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ASSESSMENT OF NO_x EMISSIONS REDUCTION STRATEGIES FOR CEMENT KILNS - ELLIS COUNTY

FINAL REPORT

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Work Order No.05-06

Prepared by:

ERG, Inc.
10200 Alliance Road, Suite 190
Cincinnati, Ohio 45242-4716

Prepared for:

Air Quality Planning Section
Chief Engineer's Office
Texas Commission on Environmental Quality
Austin, Texas 78711-3087

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This study is the work project of a panel of experts assembled at the request of the Texas Commission on Environmental Quality. This study was performed under contract to Eastern Research Group that provided overall contract management and subcontracted the outside experts and laboratory services. While each of the experts brought specific skills to this study and was the principal author of individual sections of the report, the overall study represents a team effort. The general conclusions of the study have been reviewed and are endorsed by the entire expert panel.

Walter Koucky, Senior Project Engineer - Contract Manager, Eastern Research Group

Dr. Ray Merrill, Senior Chemist, Eastern Research Group

David Gossman, FAIC, President, Gossman Consulting Inc.

Dr. Gabe Miller, Professor of Chemistry, New York University

Dr. Greg Miller, Principal, Cement Etc., Inc.

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Attachment D: Table D-1. Summary of Current US Regulations for NO_X

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1.0 INTRODUCTION

This study was conducted to explore potential NO_x emissions reduction strategies for cement kilns in Ellis County. This project included assessing existing NO_x control technologies as well as new technologies that have not been previously considered by TCEQ. This project evaluated the general performance and cost of applicable NO_x control technologies for the cement kilns present in Ellis County and further evaluated the application of these control technologies to the site-specific requirements of the kilns and raw materials present in Ellis County.

This study was initiated in order to fulfill obligations in the Dallas/Fort Worth Litigation Settlement Agreement. TCEQ, in consultation with the Plaintiffs, EPA, and Intervenor the Portland Cement Association, developed the scope of work and selected Eastern Research Group (ERG) and a panel of experts (the ERG Team) to perform this cement kiln NO_x control technologies study. This study evaluated the applicability of existing control technologies and the potential availability of new air pollution control technologies for cement kilns located in the Dallas/Ft. Worth ozone nonattainment area. This report evaluates and establishes the types of controls that may be technically applied to the three nonattainment area cement plants with specific evaluations of applicability to the 10 cement kilns located at the three plants. This report focuses largely on three active types of control technology: SCR, SNCR and NO_x Oxidation. This focus in based on the need to evaluate technologies that go beyond current requirements of 30 Texas Administrative Code (TAC) Chapter 117. Economics of these control technologies are also investigated and reported.

The intent of this study was to establish impartial parameters for the determination of applicable controls. Controls were included to the extent that they were technically feasible. Control costs and cost effectiveness values, in terms of cost per ton of NO_x controlled, were then assigned to all technically feasible controls. The ERG Team has not applied value judgments nor assessed the economic viability of technically feasible controls. The ERG Team has not excluded any control technology on the basis of cost. This study puts forward technically viable NO_x control technologies and evaluates their cost effectiveness for specific application to Ellis

County cement kilns with the intent of allowing TCEQ to have sufficient information to make control technology selections.

This report uses the USEPA report "NO_x Control Technologies for the Cement Industry" of September 2000 (EPA 2000) as a baseline for the technical analysis and as boilerplate for describing the cement industry and applicable control technologies. The ERG Team has reviewed and edited this text to reflect the Team's understanding of the processes and control techniques. As mentioned previously, this report looks at active control technologies beyond the combustion and process optimization techniques of 30 TAC Chapter 117. The EPA 2000 report evaluates Selective Catalytic Reduction (SCR) and Selective Non-catalytic Reduction (SNCR) for the cement industry. This study takes this EPA 2000 information and updates it to the present. In addition, this study conducts site-specific evaluations including control cost evaluations for the 10 Ellis County cement kilns. This study focuses on application of SCR, SNCR and oxidation technologies including LoTOx™ to control oxides of nitrogen. Energy improvements are also examined, including replacement of the seven Ellis County wet kilns with two large, modern dry process units.

1.1 Executive Summary

The tables presented below contain summaries of control technology evaluations conducted as part of this study. The summaries below generally contain conservative costs and scenarios for the selected technologies. For example, performance levels for selective catalytic reduction (SCR) and LoTOx™ oxidation are conservatively estimated at 80-85%. These technologies typically perform better than these levels in other industrial applications. However, using a slightly lower performance value presents a more conservative evaluation of control costs, allowing potential difficulties in initial application of these technologies to Ellis County cement kilns.

The tables include a column discussing the status of the control technology for the application. This column uses the Top-Down BACT terms, *available, transferable* and *innovative*, to describe the statuses of the control technologies. However, for the purposes of this report, *available* essentially means that the technology is commercially available and in use

on similar types of cement kilns. *Transferable* means that the technology is commercially available and in use on similar process equipment and could reasonably be expected to work on that type of cement kiln. *Innovative* describes technologies that have not been successfully applied to a type of cement kiln, but in the judgment of the ERG Team could be expected to work on the type of cement kiln if correctly optimized through experimental application.

