LAFARGE
NORTH AMERICA

Cement

June 2, 2006

Mr. J. Wick Havens, Chief
Division of Air Resource Management
Bureau of Air Quality
P.O. Box 8468
Harrisburg, PA 17105-8468

Re: Ozone Transport Commission's Regional
        Attainment Strategies Control Measures
        Comments Regarding Cement Manufacturing
        Sector – NO_X Control Reduction Strategy

Dear Mr. Havens:

Lafarge North America's Whitehall Cement Plant (Lafarge) appreciates the opportunity to provide written comments regarding the NOx control reduction strategy being proposed regarding the cement manufacturing sector.

Lafarge has several concerns with OTC's control measure summary for cement kilns which are stated briefly below and elaborated upon herein.

1. The recommended control measure of 2.0 lbs. NO_X/ton of clinker is not an achievable rate at each Pennsylvania cement manufacturing plant and may not even be achievable on average across the Pennsylvania cement industry.

2. The expectation that installing SNCR on all cement process types will be sufficient to reduce NOx emissions at each plant to the 2.0 lbs./ton limit is unrealistic.

3. SCR is not sufficiently developed to make it commercially available in the U.S. and; therefore, should not be considered a control technology.

4. OTC's cost estimates are flawed.

5. PaDEP should not support or impose costly and burdensome regulations on any industry sector without first demonstrating that such regulations will provide measurable, cost-effective progress toward attaining the 8 hour ozone NAAQS.

6. PaDEP should consider allowing the cement industry to opt into a system where emission reduction credits could be generated and traded.

1. <u>The recommended control measure of 2.0 lbs. NO$_X$/ton of clinker is not an achievable rate at each Pennsylvania cement manufacturing plant and may not even be achievable on average across the Pennsylvania cement industry.</u>

   It is well documented that NOx emissions from cement kilns can be highly variable from kiln-to-kiln and plant-to-plant. In fact cement kiln NOx emissions are driven by so many different operating parameters (e.g. fuel-type and firing configuration, raw material mix, and product type), that emissions for a given kiln at a single plant will experience significant variability within the normal range of operations.

   NOx formation in a cement kiln occurs by several mechanisms. Nitrogen in the fuel will oxidize to form NOx, as will nitrogen in the feed stock. These mechanisms are called Fuel NOx and Feed NOx, respectively. While these reactions do occur and contribute slightly to the over all NOx formation, the dominant NOx-forming mechanism is from heating the nitrogen rich ambient air that is pulled through the kiln. The NOx that is formed by this mechanism is called Thermal NOx.

   The raw materials in a cement pyroprocessing system undergo four steps to produce clinker, i.e., drying, preheating, calcining and incipient fusion ("burning"). All cement pyroprocessing systems utilize a rotary kiln in which the raw feed components are fused into a calcium-silicate mineral referred to as "clinker". This sintering process takes place in the high-temperature "burning zone" of a kiln system. The material temperature in the burning zone must be sufficient to complete the chemical reactions between calcium oxide and the siliceous, argillaceous and ferriferous components of the raw material mix. Although this temperature is similar in all plants, i.e., approximately 1,480^{o}C (2,700^{o}F), it is dependent on the chemistry of the raw material mix and other factors, and is not constant even in the same kiln system.

   The four pyroprocessing systems achieve the first three steps of the pyroprocess differently.

   - In a wet kiln system, the raw materials are introduced into the rotary kilns as aqueous slurry. The evaporation of the water in the slurry requires a significant amount of energy. In the early part of the last century, the wet

process replaced the original dry process during a time of low energy costs to provide a means for improved product quality through better blending of raw materials as slurry.

- When equipment was developed to adequately blend dry raw materials, an alternative to the high-energy wet process was once again available. In a long-dry kiln system, the raw materials are introduced into the rotary kiln as a dry powder. Absent the need to evaporate many tons of water each day, the dry process is more thermally efficient that the wet process.

- When it became necessary to remove particulate matter from the flue gas stream of a cement kiln, the preheater kiln system was developed to cool the flue gas so that a baghouse could be used for pollution control. In the preheater system, dry raw material mix is fed to a series of vessels arranged vertically in a tower in which the drying and preheating of the raw mix is accomplished in just a few seconds as opposed to the hour or more required in wet and long-dry kiln systems. Upon exiting the preheater tower, the raw materials are sufficiently heated so that calcination can commence immediately in the rotary kiln. The more-efficient preheater kiln system became available during a time of escalating energy prices and, for this reason, became popular for new installations and retrofits independent of the need for pollution control.

- The most energy intensive step in the manufacture of cement clinker is the calcination of the calcareous component of the raw mix. In the precalciner kiln system, a vessel is inserted between the preheater tower and the rotary kiln in which as much as 60% of the fuel is efficiently burned in direct contact with raw material from the preheater tower that is ready for calcination. After a very few seconds in the calciner vessel, the raw materials enter the rotary kiln almost completely calcined. Thermal energy efficiency is the greatest in the precalciner kiln system.

Consequently, the process temperature profiles are different in ways that can affect the generation and emission of NO$_x$. Therefore, to impose one emission standard on all four kiln types is not realistic, regardless of control technologies. The main reason for this is that not all kilns are the same. The raw materials and fuel inputs are site specific. Both of these components, along with the kiln type, have a direct impact on NO$_X$ emissions. Burnability of the raw materials that

makes up the kiln feed will differ from plant to plant and can even vary within a given plant; therefore, so will the NO$_X$ emissions.

Technologies are not often physically possible or fully effective if applied as a retrofit technology to an existing kiln, even if they are technically feasible. By contrast, control technologies can be optimized during the design and construction of a new kiln line. In these cases, engineering evaluations can determine the operation of given technology and design the new line to minimize aspects of operation and physical equipment configuration that could reduce the efficiency of the intended control. Retro-fitting controls to existing equipment does not provide this opportunity and, more often than not, adversely affects the ability of the control to perform. Furthermore, these effects are not always predictable, so the level of control demonstrated on one kiln system cannot automatically be assumed applicable to other existing kilns, particularly if they are of different process-types. Therefore, assuming that all kilns in Pennsylvania will be able to perform at NOx emission rates established at kilns in other states and/or countries is an unreasonable expectation, particularly since almost all of these are newly constructed kilns.

2. <u>The expectation that installing SNCR on all cement process types will be sufficient to reduce NOx emissions at each plant to the 2.0 lbs. /ton limit is unrealistic.</u>

With an SNCR control NOx is reacted with ammonia or urea in an environment with a specific temperature range and for a sufficient residence time. The effective temperature range for a SNCR system is approximately 1600°-2000°F. For a preheater/precalciner system, this would occur in a zone near the lowest stage of the preheater tower. Below the effective temperature, ammonia present in the gas stream does not react and "ammonia slip" occurs. Likewise, if excessive quantities of ammonia/urea are injected, some pass through un-reacted and cause ammonia slip. Either case will result in a release of ammonia from the stack and could result in producing a detached plume, causing an opacity compliance issue

If injection occurs at temperatures above the effective range, ammonia present in the gas stream will react to form additional NOx and NO$_X$ emissions may increase.

SNCR has been shown to be a viable NO$_X$ control technology on cement kilns that utilize the preheater (PH) or preheater/precalciner (PH/PC) process. However, SNCR is very dependent on temperature and residence time and, even with optimization, will only provide a certain degree of reduction prior to experiencing an ammonia slip. As explained above, NOx emissions can be highly variable between cement kilns with relatively high baseline NOx emissions may be able to demonstrate relatively high reduction percentages. Kilns with relatively low baseline emissions, however, will be challenged by the "diminishing returns" effect. Simply put, the greater concentration of NOx in a given volume, the more opportunity there will be for ammonia to react. As the concentration decreases, reaction opportunities are reduced and interferences prohibiting reactions are increased. Therefore, the implementation of SNCR on existing PH and PH/PC kilns will be very site specific. As such, the assumption that all PH and PH/PC kilns can achieve a 2.0 lb/ton emission rate is unrealistic.

For the rest of the kiln process types, SNCR is not a proven technology in the U.S. This would be an innovative control technology for these types of kilns and; therefore, reduction rates cannot be reliablely predicted at this time.

3. <u>SCR is not sufficiently developed to make it commercially available in the U.S. and; therefore, should not be considered a control technology.</u>

SCR for NO$_X$ control is not a proven technology in the cement industry. Theoretically, SCR will reduce NO$_X$ emissions by reacting NO$_X$ with ammonia (NH3) to form nitrogen and water. The exhaust gas stream is passed through a catalyst bed, typically a vanadium pentoxide catalyst where the reaction occurs. There are several considerations that must be taken into account when designing an SCR control system and estimating the capital and operating costs. Items to be considered include the following:

- Gas volumetric flow
- Amount of NO$_X$ in the exhaust gas
- Required NO$_X$ control
- Exhaust gas temperature
- Quantity of and composition of particulate in the exhaust gas (there may by catalyst poisons in the flue gas)
- Amount of SO$_2$ and SO$_3$ in the exhaust gas
- Allowable SO$_2$ and SO$_3$ oxidation rate

- Required catalyst life
- Allowable NH$_3$ slip
- Space available for equipment and tie-ins

The operating temperature within the SCR must be controlled to optimize efficiency, to control the SO$_2$ to SO$_3$ oxidation and to protect the catalyst. Operating temperatures in the SCR will range from approximately 600°-800°F. Lower temperatures may result in increased formation of ammonium bisulfate (NH$_4$HSO$_4$) as SO$_3$ reacts with NH$_3$ and water. Higher temperatures may sinter the catalyst (the catalytic components react with the ceramic substrate) thereby reducing the catalyst activation.

The current state of SCR is best summed up in the attached document that was sponsored by the Portland Cement Association. This document addresses the concerns of SCR on cement kilns.

4. <u>OTC's cost estimates are flawed.</u>

OTC suggests that installing SNCR, along with annualized costs would be less than $2,500 per ton. Lafarge believes that this cost estimation is based upon the following flawed assumptions. First, OTC suggests that all kiln types can achieve a 60% NO$_X$ reduction. As stated in item #2 above, SNCR reductions will vary greatly from plant to plant and process type. Second, nowhere in the control measure summary does OTC mention installation of SNCR costs. Rather, it references two EPA scenarios using SNCR. One is biosolid, dewatered sewage sludge and the other using the NOXOUT technology. The NOXOUT example uses urea as the agent as opposed to ammonia. Urea may not be readily available as is ammonia and the costs and reduction efficiencies will vary. Too many assumptions are taken into account for this cost analysis to be reliable.

For long wet process kilns, in order to meet the temperature requirements for the SNCR system, there are limited options:

- End of pipe technology, similar to SCR. This would be cost prohibitive due to the high fuel cost to heat the gas stream to the appropriate range.
- Injecting packets of urea into the burning zone of the kiln
- Mid kiln injection

Injecting urea into the burning zone or at mid kiln would be considered innovative technology and would require pilot testing to prove out. It would be necessary to determine the feed rate for the urea or ammonia. Injecting packets of urea will result in inconsistent conditions within the kiln, thereby reducing the overall effectiveness of the system. It will be important to quantify the actual NO$_X$ reductions achieved.

5. <u>PA DEP should not support or impose costly and burdensome regulations on any industry sector without first demonstrating that such regulations will provide measurable, cost-effective progress toward attaining the 8 hour ozone NAAQS.</u>

The economic well-being of the Commonwealth will not be advanced if the Department chooses to move forward with costly control measures that do not result in a significant contribution to attainment of the ozone standard. Unless there are assurances that significant progress will be made and that progress justifies the cost burden that will be placed on industry, the Department should not support the proposed control measures.

