May 30, 2006

David Schanbacher
Chief Engineer
Texas Commission on Environmental Quality
Bldg. F, Fourth Floor
12100 Park 35 Circle
Austin, TX 78753

Via Electronic Delivery

Re: Comments on the "Assessment of NOx Emissions Reductions Strategies For Cement Kilns - Ellis County - Draft Final Report"

Dear Mr. Schanbacher:

Enclosed please find comments on the above referenced report (the "Draft Final Report"). This letter also contains comments on the letter dated January 24, 2006, by Albert R. Axe on behalf of the Portland Cement Association (the "PCA Letter") with PCA's comments on the Draft Final Report. Both documents are presently posted on a Texas Commission on Environmental Quality ("TCEQ") website: http://www.tceq.state.tx.us/implementation/air/sip/BSA_settle.html

I am a resident of Dallas, Texas, on the faculty of a local university, and I am also involved as a advisor with local citizen groups and one of the cement plants discussed in the Draft Final Report. Please note that the views expressed in the letter are my own, they are not the views of my current employer, and this letter is not on behalf of any citizen group, cement company, or other party.

I would appreciate you posting this letter on the above mentioned website to add to the comments you have already received and to insure its distribution to any and all interested parties.

Thank you for your consideration of these comments.

Sincerely,

Al Armendariz, Ph.D.

Attachments

cc (with attachments): Karen Hill, Walter Koucky, Gabe Miller, Alvaro Linero, Marilyn Potter, Steve Pursley, Bill Neuffer, Carl Edlund, Ravi Srivastava, Michel Moser

Comments on the "Assessment of NOx Emissions Reductions Strategies For Cement Kilns - Ellis County - Draft Final Report"

SCR Is Commercially Available Technology

The Draft Final Report determines whether nitrogen oxides ("NOx") control technology options are *available*, *transferable*, or *innovative*, and it states that *"available* means that the technology is commercially available and in use on the similar types of cement kilns". The Draft Final Report concludes that selective catalytic reduction ("SCR") is *available* technology to control NOx emissions from the three dry PH/PC kilns in Ellis County, and is *transferable* technology for the seven wet kilns. On page 13 of the PCA Letter, the PCA calls the Draft Final Report's determination that SCR is *available* "inappropriate" and "not supportable."

A good test of whether SCR is commercially available for NOx control at cement kilns is the existence of SCR suppliers who can provide and guarantee performance of the technology.

Attachment 1to this letter is a memo written in 2004 by Tom Lugar, CEO of KWH Catalysts, Inc., of Wayne, Pennsylvania. In this memo, KWH Catalyst guarantees the performance (85% NOx control) of an SCR system to be installed at a proposed cement kiln in New York.

At the end of the memo, Mr. Lugar writes:

> "SCR technology has been applied for several decades to a diverse number of applications worldwide. KWH, in particular, has successfully applied the technology to such applications as coal-fired boilers, oil and gas fired boilers, municipal waste and sewage sludge incinerators, diesel/gas cogen plants, chemical plants, refineries, glass plants, biomass incinerators, and steel sinter plants. These applications span an extreme range of process gas/dust conditions and operating conditions. SCR catalyst is a mature, proven technology that can be adapted in its design formulation and configuration to a wide range of applications as has been shown with the new application on cement at Solnhofen."

Attachment 2 to this letter is a page from the KWH Catalysts website. On this page the company markets its SCR expertise and calls SCR installation at cement kilns "a tradtional field of application".

Attachment 3 to this letter is a page from the website of the Lurgi-Bischoff company of Essen, Germany. Engineers and scientists from Lurgi-Bischoff have been involved in the full-scale SCR project at the cement kiln in Solnhofen, Germany. On this page the company markets its services to the cement industry, including its "SCR-DeNOx" systems.

Attachment 4 to this letter is a page from the website of the ELEX AG company of Schwerzenbach, Switzerland. On this page, ELEX describes its SCR system for cement kilns that can achieve 90% NOx control with 90% up-time. ELEX was involved with the SCR installation at the Kirchdorfer Zementwerks in Austria that I will describe in a following section.

With at least 3 vendors marketing SCR for cement kilns, there is no question that the technology is commercially available to control NOx emissions from cement kilns. I completely agree with the designation of SCR as *available* in the Draft Final Report.

SCR Has Been Applied on Multiple Cement Kilns

The Draft Final Report discusses the application of a full-scale SCR system at a cement plant in Solnhofen, Germany, and uses the existence of the Solnhofen system to support the designation of SCR as *available* technology. The PCA Letter claims that designation as *available* is inappropriate and "is apparently based upon the existence of a single SCR system operating at the Solnhofen cement plant in Germany."

Attachment 5 to this letter is a note I received on April 18, 2006 from Mr. Marco Tinti of the Italcementi Group, a major worldwide cement manufacturer. He is participating on an EU committee that is drafting the latest version of a European guidance document on control technology for cement plants. Mr. Tinti states:

> "By the end of the year another plant, beside the one in Germany, will be equipped with an SCR system by ELEX. This plant doesn't belong to ITC Group; it is located in Monselice, small village in Padova province (close to Venice)."

So in addition to the full-scale system at Solnhofen operational since 2001, a new full-scale system in Italy will be operational by the end of this year. This full-scale SCR experience is in addition to the tens of thousands of hours of pilot-scale SCR experience at cement kilns obtained by catalyst manufacturers over the last decade (see Attachment 4).

The current and growing experience of the catalyst industry on SCR applications at cement kilns supports the designation in the Draft Final Report for SCR as *available* technology.

SCR Is a Success Where It Has Been Applied

There are at least three companies, KWH Catalysts, Lurgi-Bischoff, and ELEX AG, that are publically marketing their services to provide SCR systems to cement plants. In addition to these suppliers, others with experience in applying SCR to cement plants have testified to its success.

Attachment 6 to this letter is a page from the website of the Kirchdorfer Zementwerks, a cement plant in Austria. From 1996-1999, the plant worked with ELEX AG to test an SCR system. Concerning the SCR system, the plant writes:

> "The cement plant drew particular attention from its peers when it undertook attempts to eliminate nitric oxide emissions using the SCR technique. It was a risk experts considered bound to fail. Following a comprehensive three-year trial run, the SCR technique was eventually proven to be the most appropriate for reducing nitric oxides in the cement industry. Besides causing a stir among experts, this pioneering achievement met with broad interest, including from international circles. The number of environmental

> prizes awarded bears clear evidence of this fact."

Attachment 7 to this letter is a technical paper presented by Isabella Kossina of the Umweltbundesamt (UBA - the Federal Environmental Agency of Austria), the agency that permitted and supervised the SCR operation at Kirchdorfer. The paper was presented at the NOx Control Conference in Paris, France in March 2001, and it summarizes the success of the SCR pilot-scale trial in Austria. The summary of the paper states:

> "The application of SCR in the cement industry in crude gas configuration has been tested in Austria, Italy, Sweden and Germany. Results of a successful pilot plant trails in Kirchdorf, Upper Austria with about 3-5 % of the raw gas from the cement kiln showed that SCR allows to achieve clean gas concentrations of 100-200 mg/m^3 . The ammonia slip has been considerably below 5 mg/m^3 (half hour average, 10 % O2) and no enrichment of ammonium compounds in the dust has been proved through a trial of 13,000 hours. The loss of catalyst activity has been within the expected range."

The PCA Letter disputes the statement in the Draft Final Report that the SCR system at Solnhofen can achieve NOx emissions of 200 mg/m^3. The PCA Letter states that Solhofen's current NOx permit limit of 500 mg/m^3 shows that it is unable to achieve NOx emissions of 200 mg/m^3.

The Draft Final Report summarizes NOx emission limits within the European Union on Table 4.5.2. In this Table, the German national NOx emission limits, effective the year 2000, for cement kilns of 500 mg/m^3 for new/modified plants and 800 mg/m^3 for existing plants are presented. Attachment 8 to this letter are three pages from *Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000* (1). The European-wide NOx emission standards are established in Table II.1.1: 500 and 800 mg/m^3, for new/modified and existing cement plants, respectively. Attachment 9 to this letter are three pages from a survey conducted by the United Nations Economic Commission for Europe in December 2002 (2). The UNECE surveyed NOx regulations in Europe and on Pages 16 and 17 they show the 500 mg/m^3 German limit established in October 2002 for NOx emissions from cement plants.

The reason that the Solnhofen plant is permitted at a NOx emission rate of 500 mg/m^3 and is operated to meet this limit is because 500 mg/m^3 is the relevant German regulation. The operators and permit writers for the SCR system at Solnhofen are doing exactly what their U.S. counterparts typically do - they are meeting the exact letter of the law. There is no legal reason for them to achieve lower NOx emissions at this time.

To examine whether SCR systems on cement kilns can produce NOx emission levels as low or lower than 200 mg/m^3, as stated in the Draft Final Report, the statements of individuals closely involved with the Solnhofen project should be considered.

(1) - The full directive can be accessed at http://www.wbcsd.org/web/projects/cement/tf2/2000-76_en.pdf
(2) - The full report can be accessed at http://www.unece.org/env/documents/2002/eb/eb.air.2002.1.q.02-08.pdf.

Attachment 1 to this letter contains a memo written by Tom Lugar of KWH Catalysts, Inc. On page 3 of the memo, Mr. Lugar writes about a visit by KWH to the Solnhofen cement plant:

> "KWH had a very informative meeting at the Solnhofen Plant on February 25 [2004]. The SCR has been operating for over 24,000 hours and maintaining the German regulation requirement of not to exceed 500 mg/m^3 of NOx. The SCR is only equipped with three out of a possible five layers [of catalyst] to meet the 500 mg limit. Provision was included in the SCR design to achieve a potential future limit of 200 mg."

Attachment 10 to this letter is a paper written by Mr. Alvaro A. Linero of Tallahassee, Florida, which he presented at the 2005 Annual Conference and Exhibition of the Air and Waste Management Association (AWMA). In his paper, Mr. Linero summarizes the finding of a report co-authored by Dr. Norbert Haug of the Umweltbundesamt (German Federal Environmental Agency), Gerd Sauter of the Solnhofer Portland Zementwerke, and Dr. Gurudus Samant of Lurgi-Bischoff. In their report, the three authors state that Solnhofer is able to meet NOx emissions of 200 mg/m^3 with an ammonia use rate of 85 liters per hour. In addition, these authors evaluate the economics of SNCR vs SCR selection, and state that SCR is more economical when the desired NOx emissions are 550 mg/m^3 or lower, because of the more efficient use of ammonia in SCR systems compared to SNCR.

In his paper, Mr. Linero reports on direct communications he had with Dr. Haug in which Dr. Haug stated that "with SCR you can meet standards of 200 mg/m^3" and also that "the SCR at Solnhofen works in an excellent manner." In addition, Mr. Linero summarizes the findings of a Austrian inspection of the Solnhofen plant in July 2003. In their report, the Austrian inspectors state:

> "The reactor in the plant can be equipped with six catalyst sections of which three layers are in use. With these three, 500 mg NO_X/m^3 and less than 1 mg NH_3/m^3 are emitted. A reduction to 200 mg/m^3 is possible by variation of the NH_3 use. The actual working time of the catalyst is at present at approximately 18,000 hours with an expectation of another further 3-4 years." The same Austrian experts included their findings on SCR technology in a more comprehensive report published in 2004 by the Austrian Unweltbundesamt on waste use and emissions reductions in the cement industry."

The statements and published reports of German and Austrian regulators, Solnhofen plant engineers, and catalyst company scientists support the conclusion in the Draft Final Report that SCR technology can reduce NOx emissions to 200 mg/m^3 and that SCR technology has been successfully applied to cement kilns.

Many of The Supposed Problems with SCR Can Be Eliminated For the Ellis County Wet Kilns

The Draft Final Report discusses the success of the SCR project at the Solnhofen plant in Germany. The kiln at Solnhofen is a dry process kiln, with gas characteristics similar to the three dry kilns in Ellis County (Holcim #1 and #2, TXI #5).

The Draft Final Report in Section 4.1.1.4 also contains a site-specific analysis of SCR application to the wet kilns in Ellis County (TXI #1-#4, Ash Grove #1-#3). In this section, the Draft Final Report states that the gases from the wet kilns would have to be reheated for SCR because the gas temperatures at the stacks are below the optimum temperature for SCR operation. The cost effectiveness data presented in the Executive Summary of the Draft Final Report and in Table 4-1.2 include the costs of reheating the stack gases It is very important to note that the gases at the stacks of the wet kilns have already gone through particulate (dust) control devices. Therefore, the SCR systems proposed and evaluated in the Draft Final Report for the wet kilns are in a "low-dust" configuration. This is in sharp contrast to the installations reviewed in the Draft Final Report for the dry kilns, which are in a "high-dust"configuration.

In spite of the additional fuel required to reheat the stack gases from the wet kilns, the cost effectiveness values presented in Table 4-1.2 for TXI #1 and #4 and Ash Grove #1-#3 are in the range of $5000-$7000 per ton of NOx removed, well within common regulatory practice for NOx control cost effectiveness in ozone non-attainment areas.

Page 11 of the PCA Letter discussed some of the supposed difficulties with applying SCR to cement kilns, including dust plugging the catalyst, dust composition, dust shape, and dust loading (the amount of dust in the flue gases). These supposed difficulties are reiterated in information included as Attachment 2 to the PCA Letter. It is very important to realize that these concerns do not apply to the application of SCR to the Ellis County wet kilns in a low-dust configuration, since the gases have already been cleaned of dust. In a low-dust configuration, the application of SCR to the Ellis County wet kilns would be easier than the current successful high-dust application at Solnhofen and would also be easier than the numerous high-dust SCR applications at coal-fired power plants.

With regards to the additional need to burn fuel to reheat stack gases in a low-dust application, the cement industry in general, and the Ellis County cement kilns specifically, are experienced in the combustion of non-fossil fuels (a.k.a. "alternative fuels" or "waste fuels") including tire chips, used oils, oil filter fluff, and others. The firing of these alternative fuels in the kilns reduces the quantity of traditional fossil fuels, like coal and natural gas, that have to be fired. In addition, the firing of alternative fuels in a cement kiln results in a beneficial use of the heating value of the alternative fuels, instead of simply wasting the heating value by burning the alternative fuels in a conventional waste incinerator.