Wet kilns use more energy and have higher emissions rates than dry kilns. The only *available* wet kiln control technique fully evaluated in this study is conversion of the wet kilns to modern dry preheater/calciner units. This is a high cost alternative with a cost of approximately $11 per metric tonne (the metric tonne is the standard unit of measure for cement production and is used in this report) of clinker produced, including consideration of substantial fuel savings due to increased efficiency. As the cost of alternative controls approaches this value, there is reasonably expected to be a point where the cost of control technologies may create a substantial incentive to replace the wet kilns. This decision is complex and may require consideration of expanded production and use of alternative energy sources to be commercially justified. At the time this report was completed, Holcim of France was giving preliminary reports of trials of selective non-catalytic reduction (SNCR) on a wet kiln. While these preliminary reports do not provide sufficient information for technical evaluation of the results, this may mean that SNCR has become an available control technology for wet kilns.

Burden costs in dollars per tonne clinker produced ($/tonne) are provided to provide insight into the impacts of control costs on the cement plant's cost of product. The emissions reductions calculated in Tables 1-1 through 1-8 are based on operation of the control equipment for the entire year and not just during the Dallas/Ft. Worth ozone season. Tables 1-9 through 1-16 are based on operation of the control equipment for just the Dallas/Ft. Worth ozone season. The metric tonne is the standard unit both in the US and worldwide for measuring cement production. This causes confusion because the metric tonne is often spelled "ton". This report uses the spelling "tonne" to refer to the metric tonne (i.e., 1,000 kilograms or 2,205 pounds). Current regulations in Texas are based on pounds of NO_x per short ton (i.e., 2,000 pounds). For consistency in the technical discussions of controls and regulations in the US and worldwide, this report discusses production related information based on the metric tonne of production. To

assist in comparison with existing Texas regulations, values in pounds per short ton have been added in parentheses to the tables in this Executive Summary.

1.1.1 Control Alternatives for Holcim Inc.

Holcim operates two modern dry preheat precalcination kilns, each with an annual production capability of slightly over one million tons per year of clinker. Holcim has recently completed testing of SNCR on these kilns. SNCR performed reasonably well on Holcim #1, but additional optimization may improve performance.

Holcim #1

Holcim's Line #1 began operation in 1987. This unit is a modern design, typical of units built in the 1980's; this kiln may be a candidate for a reconstructed preheater precalcination tower to a larger, more energy efficient design (see Section 4.4.5 of the report). This reconstruction could also allow for improved staging of combustion, lower NO_x generation and improved integration with controls such as SNCR or an oxidation control technology. Without modification, Holcim #1 will likely achieve somewhat lower control performance than Holcim #2 or TXI #5 based on application of similar technologies. However, in spite of its older generation of design, Holcim #1 is currently performing nearly as well as Holcim #2. Neither Holcim #1 nor Holcim #2 is currently performing as well as TXI #5 in terms of energy efficiency or NO_x emissions rates even though Holcim #2 is approximately the same age.

Note on the conventions used in the Tables 1-1 through 1-16.

The metric tonne (1,000 kg. or 2,205 lbs.) is used by the cement industry for measuring and reporting production. Emissions are reported in short tons containing 2,000 lbs./ton. This results in a 10% difference between the metric tonne and the short ton. A controlled emissions rate of 1.1 lbs./tonne is equivalent to a controlled emissions rate of 1.0 lbs./ton. Emissions reported in tpy are in short tons per year. As Texas has used lbs./ton (based on the US ton – or short ton) in the past, these values are provided in parentheses in appropriate locations in the tables in this chapter.

Table 1-1 Summary of Technologies for Holcim #1 – Full Year Control								
Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Available	2,222	3.76 (3.41)	85%	1,888.7	0.56 (0.51)	\$1,600	\$2.60
LoTOx™	Transferable	2,222	3.76 (3.41)	85%	1,888.7	0.56 (0.51)	\$2,200	\$3.50
SNCR	Available	2,222	3.76 (3.41)	50%	1,111	1.9 (1.7)	\$1,400	\$1.30
Calciner Upgrade	Available	2,222	3.76 (3.41)	40%	888.8	2.2 (2.0)	\$2,795	\$2.70

40% for new low-NOx calciner based on literature.
Cost effectiveness for calciner upgrade calculated by ratio of burden costs using SCR data.

Holcim #2

Holcim's Line #2 began operation in 1999. Holcim #2 is a modern design, but emits substantially more NO_x than TXI #5 that was built only two years later. There may be process or combustion optimization options for Holcim #2 that can lower NO_x prior to control. Holcim has recently completed testing of SNCR on these kilns. SNCR did not perform as well as would be expected on Holcim #2 and additional optimization should improve performance.