6. <u>PADEP should consider allowing the cement industry to opt into a system where emission reduction credits could be generated and traded.</u>

Further, Lafarge suggests that a facility be allowed to generate emission reductions by financing emission reductions at any other facility in Pennsylvania at which cost-effective reductions can be achieved. Reductions generated in this way could be used by the financing facility to meet its emission targets or could be sold to other facilities needing emission credits. Under these circumstances, all emission reductions would be the property of the entity providing the financing rather than the facility at which emission reductions were accomplished. Secondary, cement plant should be allowed to enter into a bona fide trading market with other industrial sectors.

We appreciate the opportunity to comment on this significant issue. Lafarge wants to be part of the solution not part of the problem, and we look forward to working with the PaDEP to develop an equitable and workable program, which will contribute to meeting PADEP's objectives.

Sincerely,

Vince Martin
Environmental & Public Relations Manager

EVALUATION OF SUITABILITY OF SELECTIVE CATALYTIC REDUCTION AND SELECTIVE NON-CATALYTIC REDUCTION FOR USE IN PORTLAND CEMENT INDUSTRY

Robert J. Schreiber, Jr. P.E., QEP
Christa O. Russell, Jeff Evers

ABSTRACT: The portland cement industry is seeking ways to reduce emissions of nitrous oxides (NOx). Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR) are established means of reducing NOx emissions in the power plant industry. Increased attention has been paid in the past several years as to whether these technologies can be transferred to cement kilns. A number of issues can affect the technical feasibility of transferring SCR technology from the power plant industry to portland cement kiln systems. This paper presents and discusses the technical feasibility issues related to implementing SCR technology at a portland cement plant utilizing either preheater/precalciner or long wet or long dry kiln systems. The results of this assessment demonstrate that the technology is not easily transferred from the power plant industry to the portland cement industry and that substantial research and pilot testing would be required before the technology could be considered commercially available for use on cement kiln systems. By contrast, SNCR is currently commercially available for the portland cement industry and is being offered with performance guarantees, has a successful track record in Europe, and is equivalent to what SCR is predicted to achieve. For these reasons, the most dependable and effective NOx control technology currently available for modern preheater/precalciner (PH/PC) kiln systems is considered to be SNCR. SNCR is not currently commercially available for long wet or long dry kiln systems due to the inability to inject the reagent into the proper temperature zone, which is located mid-kiln.

SELECTIVE CATALYTIC REDUCTION DESIGN

Selective Catalytic Reduction (SCR) is an add-on control technology that involves reagent injection into the gas stream in the presence of a catalyst. Common reagents include aqueous ammonia (NH_3), anhydrous NH_3, and urea. In the presence of the catalyst, the injected ammonia is converted by OH* radicals to ammonia radicals (i.e., NH_2*), which react with NOx to form N_2 and H_2O. The SCR catalyst enables the necessary reactions to occur at lower temperatures than those required for Selective Non-Catalytic Reduction (SNCR). While catalysts can be effective over a range of temperatures, the optimal temperature range for SCR is 570 - 750ºF.

The SCR system, consisting of a vessel with a set of catalyst beds placed in series, is located in a part of the process where the gas temperatures are in the appropriate range during routine operation. Figure 1 is a potential configuration of an SCR system on a PH/PC kiln system. The reagent is injected at a controlled rate upstream of the catalyst using an injection grid designed to ensure relatively even distribution, good mixing, and minimum NH_3 slip.[1] The reagent reacts with NOx compounds (i.e., NO and NO_2) on the surface of the catalyst in equal molar amounts (i.e., one molecule of NH_3 reacts with one molecule of NOx) to form N_2 and water.

Note that in PH/PC kiln systems that utilize an alkali bypass, either a second SCR system will need to be installed on the bypass, or the bypass gas will need to be combined with the preheater

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[1] Slip refers to the quantity of unreacted reagent that exits the SCR reactor.
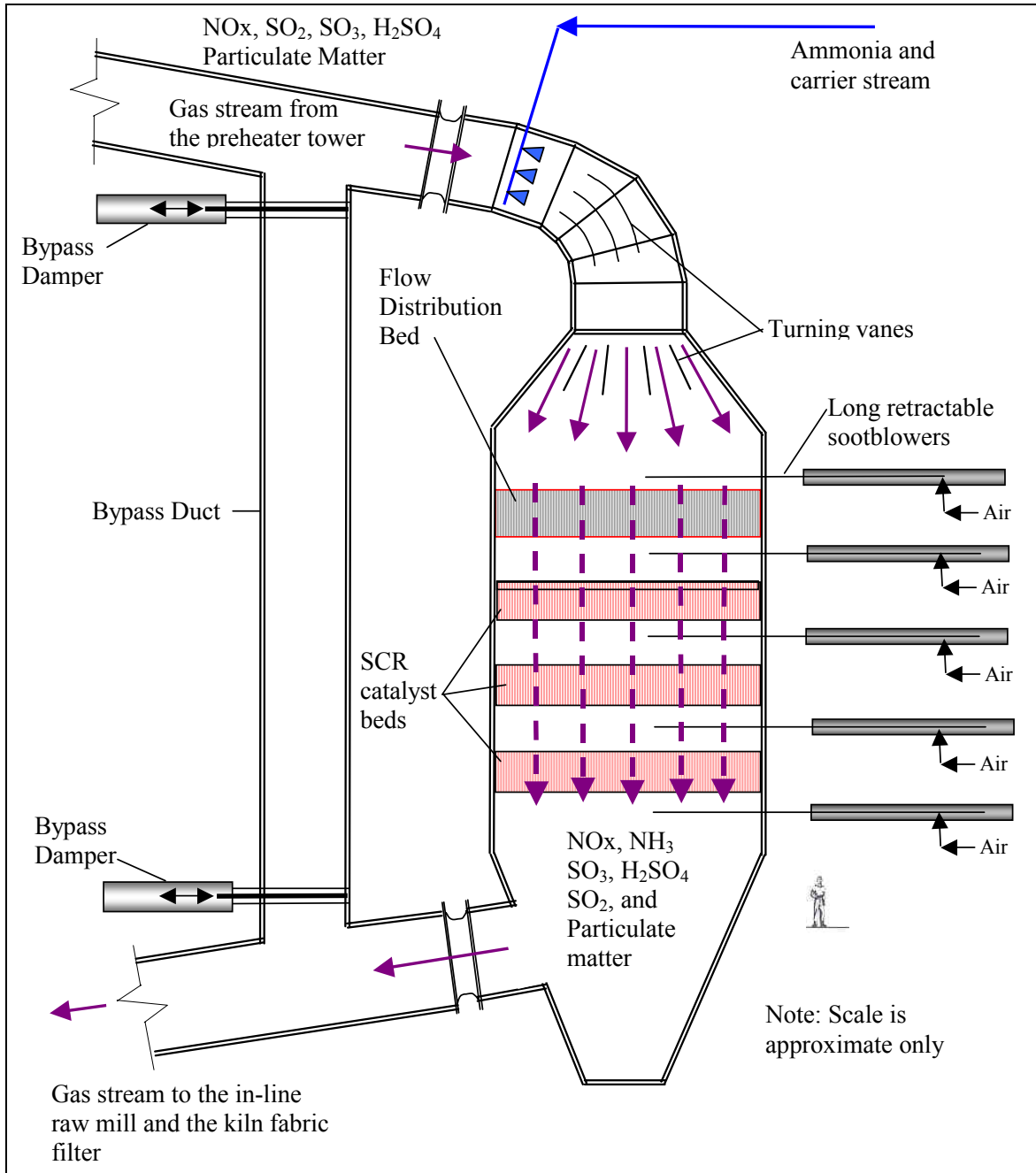
gases prior to the SCR system. In some instances, pilot testing of SCR systems on high dust PH/PC kiln systems may determine that the use of SCR at the high dust location is not feasible. In this case, the SCR would need to be located downstream of the air pollution control device (APCD). The gas stream must be reheated to the effective temperature range of the SCR.

Due to the dust loading associated with the long wet or long dry process and the existing configuration of the kilns, the SCR must be located downstream of the APCD – baghouse or electrostatic precipitator (ESP). Figure 2 shows a simplified flow diagram of an SCR system on a long wet or long dry kiln system. The gas stream must be reheated to the effective temperature range of the SCR. In addition, a sulfur-removal device, typically a wet scrubber (WLS), is placed between the SCR and the exhaust stack to control sulfur and acid mist emissions.

The catalysts used in SCR systems are usually manufactured in two forms: (1) extruded honeycombs of ceramic material with catalysts blended uniformly throughout the ceramic material; and (2) plates with coatings of homogeneously mixed or surface-deposited catalyst materials. As the gas stream passes by the catalyst, NH_3 gas is adsorbed onto active sites and reacts with NOx compounds to form N_2 and water vapor. Oxygen removes the remaining hydrogen atom to regenerate the SCR catalyst active site.

The SCR catalytic reactions occur on the surface of the catalyst structures. However, the catalyst structures are not composed of simple, flat surfaces. The catalyst is designed to have a series of large openings, termed macropores, and small openings, termed micropores. These macropores and micropores maximize the surface area of the catalyst available for reaction with NOx and NH_3.

Figure 1 - SCR System

NOx, SO_2, SO_3, H_2SO_4
Particulate Matter

Ammonia and carrier stream

Gas stream from the preheater tower

Bypass Damper

Flow Distribution Bed

Turning vanes

Long retractable sootblowers

Bypass Duct

Air

Air

SCR catalyst beds

Air

Air

Bypass Damper

NOx, NH_3
SO_3, H_2SO_4
SO_2, and
Particulate matter

Air

Note: Scale is approximate only

Gas stream to the in-line raw mill and the kiln fabric filter

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Simplified Process Flow Diagram of an SCR System for a Long Wet Process Cement Kiln