If the additional heat required to achieve flue gas reheat when using SCR in low-dust configuration at a wet kiln is matched by an increased use of alternative fuels by the kilns, then SCR can be applied with no net increase in fossil fuel use. And since there often are economic benefits to cement companies for firing alternative fuels, from payments to the cement companies from waste generators and from state tire disposal funds, there might be no net increase in

operating costs for fuel to achieve flue gas reheat for SCR at the wet kilns.

Conclusions

The current installations and growing use of SCR at cement plants in Europe and the data presented in the Draft Final Report indicate that:

- SCR is commercially available technology for cement kilns.
- SCR has been applied on multiple cement kilns.
- SCR is a success where it has been applied.
- SCR in a low dust configuration can be a cost-effective and straight-forward NOx control technology for the wet cement kilns in Ellis County, without any of the supposed dust plugging concerns of high-dust configurations.

Attachment 1 - Letter by Tom Lugar, CEO of KWH Catalysts, Inc.

KWH Catalysts, Inc.

February 27, 2004

Camp Dresser & McKee Inc.
One Cambridge Place
50 Hampshire Street
Cambridge, MA 02139

Attention: Frank Sapienza
Principle Engineer

Subject: SCR System for St. Lawrence Cement
KWH Catalysts, Inc. Response to Revisions to the Specification

Dear Mr. Sapienza:

The following is response to your questions concerning the proposed CDM revisions to the St. Lawrence Cement Greenport SCR bid specification.

1. Can KWH Catalysts, Inc. guarantee that its proposed SCR system for St. Lawrence Cement will meet the performance guarantees as stated in Appendix 1?

NOx Reduction Efficiency

KWH can meet the performance guarantee of a minimum 85% NOx reduction. However, the minimum temperature to the SCR must be 315 C versus the specified 300 C to avoid salt formation. The temperature at which ammonium salts will begin to form is really not a debatable issue. With ammonia present and the concentration of SO_3 and NOx known, salts will begin to form at a temperature dependent on the moisture content of the process gas. This is well known chemistry and easily calculated.

NH_3 Slip

KWH can meet the performance guarantee requirement of not to exceed 2 ppmvd at 3% O_2.

SO_2 Oxidation

The requirement of SO_2/SO_3 conversion of less than 1% by mole is the now typical requirement in specifications for coal-fired U.S. utility boilers since potential carry-over of SO_3 downstream can result in an acid plume out the stack. This criteria should not be applied to a cement process gas stream. The SO3 generated in the

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Phone: (610) - 293 2507(2508) • Fax: (610) - 254 9617
www.kwhcatalysts.com

process is captured by the large amount of free lime as CaO in the gas stream. SO_2 oxidation by the catalyst wil have no negative impact on the amount of SO_3 formed and subsequently captured. As an added point, there is no field test method that can measure this anyway since the SO_3 gas is totally captured by conversion to particulate calcium sulfates and sulfites as it is contacted by the free lime upstream, within, and downstream of the SCR catalyst.

Gas-Side Pressure Loss

KWH can meet the performance guarantee requirement of not to exceed 6" W.G. across the flange-to-flange SCR system.

Turndown Requirements

KWH will maintain all performance requirements listed in the Appendix with the exception of SO_2 oxidation (as explaned above) within the ranges of flow and characteristics defined in Item 1 of your letter. However the minimum temperature must be 315 C versus the specified 300 C.

Catalyst Life

Common practice for SCR catalyst is 16,000 hours and KWH would guarantee this catalyst lifetime. The Solnhofen SCR has operated successfully for over 24,000 hours. In three weeks KWH will be removing catalyst test elements from the Solnhofen reactor and conducting laboratory bench reactor tests to determine catalyst deactivation. KWH stated in its bid to St. Lawrence that it expected a 24,000 hour catalyst life. KWH would be willing to provide a 24,000 hour life guarantee but this commitment would be depend on the results of these bench reactor catalyst tests. KWH will update you on this issue when the bench reactor catalyst test results become available. A condition for the catalyst life guarantee and the following Availability guarantee is that the SCR system be equipped with a 100% bypass. This will protect the catalyst against plant upset conditions such as very low gas flow that would plug the catalyst quickly or moisture conditions at acid or water dewpoints that would form cement at the catalyst face and in the catalyst channels effectively ending the life of the catalyst. This is not an unreasonable condition as this is common practice for some pollution control equipment that are sensitive to specific plant upset conditions. For example, a bypass is commonly used for baghouses to prevent high temperature excursions from destroying the filter bags or boiler tube leaks causing permanent bag blinding.

SCR Availability

KWH can guarantee SCR system availability of 98% of the time that the cement plant is operated at stable, continuous conditions as defined in the specification for the performance guarantee criteria and provided that the SCR system is maintained and operated in accordance with the procedures and instructions stated in the KWH Operations and Maintenance Manual. Additional conditions for the availability

guarantee are that KWH will have access to the SCR system during plant outages and forced shut-downs to conduct inspections and maintenace of the SCR system and that the SCR system is equipped with a 100% bypass as described previously.

Failure to Meet Performance Guarantees

KWH takes exception to the open-ended liquidated damages requirement as stated. The Industry standard for pollution control systems, be they FGD scrubbers, bag-houses, SCRs and precipitators is typically worded as follows: "The cumulative maximum liability of Vendor with respect to all claims and costs arising out of or incurred in connection with this contract or arising out of the performance or non-performance of the supplied scope of work, whether based on contract, warranty, tort, strict liability or otherwise, shall not exceed in the aggregate an amount equal to one hundred (100%) percent of the Contract Price paid to Vendor".

2. **Maintaining the Minimum Temperature**

The inclusion, as you propose, of a bypass duct around the last preheater cyclone as a method to maintain the preheater tower exhaust gas above the minimum required temperature of 315 C, appears to be a reasonable method to address the minimum temperature issue.

3. **Solnhofen Plant Data**

KWH had a very informative meeting at the Solnhofen Plant on February 25. The SCR has been operating for over 24,000 hours and maintaining the German regulation requirement of not to exceed 500 mg/m^3 of NOx. The SCR is only equipped with 3 of a possible 5 layers to meet the 500 mg limit. Provision was included in the SCR design to achieve potential future limit of 200 mg. The 500 mg requirement is being achieved with an average NOx inlet of 2500 mg.

During the KWH meeting, Mr. Gerd Sauter, Plant Manager, stated that, if CDM wishes to obtain detailed SCR performance data and process exhaust gas and particulate/raw feed data, he would be pleased to provide this information with a confidentiality agreement in place. He invited CDM to visit the plant if they wish.

As a final comment, note that SCR technology has been applied for several decades to a diverse number of applications worldwide. KWH, in particular, has successfully applied its catalyst technology to such applications as coal-fired boilers, oil and gas fired boilers, municipal waste and sewage sludge incinerators, diesel/gas cogen plants, chemical plants, refineries, glass plants, biomass incinerators, and steel sinter plants. These applications span an extreme range of process gas/dust conditions and operating conditions. SCR catalyst is a mature, proven technology that can be adapted in its design formulation and configuration (i.e. pitch, length, etc.) to a wide range of applications as has been shown with the new application on cement at Solnhofen.

Attachment 2 - KWH Catalysts, Inc. Webpage on SCR

The SCR process for NO_X emission control

Nitrogen oxides are reacted stoichiometrically with ammonia or urea as reducing agent to form nitrogen (N_2) and water vapor (H_2O) which occur naturally in the atmosphere.

The major part of the nitrogen oxides, which is generally present as NO, is reacted according to the following reaction:

$$4\ NO + 4\ NH_3 + O_2 \Rightarrow 4\ N_2 + 6\ H_2O$$

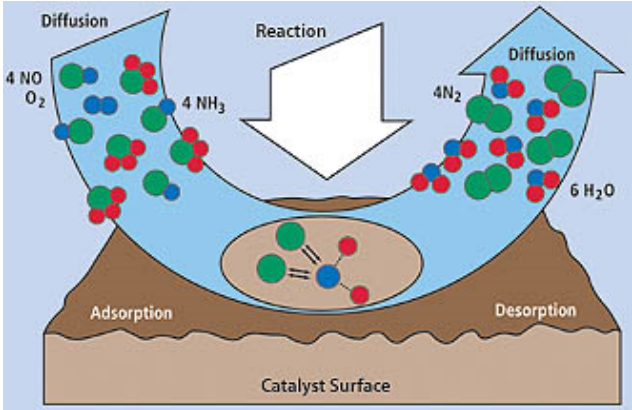
As long as a mixture of NO and NO_2 is present, the following somewhat faster reaction proceeds in parallel:

$$NO + NO_2 + 2\ NH_3 \Rightarrow 2\ N_2 + 3\ H_2O$$

In principle, these reactions can also be carried out without catalyst in a small temperature range around 900°C (1,650°F). However, under these conditions a significant proportion of the ammonia is burned to form nitrogen oxides, which severely impairs the efficiency with respect to ammonia consumption and the achievable NO_x conversion.

The SCR process makes it possible to reduce the level of nitrogen oxides by means of the reactions above in a broad temperature range between about 160°C (320°F) and just under 600°C (1,110°F), depending on flue gas conditions and catalyst type. High selectivities of almost 100% are obtained in the reaction of ammonia and, if required, NO_x conversions of well above 90% can be achieved.

Furthermore, the SCR process is extremely flexible in terms of the fuel used and the loading of the upstream combustion process.



The SCR process enables the highest degree of removal of all $deNO_x$ processes to be achieved in an economical way. In addition, it is at present the best available technology, and therefore helps to secure the future.

Traditional fields of application for the SCR technology are power stations, gas turbines, waste incineration plants, cement mills, the steel industry, chemical plants, cogeneration plants and glass works. SCR catalysts are being increasingly used in the combustion of wood and other biomass as well as in mobile combustion engines.

The wide variety of possible applications and new developments requires flexibility and tailored technology.

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Attachment 3 - Lurgi-Bischoff Webpage on Cement Industry Applications

Markets & Products

- Non-Ferrous Metallurgy
- Chemistry / FCC
- Iron and Steel
- Cement
- Glass
- Process Automation
- Spare Parts

Cement

Cement
References

In the cement production sector, we provide technologies for the following fields of application.

Due to the comparable technologies for alumina calcination also the entire field of "Aluminium" is represented here.

Gas Cleaning in Cement Mills

Kilns/Mills

- Evaporation coolers with Pulse-Jet filters or electrostatic precipitators

Clinker Coolers

- Electrostatic precipitators or air/air coolers with fabric filters

Other

- SO2 scrubbers, SCR-DeNOx
- Electrostatic precipitators or fabric filters for coal and cement mills as well as dryers
- Electrostatic precipitators for alumina-calcination

Contacts

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Attachment 4 - ELEX AG Webpage on SCR Application to Cement Kilns

Eschenstrasse 6
CH - 8603 Schwerzenbach

Tel. + 41 44 825 78 78
Fax + 41 44 825 79 79

SCR-Systems for Cement Industry

The SCR technology for Cement kilns has been successfully tested by ELEX in 3 pilot units in different Cement plants (total approx. 30'000 operating hours).

ELEX is ready to install a full-scale unit.

ELEX is Patent holder for DeNOx-catalysts (SCR) for the Cement Industry.

Definitions:
SCR = Selective Catalytic Reduction
SNCR = Selective Non Catalytic Reduction

Process description: see "DeNOx for Incinerations**"**

Requirements for a SCR-installation in cement plants

- efficiency for NOx-removal > 90%
- minimized additional energy
- no products from reaction to be diposed of
- no influence on process and products
- ammonia slip after SCR-installation < 5 vpm
- minimized pressure drop
- continous operating time >8000h
- reliability >90% per year
- to be installed during normal maintenance shut downs
- removal of other hazardous matters with the same equipment (CO, total C)

SCR system for Cement kilns

The SCR technology allows to reduce the pollution of the cement industry in a large amount. The SCR economical and ecological better at NOx reduction rates higher than 60 %.

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Attachment 5 - Letter from Marco Tinti of Italcementi Group

From: CINTI Giovanni [mailto:g.cinti@itcgr.net]
Sent: Tuesday, April 18, 2006 12:40 PM
To: Armendariz, Al
Subject: R: Cement Plants

Hi Alfredo,
the information you have got is correct. We have done some industrial tests using catalyst for NOx reduction: as Italcementi runs many lepol kilns, the basic idea was to see if this method was applicable to this type of kilns, where other proven technologies are not (SNCR, Staged combustion). The system, at least as far as the small pilot plant is concerned, works, even if with some problem, due to the presence of dust not very easy to remove. How long the catalyst lasts is a major question we didn't reply to, but, according to Haldor it seems that an annual water wash is enough in order to keep the reactivity almost constant. I am afraid I can go further in details because of confidentiality restrictions I have in this sort of communications.
By the end of the year another plant, beside the one in Germany, will be equipped with an SCR system by ELEX. This plant doesn't belong to ITC Group; it is located in Monselice, small village in Padova province (close to Venice). We all are curious to see the results.In my opinion this technology could be economically viable only if the life of catalyst is longer than 5-6 years and the cleaning problems are efficiently solved; for sure one of the main positive aspects against the more common practice of SNCR technology is that the ammonia injection point is not so delicate aspect. To be qualified as BAT this technology should be successfully applied at least on three kiln with different raw materials and production levels. Not so many information are available at the moment on the German plant and Lurgi says that it works but no information are distributed to avoid negative reaction from the clients. I am quite suspicious about this excuse. We will see.
Arrivederci
Giovanni Cinti

Da: Armendariz, Al
Inviato: martedì 18 aprile 2006 17.41
A: CINTI Giovanni
Oggetto: Cement Plants

Giovanni,

Ciao. My name is Alfredo Armendariz and I am a professor of engineering in the U.S. I read that you are helping to write the EIPPBC Cement and Lime BREF-Document. I am interested in the application of SCR technology (selective catalytic reduction) to reduce NOx emissions from cement plants. I received a note from the catalyst company Haldor Topsoe that they have tested SCR at a cement plant in Italy and that a full-scale system is in operation at a plant in Solnhofen, Germany.

Has Italcementi tested SCR at any of its facilities? If so, would you describe the tests as successful? Are you aware of any other full-scale or pilot-scale SCR installations planned or constructed in Italy or other places in Europe?

I thank you very much for your help.