Table 1-2 Summary of Technologies for Holcim #2 – Full Year Control								
Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Available	1,778	3.01(2.73)	85%	1,511.3	0.45(0.41)	\$1,900	\$2.20
LoTOx™	Transferable	1,778	3.01(2.73)	85%	1,511.3	0.45(0.41)	\$2,100	\$2.80
SNCR	Available	1,778	3.01(2.73)	50%	889	1.5(1.36)	\$1,600	\$1.20

1.1.2 Control Alternatives for TXI Cement

TXI operates five kilns, one modern dry preheat precalcination kiln and four 1960's era wet kilns. Two of the wet kilns are operated full time and two are operated as backup units about 15% of the time.

TXI #1 and #4

TXI #1 began operation in 1960 and TXI #4 began operation in 1972. These are wet kilns that use the old process of making cement from wet slurry. This makes high quality cement but uses substantially more energy to make cement. Both energy use and NO_x emissions rates are substantially higher for wet kilns than for dry process kilns. Because the kilns are of similar

size and used in a similar manner, one estimate has been created to represent both TXI #1 and TXI #4. Cost and control estimates are based on averaging the operation of these kilns; a similar approach has been used for TXI #2 and #3. A control option for replacement of the wet kilns at TXI with a new large dry kiln of equal capacity to the old wet kilns is also presented. The model for wet to dry conversion contains a calculation for fuel savings that is not entirely accurate for TXI because of the use of waste fuels in the wet kilns. However, to the extent that a new, larger dry kiln would continue to utilize a similar amount of waste fuels, the savings in fuel expressed as coal, would still provide an accurate view of a potential fuel savings. The models for TXI #1 and #4 presume that mid-kiln firing will be applied as required under the current SIP and that this will achieve a 30% reduction in NO_x emissions. This 30% assumption is based on evaluation of literature and other installations and is not intended to predict the actual ability of TXI to reduce emissions through mid-kiln firing.

Assuming mid-kiln firing reduces the emissions rate from current actual rates and decreases control cost effectiveness. As less NO_x is available for control, the cost per ton controlled is increased. However, as mid-kiln firing is already required under Texas regulations, this was deemed the proper starting place for control analysis. The analyses for TXI #1 and #4 presented below are based on an average for the two kilns and values presented below, such as emissions reductions, should be doubled to account for both kilns.

Table 1-3 Summary of Technologies for TXI #1 & #4 – Full Year Control

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Transferable	838	5.67(5.14)	85%	712.3	0.85(0.77)	\$4,900	\$12.30
LoTOx™	Transferable	838	5.67(5.14)	85%	712.3	0.85(0.77)	\$2,800	\$6.80
SNCR	Innovative	838	5.67(5.14)	35%	293.3	3.7(3.36)	\$2,100	\$2.10
Wet to Dry	Available	1,802	5.67(5.14)	65%	1,171.3	2.0(1.81)	\$6,700	\$11.00
Large 3 Kiln SCR	Transferable	1,802	5.67(5.14)	85%	1,531.7	0.85(0.77)	\$5,400	\$8.00

SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace existing capacity.

TXI #2 and #3

TXI #2 began operation in 1963 and TXI #3 began operation in 1967. Similar to TXI #1 and #4, these are wet kilns that use the old process of making cement from wet slurry. Because

the kilns are of similar size and used in a similar manner, one estimate has been created to represent both TXI #2 and TXI #3. Cost and control estimates are based on averaging the operation of these kilns. Although the kilns are physically similar to TXI #1 and #4, they are used as backup units. As backup units, these kilns have a low utilization rate (averaging 15% for the two kilns in 2004); the low utilization rate will show poor economics of control, as the fixed costs will be averaged over very small NO_x reductions. The control option for replacement of the wet kilns at TXI with a new large dry kiln of equal capacity to the old wet kilns is an option for all four kilns and has identical economics and environmental benefits as described above for TXI #1 and #4. Also, as with TXI #1 and #4, mid-kiln firing is assumed as the starting place for this analysis as this is already required by Texas regulations. The analyses for TXI #2 and #3 presented below are based on an average for the two kiln and values presented below, such as emissions reductions, should be doubled to account for both kilns.

Table 1-4 Summary of Technologies for TXI #2 & #3 – Full Year Control

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Transferable	85	3.4(3.08)	85%	72.3	0.51(0.46)	\$66,400	\$14.00
LoTOx™	Transferable	85	3.4(3.08)	85%	72.3	0.51(0.46)	\$8,000	\$11.50
SNCR	Innovative	85	3.4(3.08)	35%	30	2.2(2.00)	\$11,000	\$6.50
Wet to Dry	Available	1,802	5.67(5.14)	65%	1,171.3	2.0(1.81)	\$6,700	\$11.00
Large 3 Kiln SCR	Transferable	1,802	5.67(5.14)	85%	1,531.7	0.85(0.77)	\$5,400	\$8.00

SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace existing capacity.
The higher emissions rate of TXI 1 & 4 is used as representative of operation for combined solutions wet to dry and large single SCR.