Fuel Input

NH$_3$

Gas Reheat
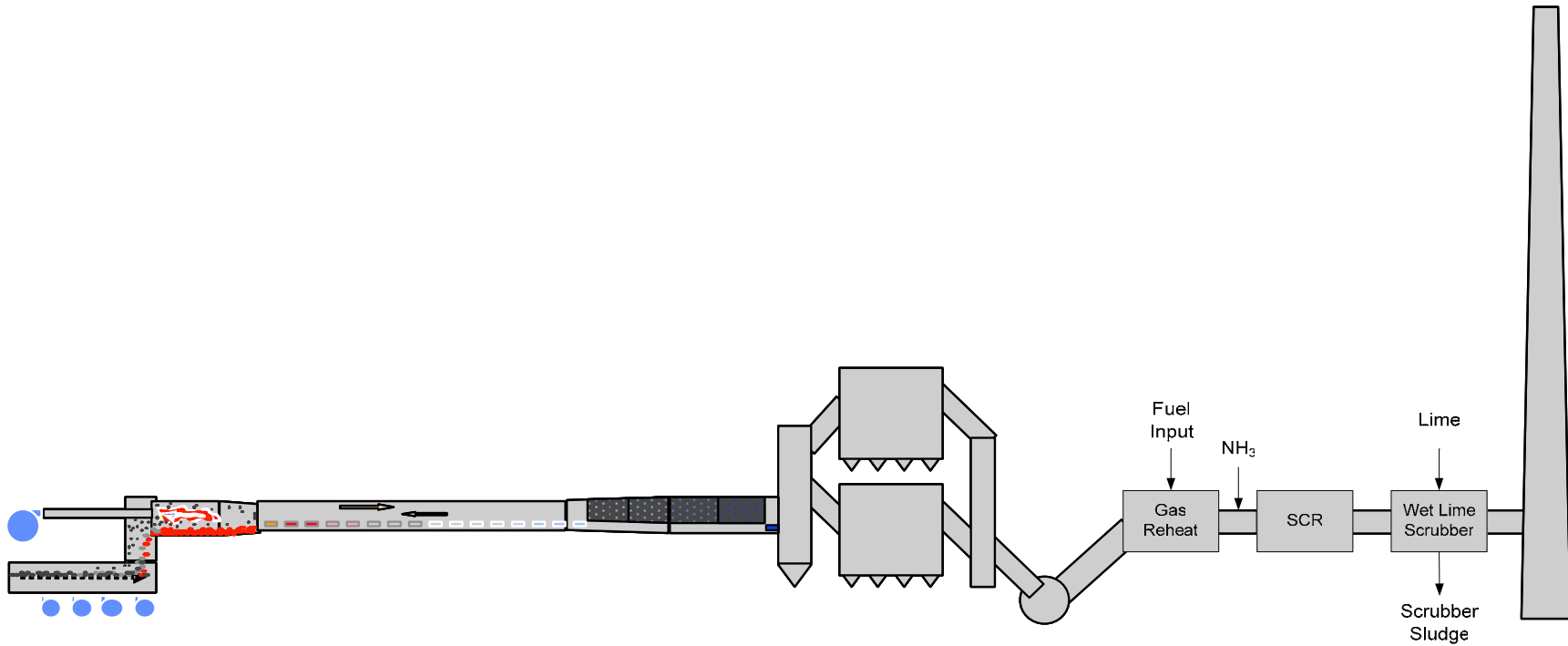
SCR

Lime

Wet Lime Scrubber

Scrubber Sludge

Figure 2

CATALYST FORMULATION AND OPERATIONAL CONCERNS

In an SCR system, the catalyst formulation, NOx reduction efficiency, and catalyst's tendency to promote SO_2 oxidation are interrelated factors that cannot be considered independently. When considering the feasibility of applying SCR to a cement kiln system, these interrelationships present unique challenges. Each of these factors are presented and discussed in the following paragraphs.

Catalyst Formulation

The catalyst used in SCR applications usually consists of: (1) a monolithic honeycomb composed of a ceramic substrate with impregnated catalyst homogenously mixed into the catalyst material; or (2) catalyst materials deposited on the surfaces of a ceramic substrate supported on a flat or corrugated plate. This metal oxide acts as a porous base with a high surface area-to-volume ratio created by the presence of microscopic pores within the metal oxide base. On this metal oxide base, typically titanium dioxide (TiO_2), one or more metal oxide catalysts are deposited in various concentrations. In SCR applications, the active catalyst material typically consists of vanadium pentoxide (V_2O_5), tungsten trioxide (WO_3), and molybdenum trioxide (MoO_3) in various combinations. The composition, also known as formulation, is tailored by the catalyst vendor to best suit a particular SCR application. Some catalyst formulations are more reactive (typically those with higher V_2O_5 contents), some limit SO_2 oxidation (typically those with higher WO_3 content and lower V_2O_5 contents), and some (such as those with higher MoO_3 contents) are less vulnerable to the poisoning effects of specific species in the exhaust gas stream.[2]

The catalyst formulation is tailored to each application based on a particular catalyst supplier's database of experience.[3] For applications that have design and operating parameters (e.g., dust loadings, poison concentrations) outside the realm of a catalyst supplier's experience, experimental laboratory and pilot-scale testing may be needed to identify the most suitable catalyst formulation for that particular application.[4] Historically, the development of a new SCR system application leading to commercial availability is a lengthy process involving laboratory and pilot scale testing, data analysis, and possibly additional testing for each new type of application or significant variant. This situation exactly describes the current development status of SCR for cement kilns. There are many unknowns that must be resolved before the technology can be considered to be commercially available. It has been estimated that an extended pilot study of 15-18 months would be required prior to design and installation of an SCR system in a cement kiln application. A catalyst supplier contacted in February 2006 would not provide a quote for SCR catalyst for a PH/PC kiln prior to conducting testing on the process slipstream to determine its impact upon the catalyst.

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[2] EPRI. 2002. State of Knowledge Concerning Fuel Impacts on SCR Performance and Longevity. Palo Alto, CA. pp. A-1–A-5.
[3] Prichard, S.G., et al. Undated. SCR Catalyst Performance Under Severe Operation Conditions. CORMETECH, Inc. p. 5.
[4] Pritchard, S.G., et al. 1995. Optimizing SCR Catalyst Design and Performance for Coal-Fired Boilers. CORMETECH, Inc., Durham, N.C. May 1995. p. 17.

In addition to catalyst composition, the physical configuration of the catalyst must also be tailored to the specific application. For *high-dust*[5] applications, a parallel-flow type catalyst (i.e., gas flow through the catalyst is parallel to the catalyst surface) is used, and typically, the gas flow is vertical rather than horizontal. The most common types of parallel-flow catalysts are honeycomb and plate types. These designs have continued to evolve as vendors have gained experience in various applications.[6] The only identified existing SCR application, at the plant in Solnhofen, Germany, has reportedly tested up to twenty different catalysts. After approximately three years of operation using the selected honeycomb catalyst, Solnhofen has replaced the first stage with a plate catalyst.

Because the catalyst necessarily comes into direct contact with the exhaust gases, it is subject to significant stresses. These stresses are greater in a context such as a portland cement in-line kiln/raw mill system where the variation in fuels, feedstocks, and operating levels is substantially greater than what is experienced at the typical coal-fired power plant. These stresses can result in catalyst deactivation, a phenomenon described in detail in the following section.

Catalyst Deactivation

As long as an SCR catalyst remains in good physical and chemical condition, NOx and NH_3 efficiently react to form water vapor and molecular N_2. When an SCR catalyst is damaged, chemically or physically, its "activity" for converting NOx and NH_3 to N_2 is reduced. This reduction in activity is termed "deactivation." The extent of deactivation can range from relatively minor to severe reductions in NOx control efficiency. When the SCR catalyst is severely deactivated, a major portion of the NOx and NH_3 passes through the SCR catalyst without reacting. Catalyst deactivation is therefore one of the most serious issues that must be addressed when applying SCR to any new source category.

In general, the five SCR catalyst deactivation mechanisms are poisoning, fouling, masking, sintering, and erosion. The impact of these deactivation mechanisms to an SCR application is dependent on the characteristics of the process being controlled, the fuels involved, and the concentration and composition of gas, vapor, and particulates passing through the SCR reactor. Each of these possible deactivation mechanisms is discussed in more detail in the following paragraphs.

Poisoning

Catalyst poisoning describes deactivation as a result of chemical reactions between the catalyst active sites and contaminants in the gas being treated. Two of the principal poisoning mechanisms experienced thus far in SCR applications involve alkaline metals (i.e., sodium and

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[5] The term *high dust* refers to installation of the SCR system prior to an air pollution control device, such as a fabric filter. This configuration is the typical design due to the need for the exhaust gases to interact with the catalyst within a narrow temperature range that cannot be reliably maintained downstream of other control devices without significant in line reheating of the exhaust stream.
[6] Pritchard, S. G., et al. 1995. Optimizing SCR Catalyst Design and Performance for Coal-Fired Boilers. CORMETECH, Inc., Durham, N.C. May, 1995. p. 16.

potassium) and arsenic trioxide (As_2O_3). In addition, compounds such as phosphorous, lead, chromium, and zinc are known or suspected catalyst poisons.

Alkaline metals react directly with the catalyst active sites to render them inert. As the active sites are blocked, NH_3 adsorption rates are reduced, thereby reducing the overall effectiveness of the SCR catalyst. The reaction of alkali metals is partially reversible only by off-site chemical treatment. Its effect can be mitigated to some extent by the catalyst formulation and catalyst type. Vanadium-tungsten catalysts are more resistant to alkaline metal poisoning than vanadium-only catalysts, and honeycomb catalysts are more resistant than coated-type catalysts. The form of the alkali metals is also important; water-soluble forms are more detrimental to catalyst activity.[7]

Arsenic poisoning should not be an issue for SCR application in cement plants due to the calcium oxide (CaO) available to react with the arsenic, limiting its availability for reaction with the catalyst.

Variations in the raw materials utilized by each cement kiln system will generate variations in the chemical and physical characteristics of the cement dust particles by each kiln type at each location and for the same kiln type at different locations. Different kiln types partition different elements at different locations within the kiln system. This impacts critical components such as alkalis (sodium and potassium) and calcium oxides (CaO), which can poison or plug catalyst pores and result in fewer active catalyst sites for NOx reduction.

Fouling

Catalyst fouling, also referred to as plugging, occurs when dust particles deposit on the catalyst surface or lodge in the pores, thereby blocking pores and active sites. In some cases, fouling may involve a subsequent agglomeration or chemical reaction to form a surface deposit that is difficult to remove.[8]

To some extent, the undesirable effects of high dust loading can be alleviated by: (1) appropriate selection of catalyst configuration and pitch;[9] and (2) ensuring even distribution of gas flow at the catalyst bed inlet. Despite a good understanding of the issues involved in plugging and fouling, this problem is still a concern for utility SCR applications, and would also be an even greater issue in cement plant SCR applications.

An evaluation of the physical characteristics of cement dust particles to that of typical fly ash from coal-fired boilers shows that, while fly ash is typically spherical in nature and of relatively consistent size, cement dust particles are larger, very jagged, and irregular in shape and size. The plugging potential for the type of particle from a cement kiln would be higher. It is also likely

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[7] Pritchard, S. G., et al. 1995. Optimizing SCR Catalyst Design and Performance for Coal-Fired Boilers. EPA/EPRI 1995 Joint Symposium on Stationary Combustion NOx Control. CORMETECH, Inc., Durham, N.C. May, 1995. pp. 9–10.

[8] Rigby, K., et al. 2000. SCR Catalyst Design Issues and Operating Experience: Coals with High Arsenic Concentrations and Coals from the Powder River Basin. Proceedings of 2000 International Joint Power Generation Conference. July 2000. p. 6.

[9] Catalyst *pitch* is a measure of the open spacing (i.e., center to center distance) between catalyst channels.

that a larger, jagged particle will erode the catalyst bed more rapidly. This critical difference has been completely ignored in several documents proposing SCR as a viable and applicable technology.

The dust loading from cement kilns, regardless of kiln type, also is higher than power plant high dust, high ash content coal systems. This increase in dust loading appears to be an order of magnitude or more (see memo in Attachment 1 which compares a cement plant dust loading to that of a coal-fired boiler burning Powder River Basin coal). In addition, during kiln upset conditions, periods of unusually high dust loading can occur. These upset conditions may result in dust buildup on the catalyst beds, plugging and blanking off portions of the catalysts, thus substantially reducing the amount of catalyst available for NOx reactions, or completely blocking gas flow and negating the operation of the SCR system and/or the kiln. The Solnhofen plant SCR system has experienced routine catalyst plugging problems.

In some situations, the dust loading from PH/PC kiln systems may make a high dust SCR system infeasible. In these situations, location of the SCR system downstream of the APCD and gas reheat would need to be evaluated.

Masking

Catalyst masking refers to deactivation resulting from the formation of calcium sulfate ($CaSO_4$) within the catalyst pore structure. The first step of this phenomenon occurs when a CaO particle becomes lodged in a catalyst pore. At this point, the catalyst is still active, and NH_3 and NOx can still enter the catalyst pore and react on the surface of the catalyst. Over time, the CaO lodged in the pore reacts with SO_3 and/or H_2SO_4 vapor[10] to form $CaSO_4$. The $CaSO_4$ formed from this reaction has a larger volume than the original CaO particle, and as the CaO particle is converted to the sulfate, the pore becomes blocked and less active. The rate at which this mode of deactivation occurs is dependent on both the CaO and SO_3/H_2SO_4 concentration in the gas being treated. This mode of deactivation would be expected to be more severe in applications where the catalyst is exposed to higher levels of CaO, such as in the cement industry.

