

PURPOSE

As requested by several EPA Regional Offices, this report will address nitrogen oxides (NO_x) controls in new cement kilns. This report will focus on staged combustion in the calciner(SCC), selective noncatalytic reduction[SNCR] and selective catalytic reduction[SCR]. Also, practices and controls that are incorporated in normal operating practices for cement kilns will also be discussed. Previous EPA documents on NO_x controls for cement kilns include "Alternative Control Techniques Document - NO_x Emissions from Cement Manufacturing" dated March 1994 (EPA-453/R-94-004) and "NO_x Control Technologies for the Cement Industry" dated September 19, 2000. The first report is available at www.epa.gov/ttn/cata/dir1/cement.pdf. The second report is available at www.epa.gov/ttn/naaqs/ozone/ozonetech/cement_nox_update_09152000.pdf.

As this report addresses only new cement kilns, this report will discuss only preheater/calciner cement kilns(ph/c kilns). This kiln type is the only type expected to be built in the future. For details on the other kiln types (wet kilns and long dry kilns) and their NO_x controls, please review the above mentioned documents.

Table 1 below presents BACT determinations since 2002. As noted here, NO_x emission limits of 2.0 lb/T are required recently.

Permit Date	Plant	Kiln type	Max Production	NOx Limit	Control Option
2002	Cemex-Victorville, CA	NA	NA	2.8 lb/T-30 day rolling avg;583 lb/hr	LNB, MSC
7/1/02	LaFarge- Buffalo, IA	PH/C	3,488 TPD	4 lb/T; 2546 TPY	GCP
9/24/02	Continental Cement-Hannibal, MO	Kiln	183 TPH	8 lb/T	SNCR; LNB;Top air duct
4/10/03	GCC Dakota- Rapid City, SD	Kiln	2,250 TPD	5.5 lb/T; 2,267 TPY	PH/PC
6/13/03	Roanoke Cement-Troutville, VA	Kiln	1.3mm TIBS/yr	982 lb/hr; 2,850 TPY	GCP and CEMS
12/11/03	Lehigh- Mason City, IA	PH/C	150 TPH	2.85 lb/T; 1,496 TPY	SNCR; LNB; Combustion controls, kiln design

NA	Az PC-Marana, AZ	5-stage PH/C	2.3 million TPY	2.3 lb/T	GCP, LNB, SC
2/04	Texas Industries-Midlothian, TX	NA	NA	2.8 lb/T -30 day rolling avg; 681 lb/hr	LNB. MSC
6/8/04	Holcim - Lee Island, MO	in-line kiln	4.83 million TPY	3.0 lb/T - first 24 mos; 2.8 lb/T after first 24 mo	SC, LNB
				2.4 lb/T after first 24 mos	SNCR, SC, LNB
7/05	Florida Rock-Newberry, FL	PH/C	125 TPH	1.95 lb/T	SNCR-ammonia;Poly sius MSC; LNB
Pending	Florida Crushed Stone- Brooksville, FL	PH/C	125 TPH	1.95 lb/T	same as above
Pending	Suwannee American-Brandford, FL	PH/C	127 TPH	1.95 lb/T	same as above
Pending	Drake - AZ	PH/C	83 TPH	1.2	same as above

GCP- Good Combustion Practices; LNB - Low NO_x Burners; CEMS - Continuous Emission

PROCESS DESCRIPTION

The process of producing cement basically consists of:

- quarrying and crushing the raw materials
- grinding the materials to a high degree of fineness
- processing the raw mix in a rotary kiln to produce clinker and
- grinding the clinker along with gypsum to a fine powder to produce cement.

Figure 1 is a depiction of a typical cement plant and steps involved in producing cement. Quarrying and solid fuel grinding are not shown in this Figure. Figure 2 is a general flow diagram at a preheater/calciner kiln cement plant.



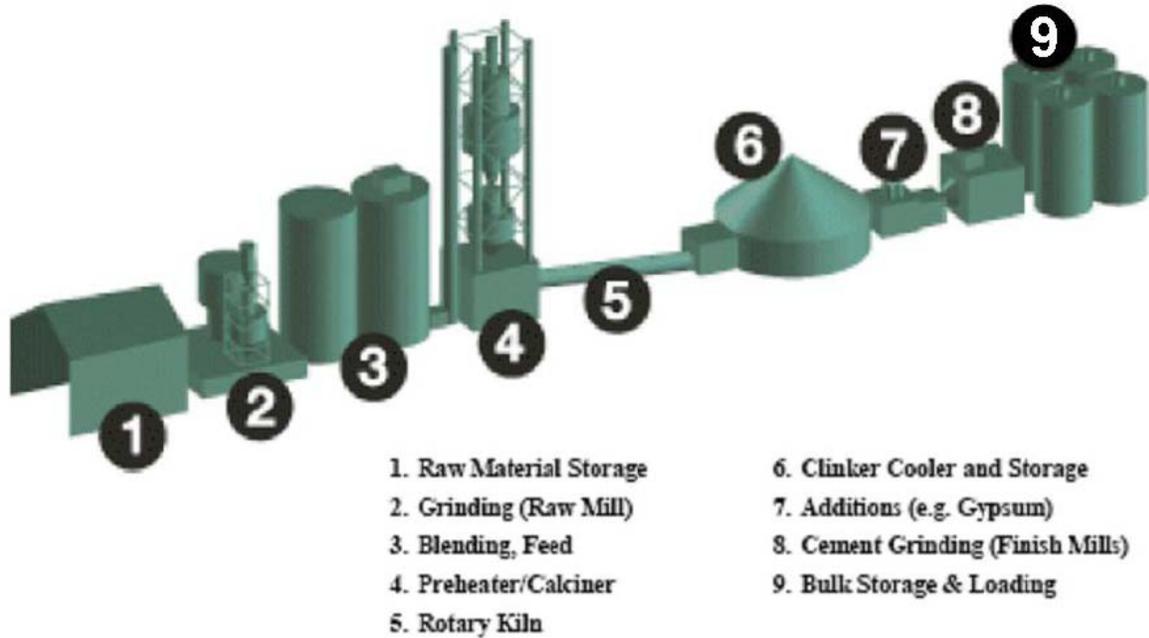
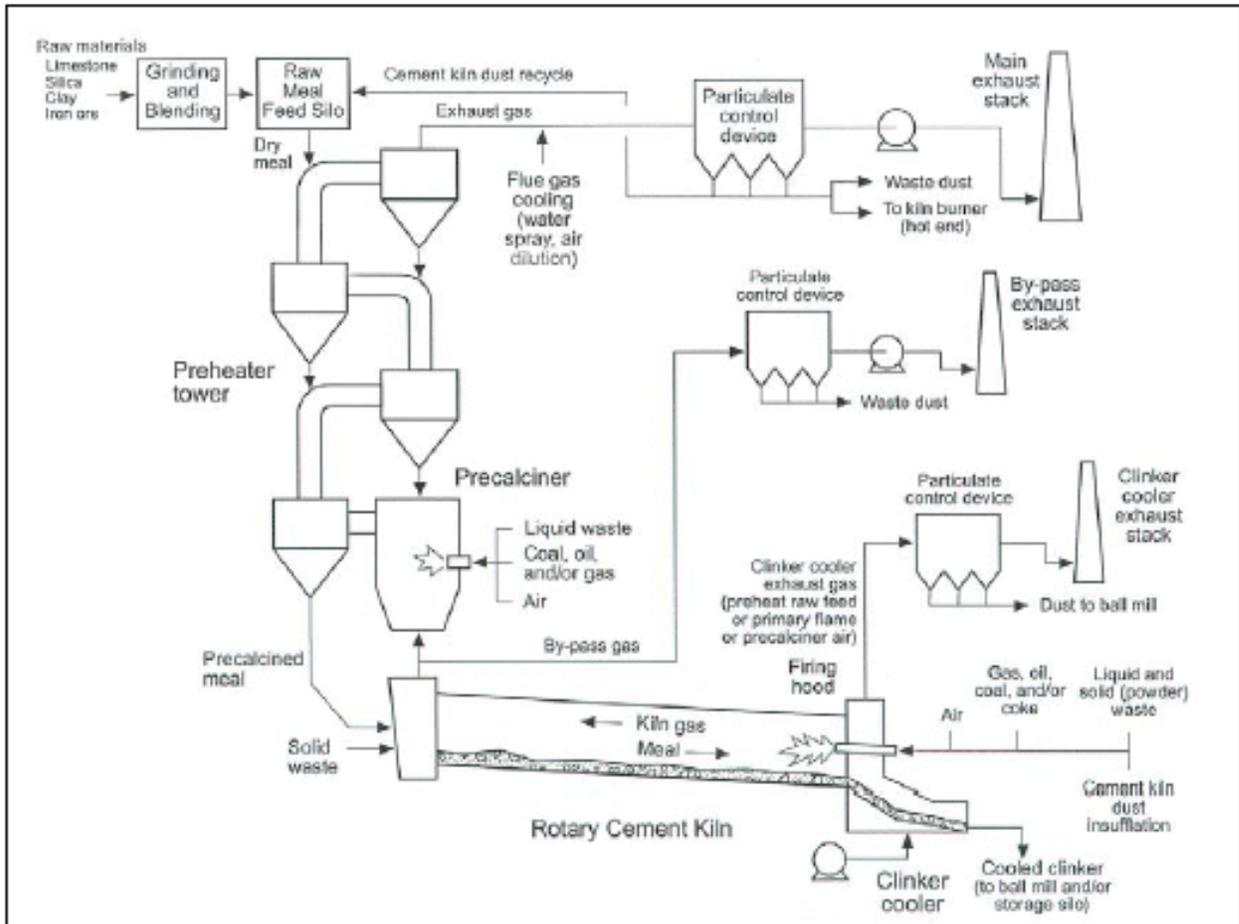


Figure 1.- Primary Operations - Cement Plant (Reference 4)

More details on the overall cement process are contained in the above mentioned two EPA documents. An excellent virtual tour of a cement plant is available at the Portland Cement Association website - www.cement.org/basics/images/flashtour.html.

Figure 2.- Primary Operations – Raw materials, Precaliner, Kiln (Reference 5)



New kilns

For this report new kilns will be described as "preheater/calcliner kilns". Often in other reports, including the two previous EPA reports, these systems were called preheater/precalcliner kiln systems. Yet, the material is nearly 100% calcined before the material enters the kiln. So, in reality the "precalcliner" is a calciner. The kiln then sinters the calcined material forming clinker. These systems have been available since 1970.

The main reasons why all new US cement kiln systems are preheater/calcliner kilns are this kiln type has increased production capacities and greater fuel efficiencies compared to other cement kiln types. Preheater/calcliner kiln systems are much larger in capacity than other kiln

types. As shown in Table 2, their capacities range from 450,000 to 1,580,000 metric tons/year with an average of 869,000 metric tons/year (111 tons/hour).

Table 2. Cement Kiln capacities(metric tons/yr) (Reference 6)

Kiln Type	Range	Average
Wet process	77,000-1,180,000	307,000
Dry process	50,000 - 590,000	265,000
Suspension preheater	223,000 - 1,237,000	406,000
Calciner	449,000 - 1,580,000	869,000

Also, the preheater/calciner kiln system is much more fuel efficient than other kiln types. Tables 3,4 show heat inputs for the various kiln types.The greater fuel efficiency is obtained using preheater/calciner kilns..

Table 3 - Heat Input for various Cement kiln types (Reference 7)

KILN TYPE	Heat Input(mmBtu/ton of clinker)	% Increase in heat input compared to preheater/calciner heat input
Long wet	6.0	45
Long dry	4.5	36
Preheater	3.8	15
Preheater/calciner	3.3	-----

Diagrams and a photo of preheater/calciner kiln systems are shown in Figures 3-6.

Figure 3 - Preheater/calcliner kiln - Suwannee American - Brandford, Florida

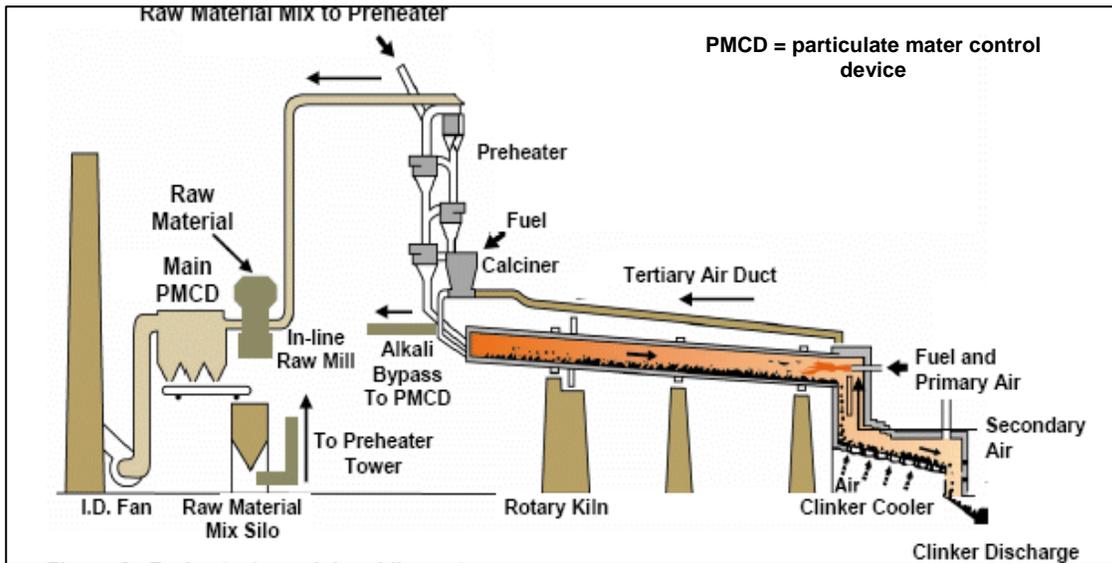


Figure 4- Preheater calciner kiln system



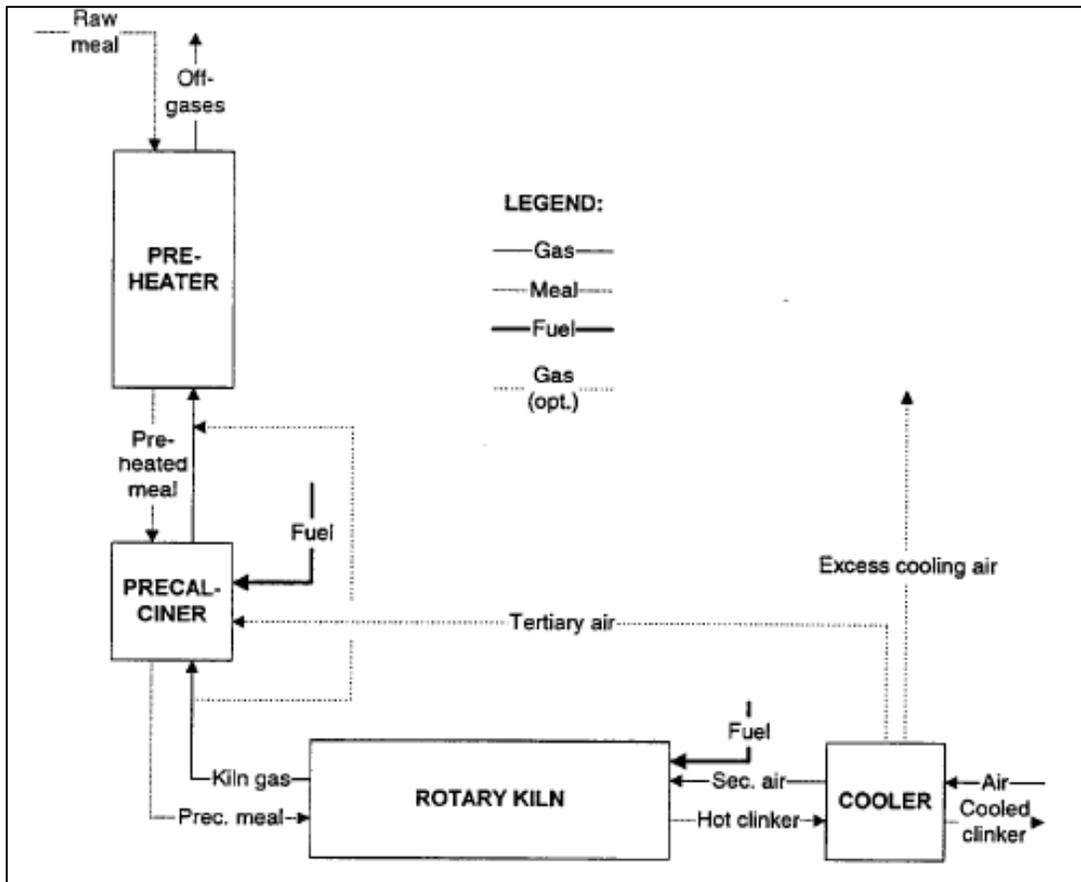


Figure 5 - Preheater/calciner kiln

Clinker, the final end product of cement processing, typically contains 66% CaO, 21 % SiO₂, 5% Al₂O₃, 3% Fe₂O₃ and 5% of other components. To produce these compounds and to obtain them in right proportions, the raw meal is pyroprocessed (burned). The processes used include preheating(drying) in 4-5 stages of cyclones, calcining in a calciner kiln and sintering in a rotary kiln.

In drying, the first stage, free water is driven from the raw meal at temperatures ranging up to 200C(390F) and with gas temperatures from 100 - 400C(210- 750 F).The adsorbed water is removed.

Next from 400-750 C (750 - 1,380 F), clay minerals are dehydrated; that is chemically combined water is expelled.

The system to perform the drying, calcining and sintering consists of 3 basic parts --

preheater, a calcining kiln or vessel and another kiln which sinters.

A. Preheater

The cold raw meal is injected into the gas flow between the upper 2 cyclone stages of the preheater. Flowing down the cyclone tower, the meal is dried and the clay minerals dehydrate and decompose. Also, any organic compounds present in the raw mill are oxidized and magnesium carbonate is calcined. In the preheater, the meal temperature is typically increased to about 700 C (1,290 F) while the temperature of the counter flowing gas is reduced from about 900C (1,650 F) to about 350C (660 F).