Sincerely,

Alfredo Armendariz

Attachment 6 - Webpage from the Kirchdorfer Zementwerks in Austria

Awards

Investments

A commitment to people and environment

3rd EBS-Silo: Use of substitue fuels to reduce fossil fuels

A Commitment to people and environment

Kirchdorfer Zementwerk is situated a little less than 600 metres from the centre of the district capital town of Kirchdorf. While the local population is highly appreciative of the cement plant as a stable economic factor and reliable employer, the emissions the plant produces have always been a delicate issue of concern.
As factory owners have been aware of their responsibility in this regard, they began launching initiatives back in 1958 and have continued to do so – some of them spectacular indeed. The first electrical filter was installed in 1958 just one year after building rotary kiln I. The dust emissions which had been so dramatic were almost totally eliminated, allowing the people living nearby to literally breathe again for the first time.
The 2-MW heat recovery plant also proved of immediate benefit. Since 1983, it has been possible to recover hot water for the thermal plant of the local district-heating system from excess cooling air: This has turned out to be a happy marriage between ecology and economy which the cement plant is still proud of.

In the 1990's the plant concentrated its efforts on noise reduction. Today this goal has largely been achieved.
The cement plant drew particular attention from its peers when it undertook attempts to eliminate nitric oxide emissions using the SCR technique. It was a risk experts considered bound to fail. Following a comprehensive three-year trial run, the SCR technique was eventually proven to be the most appropriate for reducing nitric oxides in the cement industry. Besides causing a stir among experts, this pioneering achievement met with broad interest, including from international circles.
The number of environmental prizes awarded bears clear evidence of this fact.

These recognitions by themselves served as further encouragement to stay the course. In the future, Zementwerk Kirchdorf will focus on gradually substituting natural gas and coal, its primary fuels, by appropriate residual fractions. In that respect, the production of cement clinker at process temperatures exceeding 2000°C ensures complete thermal processing and material recycling, while making it possible to conserve natural resources and considerably reduce the greenhouse gas CO_2.

Management attaches priority to purchasing test, measuring and control equipment required for compliance with environmental standards and development of new techniques. Here, no costs or effort are spared. Despite the lack of relevant legislation concerning the measurement and monitoring of mercury emissions, the Zementwerk has routinely performed these activities for the past three years. In the future as in the past, both the local population and the public at large may rely on Kirchdorfer Zementwerk's philosophy of not leaving environmental protection concerns to mere chance.

Attachment 7 - Technical Paper Presented by Isabella Kossina of the Austrian UBA

Reduction of NO_x Emissions from Exhaust Gases of Cement Kilns by Selective Catalytic Reduction

Dipl.-Ing. Isabella Kossina

Proceedings of NOx Conference, Paris March 2001

Abstract

High NO_x emissions from cement industry due to high temperatures required for the clinker burning require efficient technical measures for their reduction. Several primary and secondary techniques can be applied . The highest reduction potential can be expected from SCR technology. The Environment Agency has conducted a study about applicability and costs for SCR in the cement industry, comparing crude gas and pure gas installations. Calculated on the basis of loan conditions for environmental investments, the specific costs of SCR are below 30 ATS or 2.3 Euro/tonne clinker [UBA 1998]. In comparison costs for one ton of clinker are about 60-65 Euro. In parallel with the European discussion on emission limit values for co-incineration of waste in industrial plants several pilot tests with SCR in cement plants have been carried out in Italy, Austria, Germany and Sweden. A pilot plant trial in Kirchdorf, Upper Austria, with a pilot catalyst for 3.500 m^3/h (relation to full scale is 1:20) in the crude gas has been operated for about 13.000 hours or about two years. The reduction of NO_x emissions in the clean gas to concentrations of below 200 mg/Nm^3 half hour average has been achieved continuously. Ammonia slip under normal working conditions has been limited to 5 mg/Nm^3 and operating conditions indicate a normal catalyst life time. The presentation is aimed to show results of successful pilot trials of SCR in the cement industry and to discuss them in the light of cost considerations and the current legal situation.

1. Introduction

Due to high temperatures required for the clinker burning process in the cement industry efficient technical measures for NO_x reduction have to applied. their reduction. The highest reduction potential out of several primary and secondary techniques can be expected from SCR technology that can be either installed in the crude gas or in the pure gas. SCR has been used successfully for more than a decade in caloric power plants, waste incineration plants and in the glass, wood, paper and steel industries. This long term experience of SCR installations allows trustworthy predictions for the transferability to other areas of application. There is no doubt about the functionality and reliability of low-dust SCR with a low dust content of a few mg/Nm^3. However, pure gas installations require a re-heating of the gas stream and imply a higher volume (after the E-Filter) to be treated. For that reason, cost considerations lead to pilot tests for crude gas SCR in cement plants that have been carried out in Italy, Austria, Germany and Sweden.

2. Pilot SCR in Kirchdorf

The pilot SCR plant in Kirchdorf, Upper Austria, has been running tests for almost two years from August 1996. The treated waste gas volume has been 3.500 m^3 per hour, what is a relation of 1:20. The SCR installation consists of an ammonia supply unit (including storage tanks for liquid ammonia), the SCR reactor with three catalyst layers, cleaning units and electric heaters (required in case of a plant stand still). It has been equipped with measuring and control devices. The catalyst has been placed in the crude gas behind the cyclone preheater and in front of the rolling mill. The mill utilises the heat of the gas for drying the raw meal.

The operating conditions for the catalyst were between 300 and 400°C. The dust load was about 80g/m^3 (based on 320°C and 3%O_2). The SO_2 concentrations in Kirchdorf are typically between 150 and 300 mg/Nm^3 (half hour average, 10 % O_2) behind the cyclone preheater, but below 30 mg/Nm^3 (half hour average, 10 % O_2) behind the raw meal mill. The SO_2 concentrations mentioned above did not cause problems in the catalyst unit under running conditions. When the installation was shut down, care had to be taken that the vapour contained in the waste gases did not condense in the catalyst. This because the catalyst activity may be reduced due to reactions with water-soluble substances in the airborne dust.

Operating results of the SCR trial catalyst installation

During several test cycles the reduction of nitogen oxides has been tested. Starting from raw gas concentrations of 640 mg/Nm^3 on average (10% O_2) NO_x reductions to 100 mg/Nm^3 and even below were measured. In a report on the trail plant the company stated that any variations in the NO_x emissions can be balanced out by the targeted dosage of the amount of ammonia , so that a value of 200 mg/Nm^3 (half hour average, 10 % O_2) can safely be maintained as an upper limit.

Under the conditions mentioned above the **ammonia slip** had been considerably below 5 mg/Nm^3 (half hour average, 10 % O_2). The NH_3 requirement for the reduction of NO_x is given by the stoechiometric ratio between NO_x and NH_3 and there were no loses of any significance. The test data showed that the ammonium already in the waste gases became effective in the NO_x reduction, reducing the ammonia amount required from the tanks. In the specific test situation in Kirchdorf the ammonium present in the waste gases caused a basic reduction of the nitrogen of about 100 mg/Nm^3. On the other hand, no enrichment of ammonium compounds in the dust could be proved through the use of the SCR trial catalyst installation.

One disadvantage of crude gas SCR installations is the huge dust load of the crude gas that requires the installation of **cleaning units**. The company stated that the original susceptibility to disruption of the cleaning units has been improved but still promises potential for optimisation. By regular cleaning of the individual catalyst layers, which had been done in 15 minute intervals the **pressure loss** could be held constant between 5 and 7 mbar.

The catalyst activity has been measured after 2.246 hours of operation (1.985 operation hours with ammonia) with 92 %. This result was within the expectations of the catalyst manufacturer which had assumed an over proportional drop of activity in the first phase of operation. The trial plant has been operated for 13.000 hours and the results of NOx reduction as well as the low ammonia slip showed that there was no unexpected drop in the catalyst activity.

After stopping the pilot trail the company predicted that it will be possible to reduce NO_x emissions from cement kilns by SCR technology, but raised concern about the cost.

3. Cost Estimations

SCR Plants can be operated either as pure gas or as crude gas units. Crude gas units are installed in front and clean gas units are installed behind a suitable waste gas cleaning system, that is in cement industry usually an electric filter. The Environment Agency has conducted a study about applicability and costs for SCR in the cement industry, comparing crude gas and pure gas installations.

For an estimation of the important cost for SCR-technology in preheater cement plants the following assumptions were made:

- Capacity of cement kiln: 300,000 t clinker/a
- NO_x-reduction from 1000 to 200 mg/Nm³ at 10%O_2
- Exhaust gas: 100,000 Nm³ for Low dust SCR
- Exhaust gas: 70,000 Nm³ for High dust SCR
- Depreciation period 15 a
- Interest rate 6% and 10%, calculated for both

Table I: Investment Costs and Operating Costs for High Dust and low dust SCR under above mentioned conditions.

	Low Dust SCR		**High Dust SCR**	
	basis for calculation	**ECU / t Clinker**	**basis for calculation**	**ECU / t Clinker**
NO_x-reduction	1000 -> 200 mg/Nm³		1000 -> 200 mg/Nm³	
Investment costs	ECU 2,906,892.--		ECU 2,398,186.--	
specific investment costs		**1[+)] / 1.5[++)]**		**0.8[+)] / 1.2[++)]**
Catalyst	operating period 10 a	0.13	operating period 3 a	0.5
Maintenance and Wear		0.3		0.2
Personal costs		0.04		0.04
treated gas stream	2.3 Nm³/kg Clinker		1.5 Nm³/kg Clinker	
pressure loss	25 mbar		8 mbar	
Costs for cleaning of catalyst			periodical cleaning	0.15
Energy for reheating	77.6 MJ/t Clinker	0.24	0	0
Elektrical Energy	3.3 kWh/t Clinker	0.23	0.9 kWh/t Clinker	0.06
NH_4OH, 25 %-ig	2.7 kg/t Clinker	0.34	2.7 kg/t Clinker	0.34
Assessed Total Cost	1000 -> 200 mg/Nm³	**2.2[#)] / 2.7[##])**	1000 -> 200 mg/Nm³	**2.1[#)] / 2.6[##]**
Assessed Total Cost[o)]	1000 -> 100 mg/Nm³	**2.7[#)] / 3.3[##]**	1000 -> 100 mg/Nm³	**2. [#)] / 3.1[##]**

[+)] Interest rate of 6%
[#)] invest costs –10%; per 6%
[++)] Internal calculated interest rate of companies 10%
[##)] invest costs +10%; per 10%
[o)] assessed total costs for 100 mgNO_x/m³ HMW (ca. + 20%)

Calculated on the basis of loan conditions for environmental investments, the specific costs of SCR are below 30 ATS or 2.3 Euro/tonne clinker [UBA 1998]. The result of the calculation was that savings due to lower gas flow and not required re-heating in a crude gas installation are nearly compensated by higher catalyst costs (due to higher erosion and bigger size because of larger pores) and equipment/energy for periodical clean up of the catalyst layers.

Running costs given by several providers in November 1998 were between 1.5 and 2.2 Euro per ton of clinker. Costs including annual repayment of investment costs were reported with 2.1 and 2.7 Euro/t clinker. In the European BAT Reference Document on Cement and Lime Manufacturig investment costs are quoted with 2.5 Million Euros by ÖKOPOL and with 3.4-4.5 Million Euro by CEMBUREAU. Operating costs were calculated between 0.2 and 0.4 by ÖKOPOL for a kiln capacity of 1000 to 5000 tons of clinker per day and initial NO_x concentrations between 1300 and 2000 mg/Nm³ .

4. Legal Context in Europe and Austria

The European BAT Reference Document has been adopted by the IEF in February 2000. This document is not legally binding, but has to be considered by the authorities when issuing a permit. The European Directive on the incineration of hazardous waste contains legally binding emission limit values for cement plants, depending on the type and amount of wastes used for fuel. Currently there is ongoing activity on European level to revise the directives on waste incineration, putting requirements for incineration of hazardous and non hazardous wastes together in one single directive. The table below shows the comparison of the BAT levels for cement plants with current Austrian legislation, where BGBl Nr. 32/1999 is the transposition of the European directive 94/67/EC on the incineration of hazardous waste into Austrian law.

Tabelle 2: Comparing BAT-Standards with legally binding ones

Emission	BAT Cement[1]	Ordinance regarding incineration of hazardous Wastes (BGBl. Nr. 32/1999)[2]	Ordinance regarding air emissions from cement plants (BGBl. Nr. 63/1993)[3]
Staub [5]	20-30 mg/Nm³	34 mg/Nm³	50 mg/Nm³
Sulphur oxides as SO_2	200-400 mg/Nm³	140 mg/Nm³ 400[4] mg/Nm³	200 mg/Nm³ 400[4] mg/Nm³
Nitrogen oxides as NO_2	200-500 mg/Nm³	500 mg/Nm³ new plant 800 mg/Nm³ existing plant[6]	500 mg/Nm³ new plant 1000 mg/Nm³ existing plant
Metals	No BAT levels	[8]Cd, Tl 0,05 mg/Nm³ [8]Hg 0,05 mg/Nm³ [8]Sb, As, Cr, Co, Ni, Cu, Pb, Mn, V, Sn in total 0,5 mg/Nm³	Cd, Th, Be 0,1 mg/Nm³ each , in total 0,2 mg/Nm³ As, Co, Ni, Pb in total 0,2 mg/Nm³
HCl	No BAT levels	10 mg/Nm³	No emission limit values
HF	No BAT levels	0,7 mg/Nm³	No emission limit values
VOC /TOC	No BAT levels	50 mg/Nm³ [9] 10 mg/Nm³ from 1.1.2002 [9]	No emission limit values
CO	No BAT levels		No emission limit values
PCDD/Fs	No BAT levels	0,1 ng/Nm³ [7]	No emission limit values

[1] daily average, dry gas, 0°C, 1013 mbar, 10%O_2
Rcommendation to consider BAT levles for HCl, HF, Metalle, VOC, PCDD/Fs when the document is revised (about 2005)

[2] dry gas, 0°C, 1013 mbar, 10% O_2, half hour and daily average (§10 Abs. 1)
emissions limit values for co-incineration of waste in cement plants (waste input up to 40vH of thermal energy output), except waste woods, waste oils (§ 21 AWG), sewage sludge, used tyres, wastes defined in Ö-Norm S 2100)
Emission limit values not to be applied on start up and shut down phase if no hazardous wastes are burnt during the start up and shut down phase

[3] for conventional fuels including used tyres and rubber; half hour average as basis for ELVs, dry gas, 0°C, 1013 mbar

[4] if sulphur containing raw materials are used

[5] Minimisation of fugitative emissions is BAT; (BGBl. Nr. 63/1993): permitting authority has to set up permit conditions for fugitative emissions depending on the local situation.