Another mechanism for catalyst deactivation that can occur within the catalyst pores is masking due to condensation of ammonium sulfate and/or ammonium bisulfate in the catalyst pores. Such condensation can occur in the pores at lower operating temperatures because the reactants (NH_3 and SO_3/H_2SO_4) can concentrate in the catalyst pores, resulting in relatively high concentrations of these species. At low SCR operating temperatures, below about 300°C (570°F), formation of ammonium sulfate and/or ammonium bisulfate can lead to subsequent reactions with either the dust or the catalyst to form compounds that mask the catalyst pores. When the gas stream temperature falls below this minimum temperature, the SCR system must be bypassed. During times of bypass, there is no NOx emission control.

Sintering

Thermal sintering occurs when particles in an SCR catalyst matrix grow by joining with other catalyst particles in the matrix due to elevated reactor temperatures (i.e., above 450°C or 840°F).

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[10] Below approximately 340°C (640ºF), SO_3 rapidly reacts with water vapor to form sulfuric acid vapor.

The result of thermal sintering is a catalyst containing less access to micropores. Sintering permanently reduces a catalyst's effective surface area and its activity. The tendency for thermal sintering can be reduced by incorporation of tungsten in the catalyst formulation and by designing the SCR system to avoid high temperature excursions (i.e., incorporation of a bypass system).[11] SCR and catalyst vendors require a 100% bypass in order to provide a warranty for the system and catalyst to prevent plugging and/or sintering of the catalyst. The quotation from KWH that was included in the Friends of Hudson (FOH) comments included the requirement for a bypass to be installed. During the bypass mode, NOx emissions are uncontrolled.

Erosion

Catalyst erosion, caused by impingement of dust on the catalyst, refers to the physical deterioration of the catalyst media. The rate of erosion is a function of gas velocity, dust morphology (i.e., size, shape, hardness), angle of impingement, and catalyst properties. As the catalyst erodes, the active surface area is reduced. Erosion is typically limited to the leading edge of the catalyst, and some high-dust electric utility installations have incorporated an *inactive* or *blank* first bed to take the brunt of the erosion in the SCR system. Other countermeasures to reduce the erosion effects include flow straightening, even gas flow distribution, and hardening of the catalyst's leading edge. This mode of deactivation would also be expected to be more severe in applications where the catalyst is exposed to higher concentrations of particulate, such as experienced in the cement industry.

The high dust loading and high temperature result in high maintenance for the SCR bypass dampers at coal-fired boilers. See Steag documents contained in attachment 2. The higher dust loading at the PH/PC kilns will also likely exacerbate this problem.

DESIGN CONCERNS RELATED TO THE USE OF SCR

SO_2 Oxidation

One of the earliest issues faced by electric utilities that installed SCR systems on units firing sulfur-bearing fuels involved dealing with secondary impacts from the SCR system. Similarly, when considering applying SCR technology to the cement industry, these issues remain a concern. The most significant of these additional impacts include: (1) the formation of SO_3 in the reactor; and (2) potential impacts associated with SO_3 and the emission of unreacted NH_3 from the reactor and its potential reaction products. These effects are often interrelated because SO_3 and unreacted NH_3 can react within and downstream of the SCR reactor.

The same catalyst that promotes the reactions between NH_3 and NOx also promotes the oxidation of SO_2 to SO_3. For example, at an SCR operating temperature of 700ºF, the equilibrium relationship between SO_2 and SO_3 is such that nearly all of the SO_2 would convert to SO_3 given sufficient residence time. In practice, with modern catalyst formulations and at typical high-dust SCR space velocities, on the order of 1 or 2 percent conversion of SO_2 to SO_3

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[11] *Ibid*, p. 9.

might be expected. It is important to understand that SO_2 oxidation is dependent on other SCR design parameters. When high levels of catalyst activity are needed to target high NOx reduction efficiencies and low levels of NH_3 slip or to counteract significant catalyst deactivation rates, SO_2 oxidation rates would be expected to increase. If lower levels of SO_2 oxidation are targeted, NOx reduction, NH_3 slip, or both must be compromised. [12]

There are several reasons why industries are concerned about the level of SO_2 oxidation in an SCR reactor. In the absence of other interactions, downstream equipment that operates below the sulfuric acid dew point can experience severe corrosion. In addition, sulfuric acid mist formed in such equipment can promote the formation of a visible plume. And in extreme cases, sulfuric acid mist emissions can have severe environmental consequences.

In addition to its potential for downstream corrosion and plume impacts, SO_3 produced in the SCR system can react with NH_3 to form ammonium sulfate and ammonium bisulfate. Like sulfuric acid mist, these materials can form a fine aerosol and sticky deposits that are corrosive. Impacts on downstream equipment can include corrosion, plugging, visible plume formation, and blinding of fabric filter media.

The temperature at which ammonium sulfate and ammonium bisulfate form is dependent mostly on the localized concentrations of NH_3 and SO_3. Because both NH_3 and SO_3 are concentrated on the SCR catalyst surface, localized conditions can exist that would allow formation of sulfate compounds on the catalyst at temperatures higher than would be expected based on the bulk gas concentrations of these species. As discussed earlier, sulfate condensation on the catalyst is another potential catalyst deactivation mechanism. Thus, the SCR reactor system must be designed to ensure that the catalyst surface is maintained above the sulfate formation temperatures at all times. Some measures to avoid this problem include off-line reactor heating, bypassing the reactor when gas temperatures drop below a specific level, and withholding NH_3 injection unless the catalyst is above critical temperature levels.

For the long wet or long dry kilns, the exit gas stream will require heating from approximately 400°F to the effective range of the SCR. In order to minimize additional fuel usage, the target range for the gas reheat will be in the lower end of the SCR effective range. The effective temperature range for the SCR is 570 to 750°F. For an SCR system to be cost-effective for a long wet or long dry process kiln, it will be necessary to install a gas reheat system to heat the gas stream to the effective temperature of the SCR. Under these conditions, any SO_2 that has oxidized to SO_3 will form sulfuric acid mist. Sulfuric acid can lead to reduced efficiency, equipment corrosion, and visible emissions. Site-specific conditions, especially high sulfur raw materials, can result in high SO_2 and in some cases high SO_3 emissions. For plants with these conditions, a WLS is essential to control corrosion and to minimize the possibility of a visible plume due to formation of sulfuric acid mist. Although the WLS is essential for long-term operations of the SCR, it will result in generating calcium sulfate sludge that can either be reused onsite or will need to be disposed of in a landfill.

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[12] Cichanowicz, J. E. 1999. What You Should Know Before Specifying SCR. Power Magazine. May/June 1999. pp. 80-81.

Temperature Range, Distribution, and Fluctuation

The temperature characteristics of the gas stream to be controlled are important considerations in applying SCR technology to any source. An even temperature distribution can be important in ensuring good SCR performance. This temperature effect occurs largely because the rate of the NH_3-NOx reaction is temperature dependent. As the temperature falls, the reaction rate decreases and the NOx reduction efficiency declines. At low temperatures (below about 300ºC or 570ºF), ammonium sulfate and ammonium bisulfate can form on the catalyst surface, resulting in deactivation of part of the catalyst.[13] At high temperatures (above about 450ºC/840ºF) the catalyst can be sintered, which permanently deactivates the catalyst.[14] The SCR catalyst can be formulated to allow for operation at lower temperatures by increasing its activity, but this approach can cause problems at higher temperatures such as high rates of SO_2 oxidation and even the creation of NOx through oxidation of the injected NH_3. Temperature ranges of up to ±30ºC (50ºF) are usually considered acceptable.

In the case of a preheater-precalciner cement kiln, the exit of the preheater tower is the process location that might be most compatible with an SCR installation. Installing the SCR system at this location can present difficulties related to temperature fluctuation.

In the case of a long wet or long dry cement kiln, the gas stream exiting the APCD must be reheated to be compatible with the SCR installation. Installing the SCR system after the APCD and air heater and before the WLS provides a more uniform gas stream in the proper temperature range and would be expected to improve the operating consistency of the SCR.

An SCR design for a cement plant must be able to accommodate the potential for the adverse impacts that can occur if temperatures fluctuate outside the desired operating range. Therefore, the system must be designed and operated with a bypass for both high and low temperature excursions.

NOx Variability and NH_3 Slip

Unlike common SCR applications, such as boilers, cement kilns typically experience significant short-term variability in the NOx concentrations of the exhaust gas stream. Thermal NOx formation in a cement kiln is the prevailing mechanism responsible for NOx emissions. The rate of NOx generation due to the thermal formation mechanisms is adequately represented by the Zeldovich mechanism, which indicates that the emissions are exponentially related to the peak gas temperature. Slight changes in the peak temperatures in the kiln burner flame can have a large impact on the short-term NOx concentrations.

The extreme sensitivity of the NOx formation–peak temperature exponential relationship is one of the main reasons that the routine variability of NOx concentrations in cement kilns is considerably larger than in coal-fired boilers.

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[13] Pritchard, S.G., et al. 1995. Optimizing SCR Catalyst Design and Performance for Coal-Fired Boilers. CORMETECH, Inc., Durham, N.C. May, 1995. p.15.
[14] *Ibid*, p. 9.

There are also considerable kiln-to-kiln differences in the extent of the NOx variability and the average NOx concentrations. This is due, in part, to the differences in oxygen levels existing within the kiln and the impact of these variations on the usually highly efficient SO_2 uptake by materials within the kiln.

An SCR system applied to a cement kiln will therefore be faced with highly variable inlet NOx loadings, and would have to be controlled to ensure that the NH_3:NOx molar ratio never exceeds a value of 1.0 and preferably remains below 0.9 during these short-term NOx concentration variations. Overfeeding reagent could lead to significant NH_3 slip and the deposition of ammonium compounds in downstream equipment. The need for conservative NH_3:NOx molar ratios would reduce the overall NOx control efficiency of an SCR system in a cement kiln application.

The problem of setting reagent feed rates to an SCR system installed on some cement kilns may also be complicated by the presence of NH_3 formed by thermal decomposition of organic nitrogen compounds present in the limestone feed to the preheater tower or kiln.

The design and operation of the NH_3 injection grid is a critical component of the SCR system. The mass of NH_3 injected into the gas stream must be controlled in proportion to the mass of NOx in that stream. Thus, if one area of an SCR reactor inlet duct has a higher than average inlet NOx mass flow rate, the amount of NH_3 injected into this zone must be biased so that it is also higher than average by a proportional amount.[15] One way that SCR system suppliers have addressed this issue is by designing injection grids that allow zone-by-zone control of the mass of NH_3 injected within the ductwork upstream of the SCR reactor. Typically, these controls are set up based on an initial profiling of the reactor inlet NOx mass rates.

An additional function that may be required of the injection grids is ensuring good mixing of the injected NH_3 with the flue gas in each zone. Various system suppliers have developed designs that address this need. Alternatively, static mixing devices can be used to accomplish NH_3 mixing and distribution functions.

Start-up, Shutdown, and Malfunction Events

Installation of an SCR system on a cement kiln would expose the catalyst to transient conditions outside the realm of current vendor experience. Several possible adverse consequences are associated with such transients, including reduced average NOx control efficiency, including periods of zero control during bypass, increased risk of adverse downstream impacts, and increased risk of catalyst deactivation.