The preheater consists of a series of cyclones in a vertical arrangement. Typically, this is a four-stage cyclone system. The dry pulverized feed travels by gravity where the material is separated and preheated several times by the hot exhaust gases from the precalciner kiln. When leaving the preheater, the feed is partially(40-50%) calcined ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$).

In this cyclone tower, the meal is conveyed by the gas from one cyclone to another. In the cyclones, typically 80% of the solid phase is separated from the gas and is supplied to the cyclone stage beneath. The gas phase containing the remaining solids flows directly to the cyclone stage above. Usually, smaller double-cyclones are used in the uppermost cyclone stage on each string, giving a higher cyclone efficiency, typically 95%. (All from Reference 11)

B. Calciner

From the preheater, the material is calcined in a vessel which is a separate, typically vertical vessel attached to the preheater. This "calciner kiln" utilizes combustion air drawn from the clinker cooler or kiln exit gases. The burner utilizes about 60% of the total kiln system fuel. Coal is the most often used fuel. Almost any fuel can be used including chipped tires. The raw material is 95% calcined by the time the material leaves the precalciner kiln. This calcination begins at about 815C (1,500F) and is completed at about 950C (1,750F) (Reference 12)

In the calciner, the meal is calcined at about 900C (1,650F). Solids residence time in the preheater and calciner is about 2 minutes. After precipitation in lower cyclone stage (which is sometimes considered part of the calciner), the calcined meal enters the rotary kiln. (Ref 11)

Gas temperatures in calciner vessels are about 870 - 1,540 C (1,600-1,800F). Tertiary air is the combustion air ducted to the calciner from clinker cooler. Secondary air is hot air recovered from clinker cooler and diverted to kiln. Primary air is air entering the burner. (Ref 5)

In a preheater calciner kiln without a bypass to control alkalis, sulfur and/or chlorides, typically 60% of the fuel is burned in the calciner. As % of bypass increases(i.e. heat is lost), the total amount of fuel required increases and the amount of fuel burned in calciner increases to make up for the heat lost in the bypass gases. (Ref 12)

C. Kiln

The calcined material enters the kiln where sintering (clinkering) occurs. Clinker is produced by the chemical reaction of the dehydrated and decarbonated raw materials that occurs in the burning zone of the rotary kiln at about 1,510C (2,750F). In the clinkering process, calcium oxide reacts at high material temperatures [1,400-1,500C(2,550 - 2,730 F)] with silica, alumina, and ferrous oxide to form the silicates, aluminates, and ferrites of calcium which comprise the clinker. To achieve these materials temperatures, gas phase temperatures will be substantially higher than 1,760 C (3,200F). Oxidizing conditions must exist in the burning zone to meet clinker quality demands. About 20-25 % of the material is molten. The cement clinker continues to change in character as it passes the zone of maximum temperature. The PH/C kiln system permits the use of smaller dimension kilns since only actual clinkering is carried out in the rotary kiln. About 40% - 50% of the total fuel is burned in the kiln.; the rest is burned in the calciner. Calciner kiln operation is more stable than other kiln types because 90% of the CO₂ in the feed is removed prior to the feed entering the kiln. (Ref 13)

In the kiln, the meal is first completely calcined followed by the clinker formation reactions. The CaO is chemically combined with other minerals in the raw materials and transformed into clinker compounds in the kiln. Formation of clinker compounds require minimum initiation temperatures from about 1,200 - 1,480 C (2,200- 2,700 F). If raw materials in the kiln are not heated to these minimum temperatures, cement clinker compounds do not form. The cement clinker is a gray lava-like material about the size of golf balls. The combination of the slight inclination (typically 3 degrees) and kiln revolution causes the solid material to be transported slowly thru it.

After reaching the maximum temperature of 1,450 C (2,640 F), the clinker is discharged from the kiln and cooled in the clinker cooler. The residence time in the cooler is about 15 - 30 minutes. The purpose of the cooler is to recover heat from the hot clinker and to cool the clinker suitable for downstream equipment. (Ref 11)

The clinker is then ground or milled together with gypsum (to produce portland cement). and other additives to produce cement.

Uncontrolled NO_x Emissions

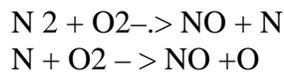
In cement kilns, NO_x emissions are formed during fuel combustion by 2 primary mechanisms :

- 1) oxidation of molecular nitrogen present in combustion air (thermal NO_x)
- 2) oxidation of nitrogen compounds in fuel (fuel NO_x) (Ref 6)

Sometimes the raw material feed may also contain nitrogen compounds which may lead to feed NO_x similar to fuel NO_x. Because of the high temperatures involved in burning or clinker formation, thermal NO_x is the dominant mechanism for NO_x formation in kiln systems.

Thermal NO_x

Thermal NO_x results from the homogeneous reaction of oxygen and nitrogen in the gas phase at high temperatures. In the overall reaction mechanism developed by Zeldovich, the 2 important steps are



The excess air used during fuel combustion can substantially affect NO formation by determining the amount of oxygen available for NO reaction. The cement kiln burning zones usually have about 5- 10 % excess air while higher excess air levels are not uncommon. Higher excess air levels result in higher NO_x .

Fuel combustion in the kiln burning zone is the primary source of thermal NO_x in cement kilns due to temperatures well above 1,400 C (2,550F). In comparison, the fuel combustion temperature in a calciner or in a kiln riser duct is well below 1,200 C (2,200 F) suppressing thermal NO_x formation. Mainly fuel and feed NO_x is formed in the preheater and calciner. Along with the combustion temperature, the gas-phase residence time and available oxygen concentration in the high temperature kiln burning zone are important parameters. Longer residence times at the high temperatures and greater amounts of oxygen in the combustion zone will increase NO_x . Once NO_x is formed, the decomposition of NO at lower temperatures, although thermodynamically favorable, is kinetically limited. (all Ref 6)

At a flame temperature of 1,870 C (3,400 F) in a rotary kiln to heat the process material to 1,480C (2,700 F), nitrogen in combustion air is oxidized to NO_x (thermal NO_x). The calciner of a calciner kiln operates near 1,200 C (2,200 F) at which the formation of thermal NO_x essentially ceases. Thus, thermal NO_x dominates NO_x formation in burning zone of rotary kiln and is a lesser factor in NO_x formation in calciner or elsewhere in this system. (Ref 14)

Fuel NO_x (Ref 14)

Fuel NO_x is formed by the oxidation of nitrogen present in fuel. About 80% of the energy requirements for the kiln systems are met by coal. Natural gas is only 3%; oil - 1%; and other fuels such as waste solvents provide 14%. Oil and natural gas have relatively low fuel bound nitrogen content whereas coal may have 1-3% nitrogen by weight. Waste-derived fuels (scrap tires, used motor oils; paint thinners, etc) are being used increasingly. The nitrogen content in these waste fuels may be significant.

Maximum possible fuel NO_x conversion can be estimated for a preheater/calcliner kiln system. As shown in Table 5, the heat input requirement for this type of kiln is 3.3 mmBtu/T of clinker. Assuming a coal heating value of 12,000 Btu/lb, 275 lb of coal would be required per ton of clinker. With a nitrogen content of 1% by weight, approximately 5.9 lb of NO (9.0 lb expressed as NO₂) would be produced per ton of clinker assuming 100 % nitrogen conversion.

The amount of fuel NO_x formed is difficult to separate from thermal NO_x as measurements indicate total NO_x formed. In general, thermal NO_x is thought to be the dominant mechanism in cement kilns. Gas burners produce more intense and hot flames compared to coal burners. Thus, gas-fired kilns may be expected to produce greater thermal NO_x as compared to coal-fired kilns. A study has indicated that gas fired dry process kilns typically produce almost three times more NO_x than coal-fired dry-process kilns.

Fuel NO_x predominates NO_x generation in the calciner and lower temperature combustion sites. Fuel NO_x also occurs in the burning zone of rotary kiln.(Ref 14)

Approximately 60% of fuel nitrogen is converted to NO_x and is dependent upon available oxygen in the flame and temperature profile of the flame. (ref 15)

Natural gas when fired in the main kiln burner has been shown to generate approximately twice the amount of NO_x per ton of clinker as coal or oil. This is not readily apparent as the adiabatic flame temperatures of coal and oil are higher than for natural gas. Also coal and oil have more fuel nitrogen than natural gas. Also, coal and oil are generally fired with a higher volume of combustion air which increases the oxygen available and thus the potential for NO_x formation. There are other factors associated with coal and oil burning that more than offset the factors mentioned above. These factors include flame shape, the luminescence of the flame and higher levels of CO and various radicals that counter NO_x formation.

Calcliner kilns burn 50-60% of the total fuel at a lower temperature [1,200 C vs 2,000 C (2,190 vs. 3,630F)]in the kiln. This leads to negligible thermal NO formation in the calciner. Thus, thermal NO_x in preheater/calcliner kiln systems is much lower than other kiln types. (Ref 11)

About 15-30% of fuel NO_x is converted in calciner in absence of tertiary air and 30-75% when tertiary air is supplied to PC. In low NO_x calciner, NO_x levels in the gases exiting the preheater are 35-50% lower than kilns without precalciners.(Ref 5)

Feed NO_x (Ref 14)

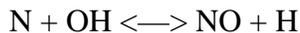
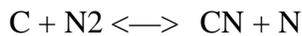
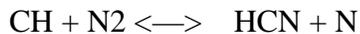
The raw materials used in cement production may contain a significant amount of nitrogen. Limestone is the major raw material with the remainder of the raw mix being clays, shales, sandstones, sands and iron ore. The nitrogen contents for various kiln feeds range from 20 to 1,000 ppm. A 100 ppm N in the kiln feed is equivalent to about 1 lb of NO_x per ton of clinker if it is all converted.

The same study mentioned above indicated that conversion of feed nitrogen to NO_x occurs mainly in the 300-800C (570 - 1,470 F) range and depends on the feed heating rate. Rapid heating rates (~ 100 C flash heating) of the kiln feed mixtures were found to give much lower conversion efficiencies, whereas a slow heating rate of kiln feed mixtures (~60 C/min) gave fairly high conversion of about 50% of bound nitrogen to NO. The explanation for this is assuming the organic nitrogen must vaporize from the sample prior to oxidation if high conversion efficiencies to NO_x are to be achieved. If heating rates are rapid, "cracking" of these volatile compounds may occur in situ. This may result in conversion of the bound nitrogen directly to N₂ before it comes into contact with gaseous oxygen, thus reducing the fraction converted to NO_x.

Feed NO_x that is, oxidation of nitrogen in feed can occur at 300 - 800 C (570 - 1,470 F). This has not been demonstrated in the field. Rapid heating of raw materials in calciner kiln system is thought to result in less NO_x feed generation than slower heating of kiln feed found in other kiln systems. Therefore feed NO_x is not likely to be a significant contributor to NO_x emissions from a preheater /calciner/kiln system.

Prompt NO_x

Prompt NO_x results from the reaction of certain free radicals generated in a HC flame with elemental nitrogen contained in combustion air. Thermal mechanism does not describe a faster, transient formation of NO in the primary reaction zone that occurs in the post-flame gas after hydrocarbon consumption.(Dissertation) This mechanism is dominant in fuel-rich premixed hydrocarbon combustion. The reactions are summarized as follows:



At most, prompt NO_x is a very minor contributor to NO_x emissions from a calciner kiln.

Because prompt NO tends to dominate when the total NO concentration in the system is low, prompt NO_x is presumed to be not important in cement kilns in which NO_x concentrations are relatively high.

Process controls that reduce NO_x emissions (refs 6,7)

How does one determine uncontrolled NO_x emissions? Should one consider the standard operating practices that all new preheater/calciner kiln systems incorporate:

- combustion zone control of temperature and excess air thru continuous monitoring of temperature and excess air
- feed mix composition
- kiln fuel type
- increasing thermal efficiency
- staged combustion in kiln
- low NO_x burners in kiln

These items are discussed on pages 5-2 - 5-8 of the ACT document and pages 54 -62 of the EC/R report. A summary of these measures follows.

- **Combustion zone control of temperature and excess air**

Continuous monitoring of CO and O₂ emissions in the cement kiln exhaust gases indicates the amount of excess air. At any given excess air level, NO_x emissions increase as the temperature of the combustion zone increases. Keeping the combustion zone temperature at a minimum value minimizes the process energy requirements and NO_x emissions.

With continuous CO, oxygen and NO_x monitors and feedback control, excess air can be accurately controlled to maintain a level that provides optimum combustion as well as lower NO_x emissions. Reducing excess air levels also results in increased productivity per unit amount of energy and thus results in indirect reduction of NO_x emissions per amount of clinker produced.

- **Feed mix composition**

Heat requirements for producing clinker are dependent on raw material composition. Experiments have demonstrated that by improving the burnability of the raw feed, the heat requirements of clinker can be reduced by 15%. Therefore less fuel is burned (i.e, less heat input per ton of clinker) and there is less NO_x per unit of product. This approach of changing feed composition may be highly site specific and may not be applicable to all locations.

- **Kiln fuel**

Using coal instead of natural gas results in lower uncontrolled NO_x emissions. The flame temperature for coal is significantly lower than natural gas which results in lower thermal NO_x emissions. In one study of dry process kilns, the average NO_x emissions decreased from 20.4 to 6.2 lb/T of clinker when the fuel was changed from natural gas to coal. According to the ACT, almost 80% of primary fuel burned in cement kilns is coal.

For ph/c kiln systems, generalized NO_x emissions for natural gas are 1.7 - 3.0 kg/T (3.7 - 6.6 lb/T) and for coal - 1.35 - 1.95 kg/T (3.0 - 4.3 lb/T). (Ref 5)

- **Increasing thermal efficiency**

As shown in Tables 6-7, the preheater calciner kiln system is the most energy efficient system for cement kilns. The energy efficiency benefit varies from 15 - 30% depending on which kiln system you are comparing the preheater/calciner kiln.

Also the thermal efficiency may be increased by improving gas/solids heat transfer; e.g., using an efficient chain system, increasing heat recovery from clinker cooler by increasing the proportion of secondary air and by minimizing infiltration of ambient air leakage into the kiln.(Ref 7)

- **Staged combustion in kiln**

The staging of fuel combustion occurs in 2 distinct zones. In the first zone, initial combustion is conducted in a primary fuel rich zone. This zone provides the high temperatures needed for completion of the clinkering reactions. Due to fuel rich conditions and lack of available oxygen, formation of thermal and fuel NO_x is minimized. In the second zone, fuel combustion is completed. Additional (secondary) combustion air is added to complete the combustion process. The gas temperature in this zone is much lower than the first zone because of mixing with cooler secondary air. NO_x formation is thus minimized in spite of the excess available oxygen in the second zone. Indirect firing kilns are required for effective staging of combustion air. (ref 7)

- **Low NO_x Burners(LNB)- Kiln**

LNB have been used by the cement industry for nearly 30 years. LNB are designed to reduce flame turbulence, delay fuel/air mixing and establish fuel-rich zones for initial combustion. The longer less intense flames resulting from staged combustion lower flame temperature and reduce thermal NO_x formation. The NO_x emission reduction is around 30%. For more details on LNB see the ACT document. All new preheater/calciner kiln systems should have LNB in the kiln.

As shown in the two earlier EPA reports (ACT and the EC/R report), uncontrolled emissions from ph/c cement kilns are lower than other kiln types. Table 9 summarizes these results. These numbers are based on data compiled for the 1994 ACT document. Calciner kilns have lower NO_x emission rates than other cement kiln types as they burn more fuel at the calcining temperature as

well as being the most energy efficient kiln type. From the ACT, uncontrolled emissions for the other kiln types are 55 - 155% higher than the preheater calciner kiln. From the AP-42, the differences range from 14 -76%.

Table 9. Uncontrolled NO_x Emissions (lb/T of clinker) - Cement Kilns

Kiln type	Range	Average/% higher than calciner	AP-42/ % higher than calciner
Wet	3.6 - 19.5	9.7 /155	7.4 /76
Long Dry	6.1 - 10.5	8.6 /126	6.0 /43
Preheater	2.5 - 11.7	5.9 /55	4.8 /14
Calciner	0.9 - 7.0	3.8 /----	4.2 /----

STAGED COMBUSTION

There are many ways a preheater/calcliner kiln system could be considered staged combustion(SC). First, the ph/c kiln system itself where first drying, calcining and finally sintering occur. Also, the kiln with a multi-channel main kiln burner with indirect firing incorporates stage combustion. The use of low NO_x precalciners which inject fuel near the kiln inlet is a form of SC. All calciners have some degree of SC. This section will only discuss SC in the calciner (SCC).

o SCC MECHANISM

NO_x formation occurs in the rotary kiln under oxidizing conditions. The various zones in the ph/calcliner kiln system are shown in Figures 11 and 12 . Fuel is then added to the kiln exhaust gas, in the kiln inlet or in the kiln riser duct so that a reducing zone (a reburning zone)is created. This promotes the reduction of NO_x to molecular oxygen. Finally in the upper part of the calciner(the burnout zone), air is added to complete burnout. (Ref 11)

SCC works by staging the introduction of fuel, combustion air, and raw meal in a manner to reduce NO_x formation and to reduce NO_x to nitrogen. It is used by all major kiln vendors to reduce NO_x generation. NO_x formed in the kiln's sintering zone is chemically reduced by maintaining a reducing atmosphere at the kiln feed end by firing fuel in this region. The reducing atmosphere is maintained in the calciner region by controlling combustion air such that the calcining fuel is first burned under reducing conditions to reduce NO_x then under oxidizing conditions to complete the combustion reaction. Controlling the introduction of raw meal allows for control over temperature in the calciner. Through these mechanisms, both fuel NO_x and thermal NO_x are controlled. The combustion chamber allows for improved control over introduction of tertiary air in the calciner region, helping to promote the proper reducing environment for NO_x control. (Ref18)

All new ph/c kiln systems are designed with multistage combustion calciners(MSC). MSC is actually the version of staged combustion as applied by Polysisus. There are several SCC variations based on fuel staging or air staging (or both) (see pp.37- 40 for descriptions). According to a Florida DEP expert , the best version of SCC would be "SCC with High Temperature Reducing Atmosphere". This is achieved when some or all calciner fuel is burned under aggressive reducing (substoichiometric air) and at temperatures significantly higher than calcination temperature. Under such conditions, the gas phase reactions that destroy NO_x proceed very rapidly and are catalyzed by raw meal. Then some additional reduction takes place at lower (calcination) temperature as you get char combustion. The lower limit of SCC w/HTRA is 2.0 lb/T.