TXI #5

TXI #5 began operation in 2001 and is the largest and most efficient kiln line in the study area. It is relatively fuel efficient and intrinsically low in NO_x emissions. The low NO_x emissions rate is a function of the design and may also be partly the result of the chemistry of the feed materials (see discussion of chemistry in the main report) that may be causing reduction of NO_x. Because of the relatively low NO_x concentrations in the offgas, the expected NO_x removal efficiencies are lower for TXI #5 than for other kilns. For example, both European and US experience with SNCR indicates that removal is less efficient at lower NO_x concentration and that practical removal is currently understood to be limited to about 200 mg/m3 or 100 ppm. For

this reason, TXI #5 is modeled for 35% control for SNCR compared to 50% for the Holcim kilns.

Table 1-5 Summary of Technologies for TXI #5 – Full Year Control

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Available	1,710	1.50(1.36)	80%	1,368	0.30(0.27)	\$2,000	\$1.10
LoTOx™	Transferable	1,710	1.50(1.36)	80%	1,368	0.30(0.27)	\$2,400	\$1.40
SNCR	Available	1,710	1.50(1.36)	35%	598.5	1.0(0.91)	\$2,300	\$0.60

1.1.3 Control Alternatives for Ash Grove Cement

ASH GROVE #1, #2 and #3

Ash Grove operates three wet kilns that began operation in 1966, 1969 and 1972. Similar to the wet kilns at TXI, these are wet kilns that use the older process of making cement from wet slurry. This makes high quality cement but uses substantially more energy to make cement. Both energy use and NO_x emissions rates are substantially higher for wet kilns than for dry process kilns. The Ash Grove kilns are currently complying with the SIP requirement for mid-kiln firing. The NO_x emissions rate at Ash Grove from mid-kiln firing of tires appears to be substantially lower than at TXI where the mid-kiln firing project has been delayed by permit issues.

Because the Ash Grove kilns are of similar size and used in a similar manner, separate discussions are not provided for each kiln. Slight differences in flow rates and emissions rates are modeled and presented in the tables below. Similar to the TXI presentation, a control option for replacement of the wet kilns at Ash Grove with a new large dry kiln of equal capacity to the old wet kilns is presented. A single, large SCR is modeled that combines the emissions and flow of the three kilns into one large control unit is modeled to demonstrate the impact on control costs. SCR is more cost effective at Ash Grove than at TXI due to higher gas temperatures and less required reheat of stack gas.

Table 1-6 Summary of Technologies for Ash Grove #1 – Full Year Control								
Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Transferable	702	5.57(5.05)	85%	596.7	0.84(0.76)	\$5,200	\$12.00
LoTOx™	Transferable	702	5.57(5.05)	85%	596.7	0.84(0.76)	\$2,900	\$7.00
SNCR	Innovative	702	5.57(5.05)	35%	245.7	3.6(3.27)	\$2,200	\$2.20
Wet to Dry	Available	2,205	5.68(5.15)	65%	1,433.3	2.0(1.81)	\$6,500	\$11.00
Large 3 Kiln SCR	Transferable	2,205	5.83(5.29)	85%	1,874.25	0.88(0.80)	\$4,200	\$10.00

SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace 3 small emissions are averaged for these scenarios.

Table 1-7 Summary of Technologies for Ash Grove #2 – Full Year Control								
Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Transferable	750	5.95(5.40)	85%	637.5	0.89(0.81)	\$5,200	\$13.00
LoTOx™	Transferable	750	5.95(5.40)	85%	637.5	0.89(0.81)	\$2,900	\$7.50
SNCR	Innovative	750	5.95(5.40)	35%	262.5	3.9(3.54)	\$2,200	\$2.30
Wet to Dry	Available	2,205	5.68(5.15)	65%	1,433.3	2.0(1.81)	\$6,500	\$11.00
Large 3 Kiln SCR	Transferable	2,205	5.83(5.29)	85%	1,874.25	0.88(0.80)	\$4,200	\$10.00

SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace 3 small.

Table 1-8 Summary of Technologies for Ash Grove #3 – Full Year Control								
Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Transferable	764	6.06(5.50)	85%	649.4	0.91(0.83)	\$5,500	\$14.00
LoTOx™	Transferable	764	6.06(5.50)	85%	649.4	0.91(0.83)	\$3,000	\$7.90
SNCR	Innovative	764	6.06(5.50)	35%	267.4	3.9(3.54)	\$2,200	\$2.30
Wet to Dry	Available	2,205	5.68(5.15)	65%	1,433.3	2.0(1.81)	\$6,500	\$11.00
Large 3 Kiln SCR	Transferable	2,205	5.83(5.29)	85%	1,874.3	0.88(0.80)	\$4,200	\$10.00

SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace 3 small.

