>2</sub> are given for the NO generated in the kiln in the primary burning zone as well as the NO<sub>x</sub> generation from the calciner. It was estimated from the NO balance that approximately 40% of the fuel nitrogen was converted to NO. The reducing zone created in the calciner, even with the kiln operated in an oxidized state, reduces around 45% of both the NO generated from the kiln and the NO<sub>x</sub> from calciner fuel. The reducing capacity of staged combustion can be increased with the presence of CO; however during testing this 45% reduction was present with at least two percent oxygen in the exit of the kiln. Finally the molar rate of the NO<sub>x</sub> as NO<sub>2</sub> is given at the exit of the system or the stack.

**Figure 20 Plant A Molar NO<sub>x</sub> Balance**



If two separate scenarios are evaluated with injection locations in the riser duct and in the upper portions of the calciner with the same NSR and reduction efficiency, the following is observed. The post calciner location will cause correspondingly greater overall NO<sub>x</sub> reduction at the stack, due to the reduction of both

fuel NO<sub>x</sub> from the calciner and the thermal NO from the kiln. Also, the calciner reducing conditions will be allowed to destroy more of the burning zone thermal NO. Table 7 shows the theoretical reductions based on a 0.7 NSR at the actual location of reduction (molar rate of NH<sub>3</sub> divided by molar rate of NO<sub>x</sub> at the location of injection), the overall NSR (molar rate of NH<sub>3</sub> divided by the uncontrolled molar rate of NO<sub>x</sub> at the stack) and a 75% efficiency of reduction at each location. The overall efficiency of the reduction of NO<sub>x</sub> is the reduction of the uncontrolled NO<sub>x</sub> versus the theoretical reduction of NO<sub>x</sub> achieved at each location. These results have been shown to be achievable with ammonia at Plants A, D, and E, illustrated in Table 7.

**Table 7: NSR versus Injection Location**

<b>Injection Location</b>	<b>Reagent Rate (gph)</b>	<b>NSR at Location</b>	<b>Overall NSR</b>	<b>Overall Reduction Efficiency</b>
<b>No SNCR Injection (Baseline)</b>	0	0	0	0%
<b>Riser Duct</b>	150	0.7	1.03	41%
<b>Post Calciner</b>	102	0.7	0.7	75%

The results demonstrate that even though each location was assigned a 0.7 NSR, to actually achieve this NSR in the riser of a kiln with high exit oxygen will require much more reagent. In addition to this, even though the riser location reduces the NO with an efficiency of 75%, this results in an overall reduction from uncontrolled NO levels at the stack of 41%. As stated earlier, this is due to the fact that this location is given no opportunity to reduce NO generated from fuel NO in the calciner. For the riser duct location to achieve the same reductions as the post calciner location a localized NSR rate of 0.865 (185 gph) would have to be utilized. Thus can be seen the advantages of utilizing SNCR at a post-calciner location. This relationship of reduction would further be exaggerated if the kiln is run with lower excess oxygen and has lower levels of kiln exit NO. The presence of unburned tires or fuel such as tires introduced in the kiln ext could lead to this situation. In these cases, locations at the exit of the calciner would be the only acceptable location for SNCR. As for preheater kilns, this issue is avoided as no additional fuel or thermal NO is generated past the burning zone. Lastly the ability for ammonia or urea to remain unreacted and circulate past the calciner if injected in the riser duct has not been demonstrated.

The third measure is to adopt multiple injection points for ammonia and/or urea. Junker<sup>16</sup> at the Slite cement plant in Sweden achieved excellent success with techniques including the use of 12 injection points, reducing the NO<sub>x</sub> emissions to about 1 lb per ton of clinker.

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