A key component of SCC is the kiln inlet burner that creates the high temperature reducing atmosphere. Some projects are considered to be SCC because they still achieve mild reducing atmosphere or maybe they have a high NO_x limit and they just run them under an oxidizing atmosphere which is easier for operations. (Ref 19)

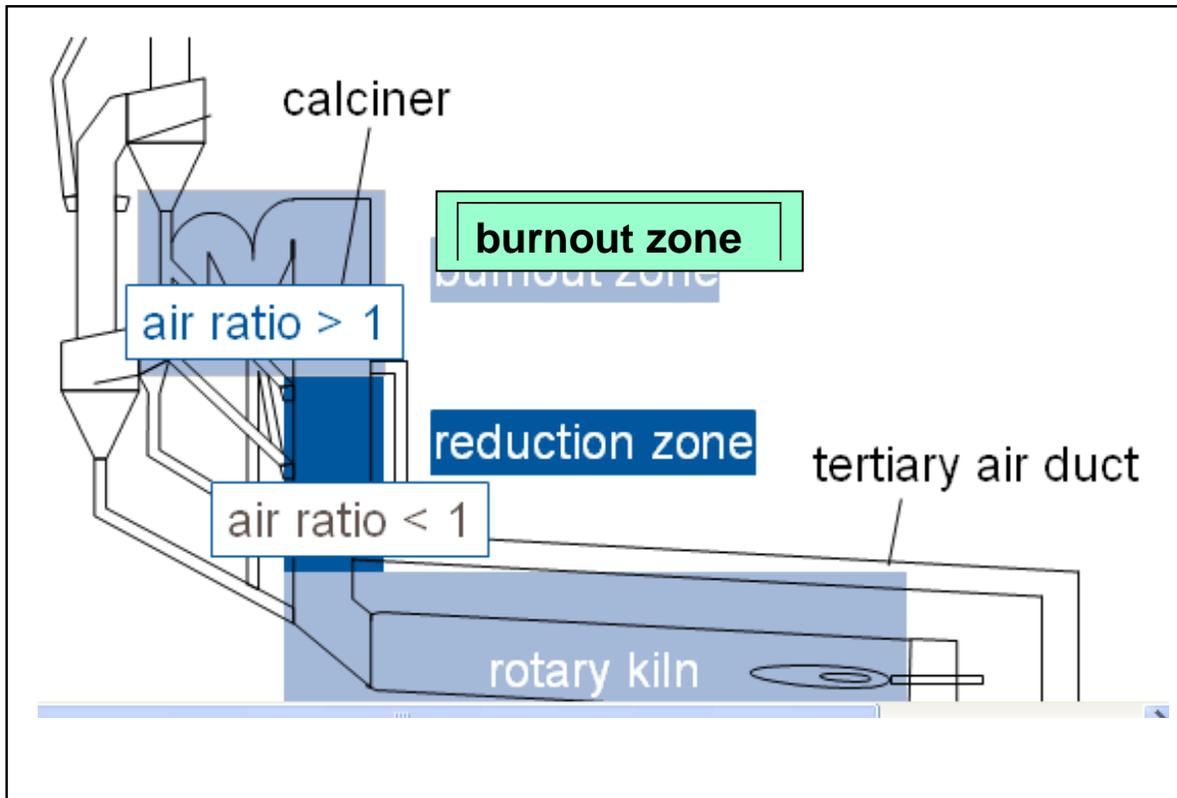


Figure 12. Principle of NO_x reduction by staged combustion in calciner

SCC involves four combustion stages. First stage is the rotary kiln where clinker burning can be optimized. The second combustion stage is the kiln feed inlet which provides reducing conditions for NO_x generated during the sintering process. In the third stage, fuel is introduced into calciner to calcine the raw meal. This calcining fuel is introduced with 3rd air to create a reducing atmosphere. The last stage is when the remaining 3rd air is introduced as "top-up air" to complete the residual combustion process. (ref 5)

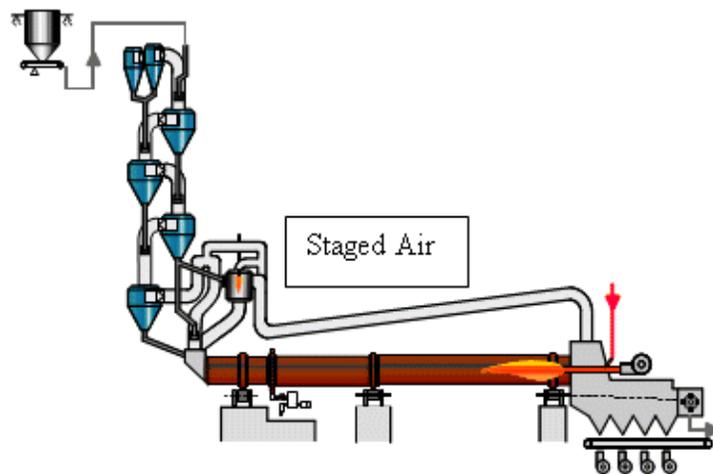
The factors affecting NO_x levels for SCC are presented in Table 11.

Table 11. Parameters affecting NO_x and Staged Combustion responses (REF 24)

Kinetic parameters influencing NO _x	Process parameter Influencing NO _x	Measures for NO reduction
oxygen concentration	air ratio	air staging
NO concentration	NO at kiln inlet	decrease O ₂ in rotary kiln
NH ₃ , HCN, HC, CO concentrations	residence time	calciner design
Same as above	mixing of gas streams	adjustment of burners, distribution of meal and tertiary air
Same as above	fuel properties	increase fineness, change fuel
temperature	temperature	meal staging

Three types of SCC (Ref10)

The first type is a staged air combustion system such as located at Suwannee American Cement, Branford, Florida (Figure 14). The calciner burner is vertically orientated in a separate combustion chamber of the type typically used for difficult to burn units such as petroleum coke. In this case it is used to burn calciner fuel (coal) in a reducing atmosphere to destroy NO_x in the kiln exhaust. The unit is supplied by Polysius and a similar calciner is the Minox Low NO_x calciner.



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Figure 14. Suwannee American Cement – Bradford, Florida – Staged air SCC(ref 10)

The second system (Figure 15) is an air and fuel staging system at Florida Rock - Newberry,

Florida. This is a Polysius multistage combustion in-line calciner. The calcination burner is mounted horizontally rather than in a separate combustion chamber. Provisions are included for a small burner in the kiln inlet housing. Instead of using the burner shown at kiln inlet, FRI burns tires.

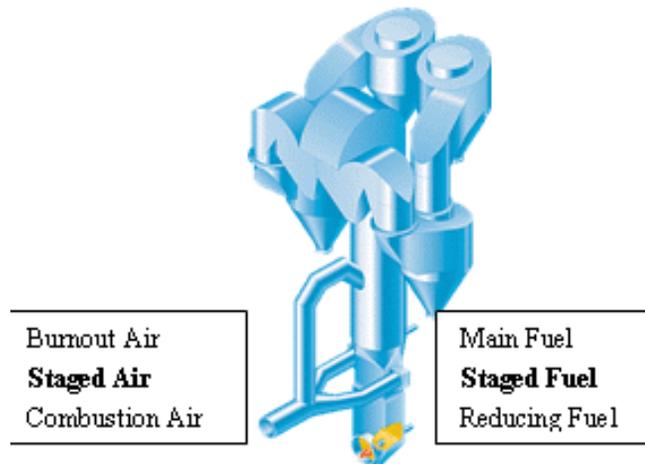


Figure 15. Florida Rock – Newberry, Florida – air and fuel staging – SCC (ref 10)

The third system (Figure 16) is a sequenced fuel and air introduction at Titan America at Medley, Florida. This is a low NO_x in line calciner. All fuel is fired in a reducing atmosphere near the kiln inlet and then all tertiary air is supplied in lower part of the calciner. Raw meal is split to several sections of the calciner. 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 NO formed in the kiln. Another important reason is as a temperature control strategy.

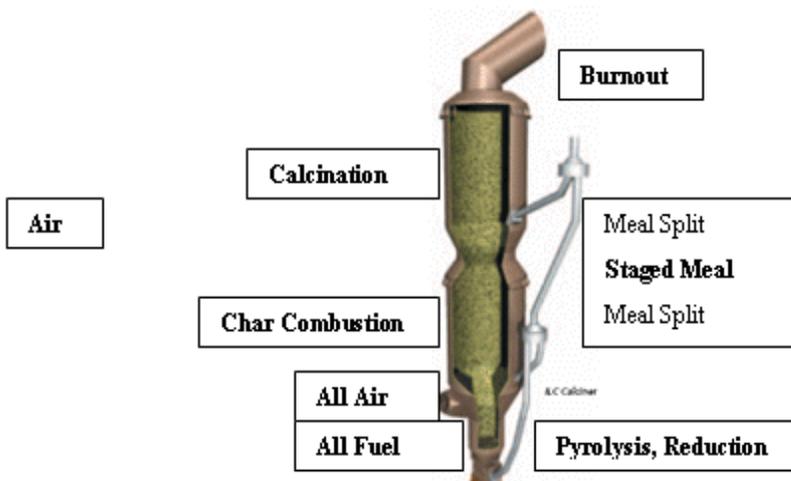


Figure 16. Titan America – Medley, Florida – sequenced fuel and air – SCC (ref 10)

Results SCC

Table 12 below is from a report done by a Canadian agency that summarizes information obtained on various US cement plants and one Canadian plant. Most of the data here represents permit data. A few plants have actual emission test data. This data reflects the results of using multiple NO_x controls including mufti stage combustion. There are 12 kilns with MSC, process controls and low NO_x burners. Their emissions range from 0.6 - 1.65 - kg/tonne (1.2 - 3.2 lb/T of clinker). The average of the 11 US kilns that have only process controls, LNB and MSC is 1.35 kg/tonne (2.7 lb/T). Several other plants used these controls plus other controls.

Table 12. NO_x Emissions Performance of Selected Cement Plants (ref 5)

Plant	Location	Year Operation	Emission Factor (kg/tonne)	Concentration (mg/Nm ³) ⁺	Control Method
Ash Grove Cement ⁽¹⁾	Durkee, OR	1998	1.8	1,070	multi-stage combustion; process control; low NO _x burner; burns whole tires in kiln
CEMEX ⁽²⁾	Brookesville, FL	2000	1.8/1.5	(750/620)	multi-stage combustion; process control; low NO _x burner
CEMEX ⁽³⁾	Victorville, CA	2000	1.4	(580)	"
GCC Rio Grande ⁽⁴⁾	Pueblo, CO	2000	1.15	(480)	"
Giant Cement ⁽⁵⁾	Harleysville, SC	2003	1.4	(580)	"
Florida Rock Industries ⁽⁶⁾	Newberry, FL	1999	1.4	(580)	"
Hanson Permanente ⁽⁷⁾	Cupertino, CA	1980	1.1	(460)	"
Hercules Cement ⁽⁸⁾	Stockerton, PA	?	1.5	(620)	and NH ₃ injection
Holcim ⁽⁹⁾	Florence, CO	2000	1.65	1,070	"
Holcim ⁽¹⁰⁾	Midlothian, TX	1997/2001	1.85/0.6	630 @ stack O ₂	tire chips burned in precalciner
Mitsubishi ⁽¹¹⁾	Cushenberry, CA	1995	1.0 – 1.25	(420-520)	40% reduction attributed to biosolids injection
RMC Lonestar ⁽¹²⁾	Davenport, CA	1989	1.0-1.25 24-h ave.	(420-520)	"
Suwanee American ⁽¹³⁾	Branford, FL	2000	1.45	(600)	"
Tarmac America ⁽¹⁴⁾	Miami, FL	2000	1.19 12-month	(500)	"
Texas Industries Inc. ⁽¹⁵⁾	Midlothian, TX	new kiln line 2001	1.4	(580)	and CemStar®
Texas Industries Inc. ⁽¹⁶⁾	Riverside, CA	Under construction	1.4	1020 @7%O ₂	"
Lafarge Canada ⁽¹⁷⁾	Richmond, BC	1999	0.6-1.2	360-610	"

⁺ Concentration data in brackets was derived from the emission factor using 2,400 Nm³ of kiln gas/t clinker (25°C, 101.3 kPa, 11% O₂, dry).

(1) Emission factor is from the Title V Permit 01-0029, dated 2001; the emission concentration of 560 ppmv (dry standard conditions) is from communication with Mark Bailey, Oregon Department of Environmental Quality

(2) Linero, Alvaro A. *What's Up with Cement Plant Permitting?*, paper # 884 presented at AWMA Conference, 2001

(3) Mojave Desert Air Quality Management District. *Engineering Evaluation for Modification of a Major Facility, New Source Review*, Southdown California Cement LLC, June 10, 1999

(4) Environment Canada communication with Ram Seetharam, Colorado Department of Public Health and Environment, July 10, 2003

(5) South Carolina, Dept of Health and Environmental Control, Part 70 Air Quality Permit, April 2003

(6) Linero, Alvaro A. *What's Up with Cement Plant Permitting?*, paper # 884 presented at AWMA Conference, 2001

(7) Environment Canada communication with Lee Colver, Hanson Permanente Cement Inc. July 18, 2003

(8) Environment Canada Communication with Mark J. Wejkszner, Pennsylvania Department of Environmental Protection, July 22, 2003

(9) Environment Canada communication with Ram Seetharam, Colorado Dept. of Public Health and Environment, July 10, 2003

(10) Linero, Alvaro A. *What's Up with Cement Plant Permitting?*, presented at AWMA Conference in 2001. Emission concentration (about 240 ppmv) is from stack tests in 2000. The emission factor of 0.6 kg NO_x/kg was a commitment by Holcim during the permitting process as a long-term NO_x performance. Holcim later stated this was an error. A permit amendment was in process as of July, 2003 that indicated a NO_x emission factor of about 1.4 kg/t for each kiln line.

(11) Environment Canada communication with M. Mizuno, Mitsubishi Materials Corporation, Japan, June 26, 2003; communication of August 20, 2003 with Alan De Salvo, Monterey Unified Air Pollution Control District provided 1998 actual emissions of 1,750 tons NO_x and emission factor of 2.25 lbs NO_x/ton.

(12) Monterey Bay Unified Air Pollution Control District, RMC Lonestar – Davenport Plant, CA. Permit No. TV16-01, Expiration Date: 12/31/03; 24-hour rolling average for NO_x limit.

(13) Linero, Alvaro A. *What's Up with Cement Plant Permitting?*, paper # 884 presented at AWMA Conference in 2001

(14) Linero, Alvaro A. *What's Up with Cement Plant Permitting?*, paper # 884 presented at AWMA Conference in 2001; 12-month rolling ave.

(15) Emission factor is from Emissions Tutorial sponsored by IEEE-LAS/PCA at Cement Technical Conference, May 4-9, 2003, Dallas, Texas.

(16) Mojave Desert Air Quality Management District, Engineering Evaluation, TXI Riverside Cement, August 5, 1999

(17) Concentration is from stack sampling over 1999- 2001; emission factor is calculated from clinker production during stack test.

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SCC results from three plants in the State of Florida are discussed in the following paragraphs.

o **Florida Rock Industries (ref 10)**

The Florida Rock Industries (FRI) kiln in Newberry, Florida has a BACT NO_x limit of 2.45 lb/ton on a 30-day rolling average basis. Data from the first half of 2004 are available. Typical emissions from the FRI kiln are between 1.5 and 2.5 lb/ton, when tires are burned near the kiln inlet. The 30-day average emissions range from 1.8 - 2.4 lb/T. The daily averages range from 1.0 - 3.7 lb/T. According to FRI, the higher values near 3 lb/ton are observed on days when tires were not available.

o **Suwannee American - Branford, Florida (ref 10)**

Suwannee American Cement (SAC) in Branford, Florida has a BACT NO_x 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 as 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.

Figure 18 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 13.

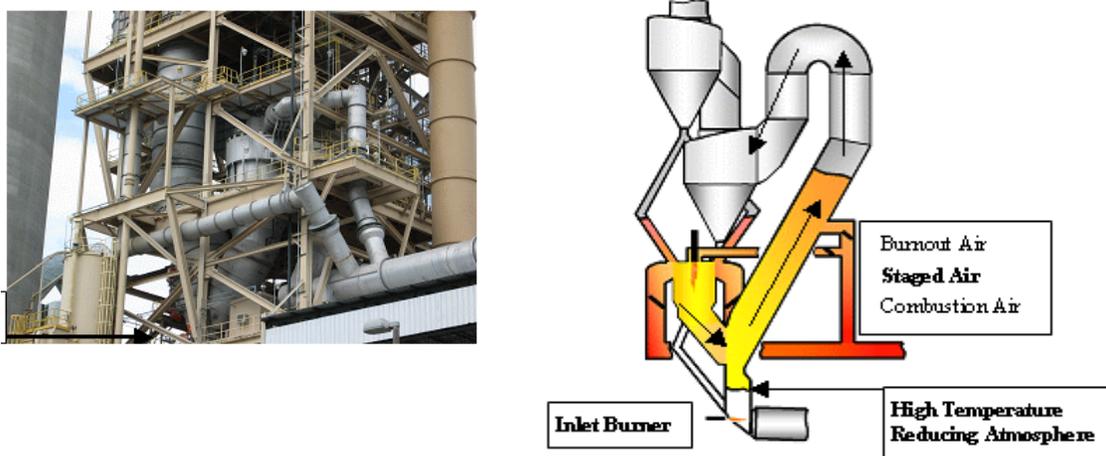


Figure 18. Suwannee American – Branford, Fl – Polysius MSC –CC with kiln inlet burner (ref

o **Titan America - Medley, Florida (ref 10)**

Compliance tests at the new 250 ton per hour Titan America kiln in Medley, Florida indicated NO_x and CO emissions at 2.0 and 0.5 lb/ton, respectively. Titan employs fewer air

cannons and does not experience the level of coating problems and stoppages reported by SAC or FRI. This calciner is not exactly a SCC. That is, it does not stage fuel (like 2 burners in calciner) or stage air (like 2 tertiary air inputs to calciner). 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.