1.1.4. Ozone Season Only Control Costs

The emissions reductions calculated in the tables below are based on operation of the control equipment during the Dallas/Ft. Worth ozone season unless otherwise noted. For example, SCR is presumed to operate only during the ozone season in the modeling. This results in a higher annualized cost effectiveness in dollars per ton of NO_x controlled as less NO_x is controlled on an annual basis. Wet kiln to dry preheat/precalciner unit conversions provide benefit for the full year and are not seasonal measures. Tables 1-9 through 1-16 are similar to Tables 1-1 through 1-8 except that adjustments have been made to represent seasonal operation.

Holcim Ozone Season Results

Table 1-9 Summary of Technologies for Holcim #1 – Ozone Season Control

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Available	2,222	3.76 (3.41)	85%	1,267.3	0.56 (0.51)	\$1,900	\$2.00
LoTOx™	Transferable	2,222	3.76 (3.41)	85%	1,267.3	0.56 (0.51)	\$2,400	\$2.35
SNCR	Available	2,222	3.76 (3.41)	50%	745.4	1.9 (1.7)	\$1,500	\$1.00
Calciner Upgrade	Available	2,222	3.76 (3.41)	40%	888.8	2.2 (2.0)	\$2,795	\$2.70

Emissions reductions are for ozone season unless otherwise noted.
40% for new low-NOx calciner based on literature.
Cost effectiveness for calciner upgrade calculated by ratio of burden costs using SCR data.
Calciner upgrade is not a seasonal ozone measure.

Table 1-10 Summary of Technologies for Holcim #2 – Ozone Season Control

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Available	1,778	3.01(2.73)	85%	1,014.0	0.45(0.41)	\$2,000	\$1.70
LoTOx™	Transferable	1,778	3.01(2.73)	85%	1,014.0	0.45(0.41)	\$2,300	\$1.90
SNCR	Available	1,778	3.01(2.73)	50%	596.5	1.5(1.36)	\$1,700	\$0.90

Emissions reductions are for ozone season unless otherwise noted.

TXI Ozone Season Results

Table 1-11 Summary of Technologies for TXI #1 & #4 – Ozone Season Only								
Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Transferable	838	5.67(5.14)	85%	477.9	0.85 (0.77)	\$5,500	\$8.90
LoTOx™	Transferable	838	5.67(5.14)	85%	477.9	0.85 (0.77)	\$3,300	\$4.70
SNCR	Innovative	838	5.67(5.14)	35%	196.8	3.7 (3.36)	\$2,400	\$1.60
Wet to Dry	Available	1,802	5.67(5.14)	65%	1,171.3	2.0 (1.81)	\$6,700	\$11.00
Large 3 Kiln SCR	Transferable	1,802	5.67(5.14)	85%	1,027.7	0.85 (0.77)	\$5,400	\$6.00

Emissions reductions are for ozone season unless otherwise noted.
SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace existing capacity, emissions reduction is full year.

Table 1-12 Summary of Technologies for TXI #2 & #3 – Ozone Season Only								
Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Transferable	85	3.4 (3.08)	85%	48	0.51(0.46)	\$96,000	\$13.50
LoTOx™	Transferable	85	3.4 (3.08)	85%	48	0.51(0.46)	\$11,000	\$10.50
SNCR	Innovative	85	3.4 (3.08)	35%	20	2.2 (2.00)	\$13,000	\$5.00
Wet to Dry	Available	1,802	5.67(5.14)	65%	1,171.3	2.0 (1.81)	\$6,700	\$11.00
Large 3 Kiln SCR	Transferable	1,802	5.67(5.14)	85%	1,027.7	0.85 (0.77)	\$5,400	\$6.00

Emissions reductions are for ozone season unless otherwise noted.
SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace existing capacity, emissions reduction is full year.

Table 1-13 Summary of Technologies for TXI #5 – Ozone Season Only								
Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Available	1,710	1.50(1.36)	80%	918.0	0.30(0.27)	\$2,200	\$0.87
LoTOx™	Transferable	1,710	1.50(1.36)	80%	918.0	0.30(0.27)	\$2,600	\$0.90
SNCR	Available	1,710	1.50(1.36)	35%	401.6	1.0(0.91)	\$2,500	\$0.45

Emissions reductions are for ozone season unless otherwise noted.

Ash Grove Ozone Season Results

Table 1-14 Summary of Technologies for Ash Grove #1 – Ozone Season Only								
Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Transferable	702	5.57(5.05)	85%	400.4	0.84 (0.76)	\$5,800	\$9.20
LoTOx™	Transferable	702	5.57(5.05)	85%	400.4	0.84 (0.76)	\$3,400	\$5.00
SNCR	Innovative	702	5.57(5.05)	35%	164.9	3.6 (3.27)	\$2,500	\$1.70
Wet to Dry	Available	2,205	5.68 (5.15)	65%	1,433.3	2.0 (1.81)	\$6,500	\$11.00
Large 3 Kiln SCR	Transferable	2,205	5.83 (5.29)	85%	1,257.6	0.88 (0.80)	\$4,600	\$7.80

SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace 3 small, emissions reduction is full year.