[6] existing installations have to comply with an emission limit value for nitrogen oxides of 500mg/Nm^3 by 1.1.2007; these emission limit value will be re-examined until 31.12.2003 by the Ministry of Environment having regard to the industry concerned

[7] as 2,3,7,8-TCDD-Äquivalent (I-TEF), 6-8-hour average

[8] for compounds and their combinations, quoted as compound

[9] 10 mg/Nm^3 may be exceeded, if it is proved that the higher levels are not caused by incineration of hazardous waste, 50 mg/Nm^3 have to be complied with anyway. TOC proven not to arise from any incineration but e.g. from raw material not to be considered.

5. Summary and Conclusions

The application of SCR in the cement industry in crude gas configuration has been tested in Austria, Italy, Sweden and Germany. Results of a successful pilot plant trails in Kirchdorf, Upper Austria with about 3-5 % of the raw gas from the cement kiln showed that SCR allows to achieve clean gas concentrations of 100-200 mg/Nm^3 . The ammonia slip has been considerably below 5 mg/Nm^3 (half hour average, 10 % O_2) and no enrichment of ammonium compounds in the dust has been proved through a trial of 13.000 hours. The loss of catalyst activity has been within the expected range. Cost estimations for full scale plants range from 3.5/4.5 Million Euro [Cemburau] to 2.5 million Euro [Ökopol]. Operating cost have been calculated between 0.2/0.4 [Ökopol] and 0.8 [UBA-Austria] Euro per ton of clinker. Running costs given by several providers in November 1998 are between 1.5 and 2.2 Euro/t clinker. Costs including annual repayment of investment costs were given with 2.1 and 2.7 Euro/t clinker. Calculated on the basis of loan conditions for environmental investments, the specific costs of SCR are below 30 ATS or 2.3 Euro/tonne clinker [UBA 1998]. In comparison costs for one ton of clinker are about 60-65 Euro. Co-incineration of wastes (hazardous and non hazardous) in cement kilns requires emission limit values to avoid a shift from waste incineration plants with stringent emission limits to industrial processes with less stringent emission limits resulting in an avoidable burden for the environment.

6. References

FEDERAL ENVIRONMENT AGENCY AUSTRIA (1997) Basic Criteria for BAT Cement

FEDERAL ENVIRONMENT AGENCY AUSTRIA (1998) BAT für Anlagen zur Zementherstellung

Draft BAT on Cement and Lime, EIPPC Bureau, 1999 and 2000

P.Bacher and HJ Gulas, Removing Nitrogen from Waste Gas of the Cement Industry by Selective Catalytic Reduction, Veitsch-Radex Rundschau 1/1998, S. 20-29

Personal Communication during visits of the Cement plant in Kirchdorf 1997 and 1999

ÖKOPOL Report 1998 Economic evaluation of NO_x abatement techniques in the European Cement Industry

CEMBURAU (1997) Best Available Techniques for the Cement Industry

Verordnung für Anlagen zur Zementerzeugung (BGBl. Nr. 63/1993)

VO über die Verbrennung gefährlicher Abfälle in gewerbl. Betriebsanlagen (BGBl. II Nr. 32/1999)

Attachment 8 - European Parliament Directive Establishing NOx Limits from Cement Kilns

DIRECTIVE 2000/76/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 4 December 2000 on the incineration of waste

THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION,

Having regard to the Treaty establishing the European Community, and in particular Article 175(1) thereof,

Having regard to the proposal from the Commission ([1]),

Having regard to the Opinion of the Economic and Social Committee ([2]),

Having regard to the Opinion of the Committee of the Regions ([3]),

Acting in accordance with the procedure laid down in Article 251 of the Treaty ([4]), and in the light of the joint text approved by the Conciliation Committee on 11 October 2000,

Whereas:

(1) The fifth Environment Action Programme: Towards sustainability — A European Community programme of policy and action in relation to the environment and sustainable development, supplemented by Decision No 2179/98/EC on its review ([5]), sets as an objective that critical loads and levels of certain pollutants such as nitrogen oxides (NO_x), sulphur dioxide (SO_2), heavy metals and dioxins should not be exceeded, while in terms of air quality the objective is that all people should be effectively protected against recognised health risks from air pollution. That Programme further sets as an objective a 90 % reduction of dioxin emissions of identified sources by 2005 (1985 level) and at least 70 % reduction from all pathways of cadmium (Cd), mercury (Hg) and lead (Pb) emissions in 1995.

(2) The Protocol on persistent organic pollutants signed by the Community within the framework of the United Nations Economic Commission for Europe (UN-ECE) Convention on long-range transboundary air pollution sets legally binding limit values for the emission of dioxins and furans of 0,1 ng/m; TE (Toxicity Equivalents) for installations burning more than 3 tonnes per hour of municipal solid waste, 0,5 ng/m; TE for installations burning more than 1 tonne per hour of medical waste, and 0,2 ng/m; TE for installations burning more than 1 tonne per hour of hazardous waste.

(3) The Protocol on Heavy Metals signed by the Community within the framework of the UN-ECE Convention on long-range transboundary air pollution sets legally binding limit values for the emission of particulate of 10 mg/m^3 for hazardous and medical waste incineration and for the emission of mercury of 0,05 mg/m^3 for hazardous waste incineration and 0,08 mg/m^3 for municipal waste incineration.

(4) The International Agency for Research on Cancer and the World Health Organisation indicate that some polycyclic aromatic hydrocarbons (PAHs) are carcinogenic. Therefore, Member States may set emission limit values for PAHs among other pollutants.

(5) In accordance with the principles of subsidiarity and proportionality as set out in Article 5 of the Treaty, there is a need to take action at the level of the Community. The precautionary principle provides the basis for further measures. This Directive confines itself to minimum requirements for incineration and co-incineration plants.

(6) Further, Article 174 provides that Community policy on the environment is to contribute to protecting human health.

(7) Therefore, a high level of environmental protection and human health protection requires the setting and maintaining of stringent operational conditions, technical requirements and emission limit values for plants incinerating or co-incinerating waste within the Community. The limit values set should prevent or limit as far as practicable negative effects on the environment and the resulting risks to human health.

(8) The Communication from the Commission on the review of the Community Strategy for waste management assigns prevention of waste the first priority, followed by reuse and recovery and finally by safe disposal of waste; in its Resolution of 24 February 1997 on a Community Strategy for waste management ([6]), the Council reiterated its conviction that waste prevention should be the first priority of any rational waste policy in relation to minimising waste production and the hazardous properties of waste.

([1]) OJ C 13, 17.1.1998, p. 6 and OJ C 372, 2.12.1998, p. 11.
([2]) OJ C 116, 28.4.1999, p. 40.
([3]) OJ C 198, 14.7.1999, p. 37.
([4]) Opinion of the European Parliament of 14 April 1999 (OJ C 219, 30.7.1999, p. 249), Council Common Position of 25 November 1999 (OJ C 25, 28.1.2000, p. 17) and Decision of the European Parliament of 15 March 2000 (not yet published in the Official Journal). Decision of the European Parliament of 16 November 2000 and Decision of the Council of 20 November 2000.
([5]) OJ C 138, 17.5.1993, p. 1 and OJ L 275, 10.10.1998, p. 1.
([6]) OJ C 76, 11.3.1997, p. 1.

ANNEX II

DETERMINATION OF AIR EMISSION LIMIT VALUES FOR THE CO-INCINERATION OF WASTE

The following formula (mixing rule) is to be applied whenever a specific total emission limit value 'C' has not been set out in a table in this Annex.

The limit value for each relevant pollutant and carbon monoxide in the exhaust gas resulting from the co-incineration of waste shall be calculated as follows:

$$\frac{V_{waste} \times C_{waste} + V_{proc} \times C_{proc}}{V_{waste} + V_{proc1}} = C$$

V_{waste}: exhaust gas volume resulting from the incineration of waste only determined from the waste with the lowest calorific value specified in the permit and standardised at the conditions given by this Directive.

If the resulting heat release from the incineration of hazardous waste amounts to less than 10 % of the total heat released in the plant, V_{waste} must be calculated from a (notional) quantity of waste that, being incinerated, would equal 10 % heat release, the total heat release being fixed.

C_{waste}: emission limit values set for incineration plants in Annex V for the relevant pollutants and carbon monoxide.

V_{proc}: exhaust gas volume resulting from the plant process including the combustion of the authorised fuels normally used in the plant (wastes excluded) determined on the basis of oxygen contents at which the emissions must be standardised as laid down in Community or national regulations. In the absence of regulations for this kind of plant, the real oxygen content in the exhaust gas without being thinned by addition of air unnecessary for the process must be used. The standardisation at the other conditions is given in this Directive.

C_{proc}: emission limit values as laid down in the tables of this annex for certain industrial sectors or in case of the absence of such a table or such values, emission limit values of the relevant pollutants and carbon monoxide in the flue gas of plants which comply with the national laws, regulations and administrative provisions for such plants while burning the normally authorised fuels (wastes excluded). In the absence of these measures the emission limit values laid down in the permit are used. In the absence of such permit values the real mass concentrations are used.

C: total emission limit values and oxygen content as laid down in the tables of this annex for certain industrial sectors and certain pollutants or in case of the absence of such a table or such values total emission limit values for CO and the relevant pollutants replacing the emission limit values as laid down in specific Annexes of this Directive. The total oxygen content to replace the oxygen content for the standardisation is calculated on the basis of the content above respecting the partial volumes.

Member States may lay down rules governing the exemptions provided for in this Annex.

II.1. **Special provisions for cement kilns co-incinerating waste**

Daily average values (for continuous measurements) Sample periods and other measurement requirements as in Article 7. All values in mg/m³ (Dioxins and furans ng/m³). Half-hourly average values shall only be needed in view of calculating the daily average values.

The results of the measurements made to verify compliance with the emission limit values shall be standardised at the following conditions: Temperature 273 K, pressure 101,3 kPa, 10 % oxygen, dry gas.

II.1.1. *C — total emission limit values*

Pollutant	C
Total dust	30
HCI	10
HF	1
NO_x for existing plants	800
NO_x for new plants	500 ([1])

Pollutant	C
Cd + Tl	0,05
Hg	0,05
Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V	0,5
Dioxins and furans	0,1

(1) For the implementation of the NO_x emission limit values, cement kilns which are in operation and have a permit in accordance with existing Community legislation and which start co-incinerating waste after the date mentioned in Article 20(3) are not to be regarded as new plants.

Until 1 January 2008, exemptions for NO_x may be authorised by the competent authorities for existing wet process cement kilns or cement kilns which burn less than three tonnes of waste per hour, provided that the permit foresees a total emission limit value for NO_x of not more than 1200 mg/m³.

Until 1 January 2008, exemptions for dust may be authorised by the competent authority for cement kilns which burn less than three tonnes of waste per hour, provided that the permit foresees a total emission limit value of not more than 50 mg/m³.

II.1.2. *C — total emission limit values for SO_2 and TOC*

Pollutant	C
SO_2	50
TOC	10

Exemptions may be authorised by the competent authority in cases where TOC and SO_2 do not result from the incineration of waste.

II.1.3. *Emission limit value for CO*

Emission limit values for CO can be set by the competent authority.

II.2. **Special provisions for combustion plants co-incinerating waste**

II.2.1. *Daily average values*

Without prejudice to Directive 88/609/EEC and in the case where, for large combustion plants, more stringent emission limit values are set according to future Community legislation, the latter shall replace, for the plants and pollutants concerned, the emission limit values as laid down in the following tables (C_{proc}). In that case, the following tables shall be adapted to these more stringent emission limit values in accordance with the procedure laid down in Article 17 without delay.

Half-hourly average values shall only be needed in view of calculating the daily average values.

C_{proc}:

C_{proc} for solid fuels expressed in mg/Nm³ (O_2 content 6 %):

Pollutants	< 50 MWth	50-100 MWth	100 to 300 MWth	> 300 MWth
SO_2				
general case		850	850 to 200 (linear decrease from 100 to 300 MWth)	200
indigenous fuels		or rate of desulphurisation ≥90 %	or rate of desulphurisation ≥92 %	or rate of desulphurisation ≥95 %
NO_x		400	300	200
Dust	50	50	30	30

Until 1 January 2007 and without prejudice to relevant Community legislation, the emission limit value for NO_x does not apply to plants only co-incinerating hazardous waste.

Attachment 9 - UNECE Survey of NOx Regulations in Europe

EXECUTIVE BODY FOR THE CONVENTION ON
LONG-RANGE TRANSBOUNDARY AIR POLLUTION

THE 2002 REVIEW ON STRATEGIES AND POLICIES FOR AIR POLLUTION ABATEMENT

THE 1988 PROTOCOL CONCERNING THE CONTROL OF EMISSIONS OF NITROGEN OXIDES OR THEIR TRANSBOUNDARY FLUXES

REPLIES TO QUESTIONS 2 – 8 OF THE 2002 QUESTIONNAIRE

Prepared by the secretariat from submissions by the Parties

Introduction

1. This document is the basis for part of the 2002 review of policies and strategies requested by the Executive Body at its nineteenth session in December 2001. It provides the answers as received from Parties in response to the 2002 questionnaire that was made available to Parties between February and May 2002.

2. The document is intended as a reference for the Draft Summary of the 2002 Review of Strategies and Policies for Air Pollution Abatement (EB.AIR/2002/1 and EB.AIR/2002/1/Add.1), and will be provided to the Executive Body, the Implementation Committee and will be made available through the Convention's web site. Answers are supplied in English below, and will be made available in the original languages in which they were submitted when this is not English.

3. This section summarizes the answers received to questions 2 to 8 of the questionnaire. Replies to one or all of the questions in this section were received by 28 Parties to the Convention. Responses to the questions were mandatory for the 28 Parties to the Protocols: Austria, Belarus, *Belgium*, Bulgaria, Canada, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Liechtenstein, *Luxembourg*, Netherlands, Norway, Russian Federation, Slovakia, Spain, Sweden, Switzerland, *Ukraine*, United Kingdom, United States and *European Community*. However, those Parties in italics failed to provide a response to the Secretariat. In addition responses were received from 4 other Parties to the Convention: Croatia, Monaco, Poland, Portugal and Slovenia (identified with * below).