On a long term average, a well operated MSC plant under reducing conditions in calciner can achieve 2.3 -2.5 lb/T. Staging can involve either the staging of fuel combustion, staging of combustion air or both. The basic MSC system operating under oxidizing conditions throughout will result in NO_x emissions of about 3.5 -4.0 lb/T. (ref 2)

The MSC system can be operated with combustion at various points being fuel-rich conditions. If a kiln inlet burner is used or if TDF is fired as supplemental fuel at kiln inlet, combustion can occur with sub-stoichiometric combustion air. This creates a reducing atmosphere around 1,000 - 1,100C (1,830 - 2,010 F). Under these high temperature reducing conditions, a good portion of NO_x generated in the kiln is converted to N₂, thus reducing NO_x emissions. This concept is similar to reburning.

European studies

An European study indicates that most current European standards [200-500 mg/Nm³ (1.0 – 2.4 lb/T)] can be met by MSC manufactured by Polysius. Another European reference states that there is a 10-50% reduction attributable to SCC that achieves emission levels <500 - 1000 mg/m³. (<2.4 - 4.8 lb/T).(ref 28)

SUMMARY OF SCC - EXPECTED NO_x PERFORMANCE

Table 15 summarizes the level of performance expected from SCC with other NO_x controls (primarily combustion and process controls) in place (e.g., LNB in kiln and process controls). As shown in this Table, the NO_x level varied considerably from 1.0 - 4.8 lb/T. **The average of these numbers [excluding those kilns that burn tires and 1.0(outlier)] is 2.7 lb/T.** This average will be used in determining cost effectiveness of SNCR and SCR.

Table 15. Summary of NO_x Performance of SCC

Source/Location	NO _x (uncontrolled) (Lb/T)	NO _x (controlled) (Lb/T)	Efficiency
11 US kilns	NA	2.2 - 3.3 (avg- 2.7)	NA
ECRA report	NA	2.4 - 4.8	NA

Florida Rock	3.5	3.0 -w/o tires;2.0-tires	17% -w/otires;43%-tires
Suwannee American	NA	2.4	NA
Titan American	NA	2.0	NA
Lone Star	2.8	1.8	35%
American Cement	NA	2.3-25(reducing); 3.5-4.0(oxidizing)	NA
European Report	NA	1.0-2.4	NA

Limitations of MSC - high sulfur

In kiln systems, that have a process mix that has a high sulfur to alkali molar ratio, the volatility of sulfur increases due to the strong reducing conditions in MSC and relatively low oxygen content in the system. Operationally, this causes severe preheater plugging to occur due to significant sulfur deposition associated with MSC operation. Thus, the required conditions needed for optimum MSC operation (low excess oxygen) conflict with the goal of preventing sulfur deposition and minimizing operational problems. Thus, a high sulfur/alkali molar feed ratio prevents the achievement of maximum NO_x reduction using MSC.

SELECTIVE NONCATALYTIC REDUCTION (SNCR)**Basis of SNCR**

A short summary of SNCR follows. Ammonia in the form of ammonia water or urea is injected at a point in the flue gas stream at a suitable temperature.. By far, ammonia solution is the reagent that has been most often used for cement kilns.(ref 5, 31) Other alternatives include anhydrous ammonia - injected as a gas; urea solutions, and ammonium sulfate. According to one reference, experience indicates that ammonia solution is most effective for PH/C applications.(ref 22)

The SNCR performance depends on temperature, residence time, turbulence, oxygen content and a number of factors specific to the given gas stream. These factors are discussed later. SNCR removes NO_x (90-95% of NO_x in flue gas is NO) by a 2-step process as follows:

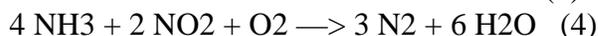
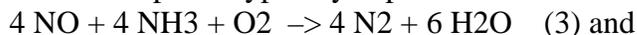
a - ammonia reacts with available hydroxyl radicals to form amine radicals and water:



b - amine radicals combine with nitrogen oxides to form nitrogen and water



These 2 steps are typically expressed as follows:



The first equation is the predominant reaction since 90-95% of NO_x in flue gas is NO. (ref 31)

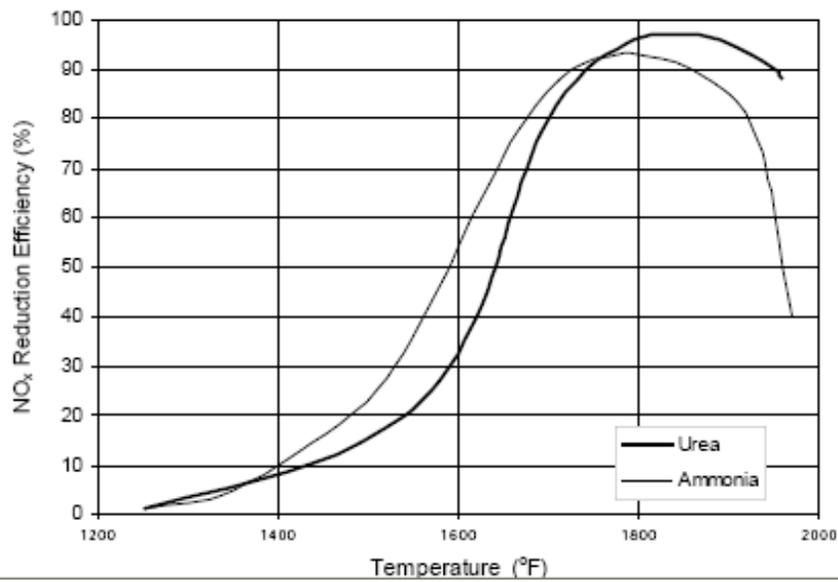
These equations suggest that SNCR will function best in an oxidizing atmosphere. Also this is shown in the next equation that in a reducing atmosphere, CO competes with ammonia for available OH radicals.

**Appropriate temperature for SNCR**

As mentioned above, the temperature window for these reactions is critical. (ref 31) Table shows the acceptable ranges from various references. At higher temperatures, ammonia will react with oxygen increasing NO_x concentrations. At lower temperatures, the rates of NO_x reduction reactions become too slow resulting in excessive ammonia slip or excessive buildup of ammonia in raw materials. The range is 870 – 1,100 C (1,600 – 2,000 F). The performance of urea and ammonia at various temperatures is shown in Figure 20. As shown in Figure 20, ammonia has a slightly higher efficiency than urea at temperatures between 760 - 930C (1,400- 1,700F). Urea has slightly higher efficiency between 950 - 1,040 C (1,750- 1,900 F).

Ref 34

Figure 20. Ammonia and Urea Reduction at Various Temperatures



Ref 33

Location of suitable temperature

For preheater/calciner type cement kilns, the likely locations for this temperature range are the cooler end of the rotating kiln, in the riser duct, and in the lower section of the cyclone preheater tower. (ref 6)

The major cement kiln manufacturer, Polysius, believes there are three possible SNCR injection points (ref 36)(see Figure 22)

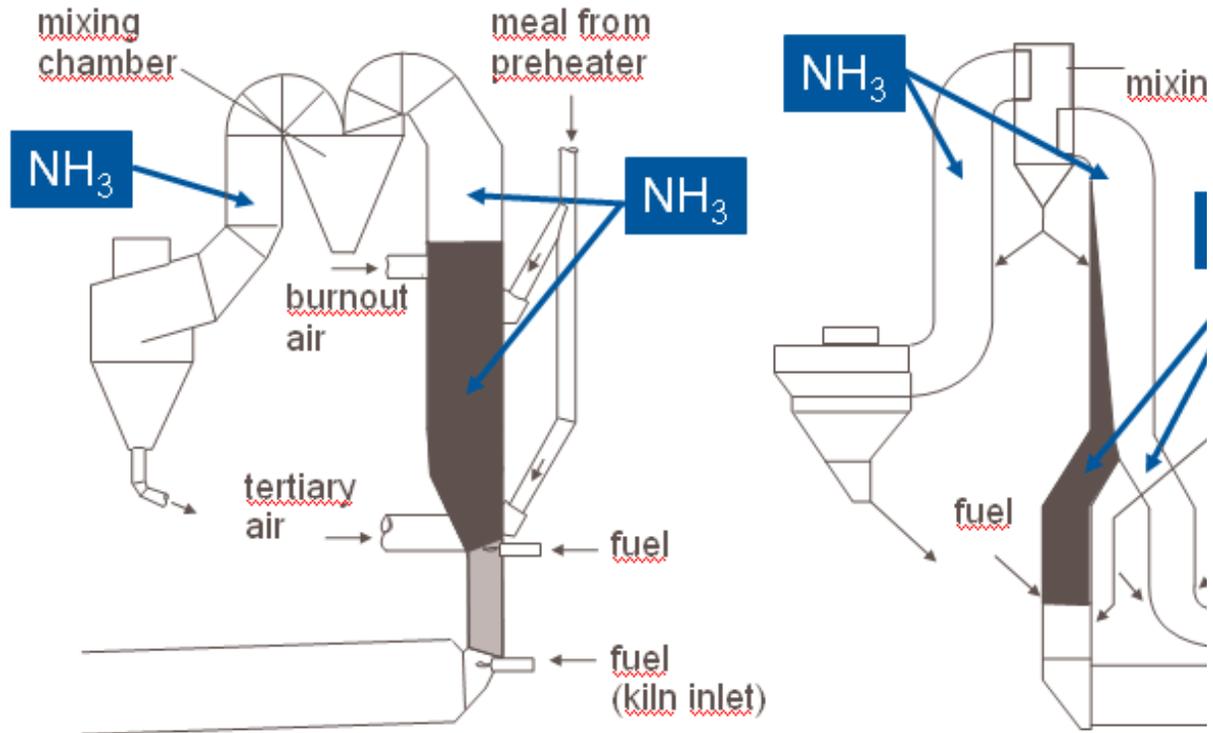
- combustion zone in part of calciner operated under reducing conditions [930-990 C (1,710 - 1,810 F)]. This location is most ideal as far as temperature.
- oxidation zone under the upper air inlet before the deflection chamber [850 -890 C(1,560 - 1,630 F)].
- area after the deflection chamber before the inlet to the bottom cyclone stage. This was found to be the best location.

Figure 22. Possible SNCR injection points

Figure 22. Possible SNCR injection points

Figure from ref 37

Optional points for adding SNCR reducing agent



OTHER FACTORS AFFECTING SNCR

Other important design and operational factors that affect NO_x reduction by an SNCR system are: (ref 38)

- residence time available in optimum temperature range
- degree of mixing between injected reagent and combustion gases
- uncontrolled NO_x concentration level
- molar ratio of injected reagent to uncontrolled NO_x .

Figure from ref 40

POTENTIAL PROBLEMS WITH SNCR

Earlier operating experience identified several concerns with both ammonia and urea-based SNCR processes. The most frequently reported is the buildup of ammonium bisulfite scale when burning sulfur-containing fuels.(ref 31) Also there is some concern about converting some NO to N₂O which seems to be more prevalent using urea than ammonia (ref 6)

One issue raised by manufacturers is the iron ore content of the limestone or sulfur content of limestone or some other aspect of limestone that will prevent SNCR from operating efficiently. (ref 31)

Sulfide or elemental sulfur contained in raw materials may be roasted or oxidized to SO₂ in areas of pyroprocessing system where sufficient oxygen is present and material temperature is 300-600 C (570 - 1,100 F). For some cement plants, SO₂ is not a problem. Uncontrolled SO₂ emissions are only about 0.10 lb/T and less than 100 TPY at Florida's PH/C kilns because there are minute amounts of sulfur in most of the available limestone. Uncontrolled SO₂ can be as much as 2 orders of magnitude greater when pyritic sulfur is present in raw materials. Unreacted ammonia from SNCR process or from raw materials reacts with SO₂ and SO₃ at temperature prevalent in the upper preheater, pollution control equipment and outside the stack. Ammonium bisulfate, ammonium sulfate and ammonium bisulfite may be formed. (ref 10)

When the kiln system is operating with the raw mill on line, the compounds condense. They go back into the feed system and to the preheater, where they vaporize again. They subsequently condense 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 PM collection device (BH or ESP). Since the PM control cannot capture the new, high concentrations efficiently, the plume becomes highly visible. When the raw mill is put back into operation, the plume is not visible. This cycle continues indefinitely. It would seem that a filter cake in a baghouse would even out these emissions more so than an ESP- so it is not a foregone conclusion that the plume will be highly visible.

If the plant has a persistent detached plume due to ammonium sulfate, it is necessary to eliminate ammonia or sulfur dioxide. Obvious method is to minimize ammonia use when SO₂ emissions are likely.

Operating the raw mill promotes SO₂ removal by limestone scrubbing under humid conditions, due in part to freshly generated limestone surface produced by grinding. Some of the SO₂ 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 SO₂ 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 SO₂ is evolved. This involves conveyance of lime from the calciner to the upper stages of the preheater. System consists

of a cyclone and some ductwork and no moving parts.

If these three SO₂ measures are insufficient, then conventional wet or dry scrubbers can be considered. The TXI Midlothian scrubber was estimated to cost \$13 million. SO₂ emissions were permitted at 1.33 lb/T of clinker. It is not certain whether SO₂ emissions are that high. If they are that high and SNCR system is installed, it might be necessary to limit ammonia slip or to further enhance SO₂ removal to avoid a detached plume.

A very fine suspension of slaked lime can be introduced into gas-conditioning tower to remove SO₂, particularly when the raw mill does not operate. The droplets react, dry and are captured by the PM controls where excess lime (from dried droplets) continues to remove remaining SO₂. (ref 10)

SNCR experience

US - early tests

According to the ACT and the EC/R reports, there was very limited experience with SNCR at cement kilns. The two US plants that were tested with SNCR and mentioned in these reports are discussed below.

A. Ash Grove Cement - Seattle, Washington (ref 41)

A week long test of a Nahlco Fuel Tech(urea) system at Ash Grove Cement's Seattle plant was performed on 10/93 on a 160 TPH 5-stage preheater/calculator under 10 different operating conditions. Using 3-4 injectors, NO_x was reduced from 350-600 lb/hr to less than 100 lb/hr. NO_x reduction was greater than 80% for most cases. Chemical utilization of urea was greater than 50%. The excellent results were attributed to a high degree of mixing and a long residence time at an appropriate temperature in the preheater tower. The average ammonia slip was 4 ppm above baseline at an NSR of one. There was virtually no effect on plant operations.

The urea reagent was injected at three ports at the top of the calciner, three ports halfway up the calciner and four ports at bottom of calciner. Gas temperature was measured at each of these ports. During tests, kiln feed rate was steady at 160 TPH; kiln fired with natural gas. Conditions covered a fairly wide range of fuel firing and excess air conditions. For a typical operating condition, gas temperature was 820 C (1,530F) at top of calciner. Temperature measured at bottom ports was 2070F. Hot gas was reduced to 840 C (1,550F) as it calcines the solids entering the calciner. Reduction of 90 % was achieved at NSR of 2. Chemical utilization was greater than 70% at NSR of 0.5 and 60% at NSR of 1.

Conclusions

At NSR of 1.5, NO_x reduction was as high as 80% and chemical utilizations were higher than 50%. High degree of mixing and long residence time at appropriate temperature contributed to

excellent process performance. Current NO_x emission limit was maintained under various kiln/calcliner operating conditions with less than 40 gallons/hr. SO₂ and CO were unchanged from baseline levels at NSR <0.7. At higher NSR, these emissions also remained near baseline levels when preheater oxygen concentration was >2.3%. However both SO₂ and CO increased slightly with increasing chemical injection rate at lower oxygen. Ammonia at exit of preheater was erratic - ranged from 6 ppm under baseline to 10 ppm at NSR of one.

Urea based process was easily installed using existing port and available resources without a plant outage. Plant operation was unaffected during testing. A commercial system should also be easily adapted to plant operations and easily maintained.

Coal or gas were the fuels used. When firing gas into the kiln and coal in calciner, uncontrolled NO_x emissions average 2.8 lb/T of material input. When gas is fired in both units, uncontrolled NO_x was 2.9 lb/T. Based on limited short term data using stabilized urea at an NSR of 0.5, NO_x was reduced ~27%. At NSR of 1.0, NO_x was reduced ~55%. (ref 7) The urea is injected at the top, halfway and bottom points of the calciner. The EC/R report indicates that under 10 different operating conditions at this same kiln, NO_x was reduced from 3.5-6.0 lb/T to less than 1 lb/T. It should also be pointed out that the 25% reduction at Ash Grove was obtained at an NSR of 0.5; 55% at NSR of 1.0. At an NSR of 2, 90% reduction was obtained.

B. LaFarge - Davenport, Iowa

Another NO_x Out system was tested in October 1998, at LaFarge's Davenport Iowa plant. Much lower NO_x reductions were obtained (10-20% from uncontrolled emissions of 350 lb/hr). (ref 6) The reasons for this lower reduction are presented below. (ref 42)

Reasons for low reduction rates

The unit is unusual due to the high proportion of heat released in calciner. At Davenport, 70% heat input is added at the calciner. At Ash Grove only 5-10% of heat input is in the calciner. Most ph/c kiln use 50% of heat input to the calciner. This difference affects the gas temperature in the calciner and the gas retention time in the 860 - 1,090 C (1,600-2,000F) range. The gas stays within this range for a longer time in the Ash Grove system. At Ash Grove, gas retention time in the precalciner is 2.7 seconds; at Lafarge 1.95 seconds. The Lafarge unit operates at 815 - 920 C (1,500-1,700F) and Ash Grove is at 840 - 1,130 C (1,540-2,070 F). The Ash Grove unit has a larger window within this range.