Table 1-15 Summary of Technologies for Ash Grove #2 – Ozone Season Only								
Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Transferable	750	5.95 (5.40)	85%	427.8	0.89 (0.81)	\$5,800	\$9.90
LoTOx™	Transferable	750	5.95 (5.40)	85%	427.8	0.89 (0.81)	\$3,500	\$5.40
SNCR	Innovative	750	5.95 (5.40)	35%	176.1	3.9 (3.54)	\$2,400	\$1.70
Wet to Dry	Available	2,205	5.68 (5.15)	65%	1,433.3	2.0 (1.81)	\$6,500	\$11.00
Large 3 Kiln SCR	Transferable	2,205	5.83 (5.29)	85%	1,257.6	0.88 (0.80)	\$4,600	\$7.80

Emissions reductions are for ozone season unless otherwise noted.
SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace 3 small, emissions reduction is full year.

Table 1-16 Summary of Technologies for Ash Grove #3 – Ozone Season Only								
Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne ($lbsNO_x$/ton)	Percent Control	Emissions Reduction from Control tpy	Controlled Emissions $lbsNO_x$/tonne ($lbsNO_x$/ton)	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
SCR	Transferable	764	6.06 (5.50)	85%	435.7	0.91(0.83)	\$6,100	\$10.60
LoTOx™	Transferable	764	6.06 (5.50)	85%	435.7	0.91(0.83)	\$3,700	\$5.70
SNCR	Innovative	764	6.06 (5.50)	35%	179.4	3.9 (3.54)	\$2,400	\$1.70
Wet to Dry	Available	2,205	5.68 (5.15)	65%	1,433.3	2.0 (1.81)	\$6,500	\$11.00
Large 3 Kiln SCR	Transferable	2,205	5.83 (5.29)	85%	1,257.6	0.88 (0.80)	\$4,600	\$7.80

Emissions reductions are for ozone season unless otherwise noted.
SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace 3 small, emissions reduction is full year.

1.1.5. Summary of Performance and Cost Modeling Assumptions

The ERG Team used best engineering judgment in determining modeling parameters from the various data available. The ERG Team relied primarily on permit materials and emissions statements submitted to the State of Texas as well as material supplied by the companies in establishing the modeling parameters used to estimate control performance, cost and cost effectiveness. The ERG Team considered long term trends to derive estimated values for factors such as annual production capacity of clinker, which was adjusted by an assumed capacity factor that may be lower than current high operating levels. Values for airflows and temperatures were not always available for the proposed control device locations and values were estimated based on temperature and moisture adjustments.

Cost effectiveness is calculated for NO_x reductions only. A wet to dry kiln conversion, calciner upgrade or the addition of a scrubber will result in reduction of other pollutants. As this study is performed to assess ozone control measures, these benefits have not been included in the cost benefit analyses. A simple spray tower that would not effectively control SO_2 is priced as part of the LoTOx^{TM} analysis for wet kilns. If a flue gas desulfurization (FGD) scrubber were added, the price would increase. However, additional benefits for other pollutants controlled would also occur. For example, adding FGD scrubbers to Ash Grove wet kilns could result in approximately 1,800 tons per year of SO_2 emissions reduction per kiln and a wet kiln conversion would result in approximately 1,300 tons per year of SO_2 reduction per kiln. Both the oxides of nitrogen and sulfur are also precursors of fine particle formation. Control technologies that remove these precursors would provide additional, unquantified benefits to regional air quality.

1.1.5.1. Kiln Replacement or Upgrading

Both kiln replacement and upgrading were considered for modeling of the wet kilns. Replacement is the only option actually modeled because none of the wet kilns is large enough to be practically upgraded to a semi-wet system. Conversion of wet to semi-wet systems has been shown to result in significant production increases and NO_x decreases, but fuel savings have proven to be limited. Upgrading the preheater/calciner tower on Holcim #1 was also considered as an option. This process line is somewhat older than Holcim #2 or TXI #5 and the design

somewhat less energy efficient. The assumed performance of Holcim #1 with a modern, redesigned low-NO_x preheater/calciner tower was based on the survey of the performance of recently constructed new facilities and the performance of TXI #5 which is using similar Ellis County limestone to make cement. Although Holcim #2 is approximately the same age as TXI #5, TXI #5 produces much less NO_x per tonne of clinker produced. The expert panel believed that a new, intrinsic low- NO_x designed tower for Holcim #1 should perform substantially better than Holcim #2 and more like TXI #5. The cost values for wet to dry conversions and for upgrading the design of Holcim #1, as well as the energy improvements, are taken primarily from Department of Energy reports. The emissions rates in tons per year of NO_x used in these model runs are based on the assumption that a large new modern dry preheater/calciner unit would replace several older units. At Ash Grove, where all the kilns are highly utilized, this represents a composite of all the kilns. At TXI, where primarily kilns #1 and #4 are used, the replacement model looks at the emissions from these units plus a small amount from kilns #2 and #3.