Question 2: **Provide information, as required by article 8, paragraph 1, on national strategies, policies and programmes developed in accordance with article 7 that specifically address the control and reduction of emissions of nitrogen oxides or their transboundary fluxes, including progress achieved under them and any changes made to them.**

Austria. According to the Industrial Code and the Clean Air Act for Steam Boilers, a license for each new or modified installation is required. The determination of emission limit values and/or measures according to best available technology (BAT) is carried out in the licensing procedure; these provisions were introduced in the 1980s. For several categories of (new and existing) stationary emission sources, explicit emission limit values and BAT requirements have been set by ordinance (see Q.s 3-5). After early introduction of strict national emission standards for cars in the 1980s, emission standards for vehicles have been improved and extended

Power generation	Fuel type	mg/m3(n)	
gas turbines	Oil 67		
gas turbines	Gas 72		
Power Stations			
50... 300 MW	Solid 428		
>300 MW	Solid 143		
50... 100 MW	Liquid 418		
100...3000 MW	Liquid 278		
>300 MW	Liquid 174		

1/ The statistical treatment can be a percentile (e.g. 95 percentile), a daily average, a monthly average, etc.
2/ Use the technical annex to the Nitrogen Oxides Protocol relating to best available technologies (BAT) as a reference.

France. Categories of stationary sources account for less than 10 per cent of total national annual emissions of NOx and do not qualify as major stationary source categories under the Protocol. The regulations applicable to new stationary sources give limit values for NOx. These regulations concern: large combustion plants; decree 27/06/90; decree of 02/02/98; decree regarding small combustion plants (2-20 MWth) of 25/07/97; decree regarding turbines and motors more than 20 MW from 11/08/99; decree regarding glassworks of 14/05/93; decree regarding cement works of 03/05/93; Decree regarding paper manufacturing of 03/04/00. France provided a table of limit values adopted 02/02/98. National emission standards by source category (for NOx) including units and anti-pollution measures are covered by the decree of 02/02/98. If the hourly flux is greater than >25kg/h, existing refineries and extensions; Agglomeration of minerals; fabrication of nitric acid; VOCs by oxidation 500 mg/m3 daily average flux, equivalent to 500 mg/m3, applicable as of 01/01/2000; 750 mg/m31.3 kg/t HNO3100 mg/m3; Permanent autosurveillance: ELV's are respected if the number of observations surpassing the ELV is less than or equal to 10 per cent of the total number of observations in one daily period and the observations last around a half-hour and if no observation surpasses the doubling of the ELV. Measures on instantaneous sampling: the ELV are respected if no result surpasses the doubling of the ELV. The limit values are expressed under normal conditions and temperatures and pressure from dry natural gas on the units of production of nitric acid (except for dry-cleaning plants). Generally the standards for NO_2 are 3 per cent for liquid and gaseous combustibles; 6 per cent for combustible mineral solids and 11 per cent for biomass and steam generators; 15 per cent for turbines and 5 per cent for motors.

Germany. Germany has national NOx emission standards for heat and power generation (according to the type of fuel) and industrial processes and applies control technologies as follows:

Source category	National emission standards	Unit & statistical treatment	Pollution control measures applied
Boilers	depending on type of plant and fuel	mgNO2/m3, daily average, related oxygen content	-
1-50 MW	solid 300-500, liquid 250-450, natural gas 200	7-11%, 3%, 3%	primary measures

> 50-300 MW	solid 400, liquid 300, natural gas 200	5-7%, 3%, 3%	primary measures, SNCR, SCR
> 300 MW	solid 200, liquid 150, natural gas 100	5-7%, 3%, 3%	primary measures, SNCR, SCR
Gas turbines	100-350 (depending on fuel and size)	15%	primary measures, water-/steam-injection
Stationary engines	-	-	-
compression ignition (diesel engines):	500-1000, (depending on fuel)	5%	water injection, SCR
spark ignition (Otto engines):	500-800, (depending on type)	5%	primary measures
Industrial processes (selection)	-	-	-
Nitric acid plants	450	-	SCR, SNCR
Fertilizers	500	-	-
Pulp mills: 50-100 MW /> 300 MW	300/150	3%	primary measures, optimised combustion techniques
Iron and steel	400-500	-	low NOx-burner
Cement	500	-	primary measures, staged combustion, SNCR, SCR
Glass	500	-	primary measures, 3R, SNCR, SCR

Greece. All large combustion plants are existing installation, conforming to Directive 88/609/CEE. Directive 96/61/CE regarding the prevention and reduction of pollution applies equally to all new large combustion plants as of October 2000.

Hungary Hungary gives a table of national emissions standards for power plants and waste incinerators.

Ireland Q.3 New stationary sources*

Source Category	National emission standards	Units & statistical treatment	Pollution control measures applied
Major new stationary source *until November 2002*[1]		Emission limit values expressed as mg/Nm^3 as NO_2	
Solid fuel 50 – 500 MW_{th} >500MW_{th} From 1 January 2016	600 500	None of the calendar monthly mean values exceeds the ELVs and 95% of all 48 hourly mean	Generally measures e.g. low NO_x burners staged burning

[1] Large combustion plant with a rate thermal input of 50 MW or more – EU directive 2001/80/EC

Attachment 10 - Technical Paper Presented by Alvaro Linero at AWMA 2005 Annual Conference

SNCR NO_X at U.S. Cement Plants. Is SCR Close Behind?

Paper # 638

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ABSTRACT

Many cement kilns recently constructed in the United States depend on staged combustion in the calciner (SCC) for nitrogen oxides (NO_X) reduction. At the same time dozens of kilns have been retrofitted in Europe with selective non-catalytic reduction (SNCR) in addition to or in lieu of SCC. After great resistance to SNCR, a number of American operators have recently yielded and now propose SNCR. This paper examines the reasons for the shift. The theory, practice, and some unexpected problems are discussed with respect to SCC. Variations of SCC are compared and contrasted. The combination of SNCR and SCC is compared with SNCR alone. Finally the specter of selective catalytic reduction (SCR), which has been commercially demonstrated at one plant in Europe, is discussed, because it may be a viable alternative to SNCR when sulfur or ammonia are present in the raw materials. Some synergistic and counteractive effects of NO_X control on other pollutants are reviewed and some possibilities for countering or exploiting these negative (counteractive) or positive synergies are suggested.

INTRODUCTION

The requirements for very high temperatures and oxidizing conditions make cement manufacturing (pyroprocessing) an inherently large generator of NO_X per unit of clinker produced. Fortunately the typical preheater/calciner (PH/C) kiln design includes some features that are compatible with lower NO_X emissions. One is indirect firing, whereby the amount of air introduced through the primary burner into the kiln sintering zone is minimized. Another is the splitting of fuel between the very high temperature region near the kiln outlet and the more moderate temperatures that prevail in the calciner.

New projects in the United States incorporate combustion innovations in the calciner that destroy NO_X produced in the kiln and minimize formation of additional NO_X. All involve refinements of staged combustion principles and fall under the category of SCC. Operational problems ultimately limit the ability of SCC to achieve low emissions.

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

Meanwhile large projects in Missouri and New York were delayed in part due to the long time that it took applicants to propose SNCR and negotiate the related permit conditions to meet the BACT NO_X emission limits required by the state environmental agencies.

Recently, three applications for new cement kilns were received in Florida. All propose SNCR to meet NO_X emission limits lower than any project outside of the state. Two of the companies conducted tests on similar existing kilns to insure that SNCR can be implemented at their facilities without operational problems or high opacity. One permanently installed SNCR on its existing kiln in March 2005 even though it can meet its NO_X limit by SCC.

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

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

The interaction of NO_X control with internal (fuel) and external (raw materials) sulfur cycles must not be underestimated. Therefore reference will be made as necessary to sulfur cycles and transformations, control of SO_2, and to a lesser extent, carbon monoxide (CO) and total hydrocarbons (THC).

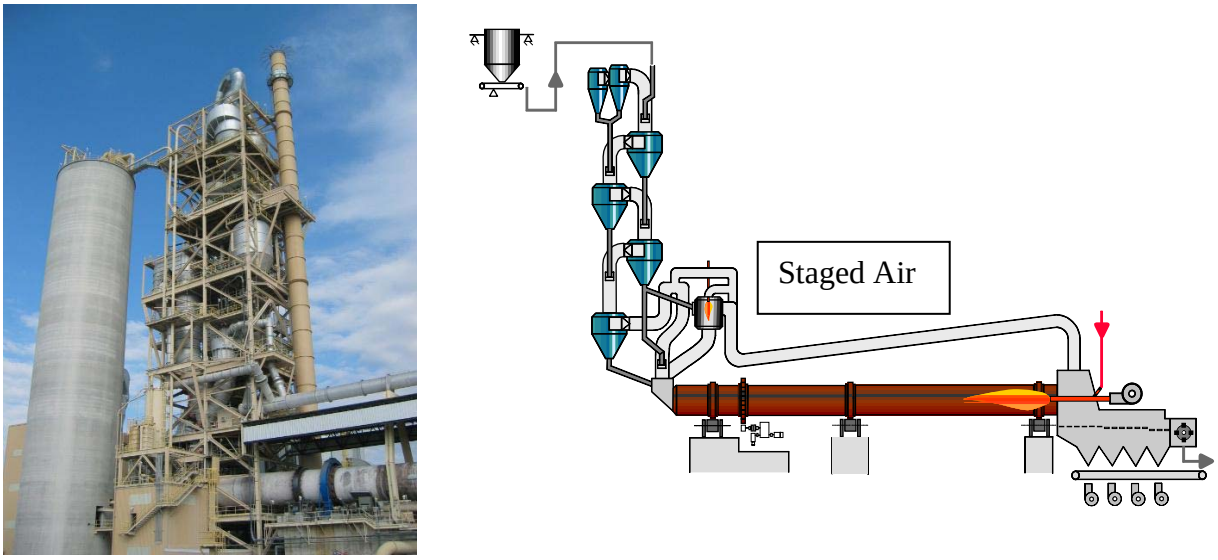
At a time of burgeoning global demand for cement and shortages in some key U.S. markets, it is important to disseminate the status of technology so that regulatory agencies and applicants are "on the same page". This will expedite permitting, protect the environment, and insure that a healthy cement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

STAGED COMBUSTION IN THE CALCINER (SCC)

Examples of SCC

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

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



The design shown in the diagram is an example of *staged air* combustion practiced at Suwannee American Cement (SAC) in Branford, Florida. The calciner burner is vertically oriented in a separate combustion chamber of the type typically used for difficult to burn fuels such as petroleum coke. In this case it is used to burn calciner fuel (coal) in a reducing atmosphere to destroy NO_X in the kiln exhaust as described below. The SAC kiln was supplied by Polysius. A similar calciner was promoted by Technip CLE as the Minox Low NO_X calciner.

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

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

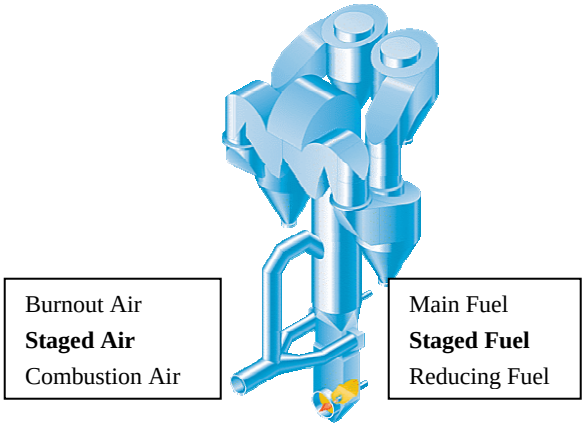
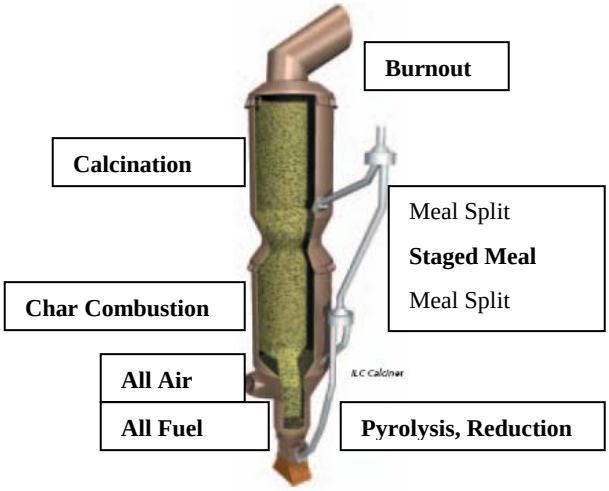


Figure 3 shows the Low NO_X in line calciner at Titan America Pennsuco Kiln No. 5 in Medley, Florida. All fuel is fired in a reducing atmosphere near the kiln inlet and then all tertiary air is supplied in the lower part of the calciner. For lack of a better term, this design by F.L. Smidth will be referred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

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



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

NO_X Reduction by SCC

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

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

$$CaCO_3 \rightarrow CaO + CO_2$$

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

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

$$CHi^* + NO \rightarrow HCN + ...$$

Where:

$i = 1, 2, 3$

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

$$NHi^* + NO \rightarrow N_2 + ...$$

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

Other reactions involving carbon monoxide (CO) or hydrogen (H_2) are also catalytically driven and destroy NO_X in this reducing atmosphere. In the subsequent burning of soot and char, the NO_X reducing reactions proceed much more slowly and some of the remaining fuel nitrogen can form additional NO_X.

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

Thus it is not enough to specify SCC (or MSC, or Low NO_X Calciner). What is actually sought is SCC with high temperature raw meal catalysis in a reducing atmosphere. Therefore SCC for NO_X reduction must specify or qualify the conditions under which it will operate.

Interactions Between SCC and the Internal Sulfur Cycle

Sulfur dioxide (SO_2) formed by burning fuel in the main kiln burner can be efficiently scrubbed out by reactions with alkali species (Na and K) or with CaO in the kiln to form stable sulfate compounds that are incorporated into the clinker.