Also, at La Farge, a significant portion of kiln flue gas is bypassed(40-60%) prior to the precalciner. Thus, roughly half of the kiln exhaust gas is not treated by SNCR. Raw material in Davenport is highly alkaline(eg -sodium, potassium) compared to the material being processed at Ash Grove's Seattle plant. The alkali bypass provides the ability to control alkali content of the clinker product. Thus anticipated SNCR control should be much less than 30 -70%. The gas exit temperature of the bypass gas is 920 C (1,700F) but is immediately quenched by adding dilution air to 430 - 780 C (800-900F). There is not sufficient time for the addition of SNCR to this gas stream(that is the alkali bypass stream). Data during the Fuel Tech tests in 10/98 indicate that

approximately 1/3 of uncontrolled stack emissions are from the bypass.

Another reason why SNCR was not effective at La Farge is because of the temperature profiles. (ref 43) No section of the calciner has ideal temperature profile for SNCR. SNCR is added to top of preheater (after Stage 4 cyclone) where the temperature is around 890 C (1,640 F). Temperature drops by 90 - 120 C (200-250F) over next 1.3 seconds as gases pass thru stage 4 cyclone. Thus, the temperature is marginally within SNCR window. Thus, there is a slight NO_x reduction. Ammonia slip was 14 ppm from the 5-6 ppm baseline. Flue gases have cooled well below the SNCR temperature window. - no reduction was found. Ammonia slip was 47-52 ppm.(all from Lanier) SNCR optimal temperature window is 860 - 1,090 C (1,600-2,000F). This window only appears in the upper calciner/lower Stage IV cyclone zone of the La Farge kiln system. The temperature in this zone of the Lafarge kiln system ranges from 860 - 920 C (1,600-1,700F) with a residence time of less than two seconds. At La Farge, the temperature of flue gas in riser between kiln exit and bottom of calciner is 815 +/-10 C (1,500+/-50 F). Peak temperature in calciner is 920 C (1,700F) and temperature at exit of calciner is 890 C (1,640F). Gas residence time in calciner is 1.95 seconds. Flue gases exit the calciner and enter stage 4 cyclone preheater (taking 1.3 seconds). (from ref 44)

At Ash Grove, the combustion gas from kiln enters the bottom of calciner at 1,120 C (2,070F). Gas temperature at top of calciner is 830 C (1,540F). Horizontal temperature profiles were essentially flat with less than 8 C (15 F) variation across the preheater cross section. Estimated residence time in calciner is 2.7 seconds. After leaving the kiln the maximum temperature reached by flue gas is 920 C (1,700F) at the middle of calciner, very near the combustion zone.

1. US Plants presently using SNCR

There are five know cement kilns in the US that are presently using SNCR on a permanent basis.

1. Hercules Cement - Stockertown, PA

The oldest existing full scale SNCR installation on a cement kiln presently operating in the US is located at Hercules Cement; Stockertown, Pa. The SNCR system uses a 19% ammonium hydroxide solution and was installed in 2001 on the K3 kiln (a preheater/calciner kiln). This kiln produces 60% of the cement production at this plant. The other kiln (K1) is a preheater kiln but a good spot for ammonium hydroxide injection could not be found for this kiln. Both kilns have LNB. (ref 45)

SNCR was installed to comply with RACT levels. The limit for all 3 kilns is 492 lbs/hr. NO_x reductions of 25%(300 ppm) have been seen using the SNCR system. Reduction rates of 11.5% are sustainable. The system has no impact on clinker production. (ref 46)

- Emission tests in 2003 show ammonia to be 13 ppmvd; 28 ppmvd@ 7% oxygen. If a good spot for injecting ammonium hydroxide solution(AHS)into K1 can be found, an overall reduction of

40-50% at stack may be seen. The annual cost for AHS is \$20,000-35,000. (ref 45)

The ammonia injection is near the bottom of calciner rather than the 180 degree bend before bottom cyclone. This location is better because of low CO and maximum oxygen. The SNCR performance might also be limited by possibility of detached plume if there are pyrites in raw material. (ref 47)

2) SEE SWANNEE AMERICAN - FLORIDA -pp.83 - 91

3. St Mary's Cement - Charlevoix, MI

On an existing preheater/calciner kiln system, SNCR was temporary installed and pilot tests were conducted in 4/05 and SNCR was utilized thru the 2005 ozone season. The plant is in the process of permanently installing an SNCR(urea system). According to state of Michigan personnel, SNCR is being installed to comply with Michigan NO_x Rule 801 which sets a limit of 6.5 lb/T(30- day rolling average) during the ozone season. (refs 48, 49)

Using urea, daily averages for the period May 1 - September 30, 2005 were obtained from the state of Michigan. The 30 day rolling averages beginning May 30, 2005 range from 4.41 - 6.38 lb/T for this period. Clinker production varied from 716 to 4,516 tons per day. There were 11 days during this period when the kiln did not operate. Most days the production range from 3,800 - 4,500 tons of clinker per day. (ref 51)

According to plant personnel, the plant uses a 40% urea solution. The kiln has a lot of up and down operations and operates typically at about 70-80 % capacity during ozone season. The calciner and kiln both are permitted to burn coal. There is a test trial permit for the firing of petroleum coke. The trial will dictate what percentage of coke will be burned in the system. There is a 10 -30% alkali bypass. The urea solution is currently injected above the kiln feed shelf and before the calciner. Other locations for injections were tested such as post calciner, upper stage of calciner and entrance to the calciner but optimum efficiency was obtained at present location. (ref 52)

4. Cemex - Brooksville, Florida (all from ref 53)

Cemex has installed SNCR on two existing preheater kilns. The kilns are not ph/c kilns but preheater kilns. SNCR is presently operating on one of the two kilns. The other kiln will start operating SNCR after obtaining a permit to test tires and petroleum coke as fuels. The system uses a 19% ammonia solution with one injection nozzle at the kiln inlet where optimum temperature for ammonia 850 - 1,150 C (1,550 - 2,100 F) is available. The oxygen content is typically 1.5 - 2.0 % at this location. There are also 3 injection nozzles in the riser duct but they are not used.

The ammonia solution injection rate for the single injection point can vary from 0-15 liters/minute or up to 0.35 lb-moles of ammonia per minute. Assuming an ammonia utilization rate of 75% based on other tests in Florida, this equates to a potential NO_x reduction of up to 15 lb-

moles per hr. A NO_x reduction of about 4 - 5 lb-moles/hr equates to a NO_x reduction from the present maximum rate of 4.0 lb/T of clinker to the proposed emission rate of 2.0 lb/T of clinker so there is assurance that the SNCR system is capable of delivering the required ammonia. The mole ratio for this reduction is 0.6 - 0.7.

The plant believes that even with the potentially greater NO_x emissions during firing of petroleum coke or coke/coal mixture, there is sufficient ammonia delivery capability with the single injection point to achieve 2.0 lb/T of clinker.

As shown on pp.9 -10, preheater kilns are less fuel efficient than ph/c kilns. Also, all fuel is burned at main kiln burner so a great deal of thermal NO_x is produced. Also the uncontrolled emission rate for ph/c kilns is lower than preheater kilns as shown on p 28.

5. Holcim, Midlothian, Texas (refs 54 -58)

The plant operates 2 preheater/calciner kiln lines. Line 1 was commissioned in 1987 and Line 2 in March 2000. The plant exceeded 1998-99 NO_x permit limits so plant was required to test SNCR. This permit limit was 1,659 TPY for the combined kilns.

Line 2 has low NO_x burner in the kiln, MSC and provisions for alternative fuels. Line 1 uses alternative fuels but does not have LNB or MSC. Wet scrubbers were added to both lines. The scrubbers were predicted to remove 25% of NO_x based on European operations. However, in the US most NO_x emissions from cement kilns are NO so little reduction using this scrubber was obtained. *According to Holcim, full scale SNCR systems began operating on April 15, 2006 on Lines 1 and 2. For Line 1, ammonia solution is added at the top of the preheater. For Line 2, ammonia solution is added at the top of the pyroclone. (5/31/06 telecon with Michel Moser; Holcim – 972-923-5808)*

In 2005, SNCR (19.5% ammonia solution), was tested on both lines. The entire airflow was tested at full load conditions and at all operating parameters (mill-up/down, scrubber-up/down.) The test period was approximately two weeks per line. Line 1 achieved on a routine basis - 40-45% reduction and Line 2 achieved 30-40% reduction. NO_x reduction was as high as 80% but at this reduction there was excessive ammonia slip and pluggage at the preheater. These numbers only establish SNCR "applicable" and "effective" levels. The new permit limits for the combined kilns for NO_x are 3,738 TPY and 1,300 lbs/hr. During the ozone season(May 1- September 30), NO_x shall not exceed 1,564 tons for the combined kilns. Also, additional SNCR testing will be done in 2006 and 2007. This testing may result in changes to the NO_x permit limits.

In the report, curves are prepared on the performance of SNCR for the 2 lines and summarized in Table 19.

Table 19. NO_x % Reductions for 2 Lines at Holcim - Midlothian, Texas

NSR

Line	0.4	0.6	0.7	1.0
1	30	43	47	60*
2	10	28	32	45*

* Sharp increases in NH3 emissions

A. US Cement Plants installing SNCR

1. Lehigh Portland Cement - Mason City, Iowa

SNCR is being installed on No. 8 ph/c kiln (150 tons of clinker/hr). As of October 2005, the SNCR has not been installed. The unit will be installed at the same time as the SO2 scrubber is installed. The plant is waiting on a shutdown period to install these controls. SNCR will operate year round.

The emission limit is 2.85 lb/T(30 day rolling average) which is a 25% reduction for SNCR .[Therefore uncontrolled is 3.8 lb/T] Also, there is a calendar monthly average limit of 5 lb/hr. The No.8 kiln also has LNB and the calciner burns fuel in substoichiometric conditions. Kiln 8 capacity is 1,050,000 short tons/yr. The preheater calciner vessel was replaced by larger vessel and all of the 4 stage cyclone was replaced with a larger more efficient vessel.

2. Holcim - Lee Island, Missouri

The expected completion date of this new plant is expected to be June 2007. Construction is expected to start in summer 2005. Project construction is estimated to take 3 years. The annual clinker production capacity will be 4.828 million tons. Based on present specifications in US, Lee Island will have annual production capacity of 5.082 million tons using one ph/calciner system. (ref 62)

No later than 24 months after commencing operation, SNCR is to be installed as innovative control technology. After installing SNCR, NO_x emissions on 12-month rolling operation will be less than 1,322.8 lb/hr and 2.4 lb/T. There will also be a summer season (May 1 to September 30) NO_x emission limit of 1,622 tons. This limit includes 530 TPY of emission reduction credits.. In no case shall NO_x emissions exceed 1,822 tons of NO_x for 5/1-9/30 from in-line kiln and raw mill system..

3. Drake Cement- Arizona

This proposed cement plant is expected to be constructed and commence operation in 2008. The nominal capacity of the ph/c kiln system is 660,000 short tons/yr. The system is a rotary kiln, 6-stage preheater, low NO_x calciner with a clinker production of 2,000 TPD. The maximum

capacity is 83 tons of clinker/hr and the kiln will operate 7,920 hrs/yr. The kiln and calciner will burn coal which will be less than 0.90 weight percent sulfur. The raw limestone has a total sulfur content <0.01 weight percent. Fuel combustion in precalciner will be 50-55% of the total energy demand of kiln system; and the rotary kiln - 45-50%. There is low sulfur in the raw material. Sulfur expressed as SO₃ is feed material -0.05%; coal-1.68% (equivalent to 0.67% of sulfur); feed material plus coal- 0.18% . One ton of feed raw material requires 0.0765 tons of coal. One ton of clinker is equivalent to 1.53 tons of raw materials. (ref 64)

The air permit application submitted in 6/04 proposed an emission limit of 2.3 lb/T on a 24-hr basis. The controls to be used were low NO_x burners in the kiln, low NO_x precalciner and multi-stage combustion. The draft permit issued by the state of Arizona has a BACT limit of 1.95 lb/T (30-day rolling average). (draft permit = 2/06) For the first 180 days after initial startup of the rotary kiln, the Nox emission limit is 2.45 lb/T on a daily rolling 30 day average. To comply with Class I considerations, the limit is 95 lb/hr on an hourly 24-hr average. Using the maximum production rate of 83 Tons of clinker/hr, this is equivalent to 1.14 lb/T. is 1.25 lb/T by SNCR. This suggests that BACT is not necessarily the lowest limit for Nox when there are other issues such as visibility to consider.

It is expected that SNCR will be introduced (ammonia in an aqueous solution) as a reducing agent in the space between the calciner and the bottom stage of the preheater which has a temperature window of 860-980C (1,580 - 1,800 F).

As described in Innovative Control Technology analysis, Drake intends to reduce NO_x to 416 TPY with voluntary limit that has been proposed as result of Air Quality Impact Analysis. Drake proposes to add SNCR in conjunction with the currently proposed BACT limit.

To meet the voluntarily accepted modeling driven limit, DC will optimize SNCR operations as well as other process and air pollution control equipment to minimize NO_x emissions. If these operations do not reduce NO_x to 416 TPY, DC will curtail production to ensure 416 TPY is not exceeded during any 12 month period.

With a six-stage preheater/calciner process with low NO_x calciner (i.e., offering multistage or stageless combustion and sufficient residence time), the NO_x emission rate is estimated to be 1.9-2.3 lb/T. As shown in DC Class 1 application, use of these combustion design features delivers an emission rate that satisfies BACT requirements. The NO_x concentration leaving the calciner and entering SNCR will not be as high as plants using current combustion technology. This has the benefit of reducing the additional NO_x reduction by SNCR that is necessary to achieve the proposed emission limit of 95 lb/hr. Therefore the portion of overall NO_x reduction attributable to SNCR is within current process capabilities with respect to both relative proportion (% controlled) and absolute magnitude (lb/hr removed).

DC has advantage of incorporating features that will improve SNCR performance as an integral part of the process design rather than retrofitting equipment. It is anticipated that this design effort building on recent developments will be successful. Therefore DC will be able to operate at NH₃/NO stoichiometric ratios of approximately 1.0. Experience at existing kilns shows holding the

ammonia slip at approximately 15 mg/nm³ or 10-12 ppm is reasonable.

4. ALSO SEE BELOW INFORMATION ON KILNS IN FLORIDA

Kilns in Florida

This section summarizes information on cement kilns in Florida that have installed SNCR, tested SNCR or plant to install SNCR. According to a Florida expert, cement production is greater using SNCR compared with multistage combustion (staged combustion in calciner under reducing conditions).



All Florida cement kilns have multi-channel main kiln burners with indirect firing (meaning low primary air blowing in the pulverized coal). These are known as low NO_x burners (LNB). All kilns listed below are also multistage combustion (MSC) calciners. MSC is actually the version of

staged combustion as applied by Polysius.

Suwannee American Cement – Branford, Florida (ref 31)

The first Florida plant to be discussed is Suwannee American Cement (SAC) in Branford, Florida. (Figure 26) This plant has tested and has permanently installed SNCR on April 2005 on a preheater/calciner kiln.

The calciner operates at about 1,090 C (2,000 F) and the kiln operates at 1,650 C (3,000 F). Both units burn coal. The preheater exhaust gases go thru the raw mill and then to a baghouse. Fly ash is injected directly to calciner and also to the top of preheater.

According to plant personnel , the advantages of using SNCR are: (ref 34)

- greater kiln stability
- prolonged periods of increased production
- fewer kiln process problems(buildup in riser duct)
- reduced NO_x
- possibility to use petroleum coke with current NO_x limits

The disadvantages of using SNCR are :

- higher than average CO
- ammonia emissions observed during raw mill down periods. Ammonia emissions may occur over longer periods of time with raw mill on.