1.1.5.2. SCR

The SCR cost model is a boiler cost model developed for use on coal-fired utility boilers. The SCR model is developed from the OAQPS Cost Manual and has been applied to other processes such as refinery FCCUs with reasonable success.

For the dry kilns, the model assumes that a location for SCR can be found where reheat of the process gas is not required. This is a high dust assumption. For the wet kilns, installation is assumed to be located after the dust collectors (low dust) and that reheat of the exhaust gas will be required. The impact of reheat of the gas on NO_x emissions was examined and found to be negligible. An increase of 5 to 10 tons per year of NO_x was estimated to occur based on modeled natural gas fuel use. As the gas reheater emissions could also be controlled by the SCR, the increase would reduce to one to two tons per year and was not included in the modeling. Based on the installation at Solnhofen (see Figure 4-1.1) of the SCR on the side of the tower, it was assumed that this configuration could work at the preheat/calciner kilns in Ellis County. The wet kilns, with the SCR located after the particulate controls were also assumed to have adequate

space available. The reheat cost model is based on the OAQPS cost model for regenerative thermal oxidizers with 70% heat recovery.

Although current assumptions for coal-fired power plants would predict 90% or better control for SCR, this assumption has been lowered to 85% for these model runs. This was done to represent a conservative approach to the cost modeling that included consideration of potential problems in applying SCR, such as higher variability of the gas stream comparing a utility boiler to a cement plant, and lack of experience in achieving high levels of control using SCR in the cement industry. Due to the lower emissions rates at TXI #5, the control efficiency was modeled at 80%. This was based on the evaluation of the current relatively low concentrations of NO_x in the TXI stack and uncertainty about SCR performance in a cement kiln at very low endpoint concentrations. These control efficiencies are not intended to define the final performance of this technology, but to evaluate costs under conservative assumptions. The actual decrease in performance, if any occurs, cannot be determined in advance. In the application of SCR to coal-fired boilers, higher levels of performance are typically achieved by increasing the amount of catalyst, and, thereby increasing the contact between reagent and catalytic material. Achieving higher control efficiencies increases the initial capital cost and maintenance costs for the unit. The lower performance rates were selected for the purposes of the cost modeling based on the engineering judgment of the expert panel and may not reflect the final capability SCR if installed at these locations.

1.1.5.3. SNCR

The SNCR cost model is also a boiler cost model developed for use on coal-fired utility boilers. The SNCR model is derived from the OAQPS cost manual and EPA's OTAG cost modeling. It has been simplified to obtain capital costs primarily on flow rates. The ERG team verified the reasonableness of these models' results for the Ellis County dry kilns by comparison to actual installations. The estimates for wet kilns are conjecture. No accurate costing can be developed without an understanding of the ultimate design of the control system. Limited information on installation of SNCR on a wet kiln in France suggests that this is a technically feasible option. Lacking any detailed information on the unit in France, controls costs were estimated based on the dry kiln model. Reagent costs are a substantial part of the annualized cost

of SNCR, so this rough cost estimate for wet kilns was still considered to be a valuable approximation.

As with the SCR control efficiencies, the cost models were run at conservative control efficiency values. A value of 50% was used for the Holcim kilns and 35% was used for TXI #5 and the wet kilns. The control efficiency of 35% at TXI was consistent with the reported performance of a European application at approximately 100 ppm. The value for wet kilns represented a reduced expectation for this experimental approach. The performance rates were selected for the purposes of the cost modeling based on the engineering judgment of the expert panel and may not reflect the final capability of SNCR if installed at these locations.

1.1.5.4. Oxidation Technologies

LoTOx™

The LoTOx™ model is based on the OAQPS model for thermal oxidation. Specific inputs to this model were developed with assistance from the BOC Group, PLC (BOC) and should produce results reasonably close to the current costs of their oxidation technology. For the dry process kilns, no scrubbers were assumed to be required as the existing scrubbers were expected to be sufficient for removal of oxidation products from the process gas. For the wet kilns, BOC provided approximate costs for installing LoTOx™ with spray towers. BOC provided generalized costs; detailed estimates on scrubber operating costs have not been developed. No cost model runs were performed for single LoTOx™ units to control multiple kilns as was done for SCR. The LoTOx™ cost model does not have the same benefit of scale for larger units as does SCR. Because little or no cost benefit would be predicted from a single, large LoTOx™ unit, no cost estimates were done for combined control of multiple kilns.

The same control efficiencies were used for LoTOx™ as for SCR. Again, this was done to make the cost estimates conservative due to lack of application of these technologies to the cement industry. BOC asserted that control efficiencies of 95% and 98% could be obtained using this technology. However, for this modeling effort, the same performance levels were modeled for LoTOx™ as for SCR. As with the SCR modeling, this was not done as a reflection

on the final performance capability of the technology, but rather to provide an equivalent and conservative basis for evaluating the cost of control.