Equation 4. Kiln SO_2 reaching the calciner and all SO_2 from burning fuel in the calciner is completely scrubbed out at the temperatures prevailing in the calciner as follows: [4]

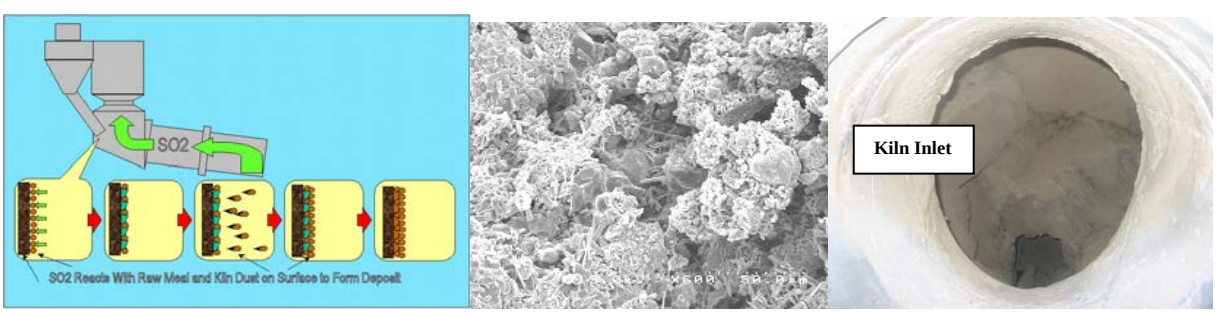
$$CaO + SO_2 \leftrightarrow CaSO_3 \text{ or } CaO + SO_2 + 0.5O_2 \leftrightarrow CaSO_4$$

At 1,045°C, the formation and decomposition reactions for $CaSO_4$ are at equilibrium at normal excess oxygen levels. At higher temperatures, $CaSO_4$ will tend to decompose. As raw materials move through the high temperature regime in the kiln, the $CaSO_4$ can break down per the above reaction releasing the SO_2 or it can fuse/react with the alkali sulfates and other species to form stable compounds that depart with the clinker.

The concentrations and flows of SO_2 build up within the internal cycle of the kiln and calciner. One of the key design and operational objectives is to manage this cycle so that solid sulfur containing compounds do not form coatings and blockages. According to one author, "NO_X abatement rates of up to 50 percent can generally be achieved with staged combustion. However the processes are critical with high circulating sulfur and alkali systems in conjunction with the reducing mode of operation and the operation can be seriously affected by the formation of coating".[5]

If there is already insufficient alkali to balance the sulfur in the system, the recirculating flow of SO_2 is greater. The diagram and the microscopic photo in the following figure are from a Taiyeho Cement presentation and depict the formation of coating that might result under such circumstances even if reducing conditions are not encountered in the calciner.[6] The second photo is from an actual kiln inlet at a cement plant in Florida. Reducing conditions do not necessarily increase SO_2 emissions but can create considerable process problems due to sulfate deposits at the kiln inlet, in the riser duct, and cyclones.[7] Creating a higher temperature near the kiln inlet to promote NO_X reduction would tend to release SO_2 per the above reactions or could cause sintering of the coatings. Also it could cause or aggravate coating tendencies in the riser and lower cyclones.

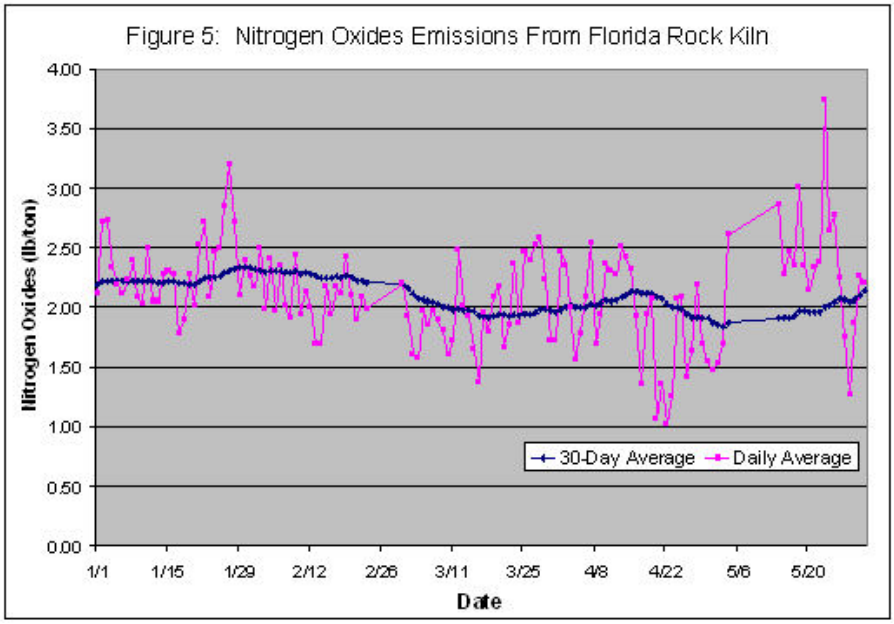
Figure 4. Coating Formation near Kiln Inlet and Microscope Photo. Nearly Choked Kiln Inlet.



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

NO_X Reduction by SCC in Florida Kilns

The FRI kiln has a BACT NO_X limit of 2.45 lb/ton on a 30-day rolling average basis. Data from the first half of 2004 are summarized in Figure 5. Typical emissions from the FRI kiln are between 1.5 and 2.5 lb/ton, when tires are burned near the kiln inlet. Assuming "baseline" emissions of 3.5 lb/ton, the NO_X reduction efficiency by SCC in a reducing atmosphere varies from 30 to 60 percent. According to FRI, the higher values near 3 lb/ton are observed on days when tires are not available. During such times, reducing conditions are maintained in the calciner, but a high temperature reducing zone near the kiln inlet is not achieved. The resulting reductions are less, all other factors being equal.



SAC has a BACT NO_X emission limit of 2.9 lb/ton on a 24-hour rolling average basis. In contrast to the FRI operation, the kiln at SAC does not fire fuel at the kiln inlet although a burner was provided for that purpose. Therefore the version of SCC at SAC achieves a reducing atmosphere in the calciner, but not a high temperature reducing zone near the kiln inlet. Under this scenario, typical emissions varied between 2.2 and 2.6 lb/ton. Assuming a baseline of 3.5 lb/ton, this version of SCC achieves reductions of approximately 25 to 40 percent.

The permit issued to SAC provided the Florida Department of Environmental Protection (DEP) with the ability to further revise the NO_X limit downward. SAC agreed to temporarily install and use the supplied kiln inlet burner with the fuel supply system to determine if creation of a high temperature reducing atmosphere could be achieved without unduly aggravating the coating tendencies. The principle of operation when using the two burners in the calciner is as follows:

"NO_X from the sintering zone of the kiln is reduced by means of a burner in the kiln inlet. The fuel is injected against the direction of flow of the kiln gases and is pyrolysed in its gas phase. In the reducing atmosphere that is formed, the NO_X is converted into nitrogen. In order to prevent new NO_X from being generated in the calciner, the calcining fuel also has to be burned under reducing conditions. This is achieved by staggered introduction of the combustion air, so that the fuel is first burnt under reducing conditions and then under oxidizing conditions. Corresponding staggering of the raw meal also favorably influences the temperature in the reducing zone".[8]

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

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

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

Parameter	**Baseline** (Before)	**KIB** (6/9/04)	**KIB** (6/10/04)	**Baseline** (between)	**KIB** (6/15/04)
KIB Coal, ton/hr	0	1.12	1.16	0	1.28
Inlet NO_X, ppm	253	159	263	229	280
Stack NO_X, lb/ton	2.19	1.61	2.22	2.13	2.17
Inlet CO, ppm	292	5994	964	383	485
ID Fan CO, ppm	219	683	122	135	457
Clinker, tph	99	100	105	105	105
Raw Meal Feed, tph	177	183	184	172	180
Kiln feed, tph	152	155	162	161	161
Stage 1 exit T, °C	857	855	867	867	872
Stage 4 exit P, in. H_2O	15.0	16.5	17.8	16.8	16.5
Stack THC, ppm	23.9	16.8	9.3	14.2	14.1

Use of the kiln inlet burner (KIB) resulted in decreased NO_X concentration at the kiln inlet and decreased NO_X emissions at the stack <u>for the short term</u> as well as increased CO concentrations at the kiln inlet and the induced draft fan. The pressure drop across the preheater increased but clinker quality was not affected. The KIB did not further affect clinker production rate, although subsequent tests show that production was already adversely affected by operating the calciner in a reducing atmosphere.

In the medium term, use of the KIB did not appear to reduce NO_X but the pressure drop remained high and clinker quality was affected. The Stage 4 (top stages) exit pressure (and other stages as well) stayed relatively high, indicative of formation of partial blockage at the orifice. A high tonnage of coal with KIB operation showed an increase of Stage 1 (bottom stage) material temperature, probably indicative of coal burning in Stage 1 (due in part to very small kiln inlet).

The temporary reduction of NO_X from 2.19 to 1.61 lb/ton verifies the capability of SCC in a high temperature reducing atmosphere to minimize NO_X emissions. The inability to maintain the low emissions and the exacerbation of operational problems verifies the potential adverse effects when operating a high temperature reducing atmosphere at the kiln inlet. Obviously this conclusion is applicable for the combination of the raw materials and fuel used at this location.

SAC advised, "Of the nine MSC systems installed in the U.S., none is using the kiln inlet burner to achieve reducing conditions. Most facilities are able to meet their NO_X limits (greater than those at SAC) without the use of this kiln inlet burner, possibly by creating reducing conditions in the same manner achieved by SAC".[10]

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

It is conceivable that process, fuel, and raw material adjustments would permit the SAC plant to use the KIB continuously to reduce NO_X emissions. For example, use of expensive natural gas in the calciner and kiln (where it would produce even more NO_X than coal), would break the internal sulfur cycle and reduce the buildup problem. As discussed in the next section, SAC chose to test SNCR to determine if low emissions could be achieved while minimizing the operational problems that occur even without operating the KIB.

Compliance tests at the new 250 ton per hour Titan America kiln in Medley, Florida indicated NO_X and CO emissions at 2.0 and 0.5 lb/ton, respectively.[11] Titan employs fewer air cannon and does not experience the level of coating problems and stoppages reported by SAC or FRI. The calciner design is shown in Figure 3. It depends on the introduction of all calciner fuel into a reducing atmosphere near the bottom of the calciner (not actually at the kiln inlet), followed by introduction of all tertiary air at a single level just above the fuel introduction point.

The manufacturer describes the design as follows: "The Low NO_X ILC design is based on dividing the meal from the second lowest preheater cyclone to the kiln riser and the calciner, which are separated by an expanded riser duct that forms a reducing NO_X zone. The calcining chamber is built (at least partially) into the kiln riser. 100 percent of the fuel is fired to the kiln riser duct. As a result, it is possible to obtain both reducing conditions and a high temperature zone in one simple system (without multiple firing points) for the lowest possible NO_X emissions.

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

It appears that all calciner fuel participates in the creation of the high temperature reducing condition. The maximum amount of kiln exhaust gas is acted upon in the shortest amount of time and at the highest possible temperature. This rapidly drives the catalytic NO_X destruction reactions and then quenches the atmosphere with lower temperature tertiary air before the NO_X forming reactions predominate. In the subsequent oxidizing atmosphere there are competing NO_X formation and destruction reactions. The duration of conditions in the calciner favorable to formation of coating (e.g. SO_2 evolution) is minimized.

The Titan America experience shows that low NO_X and CO can be attained by SCC with a high temperature reducing atmosphere without excessive coating formation. Titan applied to increase annual hours of operation and limit NO_X emissions to 2.1 lb/ton clinker on a 30-day basis.[13]

SELECTIVE NON-CATALYTIC REDUCTION (SNCR)

There are numerous references on the efficacy of SNCR for the control of NO_X. The technology has been widely practiced in the power industry, at waste-to-energy facilities and at numerous miscellaneous applications.

It suffices to state that ammonia (NH_3) is injected at a point in the process characterized by a suitable temperature window between 850 and 1050 °C depending on residence time, turbulence, oxygen content, and a number of other factors specific to the given gas stream. SNCR destroys NO_X by a two-step process as follows:

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

$$NH_3 + OH^* \rightarrow NH_2{}^* + H_2O$$

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

$$NH_2{}^* + NO \rightarrow N_2 + H_2O$$

Equation 7. The two steps are typically expressed as a single "global reaction".

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

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

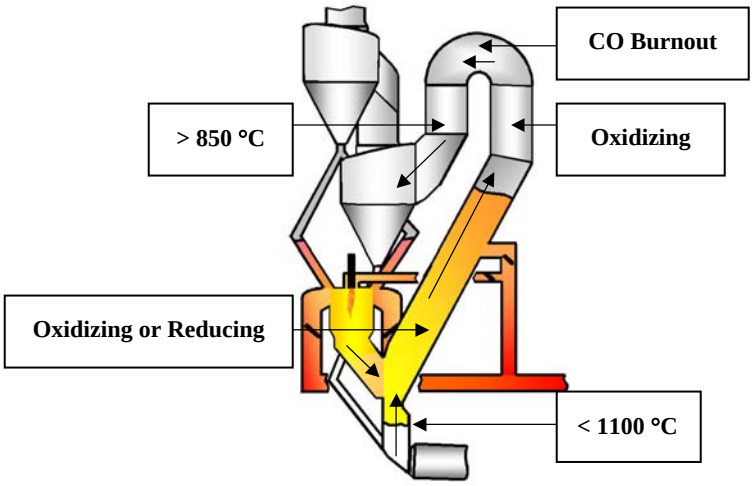
Equation 8. In a reducing atmosphere, CO competes with ammonia for available OH radicals

$$CO + OH^* \rightarrow CO_2 + H^*$$

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

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

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



Examples of SNCR

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

As of 2000, there were at least 18 kilns in Europe that had installed SNCR.[15] Most of these SNCR installations were designed and operated for NO_X reduction rates of 10 – 50 percent with NH_3 /NO_2 molar ratios of 0.5-0.9 and emissions of 500-800 mg NO_X/m^3 (~2.3 to 3.6 lb/ton). By contrast with the other European countries, the Swedish EPA limits NO_X emissions from *existing* cement plants to 200 mg/m^3 (~0.9 lb/ton).