Problems with SCR catalyst deactivation can be exacerbated by process transient conditions associated with startup, shutdown, and malfunction (SSM) events.[16] The nature of these events must be clearly understood in advance of installing an SCR system. In this way, design features

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[15] Such an uneven distribution could be due to a higher than average NOx concentration, a higher than average flow rate, or some combination of these two factors.

[16] Pritchard, S. G., et al. 1995. Optimizing SCR Catalyst Design and Performance for Coal-Fired Boilers. CORMETECH, Inc. Durham, N.C. p. 15.

and operating practices can be developed to minimize transient-related problems. For example, SCR reactors are usually equipped with bypass ducts to allow the reactor to be bypassed whenever inlet gas conditions are outside the range of desired parameters. For electric utility SCR installations, SSM transients are reasonably well understood, and current designs handle these issues in an acceptable manner. Since many power plants operate their SCR systems during ozone season only, and the SCR systems are generally installed on baseload units; startups and shutdowns of the boilers during SCR operations would be expected to be minimal. However, installing SCR on a new cement plant will create an entirely new set of transient issues for SCR operation that must be evaluated, designed for, and tested.

Cement plants are vulnerable to a variety of process upsets that are not of concern in coal-fired boiler applications. These malfunctions include, but are not necessarily limited to, preheater tower blockage and raw material feed interruption, which could result in severe gas temperature variations at the inlet to the SCR beds. These changes could occur more rapidly than the ability of the system to respond by bypassing the SCR vessel or shutting down the kiln. As previously discussed, the temperature variations can result in catalyst deactivation or sintering. It is important to understand that these types of upsets do happen in cement kilns, and SCR system suppliers have very limited experience in designing systems to accommodate these types of problems.

Because a cement kiln combines combustion with the chemical processes of calcining and clinkering, there are more system variables. Therefore, there are more complicated and time-consuming startups and shutdowns, and more varied malfunctions. The duration and frequency of SSM periods are higher than those for the combustion systems currently utilizing SCR.

SSM process events may represent one more area of technical difficulty where cement kilns, and in particular, modern PH/PC kiln systems, differ from other source groups that have successfully applied SCR. One significant effect of dealing with transient conditions is that the SCR system's NOx reduction during these events will be zero during SCR bypass. During such events, it is often unsafe from a catalyst deactivation standpoint to either admit gas to the reactor or to inject NH_3, even if flue gas is flowing through the reactor. Regulatory limits on NOx emissions, including averaging times, must be consistent with this limitation of SCR technology. Although excess emissions associated with SSM events generally do not lead to enforcement/penalties, they are generally not exempted from enforcement by current rules. Furthermore, some level of agreement in the overall control efficiency and annual and ozone season reductions anticipated by a state implementation plan (SIP) must be made in order to account for kiln operations at zero control efficiency (i.e., during SSM periods and periods of routine operations when kiln gas temperatures are outside of the acceptable SCR temperature range, resulting in SCR bypass).

Cement kilns cannot be shut down every time process conditions or malfunctions result in gas temperatures requiring bypass of the SCR. Safe kiln shutdowns require approximately 24 hours, and routinely result in loss of refractory. Loss of refractory is costly both in the cost of the labor and materials for repair, as well as lost cement production. In addition, the SCR would need to be bypassed again for at least part of the kiln startup period. Longer periods without control will likely result from kiln shutdown for malfunctions than from continued kiln operations during periods when gas temperatures fall outside of the acceptable SCR temperature range.

Gas Flow Distribution

A cement kiln SCR application presents many new challenges to control technology designers, including the problem of ensuring even gas flow distribution at the inlet to the reactor. For an SCR system to function efficiently, the gas flow distribution across the reactor cross-section must be reasonably even. The coefficient of variation (C_v) of the flow distribution is used to characterize the gas flow distribution across the reactor cross section. Cv, the ratio of the standard deviation to the arithmetic mean expressed as a percentage (see the following equation), must be less than 20% for an SCR system to function efficiently.

$$C_v = \frac{\sigma}{x} * 100$$

Larger deviations can result in increased catalyst volume requirements, increased NH_3 slip, lower NOx reduction levels, increased SCR system pressure drop, or some combination of the above.[17] In extreme cases, catalyst plugging, deactivation, and/or erosion can occur. The two primary techniques used to address the gas distribution issue include:

- Computational Fluid Dynamics (CFD) modeling to predict gas distribution and identify design measures (i.e., flow straighteners) that can be used to ensure even gas distribution; and
- Physical flow models to evaluate gas flow distribution and the effect of flow distribution devices.

Often, a combination of both computer and physical modeling and pilot testing is used because good gas distribution is critical to optimum SCR performance. The use of pre-construction flow modeling and flow straightening devices has become an essential component of many electric utility SCR applications.[18]

Obtaining an even distribution of reactants and temperature is more critical than flow distribution. The use of flow modeling and flow straightening devices coupled with the design and operation of the NH_3 injection grid are techniques that designers use to understand and minimize the impacts of uneven distribution at the inlet to an SCR reactor.

Pilot testing will be required to determine whether these design techniques can successfully address the issues of flow distribution for application of SCR to a PH/PC kiln system. The ability to successfully design, install, and operate a flow distribution system over the long term is an open question for this application because it is outside the realm of current experience. Operation of SCR systems at coal-fired power plants provides little in the way of useful background for facing this issue. The erosive effects and the nature of the flow distribution at

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[17] Prichard, S. G., et al. Undated. SCR Catalyst Performance Under Severe Operating Conditions. CORMETECH, Inc., Durham, NC. p. 17.

[18] Cichanowicz, J. E. 1999. What You Should Know Before Specifying SCR. Power Magazine. May/June 1999. pp. 81-82.

the exit to the preheater towers intrinsic to a PH/PC kiln system present design challenges unique to the portland cement industry and this kiln type.

An additional issue that must be faced if flow straighteners are placed in this location is the potential for deposition of sticky materials on these devices. As discussed earlier, certain mineral compounds have been found to form sticky deposits at the temperatures found at the exit to the preheater tower.[19,20] Even assuming that these materials do not plug and/or foul the SCR catalyst, they have potential to build up on the surface of flow straighteners, blocking gas flow. Such buildup could create additional distribution problems, and, if the material breaks loose, it could result in massive blocking of catalyst channels. These sticky deposits can also accumulate on the bypass damper, creating operational and maintenance problems.

An important issue related to the subject of sticky deposits and buildup is that there is no way to predict if the dust in the preheater tower exhaust gas will exhibit these properties. The potential is very real for this problem to occur with a cement kiln, but one cannot tell if the problem will occur, or the extent of the problem, until after the plant begins operation.

If such deposits occur, SCR performance would be greatly impaired, potentially rendering the SCR system virtually inoperable. Pilot testing would be necessary prior to the design and installation of a full scale SCR system on a PH/PC kiln system.

EUROPEAN SCR PILOT PLANT FOR PREHEATER KILN

There is only one large-scale installation of SCR on a cement plant in the world. This installation is at the Solnhofen Cement Works in Solnhofen, Germany. The Solnhofen plant is a dry process preheater kiln, as opposed to the more fuel-efficient and more environmentally friendly PH/PC kiln systems that are the dominant design for new plants in the United States.

Information from available literature and from direct communications with a cement industry expert conflict with claims made in various reports regarding the overall average control efficiencies achieved at Solnhofen. Mr. Mark Terry, President of Polysius USA, a cement plant design and manufacturing company, has spent time at the Solnhofen facility, and studied the application of SCR at that location. Attachment 3 contains correspondence from Mr. Terry to R.J. Schreiber regarding Solnhofen operations.

A review of permitting documents for the Solnhofen facility also does not support all of the statements and conclusions in reports justifying the applicability of SCR to the cement industry. Attachment 4 contains these permit documents. According to the permit records, in 1990 the facility was permitted to emit 950 mg/Nm3 NOx. No SNCR or SCR systems were installed at that time. Thus, the baseline (or "uncontrolled NOx emissions rate") for Solnhofen is 950 mg/Nm3, not 1050 mg/Nm3 as in stated in the referenced reports . (The overstatement of the baseline results in an overstatement of the control efficiencies.) An SNCR system was permitted and installed at Solnhofen in 1995, and the authorized emission rate was reduced to 850

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[19] Berube, R. A. 1996. Effective Temperature Control for Cement Kiln Off-Gases. TurboSonic, Inc., Waterloo, Ontario. March, 1996. p. 2.

[20] Gutzwiller, L., et al. Undated. Cement Plant Preheater Fan Buildup Control. Robinson Industries, Inc. p.1.

mg/Nm3. The permit for the installation of the SCR unit, issued in 2000, states that the SCR systems would be installed with a goal of achieving an emission rate of 200 mg/Nm3. This goal was not achieved, as the operating permit issued in 2002 after the SCR system was built and operating set a NOx limit of 500 mg/Nm3.

Little, if any, written documentation via continuous emissions monitoring systems (CEMS) or stack testing data is available for Solnhofen that could be used to verify the SCR inlet concentration to calculate control efficiency. However, Mr. Terry had indicated (see Attachment 3) that the plant's baseline emissions rate ranges from 700 to 1400 mg/Nm3.

Although the Solnhofen plant had a goal of operating at 200 mg/Nm3 and that rate was achieved in a short-term test, this rate has not been sustainable during long-term operations. According to the 2004 annual emissions report for Solnhofen, the plant only achieved the permitted 500 mg/Nm3 NOx emissions rate 72.3% of the time. In other words, Solnhofen exceeded its permitted limit of 500 mg/Nm3 nearly 28% of that year, the third year of full-scale operations. An emissions rate of 500 mg/Nm3 equates to a NOx emissions rate of approximately 2 lb/ ton of clinker, a rate that is already being achieved by several PH/PC kilns in the United States both with and without SNCR. The Solnhofen report indicates that the measures to be taken to correct future excursions are to "Improve operations of the unit." One must assume that, if the plant could have routinely operated at 200 mg/Nm3, the excursions of the 500 mg/Nm3 limit could easily have been avoided. The Solnhofen 2005 annual emissions report, which became available in March 2006 at http://www.spz-solnhofen.de/, indicates that the plant complied with the 500 mg/Nm3 limit 90.8% of the time in 2005. (See Attachment 5.) While this is an improvement, such excursions are not acceptable under regulations in the United States.

Discussions with Mr. Terry cast even greater doubt on the control efficiency for SCR at Solnhofen contained in referenced reports. While Mr. Terry was at Solnhofen, the facility operated both SNCR and SCR systems. Although the SCR served as the primary NOx control technology, its inherent process constraints limited its reliability and required the plant to utilize SNCR as a backup system. When the preheater exhaust temperatures fall outside the allowable SCR temperature range or the catalyst beds become plugged, the SCR is bypassed and SNCR is initiated to control the NOx emissions. Mr. Terry indicated that the SCR system exhibited serious plugging problems and that extensive catalyst cleaning requirements were developed. Routine catalyst cleaning has been described as taking two shifts to complete, along with further acoustic cleaning overnight. The cleaned SCR has a pressure drop of about 4 mbar, but over a period of one to two weeks, the top two layers of the catalyst bed will gradually foul with preheater dust. Once the pressure drop reaches 14 mbar, the SCR is bypassed and SNCR initiated. The SCR system is also bypassed for both high (greater than 400°C) and low temperature (less than 320°C) in order to protect the catalyst from either thermal destruction, plugging, or to avoid excessive ammonia slip. Operation in bypass mode likely accounts for some of the excursions, and the catalyst plugging and the resulting cleanout may account for the balance of the excursions. Mr. Terry also indicated that the data collected at Solnhofen indicates that a maximum control efficiency of 70% occurs at a molar ratio of 1 mole NH_3 to 1 mole of NOx and levels off after reaching 70% regardless of an increase in ammonia injection. Conversely, SNCR testing conducted by Polysius has demonstrated that an increase in molar

ratio beyond 1:1 further increases the control efficiency and that it does not level off, as seen with the Solnhofen SCR system.