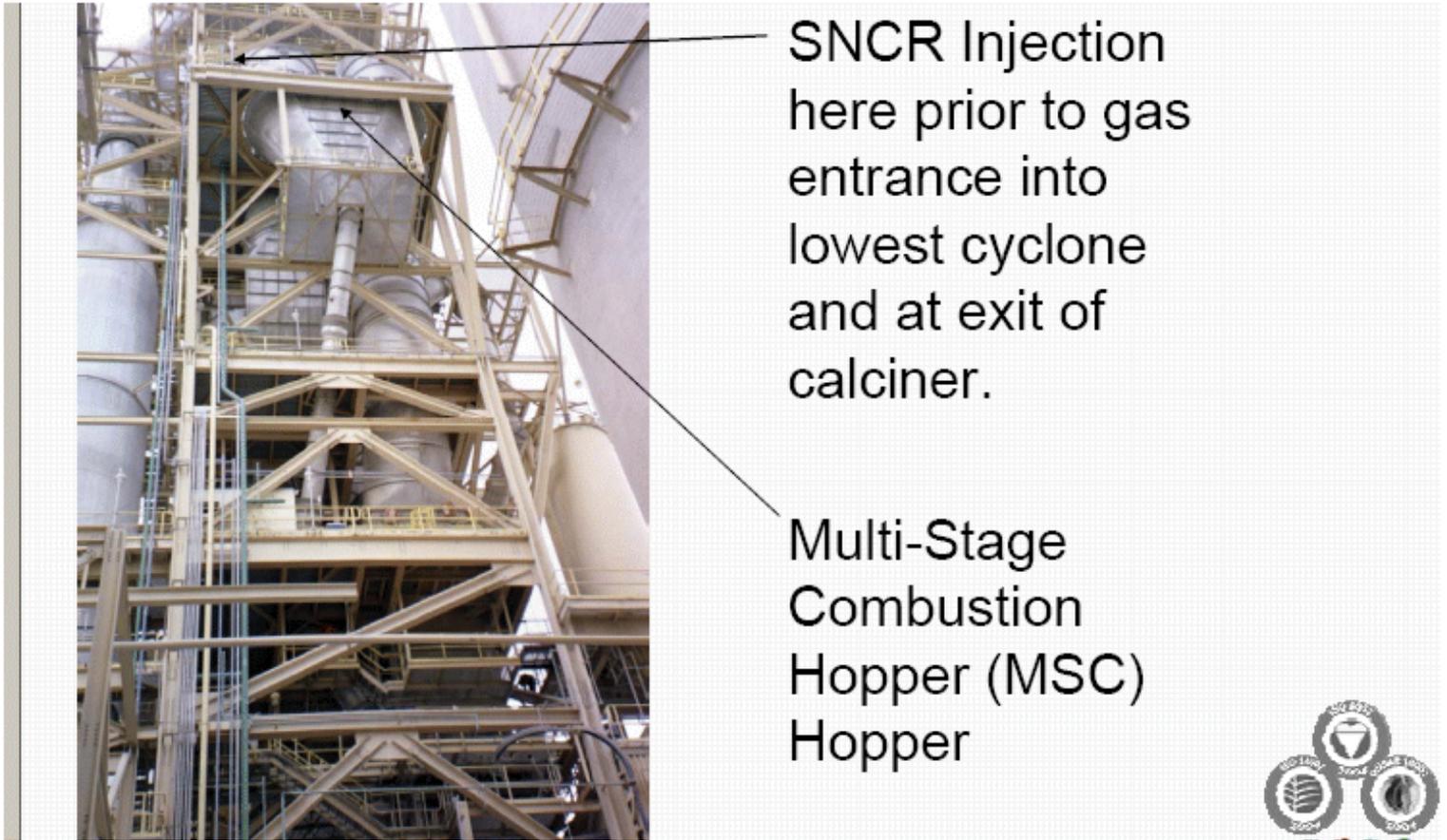
In selecting where to inject the ammonia solution , it is important to separate the NO

reduction reaction from combustion. This is ensured when the ammonia solution injection is done as close as possible to the bottom stage cyclone. The actual injection location where ammonia was injected at Suwannee is shown in detail in the following figures. The injection nozzle is shown on Figure 29. One of the four injection ports is shown on Figure 26. Overall depiction showing ammonia injection are shown in Figures 27-28. (ref 34)

Figure 26. SNCR Injection location – Suwannee American – Branford, Florida

Figure 26 - Ammonia Injection port - Suwannee American





Figures 27 - 28 - Ammonia injection -Suwannee American

. The ammonia injection location was verified thru previous testing in recent years by Polysius on kilns in Europe similar to that of SAC. This has been demonstrated as the best location for Polysius multi-staged combustion and MSC- combustion chamber kilns. The location is in the later portion of the calciner prior to the stage 1(lowest) cyclone and just beyond the MSC deflection chamber. Temperatures at this location were verified prior to testing and ranged from 870 - 910 C (1,600 -1,675F) with oxygen around 2%. This location provided optimal residence time at the needed temperature and oxidizing atmosphere as well as turbulence for mixing of ammonia solution.

(ref 66)



At this location, gas temperature averaged 860C (1,580 F) which is at the low end of temperature range for SNCR. With the temperature at lower end of range, CO emissions are minimal. With temperatures in the higher end of range, reactivity of NH_2 improves but CO after the injection is much higher. In addition, if ammonia is injected in too high temperature gases, one might create NO molecules may form instead of N_2 . (ref 34)

Full scale SNCR tests on the existing kiln were conducted. There was no problem reaching 2.0 lb/T while operating at 3.0-3.5 lb/T of clinker at kiln exit. SNCR in conjunction with MSC and separately from MSC was also tested. Both worked fine.

For 2 days prior to ammonia injection, normal NO_x emissions utilized MSC in conjunction with LNB resulted in NO_x of 2.4-2.5 lb/T. SAC utilizes the MSC and the combustion chamber to create reducing conditions. SAC frequently encounters process problems caused by this type of operation; that is strong reducing conditions and high CO at kiln inlet. Most typically, the problems consist of buildup in riser duct (lowest portion of the calciner prior to the entrance of the kiln). During establishing the baseline, SAC experience some operational problems that can be noted by abrupt changes in clinker production. These signify process upsets or problems. However, overall operations were satisfactory. (ref 66)

Conclusions

2.0 lb/T or below was achieved with SNCR with and without MSC. Increased process stability was realized during both testing periods which led to increase production. The plant achieved high ammonia utilization rates -close to stoichiometric reductions.

SNCR will promote stable kiln operation with the use of various approved fuels and to allow increase in production rate. When operating the kiln with higher exit oxygen levels, increased thermal NO_x is generated in the kiln and typically NO_x stack emissions increase. The excess NO_x generated in kiln is reduced by the reaction with ammonia. SNCR emissions were around 2.0 lb/T while operating with 3.0- 3.5 lb/T at kiln exit. (ref 35)

Since the November 2004 testing and the permanent installation of SNCR, the plant is achieving 2.4 lb/T(30 day) and 2.9 lb/T (24-hr). There are very low SO₂ and VOC emissions. The plant has determined that SNCR and moderate MSC is the least expensive way to achieve these levels. The plant will not use the already installed multistage combustion in the calciner because SNCR is so efficient and process-friendly for their installation. Production has increased after installing SNCR. The plant is meeting the 2.4 lb/T limit while injecting only ½ the theoretical amount of ammonia needed to neutralize NO_x. (refs 35, 67, 68)

Ammonia slip

Ammonia slip during raw mill down periods presents the possibility of detached plume problems since raw mill operates as a scrubbing device for SO₂. Raw mill down periods could lead to both SO₂ and ammonia emissions. (refs 10,34)

Florida Rock – Newberry, Florida



Figure 30. Florida Rock – Newberry, Florida

Florida Rock (FRI) at Newberry, Florida is another plant that installed SNCR for testing purposes. However, SNCR is not being presently used as the kiln can achieve low NO_x levels with multistage combustion (see pp. 30 -57). This modern ph/c kiln was designed by Polysius Corp and is shown on Figure 30. The plant has a permitted clinker production rate of 2,650 TPD(110 TPH). Both kiln and calciner are fired with coal. The kiln uses air and fuel staging on a Polysius multistage combustion 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. Instead of using a burner at the kiln inlet, FRI burns tires. Full scale SNCR tests were conducted on the SNCR application on this existing kiln. The kiln had no problem reaching 2.0 lb/T. The December 2004 testing is described in detail below. (ref 10)

The following Tables 21-22 summarize the emission test results.

Table 21. With tires - Florida Rock - Newberry, Florida - 12/04

Uncontrolled NO _x (lb/T clinker)	Controlled NO _x (lb/t clinker)	Molar Ratio(NH ₃ /NO _x)	NO _x reduction (%)
--	--	---	-------------------------------

3.1	2.1	0.12	34
2.9	1.8	0.19	39
3.2	2.1	0.25	35
3.3	1.5	0.51	54
3.3	1.1	0.64	68
3.2	2.0	0.34	39

Table 22. Without tires - Florida Rock - Newberry, Florida - 12/04

Uncontrolled NO _x (lb/T clinker)	Controlled NO _x (lb/t clinker)	Molar Ratio(NH ₃ /NO _x)	NO _x reduction (%)
4.5	4.2	0.09	7
4.2	3.5	0.21	18
3.7	2.6	0.35	29
3.6	1.9	0.47	47
3.6	0.9	0.80	76
3.2	0.6	1.04	82

At lower molar ratios(<0.5), NO_x efficiency was greater when tires were used compared to the efficiencies when tires are not burn. At molar ratios of ~0.5, 50 % control was achieved with or without burning tires. These data also show NO_x is reduced by approximately 0.8 lb-moles with the injection of 1.0 lb-mole of ammonia(ammonia utilization rate of 80%.) without burning tires.

3. CEMEX – Brooksville, Florida

CEMEX in Brooksville Florida just started up SNCR on both kilns. See p. 77 for more details on the SNCR system. (ref 25)

Projected Florida Kilns to install SNCR

1. Florida Rock Industries (FRI) - Newberry, Florida (ref 71)

FRI plans to install a new ph/c kiln in a couple of years. The kiln will be a Polysius Multi-stage calciner and will use SNCR in conjunction with multi-stage combustion.

The following information is from the issued permit. The kiln will have a capacity of 206 TPH of material feed dry basis to preheater; 125 TPH of clinker production; and 138 TPH of portland cement production.

The NO_x emission limit will be 1.95 lbs/T of clinker (243.8 lb/hr) on a 30 day rolling average. For the first 180 operating days, kiln shall not exceed 2.4 lb/T clinker (30 days rolling average). As the project was subject to PSD review and BACT determinations for NO_x, PM, PM10, SO₂, CO and VOC, the other limits are :

- PM - 0.23 lb/T
- PM10- 0.20 lb/T
- SO₂ - 0.23 lb/T
- CO - 3.6 lb/T
- VOC - 0.12 lb/T
- Hg - 122 lb/yr

2. Suwannee American Cement - Brandford, Florida (refs 31, 35, 66, 67, 73)

The company has submitted an application for a new kiln. The new kiln system is very similar in design to the existing ph/c kiln system that is described on pp. 83-86 . The new kiln will have a capacity of 215 TPH of material feed to preheater and 127 TPH of clinker production. Annual dry preheater feed will be limited to 1.789 million tons during any consecutive 12-month period and 1.055 TPY of clinker during any 12 consecutive months. Raw materials and additives are the same as the existing kiln system - limestone, fly ash or other alumina sources, sand or other silica sources and iron or other iron sources. Up to 45 TPH of fly ash may be injected into the calciner.

For NO_x control, the plant proposes to use indirect firing, low NO_x burners, stage combustion and SNCR. The project is subject to PSD preconstruction review for CO, NO_x, PM/PM10, SO₂, and VOC. A summary of the proposed BACT standards for this kiln is shown on Table 23.

Table 23. BACT Determinations - Suwannee American Cement - Brandford, Florida - 11/05 (ref 73)

Pollutant	Emission Standards(Lb/T of clinker)	Emission Standards (Lb/hr)	Averaging Time
CO	2.90	368	30 - day rolling average - CEMS
NO _x	1.95	248	Same as above
NO _x (initial startup)	3.0	381	Same as above

PM/PM10	0.10(of dry preheater feed material)	21.5	Average of 3 - 1hr test runs
	10% opacity		6-minute average w/ COMS
SO2	0.20	25.4	24-hr rolling CEMS average
VOC	0.12	15.2	30-day block CEMS average

3. Rinker/Florida Crushed Stone Brooksville, FL (ref 74)

This is a new line that is expected to be completed by 2007. It will have a capacity of 206 TPH of material feed dry basis to preheater and 125 TPH of clinker production.

The NO_x emission limit will be 1.95 lbs/T of clinker (243.8 lb/hr) - 30 day rolling average. Project was subject to PSD review and BACT determinations for NO_x, PM, PM10, SO₂, CO and VOC. These limits are:

- PM - 0.23 lb/T
- PM10- 0.20 lb/T
- SO₂ - 0.23 lb/T
- CO - 3.6 lb/T
- VOC - 0.12 lb/T
- Hg - 122 lb/yr

The proposed NO_x control is SNCR with multi-stage combustion. SNCR will operate in conjunction with MSC(including reducing conditions at PC as needed).

4. Sumter Cement Company - New Center Hill, Florida (ref 75)

Preheater calciner kiln system has a capacity of 353 short tons/hr as feed to the preheater or 208 tons/hr of clinker production. The expected operating hours are 7,883 hrs/yr. Raw materials and additives to the kiln include limestone, fly ash, sand and steel slag. Fly ash may be injected through the calciner burner. There will also be an in-line raw meal that simultaneously dries raw materials using the exhaust gas from the kiln, ph/c and clinker cooler.

The calciner will be designed to accommodate introducing fly ash and non-hazardous waste through the calciner burner. The burner will contain a specific chamber or nozzle within the burner for simultaneous introduction of coal, petroleum coke, fly ash and non-hazardous wastes. Petroleum coke typically has a lower reactivity and typically requires the longest retention time in the calciner.

Tires, either whole or shredded, may be used and injected via an airlock/gate system into the material inlet of the kiln. The tires produce a localized reduction zone around the tire fuel which

assists in NO_x reduction. The proposed tire gasification system would produce a combustible gas that would be injected into the kiln inlet or calciner region.

Primary fuel firing scenario has 55-60% of total heat input in calciner and 40-45% in the kiln main burner. This ratio will remain fairly constant. When tires are used, they may account for up to 15% of calciner heat input. When using tire gasification, up to 40% of the calciner fuel may be supplied.

Primary fuel for kiln and calciner burners will be ground bituminous coal and petroleum coke. Burners will be designed to burn non-hazardous liquids such as fuel oil. These fuels could produce up to 50% of total heat input in each burner. Solid nonhazardous waste may be used in the calciner burner and produce up to 50% of total heat input.

To control NO_x, the plant will use a form of MSC (i.e. reducing zone), low NO_x burners in the kiln and SNCR. The Florida Agency determined that 1.95 lb/T(30 day rolling average) is BACT for this project.

5. American Cement Company - Sumterville, Florida (ref 76)

Proposed BACT determined by the Florida DEP for this ph/c kiln is 1.95 lb/T (30 day rolling average). NO_x controls will be SNCR, low NO_x burners in the kiln, kiln design and MSC. MSC will be used to function with either fuel staging or combustion air staging and will have flexibility in meal splitting.. Kiln design is the preheater/calciner kiln system. The plant is designed for 1,150,000 TPY.

Coal and petroleum coke will be burned in both the kiln and calciner. Ratio of coal to pet coke burned will depend on process conditions such as material build up, feed alkali content and heating value of the fuel. Petroleum coke will not exceed 25-30% of pet coke/coal fuel mix.

Field tests by Polysius, the major cement kiln manufacturer, demonstrated that a 65-70% NO_x reduction was achieved using a 25% ammonia water solution at a molar ratio of 1. In comparison a 68% urea solution achieved only a 35-40% reduction at the same molar ratio. At a higher molar ratio than 1, ammonia slip becomes a problem. (ref 30)

SNCR - FOREIGN EXPERIENCE – EUROPE, JAPAN, TAIWAN

SNCR has been applied to more than 30 German kilns which includes rotary kilns with cyclone preheater and rotary kilns with grate preheater as well as kilns with staged combustion in the calciner. SNCR is increasingly being applied at cement plants in other European countries.

To achieve high reduction rates, usually a stoichiometric ratio >1 is required. The target value is often a low concentration as low as 200 mg/m³(~1 lb/T). Ammonia slip may occur that can increase when there is not combined drying and grinding. Otherwise a considerable amount of

ammonia is deposited in the raw meal. Experience in numerous kilns indicates that this ammonia deposition is not detrimental to product quality. 25% ammonia aqueous solution is still considered the standard reducing agent. In many cases waste water is used as reducing agent

The experience with SNCR in cement kilns is more extensive than that in the USA. Most European kilns with SNCR are the ph kiln type with a few ph/c kilns. According to one source, SNCR is installed at 25 German kiln systems of different designs. Another reference states that there are presently 19 European cement plants with SNCR. Seventeen of these plants are preheater or traveling grate types. The two plants of ph/ c kiln type that use SNCR are located in Sweden. (refs 22,24)

New kilns in Europe have to comply with an emission limit of 500 mg/nm³(2.3 -2.5 lb/T). For existing plants, the limit is 800 mg/nm³ (3.7 -4.0 lb/T). Government agencies and cement industry organizations have collaborated into jointly funded studies to evaluate controls such as MSC, SNCR and SCR. (ref 78)

An European report indicated that SNCR on cement can achieve below 200 mg/m³ (80-85% control) if initial concentration is not higher than 1000 -1300 mg/m³. At one 2000 tonnes/day (2,205 TPD) plant, a molar ratio of 1.0 produced reductions of 80% without any increase of ammonia. Most SNCR applications are designed and or operated at NO_x reductions of 10-50% with NH₃/NO₂ ratios of 0.5-0.9. The controlled emission levels are 500-800 mg NO_x /m³. NO_x reductions up to 90% may be achieved at NSR of 0.7-0.8 and ammonia slip = 5 mg/m³. Based on experience in Europe, ammonia solution is the best agent for preheater/calciner kilns. (ref 22, 24)

JAPAN/TAIWAN (ref 5)

There are also ten cement plants in Japan and one in Taiwan with SNCR. Detailed information was available on an existing Taiwan plant using urea with 2 coal fired kilns each at 90 tonnes/hr (99 TPH). The goal was to reduce NO_x below 500 ppm. A summary of the results is shown on Table 24 .

Table 24. SNCR at a Taiwan cement plant

	Kiln A	Kiln B
NO _x baseline; ppm	389 - 412	525
Annual NO _x reduction (%)	>50	46
Controlled NO _x ; ppm	185 - 203	284

SUMMARY OF SNCR PERFORMANCE

Table 25 below summarizes the performance of ph/c cement kilns (except the Cemax

plant that has a preheater kiln) that have installed SNCR. Most SNCR systems use an ammonia solution. It appears that an emission level of 2.0 lb/T is achieved with an NSR of 0.5. At higher NSR ratio of 1.0, NO_x could be reduced to around 1.0 lb/T. Recall from p. that the uncontrolled NO_x (after SCC, LNB in the kiln and process controls) is 2.7 lb/T. So on average, SNCR achieves 35% reduction at NSR of 0.5 and a 63% reduction at NSR of 1.0. Ammonia slip may be a problem as the NSR is increased.