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

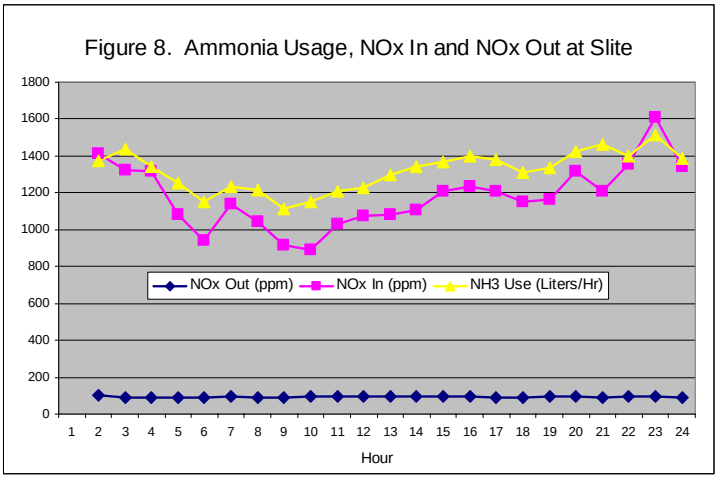
"Petro Miljö erected the unit during the autumn of 1996. The unit consists of a tank for storing 25 percent ammonia solution, pumping gear for ammonia and water, mixing modules to achieve the correct ammonia solution, and injection equipment for atomising and distributing the agent into the gas flow.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

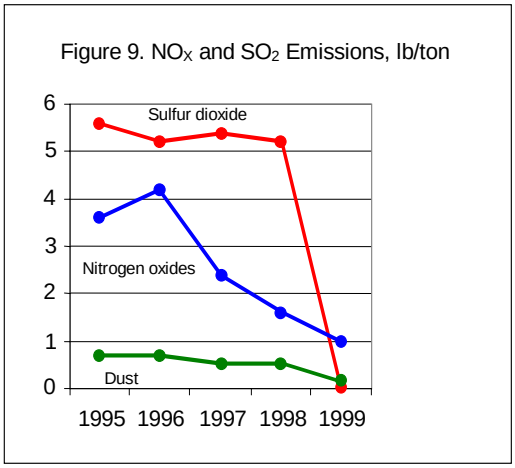
"The unit was designed to achieve at least 80 % reduction of NO_X. The investment cost was about 1.1 million euros (0.55 million euros for the SNCR installation and another 0.55 million euros for the ammonia water storage) and the operating cost is about 0.55 euros/tonne of clinker. The total cost (investment + operating costs) is less than 0.6 euros/tonne of clinker." The kiln has a production capacity of 5,800 metric tons per day. The conclusions are:

"After more than three years of operation, the initial NO_X emission level of approximately 1200 mg/m^3 has been reduced to approximately 200 mg/m^3 with a molar ratio of 1.1-1.2. At an NH_3/NO molar ratio of around 1.0 the NO_X level has been reduced by about 80 percent.

"The results show that it is possible to reach a degree of purification of over 80% without having any slip of ammonia or higher levels of N_2O. No increase in CO emissions have been measured and no traces of any NH_3 have been found in the cement".

Based on Figure 8, it takes 1,200 to 1,400 liters per hour (L/hr) of 25 percent ammonia to reduce NO_X from 1,200 to 200 mg/m^3 (~0.9 lb/ton, 100 ppm). Figure 9 shows the annual improvement in NO_X and SO_2.





One important point is that the reduction in NO_X occurred concurrently with reductions in previously high SO_2 (over 5 lb/ton) by the installation of a scrubber. Without the scrubber and at the target NO_X removal efficiencies, there would be a potential for a visible detached plume because of the high NH_3/NO molar ratio and the high SO_2 emissions (when not controlled).

According to the Gotland Environmental Director, "the Slite plant has a big stake in showing the highest possible reduction because there is a discussion going on in the Environmental Court if they should decide that the plant has to install SCR technology to further reduce the emission of NO_X". The findings are corroborated in Scancem's 1998 Environmental Report as follows:

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

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

"The base emissions without the addition of NH_3 were scattered very widely between 400 and 800 mg/m³ (~1.8 and 3.6 lb/ton). The emission values were lowered from the initial value of 500 mg/m³ (~2.3 lb/ton) in steps to 250 mg/m³ (~1.2 lb/ton) by adding ammonia, which corresponded to abatement rates of 38 to 68 percent". Examination of the time series shows that emissions were further reduced to less than 100 mg/m^3 (~0.5 lb/ton) by using 250 L/hr of 25 percent ammonia solution but at a high NH_3/NO ratio and slip potential. Presumably this occurred on the smallest (1,900 metric TPD) kiln. The greatest NO_X reduction occurred when ammonia was injected after the final air stage and after full mixing in a subsequent deflection chamber. Introduction of ammonia prior to the chamber or in the reducing atmosphere was less effective.

Interactions Between SNCR and the External Cycle

Sulfide or elemental sulfur contained in raw materials may be "roasted" or oxidized to SO_2 in areas of the pyroprocessing system where sufficient oxygen is present and the material temperature is in the range of 300-600°C.[19,20] Uncontrolled SO_2 emissions are only about 0.10 lb/ton and less than 100 tons per year at the Florida PH/C kilns because there are only minute amounts of sulfur in most of the available limestone. Uncontrolled SO_2 emissions can be as much as two orders of magnitude greater where pyritic sulfur is present in the raw materials. Unreacted ammonia from the SNCR process or from raw materials reacts with SO_2 and SO_3 at temperatures prevalent in the upper preheater, pollution control equipment, and outside the stack.

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

$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4$$

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

$$2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4$$

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

$$NH_3 + SO_2 + H_2O \rightarrow NH_4HSO_3$$

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

If a plant has a persistent detached plume that is attributable to $(NH_4)_2SO_4$ it is necessary to get rid of <u>one</u> of the two reactants that ultimately form $(NH_4)_2SO_4$ - either the NH_3 or the SO_2.[22] The obvious method of avoiding the feared plumes when using SNCR is by minimizing ammonia use when SO_2 emissions are likely.

Operating the raw mill promotes SO_2 removal by limestone scrubbing under humid conditions, due in part to freshly generated limestone surface produced by grinding. Some of the SO_2 generated in the top preheater stages is also scrubbed out by small amounts of free CaO that are carried back from hotter zones by combustion flue gases.

Another SO_2 removal technique is to extend the inherent self-scrubbing (by CaO) that occurs in the calciner to the upper sections of the preheater where pyrite-derived SO_2 is evolved. This involves conveyance of lime from the calciner (by differential pressure) to the upper stages of the preheater. The system consists of a cyclone and some ductwork and involves no moving parts.[23]

A very fine suspension of slaked lime can be introduced into the gas-conditioning tower to remove SO_2, particularly when the raw mill does not operate. The droplets react, dry, and are captured by the particulate control equipment where excess lime (from the dried droplets) continues to remove remaining SO_2.[24]

If the three SO_2 measures are insufficient to achieve permitted SO_2 requirements, then conventional wet or dry scrubbers can be considered. The TXI Midlothian scrubber system was estimated to cost $13,000,000. Emissions of SO_2 from the new kiln were permitted at over 1,300 tons per year and 1.33 lb/ton of clinker.[25] It is not certain whether SO_2 emissions are actually as high as permitted. If they are that high and an SNCR system were installed at such a plant for additional NO_X control, then it might be necessary to limit ammonia slip or to further enhance SO_2 removal to avoid a detached plume.

SNCR Experience in Florida Kilns

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

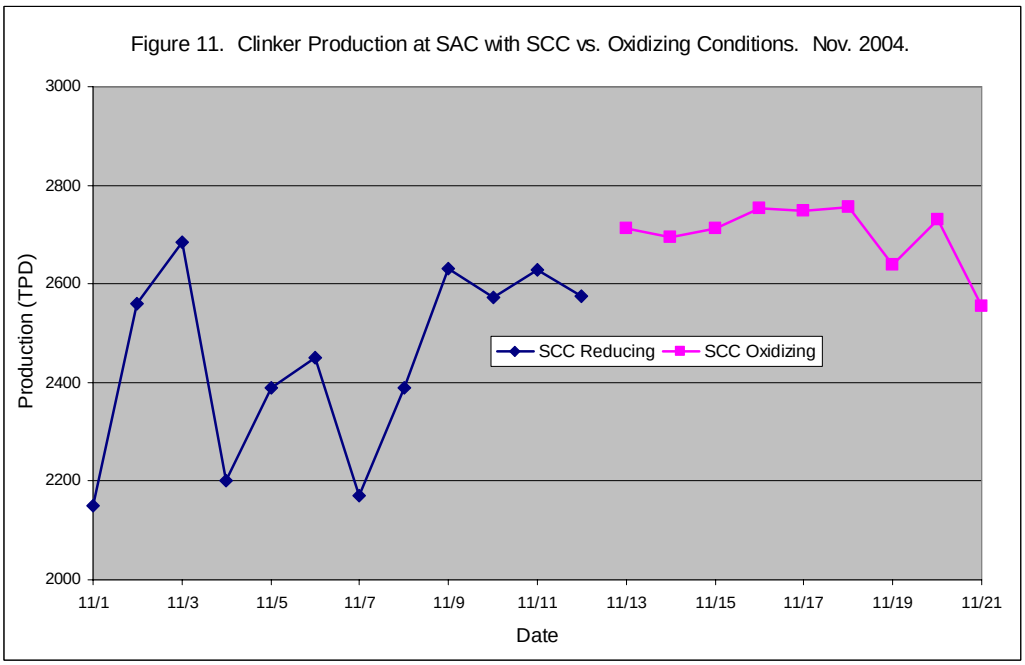
Figure 10. Aqueous Ammonia Supply Truck, Compressed Air, One of Four Ports, An Injector

Not shown is the metering system or the additional continuous emission monitoring equipment. Referring back to Figure 6, four ports were installed after the bend in the duct work following the top air injection branch for tertiary air. This setup is relatively simple. It is noteworthy that it suffices for treatment of all of the exhaust gas from the calciner and not just a slip stream. In fact at times a single injector sufficed for adequate NO_X control.

One would expect the NO_X at the stack outlet to be the parameter of greatest interest. Those results were actually expected by the author per the discussions of previous trials and commercial installations. In fact the most interesting parameter is clinker production.

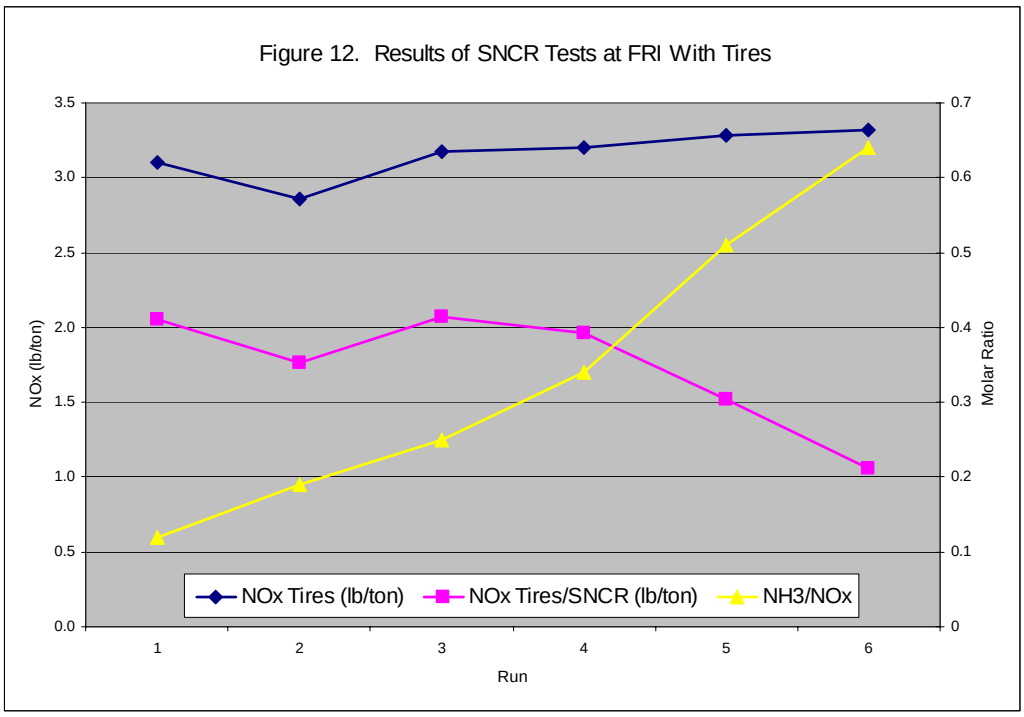
Figure 11 is a graph of the clinker production time series. The series on the left hand side reflects operation of the kiln under SCC with a reducing atmosphere. Ammonia injection began on November 8 with a less aggressive reducing atmosphere. The one on the right hand side reflects operation of SCC with an oxidizing atmosphere. As anticipated, operating the calciner in an oxidizing atmosphere rather than a reducing atmosphere caused less coating formation, plugging and stoppages. Daily production was sustained at a higher level by operating the calciner in a less reducing atmosphere and then at an even higher level in an oxidizing atmosphere. While not unexpected, it is a real eye-opener and incentive to find means other than SCC with a reducing atmosphere to control NO_X at this kiln.

The permitted emission rates were easily achieved by SNCR whether or not the calciner was operated in an oxidizing or reducing atmosphere. SAC received a permit to: permanently increase production from 105 to 120 tons of clinker per hour; meet an additional NO_X limit of 2.4 lb/ton on a 30-day basis; keep the daily 2.9 lb/ton limit; install an SNCR system; and inject fly ash directly into the calciner.[26] Operation under the terms of the new permit began on April 1, 2005.