The 2004 and 2005 operational data indicate that the 200 mg/Nm3 emission rate was demonstrated only during short-term testing. That fact, along with the information indicating that the plant alternately utilizes both SCR and SNCR, bring into question the control efficiency and NOx emissions rate routinely achievable for the Solnhofen plant using the SCR technology.

All of the publicly available information regarding the Solnhofen plant SCR installation was assessed for this report. Based upon those data, it is apparent that there are significant differences between the Solnhofen plant and portland cement plants being constructed in the United States. A key difference is the type of kiln system. However, also of great importance are the difference in the type of raw materials used and the stack gas conditions. For example, the limestone used in the Solnhofen plant contains much higher latent levels of ammonia than what is typically encountered in the United States and particularly in the Western United States. In addition, the levels of pyritic sulfur present in the limestone used by the Solnhofen plant are very low, limiting the potential for catalyst poisoning. The Solnhofen plant required an extensive pilot study to determine the SCR catalyst and system design best suited to the plant's raw material and stack gas conditions. The difference in kiln types and locations creates significant differences in the stack gas and raw material constituents and characteristics that will require a substantial new pilot study before the technology can be applied to a cement kiln system in the United States. Discussions with experts familiar with SCR system design indicate that a 15-18 month pilot study would be necessary prior to design and construction of the full-scale SCR system.

It does not appear that the long-term demonstrated performance of the SCR system at Solnhofen results in a lower demonstrated NOx emission rate than that achievable with SNCR. The SCR-equipped Solnhofen kiln system has a German regulatory NOx emissions limit of 500 mg/Nm. This emission rate is approximately equivalent to 2.0 lbs NOx/ton clinker. Recent domestic permit determinations have concluded that BACT for portland cement plants with PH/PC kiln systems is 1.95 lbs NOx/ton clinker, based upon the use of SNCR and multi-staged combustion (MSC). At least two new PH/PC portland cement plants in the United States are operating successfully with SNCR. Another is undergoing shakedown, and several successful pilot tests have been completed at other United States cement plants using PH/PC kiln systems. SNCR manufacturers are currently offering with performance guarantees, which are based upon a combination of process equipment design and SNCR, to meet 1.95 lbs NOx/ton clinker. SNCR does not present the problems associates with SCR because of the absence of the vulnerable catalyst. Therefore, the commercially available SNCR technology offers NOx control equal to that envisioned for SCR, but without the significant performance concerns.

The Solnhofen system can cause increased impacts attributable to SO_3. The Solnhofen[21] SCR system appears to oxidize a significant fraction (more than 50%) of the SO_2 present at the SCR system inlet. Raw materials in many areas of the United States contain significantly higher concentrations of pyretic sulfur than those existing at Solnhofen. The higher raw material sulfur will exacerbate the SO_2 oxidation. As discussed above, the oxidation of SO_2 to SO_3 causes

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[21] Solnhofer Cement Works in Solnhofen, Germany.

significant long-term concerns both to the control device and in-line structures as well as to air quality. The use of increased catalyst in an effort to improve control device performance is expected to increase the rate of SO_2 oxidation, thereby resulting in potential corrosion and visible emission issues.

SELECTIVE NON-CATALYTIC REDUCTION DESIGN

Selective, non-catalytic reduction (SNCR) involves the use of an ammonia-containing solution with NOx in the preheater tower within the optimum temperature range of 1,600–2,000°F. The ammonia-containing solution may be supplied in the form of anhydrous ammonia, aqueous ammonia, or urea. The primary reactions include:

$$NH_3 + OH^- \rightarrow NH_2 + H_2O$$
$$2\ NH_3 + O^{2-} \rightarrow 2\ NH_2 + H_2O$$
$$NH_3 + H^+ \rightarrow NH_2 + H_2$$
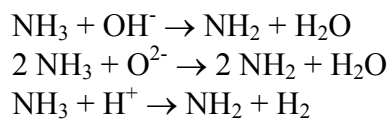
Whereupon NH_2 has been formed by any of the above mechanisms, reduction of NO occurs:

$$NH_2 + NO \rightarrow N_2 + H_2O$$
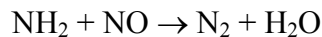
Both laboratory work and field data show NH_3 slip to be a strong function of temperature.

The following factors influence the control effectiveness of SNCR:

- Temperature and oxygen availability (i.e., location);
- The baseline, or uncontrolled NOx concentration;
- Mixing;
- Reagent to NOx Ratio (i.e., molar ratio);
- NH_3 accumulation;
- Excess ammonia emissions; and
- Ammonium salt formation.

Importantly, based on the current state of knowledge, these technical differences usually do not result in an SNCR system's "inability to perform" but instead present a "level of performance" question.

At temperatures lower than 1,600°F, the reaction rates are slow, and there is potential for significant amounts of ammonia to exit or "slip" through the system. This ammonia slip may result in a detached visible plume at the main stack, as the ammonia will combine with sulfates and chlorides in the exhaust gases to form inorganic condensable salts. The condensable salts can become a significant source of condensable PM_{10} emissions that cannot be controlled with the baghouse.

Based on research conducted at several cement plants, the combination of ammonia, chlorine, and SO_2 in quantities greater than 10 ppm each results in an extremely high risk of a detached visible plume

At temperatures within the optimal temperature range, the above reactions proceed at normal rates.

At temperatures above 2,000°F, the necessary reactions do not occur. In this case, the ammonia or urea reagent will oxidize and result in even greater NOx emissions. In addition, SNCR side reactions can form a precipitate, resulting in additional reagent usage, preheater fouling, and kiln upset. Ammonia reagent may react with sulfur in kiln gases to form ammonium sulfate. Ammonium sulfate in the preheater can create a solids buildup. Ammonium sulfate in the kiln baghouse dust recycle stream may adversely affect the clinker quality and the kiln operation.

The optimal temperature window for application of the SNCR process occurs somewhere in the preheater system. Temperature fluctuations at various points in the preheater are common during normal cement kiln operation.

Therefore, selection of the proper temperature band for ammonia or urea injection is critical to the performance of SNCR. On-site system testing of approximately one week duration is performed to determine the number and location of the ammonia/urea injection nozzles in order to optimize NOx control efficiency.

For SNCR to work effectively, the exhaust stream being treated must have a relatively high concentration of NOx as opposed to other potential reactants with which NOx would compete to react with NH_2*. The presence of competing reactants in the exhaust stream may result in less NH_2* to convert NOx to its non-polluting forms. This would reduce the effectiveness of the SNCR process.

SNCR requires an oxidizing or fuel-lean atmosphere to reduce NOx emissions. In a fuel-rich environment, the fuel (e.g., CO) will compete with NH_3 for OH* radicals, thus reducing NOx control effectiveness. In addition, ammonia interferes with the complete oxidation of organic compounds in the fuel, potentially causing a rise in CO emissions. These three conditions must be met for SNCR to be effective in NOx reduction.

The successful application of SNCR also depends on the accurate injection of the optimum quantity of reagent NH_3. Insufficient reagent will not result in effective control, while excess reagent will result in ammonia pass-through and emission (referred to as ammonia "slip"). Ammonia is typically injected in approximately equal molar quantities relative to the NOx present in the gas stream. While this injection ratio can theoretically result in conversion of 80% of the NOx with an ammonia slip of 10 ppm or less, there is a strong potential for the formation of a detached plume resulting from the presence of chlorides and sulfates in the exhaust gas stream. These compounds are present in the raw materials and are released in the kiln system.

Recent tests have been conducted on two different PH/PC kilns in Florida. The testing at Suwannee American Cement indicated a range in a NOx reduction at various molar ratios. NOx

reductions of around 55% were achieved at the tested ammonia injection rates. Suwannee American Cement has operated a permanent SNCR system since April 2005 and achieved the same long-term efficiencies and NOx reductions as those achieved during the initial tests. Testing at Florida Rock was conducted at two different operating scenarios. The testing with tires as a portion of the fuel resulted in NOx reductions that ranged from 34% to 68%. When the plant tested without tires, the range of control efficiencies was 65% to 82%.

In addition, two plants in Sweden have been complying with the Swedish emission limit of 200 mg/Nm3 using SNCR technology. These represent control efficiencies of 80%-85%, although the molar ratios are high and ammonia slip was avoided due to unique circumstances with these facilities. Testing conducted by the Research Institute of the Cement Industry in Dusseldorf, Germany has indicated a range of control efficiencies from 15% to 75% for SNCR. Clearly, the more recent data from fully operational SNCR systems indicate that higher control efficiencies are possible, at least for current designs and with certain raw material characteristics. The results for PH/PC kilns may vary due to the significant differences in raw materials between kiln locations. Recent tests at the Midlothian Holcim plant with oversight by Texas Commission on Environmental Quality (TCEQ) indicated optimum control efficiencies between 35% and 45%. It is important to note that the tests conducted in Europe do not indicate whether high opacity or detached plume problems occurred while operating SNCR systems at the stated control efficiencies. In general, European opacity requirements, where they exist, are less stringent than United States opacity standards.

SNCR has been limited in application to PH and PH/PC kilns as there are logistical issues with injection of ammonia or urea at the proper temperature zone in long wet or long dry kilns. However, one long wet kiln in France has tested an SNCR system. Little information is currently available. However, the use of SNCR to control NOx emissions from long wet or long dry plants may be possible using innovative ammonia/urea injection technologies.

SNCR technology is very application sensitive, and the amount of achievable NOx reduction depends on site-specific operating conditions. However, vendors currently indicate a willingness to guarantee levels of approximately 1.95 lb. NOx/ton clinker through the use of process equipment design combined with SNCR.

COMMERCIAL AVAILABILITY OF SCR FOR CEMENT PLANT INSTALLATIONS

The most recent, extensive evaluation of vendor commitment regarding SCR application on a cement kiln system was compiled by St. Lawrence Cement Company in support of their proposed Greenport, New York plant. The St. Lawrence Cement Company assessment and related documents were reviewed as part of this assessment. These materials are considered current since the evaluation was compiled less than three years ago.

The vendors included in the evaluation were KWH Catalysts, Inc. (KWH)[22], Lurgi PSI Inc. (Lurgi)[23], Babcock & Wilcox (B&W)[24], and Alstom Power Inc. (Alstom)[25]. The vendors

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[22] KWH supplied catalyst to the SCR demonstration plant in Solnhofen, Germany, and has also indicated that SCR is commercially available for application to cement kilns in the United States.

included in the evaluation cover the key supplier categories, including all of the organizations with direct experience at the Solnhofen demonstration plant, as well as major suppliers with diverse and significant experience in other SCR applications.

In parallel with identifying potential SCR system suppliers, a Bid Specification was developed to be used as the basis for soliciting bids from the potential suppliers. The Bid Specification is primarily a performance-type specification, in that it defines performance requirements for the system without specifying details about how the vendor is expected to meet the performance requirements. Following is a summary of the key performance specification requirements included in the Bid Specification.

NOx Reduction
Vendors were requested to provide a system designed to achieve a 90% NOx reduction on a 30-day rolling average basis. This value was selected based on performance claims made by KWH.

NH$_3$ Slip
Vendors were requested to provide a system designed to operate with NH$_3$ slip from the SCR reactor of 2 ppm$_{vd}$ @ 3% O$_2$ or less. This value was selected based on performance claims made by KWH.