Table 25. SNCR SUMMARY

PLANT/SOURCE	Control Level(lb/T)	% Efficiency	NSR
3 European kilns(p68)	NA	25-50;35-60;42-72	0.6; 0.8; 1.0
Ash Grove, Seattle(p.73)	2.2; 1.3	25; 55	0.5; 1.0
Hercules; PA (p.75)	300 ppm~3.0	12-25	NA
Cemex; FL-preheater kiln(p.78)	2.0	50	0.6 - 0.7
Suwannee American(p.88)	2.0	33-50	NA
Florida Rock (p.94)without tires	1.9; 2.6	47; 29	0.47; 0.35
Florida Rock with tires	2.1	34	0.12 - 0.25
Holcim – Texas (2 kilns)	NA	47, 32	0.7
European Report(p.102)-achievable	1.0	80-85	NA
European Report - actual operation	2.5 - 4.0	10-50	0.5-0.9
Skovde, Sweden(p.103)	0.5- 1.0	80-85	1.0 - 1.1
Slite, Sweden (p.103)	1.1	80	1.0
Taiwan-2 kilns (p 104)	194;284 ppm~2.0;2.9	50; 46	NA

MSC +SNCR

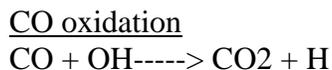
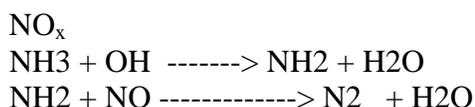
Most if not all new ph/c kiln systems will have some form of stage combustion. One form of MSC is shown in Figure AAAA. This section will present studies on the effect of the combination on MSC and SNCR. In a MSC calciner, part of the calciner fuel is introduced at the kiln inlet to reduce the NO generated in the kiln. The adjustable division of the tertiary air allows part of the calciner to be operated under sub-stoichiometric conditions. This leads to reduced NO formation from fuel nitrogen and depending on the type of calciner fuel used, to the reduction of more of the NO produced in the kiln.

One European reference states that considerable CO is formed in staged combustion but burns out for the most part in the area of the mixing chamber and the bottom cyclone stage. Operation of the SNCR, substantially impairs CO burn-out. During SNCR trials, CO rose from 0.02 to 0.05%. (refs 22,24)

Causes for the interaction between SNCR and CO burn-out rate have not been identified. SNCR and CO decomposition both require OH radicals. As a rule it seems advisable to create separate reaction zones for SNCR and SC. If SNCR is installed in a n existing precalciner kiln, this can be implemented by injecting the reducing agent at a point where coburing has progressed sufficiently. Design of new calciners should allow for sufficient gas residence time - allowing CO burnout and SNCR reaction to take place consecutively.

An European study was undertaken to study the combination of SNCR and staged combustion as an "emerging technique". It was assumed this combination could attain NO_x emissions of 100 -200 mg/m³. (ref 37)

The report states that there are competitive reactions of MSC and SNCR. These reactions are listed below. These are also shown on pp.59-62 of this report.



Four different kilns were tested to evaluate the effects of SNCR on ph/c kilns with stage combustion.. The results are summarized below. As shown in this Table, NO_x reductions attributable due to only SNCR varied from 45 - 65%. CO emissions increased when the NSR was at least 1.2 and NO_x reduction due to SNCR is at least 50%.

Table .EFFECT OF SNCR ON EMISSIONS WITH STAGED COMBUSTION

Kiln	B	B	D	M	X	X
NSR	0.6	0.9	1.2	1.5	2.5	2.7
NO _x RED due to SNCR (%)	47	45	50	65	65	65
CO INC(ng/m3)	0	0	125	375	290	950

315 - Figure 34 is summarized in Table 26 that summarizes the injection of ammonia in the burnout zone.

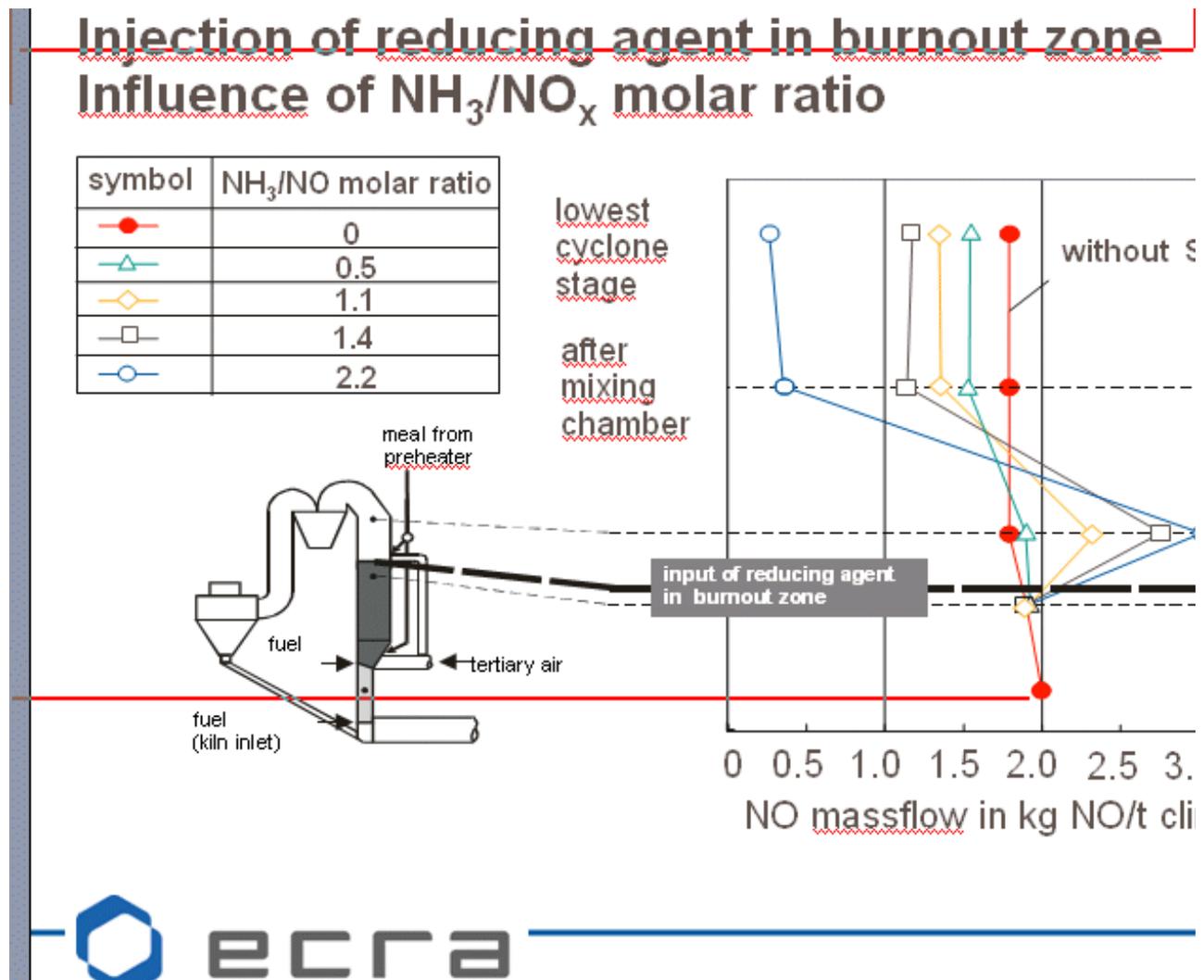


Table 26. Impact of injecting Ammonia in burnout zone

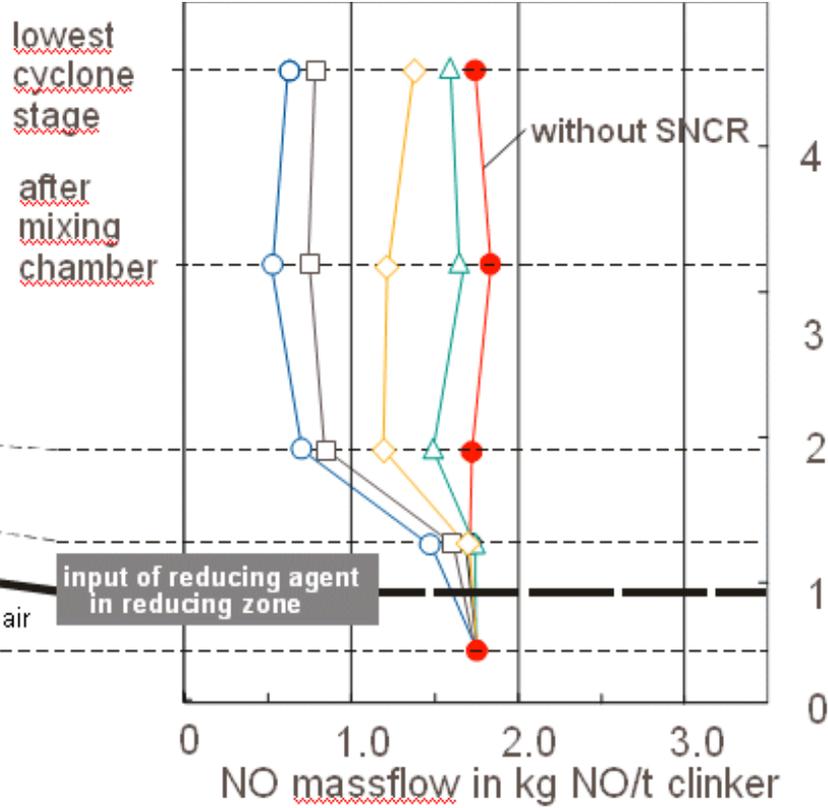
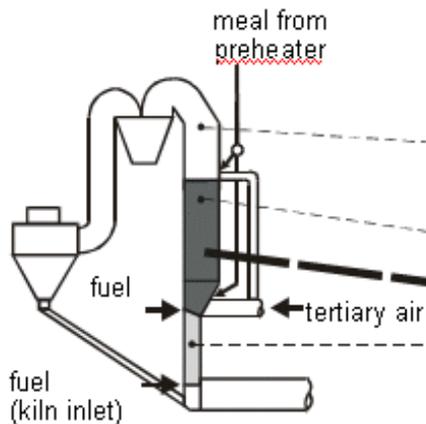
NSR	After mixing chamber NO(kg/T)	Lowest cyclone stage NO(kg/T)
0	1.8	1.8
0.5	1.6	1.6
1.1	1.3	1.3
1.4	1.1	1.1
2.2	0.4	0.3

The injection of ammonia in the reducing zone(Figure 35) is summarized in Table 27.

Table 27. Impact of injecting Ammonia in reducing zone

NSR	After mixing chamber NO(kg/T)	Lowest cyclone stage NO(kg/T)
0	1.8	1.7
0.7	1.6	1.6
1.4	1.2	1.5
2.0	0.8	0.8
2.7	0.6	0.7

symbol	NH ₃ /NO molar ratio
●	0
△	0.7
◇	1.4
□	2.0
○	2.7



The report had the following conclusions on the combination (MSC/SNCR):

- MSC/SNCR is feasible
- CO burnout and SNCR process affect each other
- CO can increase
- Optimum point for feeding reducing agent should be determined for each plant

The report had the following conclusions on the interaction of SC with SNCR:

- higher ammonia input into combustion chamber, more retarded the CO burnout
- CO can increase if residence time is too short after injection
- calciner design - plus 1-1.5 seconds residence time for SNCR
- input of reducing agent can be limited due to CO increase. CO increase can be avoided by increasing air ratio in the reduction zone (less air staging).

Solution – improve CO burnout by increasing air ratio in the reduction zone (less air staging)

According to a Florida DNR employee, a cement kiln in Florida would operate very comfortably at around 3.6 to 4 lb NO_x/ton in a PH/C kiln with oxidizing conditions in the calciner. Every bit of effort towards SCC and then towards high temperature reducing atmosphere costs something in terms of increased coatings, pluggage, size of calciner and higher preheater to accommodate the bigger calciner. Somewhere between 1 lb/ton and 4 lb/ton is an appropriate point called BACT for the given kiln. There will be some sort of least cost combination of SCC and SNCR or just one or the other. The expert believes that BACT will be much closer to the lower end of the range than the higher end. (ref 19)

Krupps Polysius carried trials that indicated that the combination of MSC with SNCR can achieve these values.(i.e., 800 mg for existing kilns and 500 mg/nm³ for new kilns). (ref 81) The MSC calciner is characterized by kiln inlet burner, staggered tertiary air introduction, staggered meal introduction and deflection chamber located before the first cyclone. Best results for NO_x reduction were obtained by injecting ammonia solution before and after the deflection chamber. Smallest plants show the best reduction rates. This is essentially attributable to the fact that mixing of a small amount of liquid into a large gas volume becomes more difficult. A reduction occurs only above a molar ratio of 0.2; below this it cannot be ruled out that part of ammonia oxidizes and thus reduces the reduction effect to such an extent that it is practically 0.

A CO increase is also linked to molar ratio. With molar ratios of less than 1, CO increases are in the order of 150-350 mg/m³. Above molar ratio of 1, CO increases can reach 600-800 mg/m³ depending on molar ratio. This CO increase is not characteristic of combined MSC/SNCR process; but to SNCR process itself.

The use of MSC/SNCR becomes economically attractive at total reduction rates above 35-45%. MSC leads to reduction in basic emission load reducing ammonia requirements for SNCR. SNCR allows kiln operation without direct coupling to emission limits, leaving the kiln operator more freedom of action.

Selective Catalytic Reduction (SCR)

There is presently one cement plant in the world using SCR - a preheater kiln in Solnhofer in Germany. This plant will be discussed in detail later.

Process Description

SCR is the process of using ammonia in the presence of a catalyst to selectively reduce NO_x emissions from exhaust gases. The SCR process has been used extensively on gas turbines, IC engines and fossil fuel-fired utility boilers. In this system anhydrous ammonia, usually diluted with air or steam, is injected through a catalyst bed to carry out NO_x reductions. A number of catalyst materials have been used such as titanium dioxide, vanadium pentoxide and zeolite-based materials. The catalyst is typically supported on ceramic materials, e.g., alumina in a honeycomb monolith form. The optimum temperature for the catalyst reactions depends on the specific catalyst used but occurs in the range of 300-450C (570-840F). This can be higher than typical cement kiln flue gas temperatures especially in plants that use heat recovery systems, or use a baghouse for PM control.(refs 7, 82)

The two principal reactions are:

$4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O}$ (predominant reaction as most NO_x is NO)

$4 \text{NH}_3 + 2 \text{NO}_2 + \text{O}_2 \rightarrow 3 \text{N}_2 + 6 \text{H}_2\text{O}$

Ammonia is typically injected to produce a NH_3 : NO_x molar ratio of 1.05-1.1:1 to achieve NO_x conversion of 80-90% with an ammonia slip of about 10 ppm of unreacted ammonia in gases leaving the reactor. (ref 6)

In an SCR system, ammonia is typically injected to achieve a NO_x conversion of 80-90% with an ammonia slip of about 10 ppm of the unreacted gases leaving the reactor. The NO_x removal efficiency depends on the flue gas temperature, the molar ratio of ammonia to NO_x and the flue gas residence time in the catalyst bed. All these factors must be considered in designing the desired NO_x reduction, the appropriate reagent ratios, the catalyst bed volume and the operating conditions. As with SNCR, the appropriate temperature window must be maintained to assure that ammonia slip does not result in a visible plume. (refs 7,82)

SCR can be installed at a cement kiln at 2 possible locations:

- 1) after the PM control device - low dust exhaust system.
- 2) after the last cyclone without ducting as a so-called "high-dust" set-up.

The advantages of a "low dust" set-up are longer catalyst life and lower danger of blockage. The disadvantage is additional energy costs required to heat the cooled exhaust

to achieve proper reaction catalyst temperatures.

The advantage of high dust-set-up is that exhaust gas temperature after cyclone is more or less equal to the temperature required by the catalyst. Additional heating is not required. However a high dust SCR installation which is used for most boilers using SCR is not recommended because the high calcium content of the dust in cement kilns forms deposits on the catalyst and reduces efficiency below acceptable levels. (ref 82)

The optimum temperature for catalytic reactions depends on the specific catalyst used and is usually 300 - 450 C(570 - 840 F). This temperature range is higher than typical cement kiln gas flue temperatures especially in plants using heat recovery systems of baghouses for PM control.
(ref 7)

The catalysts may be fouled or deactivated by the PM in the flue gas. The use of soot blowers would help alleviate this problem. Also the presence of alkalis and lime as well as sulfur dioxide in exhaust gas is of concern. It was felt that due to fouling problems, SCR must be installed after the PM control. This would require flue gas reheating as the temperature of kiln exhaust after PM control is lower than typical SCR operating temperatures. The ACT also noted that there have been recent developments on sulfur tolerant SCR catalysts that limit SO₂ oxidation to less than 1 %. (ref 7)

Early Pilot Tests

In 1976, Hitachi Zosen, an SCR manufacturer, conducted three test programs on 2 suspension preheater kilns and a wet process kiln. Each was tested for 5,400 hours. ESP's were used to remove PM before the flue gas entered the SCR unit.(ACT- p.5-14) Also, a heat recovery system with supplemental fuel firing was used to raise the flue gas temperature to the required reaction temperature. Slipstreams of about 3,000 scfm were treated with initial NO_x removal efficiencies of 98%. However after about 5,400 hours of operation, NO_x removal efficiencies dropped to about 75% due to catalyst coating. ACT-5-15 The ACT document concluded that SCR is a possible technology for cement kilns and NO_x reductions were projected to be 80 -90% regardless of kiln type. Also, the ACT document stated that installing an SCR would require an efficient PM collection device as well as reheating exhaust gases to appropriate temperature. (ref 7)

Pilot plant trials (3% of flue gas) have shown promising results in Austria, Germany, Italy and Sweden. At least three European suppliers offered full scale SCR to the cement industry with performance guarantees of 100- 200 mg/m³(0.2 - 0.4 lb/T of clinker). The report noted that a full-scale SCR demonstration plant was being built in Germany with government support. Also, a full scale SCR plant was under consideration in Austria (ref 6)

Pilot test – Austria (ref 83)

A pilot test was conducted in Kirchdorf, Upper Austria using a slipstream of

3,500 m³/hr. The pilot plant was operated starting in 1996 for about 13,000 hours or about 2 years. NO_x was reduced continuously to 200 mg/Nm³ half hour average. Ammonia slip was under 5 mg/Nm³.

Liquid ammonia was the reagent used and the SCR unit had 3 catalyst layers. The catalyst was placed prior to PM control. The gas temperature was between 300 - 400 C (570 - 750 F) with a dust load of 80 g/m³. SO₂ concentrations were typically between 150 -300 mg/Nm³.