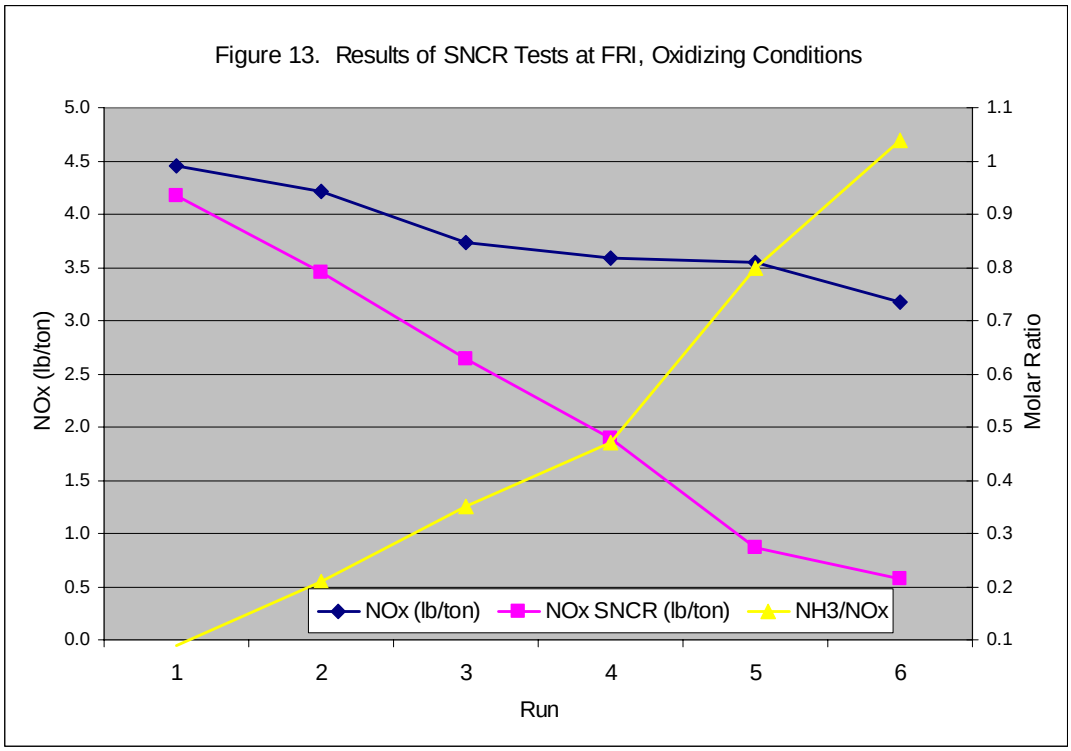


The requested NO_X limits can be achieved using SCC with a high temperature reducing atmosphere without SNCR. However, SAC will typically operate the calciner in an oxidizing atmosphere and use SNCR to maintain higher production capacity. The will also allow SAC to use the combustion chamber to burn petroleum coke blends as already allowed while meeting permitted NO_X limits.

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



The results indicate very substantial NO_X reductions by SNCR compared with NO_X emissions burning tires alone (representative of SCC in a mildly reducing atmosphere) even with molar ratios much less than 1.0. The following chart summarizes results of tests conducted while the calciner was operated in an oxidizing atmosphere.



Under oxidizing conditions, baseline emissions were greater than they were when tires were used. Very low emissions were achieved at molar ratios approaching 1.0. The baseline emissions also tended to decline probably due to recirculating NH_3 from previous runs.

SELECTIVE CATALYTIC REDUCTION (SCR)

There are hundreds of examples of SCR for the control of NO_X. Numerous installations exist in the United States, Europe and Japan. Most of the projects have been conducted in the electric power industry for a wide selection of fuels, energy cycles, and operating conditions.

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

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

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

The SCR system supplier, respected company personnel, and the director of the section within the German Federal Environmental Office (FEO) responsible for regulating the cement industry prepared a paper which was presented at the 2001 Paris NO_X Conference.[27] Among the findings were:

- Catalyst pitch should be greater than 8 mm for easier cleaning;
- NO_X in the exhaust gas is reduced by 30 percent with <u>no</u> ammonia use, relying on its presence in local raw materials; and
- NO_X reduction rates above 90 percent, with NH_3 slip less than 5 ppm, can be achieved.

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

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

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

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

- The system reduced raw material NH_3 that might otherwise have been converted to "raw material NO_X";
- Slip was contained to less than 1 mg/m^3; and
- Reductions of hydrocarbons and SO_2 on the order of 50 to 70 percent were also attained.

The NH_3 (25% aqueous solution) consumption rates needed to reduce NO_X concentration from 1200 mg/m^3 to 800, 500, and 200 mg/m^3 were 46, 64, and 85 liters L/hr respectively. By comparison, the Slite kiln consumes around 1200 L/hr to achieve 200 mg/m^3 on a kiln about four times the size of the Solnhofer installation. Correcting for size, it *appears* to take less than one-third as much ammonia to achieve 200 mg/m^3 by SCR at Solnhofer compared to SNCR at Slite. The difference must be accounted by raw material ammonia and more efficient reactions at Solnhofer.

The authors made cost comparisons between SCR and SNCR to reduce NO_X from 1,200 to 800, 500, and 200 mg/m^3. In doing so, they made the following assumptions: clinker production is 480,000 metric tons per year; the facility operates 7,500 hours per year; the SCR system costs 2.5 million Euros; an SNCR system costs 1.0 million Euros; and the catalyst will last 3-4 years.

The costs for control by SNCR varied from approximately 0.40 to 1.40 Euros per ton of clinker for NO_X reduction to values between 800 and 200 mg/m^3. The costs for control by SCR varied from approximately 0.80 to 1.00 Euros per ton of clinker for NO_X reductions to values between 800 and 200 mg/m^3. For reference, the author of the Slite paper estimated only 0.60 Euros per ton of clinker to achieve 200 mg/m^3 at the much larger Swedish installation.

According to the German analysis, the crossover point is at approximately 550 mg NO_X/m^3. This means that for objectives less than 550 mg/m^3 (roughly 2.5 lb/ton of clinker), SCR is the more economic option. The reductions in THC, SO_2, and NH_3 emissions as well as the reduction of the potential for plume opacity emissions make the SCR option even more attractive where significant amounts of sulfur, organic matter or ammonia are present in the raw materials.

Early on during the commercial demonstration, the German official advised this author, "with SCR you can meet NO_X standards of 200 mg/m^3".[30] More recently he advised the author, "the SCR in Solnhofen works in an excellent manner".[31] It is noteworthy that the plant had an SNCR system prior to installing the SCR unit. They can achieve their permitted emission limit with either technology but continue to use SCR.

According to the Cement Industry Research Institute of the German Cement Works Association the status of SCR is as follows: "As with the SNCR process, a suitable reducing agent, such as ammonia, is injected into the exhaust gas flow. Owing to the catalyst, however, the reduction reaction takes place at a lower temperature range of 300 to 400 °C and results in a higher yield and lower NH_3 slip.

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

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

"The economic efficiency of the SCR process will have major influence on the extent to which the process will be applied for NO_X abatement at cement works in the future. Apart from capital costs as well as the consumption of reducing agent and power, the service life of the catalyst will substantially determine overall costs. After one year of operation, the catalyst's loss of activity was fairly low. The operator therefore reckons with a service life of 3 to 4 years".[32]

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

"The reactor in the plant can be equipped with six catalyst sections of which three layers are in use. With these three, 500 mg NO_X/m^3 and less than 1 mg NH_3/Nm^3 are emitted. A reduction to 200 mg/m^3 is possible by variation of the NH_3 use. The actual working time of the catalyst is at present at approximately 18,000 hours with an expectation of another further 3-4 years." These experts included their findings on SCR technology in a more comprehensive report published in 2004 by the Austrian FEO on waste use and emissions reductions in the cement industry.[34] During 2003, the plant emitted less than 500 mg NO_X/m^3 on 95.6 percent of operating days.[35]

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

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

The author believes that the possibility of combining SNCR with a small or "trim" SCR system should be assessed when very low emissions are required. Under such a scenario, this would reduce the NH_3 use required by an SNCR system while avoiding the capital costs and footprint of a large SCR system. Such options are sometimes used for power plant control equipment retrofits, especially when space is at a premium.

CONCLUSION

SCC with a reducing atmosphere is an excellent NO_X control option when moderate levels of control are required and there is a good balance between fuel sulfur, alkali, chlorides, etc.

There are considerable unaccounted costs for SCC not apparent during design. These become more evident with the realities of available fuels and raw materials, particularly when low NO_X emissions are required. SCC requires larger calciners and long ducts with costly structural impacts on the entire preheater structure. The costs associated with possible operational difficulties and lower production must be considered when compared with SNCR.

SNCR is a technical and economic alternative to SCC with a reducing atmosphere, particularly when there are imbalances between sulfur and alkali or other phenomena that cause coating formations. SCR is a technical and economic alternative to SNCR particularly when sulfur or organic matter or ammonia are present in the raw materials or when very low NO_X emissions are required.

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DISCLAIMER

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

KEY WORDS

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

REFERENCES

[1] Sprung, Siegbert. Technological Problems in Pyroprocessing Cement Clinker: Cause and Solution. Beton Verlag. 1982.

[2] Thomsen, K.; Jensen, L.S.; Schomberg, F. "FLS-Fuller ILC-Low NO_X Calciner Commissioning and Operation at Lone Star in St. Cruz in California," *Zement Kalk Gips International*, **1998**, 10, 542-550.

[3] Terry, Mark S. "BACT: What is available with Today's Technology," *Krupp Polysius Technical Seminar*. 1999.

[4] Miller, F. M.; Hawkins, G. J. "Formation and Emission of Sulfur Dioxide from the Portland Cement Industry" in *Proceedings of the 93rd Air and Waste Management Association Conference.* 2000. San Diego, CA.

[5] Xeller, H. "New Developments in NO_X Abatement in the Cement Industry, Part 2", *Zement Kalk Gips International*, **1998**, 4, 208-218.

[6] Presentation. Waste Management Technologies in Japanese Cement Industry. Taiyeho Cement, Taiyeho Engineering, CTI/Industry Joint Seminar, February 2004.

[7] Reference 4.

[8] Brochure. DOPOL^R '90 Preheater and PREPOL^R Calcining System. Krupp Polysius.

[9] Electronic mail transmission from F. MacGregor Miller, PhD., Cement Etc., to A. A. Linero, Florida DEP. Inquiry regarding Paris 2001 Presentation. May 13, 2002.

[10] Electronic mail transmission from Joe Horton, Suwannee American Cement, to A. A. Linero, Florida DEP. Response to Control Technology Information Request. February 25, 2004.

[11] Source Test Report. Pennsuco Cement Kiln PK5 – Titan America, Medley, Florida. October 20-22 and November 4-5, 2004.

[12] Brochure. Dry Process Kilns. F.L. Smidth.

[13] Application. Titan America Cement. Hours of Operation Increase and Emission Limit Adjustments. Pennsuco Cement Plant, Medley, Florida. April 2005.

[14] Sun, W.H.; Bisnett, M.J.; Kirk, D.W.; Steuch, H.E.; Hille, J. "Reduction of NO_X Emissions from Cement Kiln/Calciner through the Use of the NO_XOUT^R Process," In *Proceedings of the AWMA International Specialty Conference on Waste Combustion in Boiler and Industrial Furnaces*, April 21, 1994.

[15] Institute for Prospective Technological Studies, *Reference Document on Best Available Techniques in the Cement and Lime Manufacturing Industries*; European Integrated Pollution Prevention and Control Bureau: Seville, Spain, March 2000.

[16] Junker, P., Director of Environmental Protection for Gotland County, Swedish EPA. "Reduction with SNCR Technology at Slite Cement Plant", In Proceedings of the *Paris NO_X/N_2O-conference*, March 21-22, 2001.

[17] *Scancem 1998 Environmental Report*, Scancem: Malmo, Sweden, 1999.

[18] D. Rose, K. Adler, R. Erpelding, "NO_X abatement with the SNCR process in kiln plants with staged combustion," In *Polysius Teilt Mit 218, 35th Polysius Cement Day*, Hannover, Germany, April 2001.

[19] Miller, F. M.; Young, G. L.; von Seebach, M., *Formation and Techniques for Control of Sulfur Dioxide and Other Sulfur Compounds in Portland Cement Kiln Systems*; Portland Cement Association: Skokie, Illinois, 2001.

[20] Greer, W. L., *Interactions Among Gaseous Pollutants from Cement Manufacture and Their Control Technologies*; Portland Cement Association: Skokie, Illinois, 2003.

[21] Reference 4.

[22] Miller, F. M. "Management of Detached Plumes in Cement Plants" in *Proceedings of the 2001 IEEE-IAS/PCA Cement Industry Technical Conference.*

[23] Letter and attachments from Walter Greer, Ash Grove Cement, to John Ramsey, Kansas Department of Health and Environment, re: Sulfur Absorbing Enhancements at the Chanute Plant, dated May 14, 1999.

[24] SO_2 Removal and Secondary Plume Abatement – MicroMist Micro-fine Lime^{TM} Semi-dry Injection Systems. Product Information Brochure. EnviroCare International: Novato, CA, 1998.

[25] Texas Natural Resources Conservation Commission. Technical Review – New Kiln and Modification of Existing Plant at Texas Industries, L.P. Midlothian Cement Plant. Permit No. 1360a. August 1998

[26] Florida Department of Environmental Protection. Production Increase, Fly ash Injection, and SNCR at Suwannee American Cement Plant. Final Permit Modification. March 15, 2005.

[27] Haug, N., Dr. Ing.; Sauter, G., Dipl. Ing.; Samant, G., Dr. Ing., "New developments of High Dust–SCR Technology in the Cement Industry Results of Pilot Tests in Solnhofen and Development State of a Full Scale SCR Unit", in Proceedings of the *Paris NO_X/N_2O Conference*, March 21-22, 2001.

[28] Kossina, I., Dipl. Ing., "Reduction of NO_X Emissions from Exhaust Gases of Cement Kilns by Selective Catalytic Reduction", In Proceedings of the *Paris NO_X/N_2O Conference*, March 21-22, 2001.

[29] Haug, N., Dr. Ing.; Sauter, G., Dipl. Ing.; Samant, G., Dr. Ing., "Einsatz der High-Dust-SCR Technologie in der Zementindustrie", in VDI Vortrag 2002.

[30] Electronic mail transmission from Norbert Haug, Dr. Ing., German Umweltbundesamt, to A. A. Linero, Florida DEP. Inquiry regarding Paris 2001 Presentation. May 13, 2002.

[31] Electronic mail transmission from Norbert Haug, Dr. Ing., German Umweltbundesamt, to A. A. Linero, Florida DEP. Cement NO_X Emission Standards. August 31, 2000.

[32] Forschunginstitut der Zementindustrie. *Environmental Protection in Cement Manufacture*; Verein Deutscher Zementwerke: Düsseldorf, Germany, 2004.

[33] Austria Unweltbundesamt. Web Report - Erste Anlage zur Katalytischen Entstickung (SCR) in Einem Zementwerk. **www.umweltbundesamt.at/umwelt/industrie/branche/mineral/zement** accessed on January 16, 2005.

[34] Szednyj, I., Dipl. Ing., Schindler, I,. Dipl. Ing.; Berichte 237 - Aktuelle Entwickungen Hinsichtlich Abfalleinsatz und Emissionsminderungungstechniken in der Zementindustrie. Unweltbundesamt GmbH. Wien. 2004. 107 pages.

[35] Solnhofer Holding AG. Web Report Summary Table. Unterrichtung der Öffentlichkeit gemäß der 17. BlmSchV über den Betrieb des Zementwerkes. **www.spz-solnhofen.de** accessed on March 29, 2005.