SO$_2$ Oxidation
Vendors were requested to provide a system designed to ensure that SO$_2$ oxidation in the SCR system is 0.5 mole % or less. A value of 0.5 mole % oxidation was selected because this level of oxidation is common in coal-fired boiler SCR designs.

Gas-Side Pressure Loss
Vendors were requested to provide an SCR system designed such that the flange-to-flange gas-side pressure loss across the system would not exceed 6 inches of water. This value was selected because it is on the high end of coal-fired boiler SCR system pressure losses.

Turndown Capability
Vendors were requested to provide an SCR system capable of maintaining all performance requirements over the range of temperature and flow conditions expected in the preheater tower exhaust gas stream.

Catalyst Life
Vendors were requested to guarantee an average catalyst life of 24,000 hours of operating time. This value was selected based on typical catalyst life guarantees provided by vendors for coal-fired boiler applications.

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[23] Lurgi is the United States arm of the German engineering firm that was involved in the construction of the Solnhofer SCR demonstration system.
[24] B&W is a major supplier of SCR systems for coal-fired boilers in the United States.
[25] Alstom is also a major supplier of SCR systems for coal-fired boilers in the United States.

SCR System Availability
Vendors were requested to provide an SCR system designed to be highly reliable and available at least 98% of the time that the kiln is in operation.

Minimum Acceptable Performance
Vendors were requested to provide a guarantee the SCR system could meet a minimum performance level of 60% NOx reduction on a 365-day rolling average basis.

An evaluation of each of these precise bid criteria is necessary to determine if SCR and its site-specific resulting emission rate are commercially available. Nonetheless, the Bid Specification provided vendors with the opportunity to take exception to any or all of these performance requirements provided they supplied a detailed explanation as to the reason for and exact nature of the exception.

In addition to meeting the performance requirements listed above, additional information related to direct cement kiln SCR application experience, either pilot or full-scale, was requested from each vendor to allow an evaluation of the adequacy of the proposed SCR system design, as well as the vendor's relevant experience in designing SCR systems. The information request included providing, at a minimum, data on process conditions, design features, operating history, catalyst activity, and performance results over time, SO_2 oxidation rates, and NH_3 slip rates. Following is a summary of the responses received from each of the vendors.

Lurgi and B&W
Lurgi was involved in the construction and German patenting of the Solnhofen SCR demonstration project, and B&W is one of the largest suppliers of SCR systems for coal-fired boilers. Both Lurgi and B&W declined to provide bids. Lurgi's reason for not bidding was its determination that it is not currently in a position to make a *commercial release* of its SCR technology for cement kilns. B&W initially indicated its intention to provide a bid, but in the end declined.

KWH
KWH submitted a "Budgetary Bid Proposal" in response to the original Bid Specification. After requests for additional information and clarifications concerning the proposal, KWH ultimately responded by stating that, due to *technical uncertainties for the SCR/catalyst supplier* surrounding the application of SCR, KWH *cannot now supply a commercial SCR system.* However, KWH did propose an *alliance agreement* to support a pilot SCR test program before a full-scale SCR system can be designed.

Alstom
Alstom submitted a proposal containing "preliminary technical data and indicative information," which was not a firm quote or offer to perform the work. Alstom responded with an addendum to their proposal after requests for additional information and clarifications. In the end, Alstom failed to provide adequate guarantees; avoided specific questions; demonstrated its inexperience with cement kilns through inaccurate, cursory statements; refused to fully address patent issues; and took a wait-and-see position on technical issues that must be addressed prior to commercial availability.

In summary, four vendors were asked to provide proposals for a PH/PC cement kiln application of an SCR system. Of these four, two, Lurgi and B&W, did not provide any proposal, with Lurgi stating that their technology was not yet ready for commercial release. A third with relevant experience from the Solnhofen demonstration plant, KWH,[26] indicated that technical uncertainties prevented them from designing an SCR system without pilot plant testing. Only Alstom provided a proposal that even suggested SCR could be supplied for a cement kiln system. However, careful review of the Alstom proposal, albeit *preliminary technical data and indicative information*, shows that Alstom has not offered a commercial SCR system viable for a cement kiln system application.

In February 2006, Cormetech, a catalyst vendor, and Peerless Manufacturing, an SCR equipment vendor, were provided with typical PH/PC kiln gas parameters and requested to provide a quote for an SCR system to reduce NOx emissions by 80%. Cormetech declined to provide a quotation for the catalyst without first performing tests on a slip-stream. The explanation and test requirements are as follows:

"Attached is our budgetary proposal for a complete SCR system including the aqueous ammonia storage and handling system for the long wet cement kiln only. From the catalyst supplier's assessment of the PH/PC kiln, the high dust loading in that application requires a slip-stream type of field test be performed first before producing a design (and quote) of catalyst for the system. The combination of the high particulate loading and the CaO could result in very severe catalyst deactivation rates; and the field test would help us to quantify this deactivation rate. This would entail diverting a stream of flue gas through an apparatus that contains catalyst to simulate full-scale conditions. The catalyst would be exposed to these operating conditions over a period of several thousand hours. At certain time increments, catalyst samples would be removed from the slipstream reactor and sent to the catalyst supplier for analysis. We can supply more information related to the slipstream testing as well as a quotation to perform such a test if desired." See email contained in Attachment 5.

In recent discussions with another SCR system engineering firm, which supplies SCR systems to the power industry, the need for a 15- to 18-month pilot test prior to the design of the full-scale system was confirmed. In the event that the pilot test for a high dust PH/PC system proves a high dust SCR to be infeasible, a second 15- to 18-month pilot test would be required for the low-dust, post APCD system.

Given the above, one must conclude that a single, large-scale cement plant installation with a different kiln system type, using different raw materials, and with operating conditions that are distinctly different from those associated with modern PH/PC kiln systems is not enough to allow the technology to be applied in the United States without first conducting an extensive pilot study to evaluate performance.

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[26] KWH teamed with Elex, a German engineering firm who was responsible for some aspects of the Solnhofer installation. Elex holds a patent covering certain applications of SCR to cement kilns in the United States.

COMMERCIAL AVAILABILITY OF SNCR FOR CEMENT PLANT INSTALLATIONS

SNCR is commercially available for control of NOx emissions from PH/PC cement kilns in the United States. SNCR has been routinely used to control NOx emissions from cement kilns in Europe for several years. There are currently at least two cement kilns in the United States utilizing SNCR to control NOx emissions. Vendors have indicated that they will guarantee a combination of process equipment design and SNCR for cement plants at levels of approximately 1.95 lb. NOx/ton clinker. However, SNCR technology for a long wet or long dry kiln application is not currently commercially available and would be considered "innovative" technology.

CONCLUSIONS

SCR is currently not commercially available for cement kiln systems. The limited available data indicate that SCR can achieve NOx emissions reductions from a preheater kiln system such as that used at the Solnhofen plant. However, while the Solnhofen plant has demonstrated that SCR can be made to work for one type of kiln, it required an extensive pilot study to determine the SCR catalyst and system design best suited to the plant's raw material and stack gas conditions. Solnhofen continues to experience operational problems related to dust plugging, necessitating frequent bypassing of the SCR system during cleaning cycles. The difference in kiln types and locations creates significant differences in the stack gas and raw material constituents and characteristics that will require a new pilot study.

The available data do not suggest that SCR is commercially available and the best NOx control technology for PH/PC kiln systems. Because of the susceptibility of the catalyst to physical and chemical harm that degrades performance, and its temperature sensitivity, SCR is not expected to reduce NOx emissions to appreciably lower than the 2.0 lbs/ton clinker level required of the Solnhofen plant. Such an emission rate could only be achieved after substantial site-specific testing, and long-term reliability is suspect. In contrast, a combined SNCR/MSC system is installed and operating in at least two PH/PC kiln systems in Florida

The Clean Air Act and NSR rules (40 CFR 51.165(a)(xiii) define LAER (Lowest Achievable Emission Rate) as:

> "That rate of emissions which reflects – (A) the most stringent emission limitation which is contained in the implementation plan of any State for such class or category of source, unless the owner or operator of the proposed source demonstrates that such limitations are not achievable, or (B) the most stringent emission limitation which is achieved in practice by such class or category of source, whichever is more stringent."

Therefore, LAER is by definition an emission limitation rather than a control efficiency or control technology.

The definition of BACT (Best Available Control Technology)(40 CFR 52.21(b)(12) is defined as:

"An emissions limitation (including a visible emission standard) based on the maximum degree of reduction for each pollutant subject to regulation under the Act which would be emitted from any proposed major stationary source or major modification which the Administrator, on a case-by-case basis, taking into account energy environmental and economic impacts and other costs, determines is achievable for such source or modification through application of production processes or available methods, systems, and techniques, including fuel cleaning or treatment or innovative fuel combustion techniques for control of such pollutant. In no event shall application of best available control technology result in emissions of any pollutant that would exceed the emissions allowed by any applicable standard under 40 CFR Parts 60 and 61."

BACT allows a control technology to be eliminated based upon energy, environmental and economic impacts, and other costs; LAER does not. Therefore, and emission limitation that meets the definition of LAER would be lower than or equal to BACT.

The SCR system at Solnhofen has demonstrated compliance with an emission limitation of 500 mg/Nm3, which is equivalent to 2 lbs NOx/ton clinker produced[27]. Suwannee American Cement has been operating a combined MSC/SNCR system to comply with an emission limitation of 2.4 lbs NOx/ton clinker on a 30-day average. Florida Rock Industries currently complies with a 2.45 lb/ton NOx limit on a 30-day average without the use of SNCR, utilizing staged combustion promoted with firing of tires in the kiln inlet. Testing at this facility and others has demonstrated that emissions rates of 2 lbs NOx/ton clinker are achievable with combined MSC/SNCR systems. The Florida Department of Environmental Protection (FDEP) issued five permits for new kiln lines under construction or in the initial phases of construction, all with NOx emissions limitations from the kilns of 1.95 lbs NOx/ton clinker. These systems have been guaranteed to achieve this emission limitation. All of these plants propose the use of MSC combined with SNCR to comply with the NOx limitation. Although these limitations have been proposed as BACT limits, they arguably would meet the definition of LAER. They represent the most stringent limitations found in an approved permit, and are more stringent that the lowest emission rate demonstrated in practice (Solnhofen). Therefore, an emission limitation of 1.95 lbs NOx/ton clinker represents LAER and BACT.

In summary, there remain substantial operational and design issues associated with the use of SCR on cement kiln systems, and the control technology is not believed capable of maintaining long-term emissions significantly below the rates achievable by the more dependable SNCR technology. Therefore, the conclusion of this assessment is that SNCR is the better technology to apply to cement kilns seeking to limit NOx emissions for the following reasons:

- SNCR does not require a lengthy pilot study prior to final design and installation; SCR does. The SNCR test period lasts approximately one week. Each SCR pilot test would last as long as 18 months.

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[27] Friends of Hudson. Response to St. Lawrence Cement's Supplemental LAER Analysis. March 24, 2004. p.8.

- SNCR is a demonstrated technology within the cement industry for PH/PC kilns and, as such, has minimal to no implementation issues. SCR is not commercially available for PH/PC kiln systems.
- Based on an evaluation of the two technologies for PH/PC kilns, SNCR is able to achieve an equivalent or better level of control at startup. Whereas, SCR will have minimal control until such time as the pilot study is completed and the full-scale system is designed, constructed, and becomes operational. Therefore, approximately three years could pass during which there would be minimal NOx control with the SCR system. BACT controls are required to be in place at the startup of the kiln system.
- SCR systems are required to have a bypass to protect the catalyst during adverse temperature or dust loading conditions. Therefore, there will be periods of time at facilities equipped with SCR where there will be no NOx control.
- SNCR can be provided with a vendor guarantee. It is our understanding that SCR vendors cannot offer a meaningful guarantee without conducting a pilot study before full-scale system design.
- SNCR combined with MSC can meet a LAER/BACT emission limitation of 1.95 lbs NOx/ton clinker produced. SCR has not been demonstrated to achieve a lower emission rate.