Some inlet concentrations of 640 mg/Nm³ (~ 2.6 lb/T) were reduced to 100 mg/Nm³(~0.4 lb/T) and below. Ammonia slip was considerably below 5 mg/Nm³. After 2,200 operating hours, catalyst activity was 92%. The pilot was operated for 13,000 hours with low NO_x emissions, low ammonia slip and no unexpected drop in catalyst activity.

SCR Installation

As mentioned above, there is one known cement kiln using SCR in the world. The plant is Solnhofer in Germany. The cement kiln is a preheater kiln not a preheater/calcliner kiln. The plant produces 500,000 tonne/yr (555,000 TPY)of cement.

First, a pilot scale demonstration was conducted in 1997-99 at Solnhofer. The SCR unit was installed after preheater in temperature between - 300-340 C (570 - 640 F). The pilot demonstration showed the following:

- catalyst pitch should be greater than 8 mm for easier cleaning
- NO_x was reduced by 30% with no ammonia usage but from the ammonia in the raw materials
- NO_x reduction rates above 90% were achieved with ammonia slip less than 5 ppm

In 2000, commercial SCR was installed at Solnhofer. A picture of this unit is shown below(Figure 36). The SCR installation is a high dust installation (that is, the SCR reactor is

located before the PM control device) and uses a 25% aqueous ammonia solution . The system reduced raw material NH₃ that might have otherwise been converted to raw material NO_x . Also, ammonia slip was less than 1 mg/m³. Reductions of hydrocarbons and SO₂ in the order of 50-70% were also attained.

Reactor can be equipped with 6 catalyst sections of which 3 layers are used. Using these three layers, 200 mg/m³ (~ 0.8 lb/T) of NO_x is achieved from an inlet of 1,050 mg/Nm³(4.2 lb/T) ; or 80% control. Less than 1 mgNH₃/m³ is emitted. At the end of 2003, the catalyst had logged 20,000 - 25,000 hrs with no discernable problems. The expected catalyst life was 3-4 yrs. Catalyst guarantee was for 16,000 hrs.

NO_x standards are 1000 mg/m³ on a half-hr basis and 500 mg/m³ on daily basis.(~ 4.6 and 2.3 lb/T). The plant emits less than 2.3 lb/T on 95.6 % of operating days. (all –ref 10)

Prior to installing SCR, the Solnhofer plant, with SNCR was achieving 700 -800 mg/Nm³(~ 2.8 - 3.2 lb/T of clinker). With SCR, the plant has been achieving 200 mg/Nm³ (0.8 lb/T of clinker). Based on uncontrolled NO_x emission rate of 1,050 mg/Nm³(4.2 lb/T of clinker). The controlled emission rate corresponds to a NO_x control efficiency of 80%. Greater than 80% control is typically achieved. According to KWH, the problem of fouling from heavy dust loading has proven to be quite manageable with regular catalyst cleaning. The gas temperature inlet to the SCR unit is 320 -340C (610 - 640 F). (refs 82, 84)

The plant has CEMs for chlorides, PM, SO₂, NO_x and Hg. The kiln also has an SO₂ standard of 0.23 lb/T on daily basis. This value is met 100% of the days. In a cement plant, the SO₃ formed at the location of the catalyst subsequently reacts with limestone in the raw mill. Also the catalyst efficiently utilizes ammonia (including ammonia in the raw material) so it is not available for detached plume formation. (ref 85)

ISSUES/SOLUTIONS USING SCR AT CEMENT KILNS – SAINT LAWRENCE CEMENT EXPERIENCE

St. Lawrence Cement(SLC) proposed to construct a new ph/c kiln at their facility

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



in Greenport, NY. Recently, SLC has decided not to construct this kiln. The following summarizes information developed during this process.

Most SCR systems are designed to operate between 315 - 390 C (600-750F). For the Greenport project, the SCR system would have been located downstream of the preheater cyclones and prior to the roller mill. According to the Mechanical Process Flow Sheet prepared by Krupp, the process exhaust temperature is 320 C (608F) at this location which is ideal for SCR. Also, it was believed that SCR would not interfere with or affect the cement manufacturing process. (ref 86)

The following presents various problems/issues that SLC raised to New York State that may occur if SCR was required for this cement kiln. A contractor to the Friends of the Hudson (FOH) provided responses to these concerns to the state of New York. Also, issues and responses on this subject that are contained in the Draft Ellis County 12/05 Report are also discussed

SO₂ Oxidation

SLC believed there were detrimental impacts due to significant levels of SO₃ in the SCR flue gas due to the oxidation of SO₂ by SCR catalyst. This can cause catalyst pore masking, formation of ammonium salts which can plug downstream equipment and acid mist emissions.(ref 87)

It is argued that high SO₃ concentration could lead to catalyst deactivation and other serious problems relating to SO₂ oxidation. A high SO₃ concentration (10-20 ppmv) when coupled with the high calcium level in the cement kiln flue gas could purportedly cause deactivation of the SCR catalyst due to the masking effect of calcium sulfate. In addition any SO₃ that does not react with the calcium could react with any unused NH₃ to form ammonium sulfate or ammonium bisulfate the could cause fouling of downstream equipment. Sulfur in the raw meal can be in several forms - calcium sulfate, magnesium sulfate and sulfites such as pyrites or organically bound sulfur. Only the volatile sulfur compounds(namely the sulfides and organically bound sulfur) are oxidized and released in the preheater as SO₂. (ref 84)

With respect to these concerns, SCR success at a number of coal-fired boilers show that SCR systems can be designed for high calcium and high sulfur flue gases. SCR catalyst suppliers have indicated that Ca SO₄ formation does not pose a major concern as they believe that the SO₃ generated in the process is captured by the free lime in the gas stream. Thus, SO₂ oxidation by the catalyst will have no negative impact on the amount of SO₃ formed and subsequently captured.

FOH responded that data from Solnhofer indicated that the SCR process eliminates 50-70% of SO₂. It is unclear where in the process the SO₂ removal occurred. The SO₂ removal could occur due to adsorption of SO₂ in the BH that replaced an ESP. (ref 86)

Also, the catalyst at Solnhofer has completed 24,000 hours of operation without any plugging problems or acid mist emissions. The presence of high SO₃ concentration has not led to catalyst deactivation and other problems at facilities with high calcium and high sulfur flue gases based on experience at various coal fired plants.(Friends of Hudson (FOH) (ref 88)

High CaO loading and potential masking? CaSO₄ formation

SLC believed that SO₃ oxidation could lead to catalyst masking by CaSO₄ formation and generating significant levels of sulfuric acid mist. Greenport will have SO₂ concentration of 177 mg/Nm³ (600 ppmv) in the preheater exhaust gas. With 0.5-2.0% SO₂ oxidation, a high SO₃ concentration of 8-17 ppmv could result. This high SO₃ concentration along with high calcium level in the cement kiln flue gas would deactivate SCR catalyst due to masking effects of calcium sulfate. (ref 87)

FOH responded that catalyst plugging problems can be prevented by managing the type and frequency of soot blowing and using a heated, compressed air blowing system (ref 86)

Ammonium bisulfate

SLC stated that SO₃ that does not react with calcium would react with any ammonia slip from the SCR unit to form ammonium sulfate or ammonium bisulfate which could cause fouling of downstream equipment. According to SLC, Solnhofer has not had to face SO₃ concentrations of this magnitude because inlet SO₂ is so low. (ref 87)

Also it is argued that ammonium salts could increase condensible particulate matter levels making it difficult for a facility to meet its PM limits. (ref 84)

In SCR systems with SO₂, NH₃ and moisture present, ammonium salts will form at temperatures below 301 - 307 C (580 - 590F). The best way to prevent their formation is to continuously control the SCR inlet temperature such that it is always 312 C (600F) or greater. Regarding the possible release of SO₃, catalyst manufacturers report that SO₃ gas is totally captured by conversion to particulate calcium sulfates and sulfites as it is contacted by free lime upstream, within and downstream of the SCR catalyst. Thus the formation of undesirable byproducts should be inherently controlled by the free lime in the system and can be further controlled by the free lime in the system and by controlling the SCR inlet temperature. (ref 86)

FOH responded that ammonium salts will form at temperatures below 300 - 307 C (580-590F). The plant can continuously monitor SCR inlet temperature to assure that the temperature is always 310 C (600F) or greater. (From Ellis Co - drat report -12/05 - There is also concern on the possible formation of ammonia salts, which can form in SCR systems at temperatures below 580 - 590 F. This problem can be avoided by keeping the SCR inlet temperature at 600F or greater.) Another option is the use of cyclone preheater bypass duct. FOH- 3/04 - p.39 - Also, Solnhofer has much higher SO₂ emissions than

SLC estimates. (between 733 - 1,700 mg/Nm³) (ref 88)

Alstom guarantees SO₃ oxidation rate of <0.55. Also, the rate of CaSO₄ formation must be considered. Any SO₃ formed would have to diffuse thru gas film surrounding the CaO particle then diffuse into the CaO particle and finally react with CaO to form CaSO₄. These reactions take considerable time - several hours. Soot blowers can remove CaO dust on catalyst every 15-20 minutes to help prevent CaSO₄ formation in catalyst pores. (ref 89)

Water soluble alkali - alkali poisoning - catalyst deactivation

SLC believed that there is a need to look at total quantify of poisons and availability of catalyst poisons reaching the vanadium pentoxide in the SCR catalyst. (ref 87)

Poisoning occurs when contaminants in the gas being treated react with the catalyst, resulting in catalyst deactivation. It's been argued that SCR in a cement plant will be subject to poisoning, principally from sodium, potassium and arsenic trioxide. Phosphorous, chromium and lead compounds can also poison an SCR catalyst but these are expected to be present in lower concentrations at cement kilns. However the typical concentration of sodium oxide in the particulate matter of certain coal fired utility is greater than double the Na₂O concentrations in the PM of the average cement plant as well as the maximum Na₂O concentration can be significantly greater than the maximum expected concentration of Na₂O in the average cement plant. Similarly As₂O₃ concentraion of flue gas of typical coal fired plant is well above the typical concentration expected from the average cement plant. (ref 84)

Additional discussion item on the solubility of Na and K in the fly ash and the form of fly ash particles. It is argued that in cement ph/c kilns, materials such as sodium and potassium compounds may be present in relatively elevated concentrations on particle surfaces in "water soluble" form that can contact the SCR surface of the catalyst bed and therefore poison the V₂O₅ "active ingredient" in the SCR bed. It is argued in coal fired boilers, the sodium and potassium are to a major extend trapped within a glass-like fly ash particle. It is widely known however that fly ash particles from coal-fired boilers are in the form of tiny spheres and during combustion, the particles are actually liquid and spheres are formed as tiny bubbles by evolved gases trying to escape. Boilers are designed to cool the molten particles to a solid state such that they can be easily removed from boiler tubes. However, depending on the fly ash temperature and its chemical composition, some fly ash will deposit in various sections of the boiler. The deposits that form at the back end of the boiler (on the economizer and air heater) are called "low temperature deposits".

Low temperature deposits are usually characterized by low pH; many contain hydrated salts and for most bituminous coals are water soluble. Therefore, coal-fired boilers do have fly ash deposits in the economizer section of the boiler that are water soluble. However, deactivation has not been found to occur. Also, SCR systems have been installed on oil-fired boilers despite the relatively higher levels of water soluble alkaline

metals found in the fly ash from such boilers.

FOH stated that data from a Kansas City coal fired power plant with SCR has more than double the Na_2O concentration in PM. Also, there is 2.3-2.5 time the As_2O_3 concentration in Somerset unit with SCR. (ref 88)

The corrosive layer of fly ash deposits is fly ash which has Na_2O - 0.1-14%; K_2O - 0.2-3.0%. These are water soluble. The predominance of SO_3 gives deposit its acidic property but water soluble alkali are still present in significant concentrations. Thus flyash from coal fired boilers contains water soluble alkali that could deactivate an SCR catalyst. But SCR catalysts on coal fired boilers have not been deactivated from alkali poisoning as catalyst suppliers have developed catalysts. (Ref 89)

Sticky deposits are primarily due to alkali salts (primarily potassium and sodium chloride and sulfates) which will significantly be removed by the alkali sulfur reduction system. Also, Alstom stated that sticky deposits can be addressed thru the type and frequency of soot blowing. (ref 88)

Various coal-fired plants have successfully used SCR despite concentrations of various catalyst poisons higher than those expected at Greenport. Oil-fired boilers are using SCR despite the presence of water soluble flyash, suggesting alkali in cement kiln flyash is unlikely to deactivate the catalyst. (ref 88)

SLC stated that alkali from coal combustion is trapped in glass-like ash particles and is therefore unavailable to poison the catalyst. (Ref – 87)

FOH replied that no analytical or quantitative data was provided to evaluate this comment.

Flyash from coal fired boilers are in tiny spheres that during coal combustion are actually liquid. (ref 88,89)

SLC also stated that potassium, the main form of alkali in Greenport, is usually not considered a water soluble alkali with respect to the sintered flyash deposits (ref 87)

FOH responded that potassium is present in coal-fired boiler flyash and hence would be available to deactivate SCR catalysts. However, SCR catalysts on coal-fired boilers have not undergone catalyst deactivation from alkali poisons. (ref 89)

High dust loadings

SLC wrote that larger SCR systems do not have the high dust loadings expected at Greenport (ref 87)

According to FOH, Kansas City P&L has ½ the dust loading at Greenport

(32.7gr/Nm³ vs. 60 gr/Nm³). Also, the gas flow rate is 23 times the proposed Greenport unit (8,860,000 Nm³/hr vs. 381,000 Nm³/hr).FOH -7/04 . Also, Solnhofer operates at dust load of 80 g/Nm³, which is 20 grams higher than the loading anticipated for Greenbelt. (ref 88)

NO_x inlet variability/NH₃ slip

SLC believed that NO_x variations are greater at cement kilns than for power plants. Also, there are considerable differences among cement kilns. It is impossible to draw conclusions from information on one plant. (ref 87)

FOH replied that this NO_x variability has greater risk in SLC's proposed MSC +SNCR than for SCR. SNCR must instantly increase ammonia feed rate in direct proportion to NO_x concentration. The SCR catalyst acts like a reservoir to store excess ammonia which is able to handle the sudden peaks in inlet NO_x concentration. (ref 89)

SLC was not aware of any data that quantifies the extent of the ammonia reserve and compares this on a mole basis to the duration and magnitude of NO_x concentration spikes in cement kilns. (ref 87)

According to FOH, KWH and Alstom each guarantee a low ammonia slip of 2 ppmvd. Solnhofer's achieves 500 mg-NO_x /Nm³ (2.3 lb/T of clinker) and less than 1 mg Nm³ of ammonia. (ref 89)

Coal-fired boilers have been operating SCR systems successfully for years despite considerable NO_x fluctuations in their flue gases. SCR suppliers typically guarantee a NH₃ slip of < 2 ppmv for any coal-fired boiler. Also, the Solnhofen data indicates that with all of inherent variability has achieved a high degree of NO_x control with low ammonia slip. Data indicates SCR inlet varies from 4.6 - 9.3 lb/T (1,000 - 2,030 mg/Nm³) while outlet varies from 1.4 - 3.3 lb/T (300 - 726 mg/Nm³). Average outlet NO_x concentration is less than 2.3 lb/T (500 mg/Nm³). However, at these variable conditions, NH₃ slip has been maintained in 1-2 ppmv range. (ref 84)

Catalyst plugging/fouling (all ref 84)

Catalyst plugging/fouling involves the accumulation of dust that blocks access to pores of the catalyst. It is argued that high dust loadings could plug or foul the SCR catalyst beds. However, the Solnhofen SCR system has operated at a relatively high dust loading, 80 g/Nm³. The level of NO_x removal shows that high dust loading can be managed to avoid catalyst plugging and fouling while maintaining high levels of control. Related to the plugging and fouling issues, it is argued that "sticky deposits" in preheater exhaust gas could foul and plug the SCR catalyst. Specifically, certain cement kiln operations could be prone to producing sticky deposits at exactly the temperature ranges in which SCR systems operate. Sticky deposits are a wide spread problem for cement kiln induced draft fans. In many plants is an extremely hard, layered, brick-like buildup that is associated with impingement of particulate at high velocity against the rotating

parts of the fan impeller.

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

For instance, gas velocities through an SCR system are typically less than 6.2 meters/sec (1,220 ft/min); whereas peripheral gas speed at the kiln ID rotor inlet is approximately 15,000 ft/min. Possible problems relating to thermal sintering and catalyst erosion have been addressed by advances in catalyst technology and proper system design. The problem of thermal sintering has been avoided by the incorporation of tungsten in the catalyst formulation and also by providing a bypass around the SCR system so that the catalyst is not exposed to high temperature excursions. Hardening the leading edge of the catalyst and also arranging the catalyst bed so that the airflow is parallel to the catalyst channels have addressed catalyst erosion.

Temperature related factors leading to lower SCR NO_x Removal Efficiencies (ref 84)

These factors are :

- 1) - an acceptable normal operating temperature
- 2) - even temperature distribution
- 3) - avoiding temperature extremes (which may lead to catalyst deactivation or sintering)

Low temperatures can lead to lower NO_x reduction efficiencies and/or higher catalyst activity (leading to possible SO₂ oxidation) and to possible ABS/AS formation in the catalyst pores.

To address the concerns on the slightly lower than desirable temperature, equipment can be installed to ensure a temperature of at least 315 C (600F) entering the SCR system. Such control systems are commonly used on boiler air supply systems and economizer bypass ducts. The SCR reactor should also have an automatically activated bypass duct around the SCR reactor, so for high temperature fluctuations (> approximately [430C] 800F) automatically controlled dampers would send the hot flue gas to a reactor bypass duct, thus preventing any damage to the SCR catalyst. Thus, temperature issues should be addressed with simple process reconfigurations.

To address normal operating temperatures and temperature fluctuations, FOH recommends that a bypass system be installed that would divert a quantity of gas from the gas duct between the 4th and 5th stage of preheater. (ref 89)