ATTACHMENT 1

Dust Loading Comparison
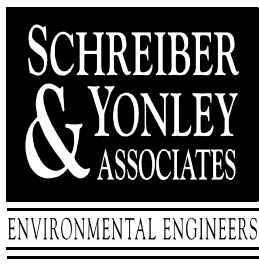
MEMORANDUM

TO: **File**

FROM: **Jeff Evers**

DATE: **JANUARY 20, 2006**

RE: **Comparison of dust loading for cement operations and boilers**
===

Based on data from F. L. Smidth (FLS), typical dust loading to the air pollution control device (APCD) for cement operations are as follows:

Long Wet Kilns: 2 – 7.5 gr/acf (units are grains per actual cubic foot)

Preheater/Precalciner (PH/PC):   10 – 20 gr/acf

[F. L. Smidth designs and installs cement kiln systems and plants worldwide, and has been doing this type of work for over 120 years.]

Actual data from a PH/PC cement system and from a Powder River Basin (PRB) fired boiler can be compared to the typical dust loading from FLS.

Type of combustor	Dust Loading (gr/acf)
FLS typical long wet kiln	2 – 7.5
FLS typical PH/PC system	10 -20
Actual PH/PC cement system	28.5
Actual PRB fired boiler	2.5

To make a more direct comparison, the volumetric flow should be converted to dscf (dry standard cubic feet). After converting, the comparison is as shown.

Type of combustor	Dust Loading (gr/dscf)
FLS typical long wet kiln	4.2 - 15.5
FLS typical PH/PC system	20.1 - 40.2
Actual PH/PC cement system	57.8
Actual PRB fired boiler	6.7

ATTACHMENT 2

steag

encotec
America
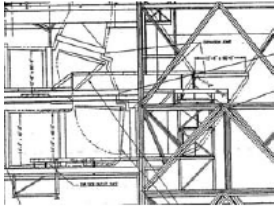
SCR Reactor Bypass:

- **Requirement for Bypass:**
  - **Seasonal operation (if applicable)**
  - **Multiple start-up and shutdown (below acid dew point)**
  - **Fast start-up**

- **Disadvantages:**
  - **Dampers are major maintenance item due to high temperature and dust loading**

- **Damper types:**
  - **Louver dampers**
  - **Diverter or flap dampers**
  - **Guillotine dampers**

- **Critcal is SCR suitable damper design**

ATTACHMENT 3

Hi Bob,

It was nice talking with you again today. After our discussion, I could tell it would be better if I tried to document my observations from my visits to Solnhofen . As mentioned, the Solnhofen facility in Southern Germany has been using the SCR technology for a number of years and is identified as the prototype facility for use of SCR in cement manufacturing operations. Since there is little published data on the actual operations of the facility, I will try to summarize what I have learned about their operations from my last couple of visits.

The Solnhofen cement manufacturing facility uses a 4-stage preheater kiln (with no precalciner) for cement production, producing around 1500 metric tons per day of clinker. The kiln uses oil and waste fuels as substitute fuels to fire the kiln, and exhibits little alkali or sulfur in the raw materials used for production. Uncontrolled NOx emissions from the kiln system are relatively low at 700-1400 mg/m3. As noted above, the facility uses SCR as their primary NOx control technology, but also employs the use of SNCR as their secondary or back up control technology for NOx, with two injection locations in the preheater tower. The selection of the overall control equipment, in addition to deriving and maintaining satisfactory operating conditions for the equipment at this facility, has been very challenging.

The catalyst selection for the SCR technology was a challenging part of developing the system, with numerous trials taking place before an acceptable design was selected. The SCR includes a multiple stage honeycomb and plate catalyst bed of primary titanium dioxide and about 2% vanadium pentoxide which utilizes the catalyst beds as necessary to control of NOx to achieve the permitted limit of 500 mg/m3. The low sulfur and low alkali content of the exhaust gas and dust from the kiln system has allowed this catalyst to work some of the time with extensive cleaning, but it took 3 years of pilot testing and one year of operations to debug the system in order to maintain more consistent operations of the equipment. Probably the main reasons that their system works as well as it does are the Bavarian raw materials, which are low in alkalis and sulfur (which cause plugging of the catalysts) and easy to burn.

During start-up/debugging of the SCR catalyst operations, the facility developed an extensive and unique system of catalyst dust cleaning. Cleaning activities for this challenging environment include significant use of high-pressure air, reverse heated compressed air flow, air cleaning valves and low frequency acoustical horns. In addition to the extensive automated cleaning activities, it is still necessary to perform a substantial amount of regular manual cleaning activities (taking two shifts to accomplish the cleaning in conjunction with overnight cleaning with acoustic horns). Generally, they can run for 7 to 14 days before the upper two layers of the catalyst are plugged requiring 24 hrs of cleaning activities on the catalyst to return the system back into full operation. The actual timing between cleaning is determined by the pressure drop across the catalyst bed, which is evaluated through monitoring. If the pressure drop is too high the system is bypassed for cleaning, and SNCR serves as the back up NOx control system. This particular problem is a main contributor to the reliability issues associated with such high dust, SCR systems.

The SCR technology is also very temperature dependent, and the Solnhofen facility has to operate in a narrow temperature window due to the specific composition of the catalyst material.

Temperatures must be maintained below 400°C to prevent damaging the catalyst, and above 330 ^{o}C to stay in the effective working range of the catalyst material . At temperatures outside of the 330 - 400 ^{o}C operating window, the catalyst bed is bypassed and SNCR is started as their back up system.

The data I have on the catalytic operations of the SCR system at Solnhofen indicates that the control efficiency peaks and levels off at 70% NOx reduction at a molar ratio of 1:1 and the removal efficiency does not increase with more ammonia usage. This would indicate a maximum efficiency for their SCR control as less than the 80-90 percent reported in some documents. In contrast, there is also data (graphs attached) that shows SNCR(red line) is capable of meeting and exceeding this control efficiency in some instances, and it is not limited to the 1:1 molar ratio as found at Solnhofen(blue dots). Also many of the SNCR test in both the United States and Europe have indicated good results (greater than 60% control). It is important to note that these results are also dependent on kiln specific chemical and physical limitations.

Je

Some of the issues with using SCR technologies developed from transfer of the technology from the power industry to the cement industry. The cement industry exhibits higher dust loading, and different types, shapes and chemistry of the dust. Power plant dust is fine, spherical, and typically lower in calcium oxide and alkalis than cement kiln dust(pictures of dust attached). Cement kiln dust is coarser and larger, which will exasperate plugging, fouling and poisoning of the catalyst. Cement kiln dust loading is also about ten times higher than the typical power plant high dust applications.

I know this was sort of long winded ; but such a topic is difficult to describe with a few bullet point. I hope it helps. If you need anything else or have any questions, just give me a call.

Best Regards,

Mark

_____

ATTACHMENT 4

SOLNHOFEN PERMIT ON CD

ATTACHMENT 5

Unterrichtung der Öffentlichkeit gemäß der 17. BImSchV über den Betrieb des Zementwerkes

1. Eigentümer der Anlage: **Solnhofer Holding AG**

2. Betreiber: **Solnhofer Portland-Zementwerke GmbH & CO.KG**

3. Berichtszeitraum: **01.01.2005 - 31.12.2005**

4. Rauchgasreinigungen:

- Entstaubung: Gewebefilter

- Entstickung : Katalysator SCR-Verfahren, Reduktionsmittel NH4OH

5. Abfall-Mitverbrennung:

- genehmigter Einsatzstoff : BPG   (produktspezifische Abfallstoffe)

6. Kontinuierlich gemessene Emissionen/Verbrennungsbedingungen und deren Bewertung:

alle Zahlen als mg/m³ i.N. trocken (,=Milligramm pro Kubikmeter trockenes Abgas im Normzustand bei einem Bezugssauerstoff von 10,4 %)	Halbstundenmittelwerte		Tagesmittelwerte	
	Grenzwert	Einhaltung in %	Grenzwert	Einhaltung in %
Staub	40	100	20	98,5
Chlorwasserstoff	60	100	10	83,7
Schwefeldioxid	200	100	50	100
Stickoxide	1000	99,5	500	90,8
Quecksilber	0,05	95,2	0,03	91

Maßnahmen gegen zukünftige Überschreitungen:	Staub:	Alle gasberührende Metallteile korrosionsbeständig ausführen
	NOx :	Bessere Brennbedingungen durch Einsatz eines neuen Ofenbrenners sowie weitere Optimierung der SCR-Anlage
	Chlorwasserstoffe:	Chloreintrag durch Sekundärbrennstoffe erheblich mindern
	Quecksilber :	Optimierung der kurzfristig ändernden Rohmaterialzustände

7. Einzelmessungen und deren Bewertung

Die Messungen wurden durch eine nach § 26 BImschG zugelassene Meßstelle durchgeführt

Parameter	Einheit	Grenzwert	Mittelwert	Maxwert der Messreihe
gasförmige anorg. Fluorverbindung	mg/m³	4	n.n	
Quecksilber und seine Verbindungen	mg/m³	0,05	0,002	0
Cadmium und seine Verbindungen	mg/m³	0,015	n.n	
Thallium und seine Verbindungen	mg/m³	0,015	n.n	
Nickel und seine Verbindungen	mg/m³	0,15	<0,002	0
Summe aus Antimon, Arsen, Blei, Chrom, Kobald, Kupfer, Mangan, Nickel, Vanadium, Zinn und deren Verbindungen	mg/m³	0,4	0,01	
Summe aus Arsen, Cadmium, Chrom, Kobalt und deren Verbindungen	mg/m³	0,05	<0,001	0
Benzol	mg/m³	5	0,7	
Dioxine und Furane: Toxizitätsäquivalente	ng/m³	0,05	0,003	0

8. Ansprechpartner bei Rückfragen:

Landratsamt Weißenburg/Gunzenhausen	Herr Löffler	Tel.: 09141/902-319
	Herr Schott	Tel.: 09141/902-324

Solnhofer Portland-Zementwerke   Herr Sauter   Tel.: 09145/601-220

http://www.spz-solnhofen.de/
3/7/06

ATTACHMENT 6

Jeff,

Attached is our budgetary proposal for a complete SCR system including the aqueous ammonia storage and handling system for the long wet cement kiln only. From the catalyst supplier's assessment of the preheater/precalciner kiln, the high dust loading in that application requires a slip-stream type of field test be performed first before producing a design (and quote) of catalyst for the system. The combination of the high particulate loading and CaO could result in very severe catalyst deactivation rates; and the field test would help us to quantify this deactivation rate. This would entail diverting a stream of flue gas through an apparatus that contains catalyst to simulate full-scale reactor conditions.   The catalyst would be exposed to these operating conditions over a period of several thousand hours. At certain time increments, catalyst samples would be removed from the slip-steam reactor and sent to the catalyst supplier for analysis. We can supply more information related to the slipstream testing as well as a quotation to perform such a test if desired.

Regards,

Paul Hoeller
Applications Engineer
Environmental Systems
Peerless Mfg. Co.
Phone: (214) 353-5527
Fax: (214) 351-0194
Email: phoeller@peerlessmfg.com