The accuracy of OAQPS cost modeling approaches is typically within 30% or so for instances where parameters are accurately defined and the process well known. This is a useful tool for comparing different technologies. However, closely scrutinized vendor quotes should be the basis of any final comparison of technologies. Minor differences in modeling results are likely to be the product of assumptions regarding cost of electricity or reagents. For example, for Holcim #2, the cost of SCR was predicted to be $1,700 per ton of NO_x and LoTOx™ was modeled at $2,100 per ton.

A relatively small difference in the cost effectiveness for SCR and LoTOx™ should not be viewed as significant without understanding the contributing factors. Reagent cost and control efficiency assumptions can account for these differences. Cost for ammonia reagent is currently very volatile due to relatively high natural gas costs. A value of $500 per ton was used to reflect higher costs experienced in 2005, but not the currently higher short-term prices. If current high prices persist, the cost difference between these two technologies would be negligible. If LoTOx™ proves better at responding to fluctuations in NO_x concentrations and achieves a higher level of control than SCR, this would also tend to push cost effectiveness of the two technologies closer together. Differences of 20% in the cost effectiveness of two technologies should not be a basis for selecting one technology over another. If initial modeling results produce similar economic and performance values, both technologies should be considered for vendor pricing unless other factors dictate a clear preference for one over the other. Other factors, such as a determination that reheat was needed for application of SCR to dry kilns, would have a substantial impact and the two technologies would no longer appear equivalent in cost effectiveness.

Other Oxidation Technologies

There are other oxidation technologies using hydrogen peroxide or other chemical reagents. Most of these technologies are new; relatively low temperature end-of-pipe control techniques. As mentioned under the discussion for SCR above, the cost for ammonia reagents is

currently higher than it has been historically. Other oxidation technologies may allow use of lower cost reagents that may improve cost effectiveness for plants with existing wet scrubbers. There is one higher temperature hydrogen peroxide technology that may be able to be implemented inside an existing precalciner system, although it still requires a wet scrubber. At current hydrogen peroxide commodity prices, one of these alternative technologies may be more cost effective than ozone or ammonia based reagent alternatives. None of these technologies was found to have been used on a cement kiln or comparable system. Therefore, costing of these options was not attempted. All of these systems should be considered innovative but should not be ruled out of consideration, as a lower cost reagent would have a substantial impact on annual control costs.

1.1.6. Evaluation of Chemistry and Process Variables on NO_x Formation

As part of the overall evaluation of the potential to control, correlate and predict NO_x formation in the Ellis County Kilns, short-term process and emissions data were evaluated. These analyses were performed on data that was considered confidential business information and are, therefore, not summarized or reported. The statistical correlations evaluated included comparison of NO_x emissions rate to:

Kiln Feed of SiO_2,

$Al2O_3$,

Fe_2O_3,

CaO,

MgO,

SO_3,

Na_2O,

K_2O passing 200 mesh,

Clinker K_2O,
Production rate,
Coal/Coke passing 200 mesh,
Chain zone temp, and
Kiln drive amps.

In addition, graphs were produced looking at the relationships between gaseous pollutants and NO_x emissions rate. The conclusion of this investigation was essentially negative. None of the

process parameters and relations to formation of gaseous pollutants that were evaluated produced any relationships that indicated the potential for further control of NO_x beyond the control measures already in place (with the exception of the wet kilns at TXI that are not yet permitted for mid-kiln injection while burning hazardous waste). Furthermore, these parameters did not indicate that changes in feed constituents had an adverse or positive correlation to NO_x emissions rate.

This investigation did not show any correlations between feed and process materials and NO_x formation rates that would prohibit the use of the control technologies and techniques reviewed in this report. This investigation did not show any direct relationships between feed materials and NO_x formation rates that could potentially be exploited to further reduce NO_x emissions rates through process modifications. However, one interesting aspect of the investigation of the chemistry of the feed materials was a strong suspicion that nitrogen bearing feed materials present in Ellis County may be producing some limited non-selective non-catalytic reduction of NO_x. The exact nature of the material was not identified in this study. Similar effects have been noted in other kilns being fed materials such as nitrogen bearing sands. This may help to explain the current low NO_x emissions rates of TXI #5. This is discussed in Section 5.2 of this report. The chemical analyses of the feed materials was requested by the three plants to be treated as confidential business information and the site specific information is not included in this report for that reason. Generally summaries of the overall characteristics based on averages for all three plants are presented in Sections 5.1 and 5.2 of this report.

1.1.7. Summary of Environmental and Other Impacts

Sampling of the materials fed to the kilns was conducted and is summarized in Section 5 of this report along with characterizations of the kiln feed materials supplied by the cement plants. This testing showed that the materials fed to the Ellis County kilns was substantially uniform for the purposes of evaluating the impacts of feed materials on control equipment. Although there was variation, the variation between different samples, wet and dry kiln feed and the different Ellis County plants was not considered by the experts evaluating the individual control technologies to be significant enough to impact any of the control determinations. The main concerns were levels of sulfur and organics in the feed materials and the resulting

concentration of sulfur oxides, hydrocarbons and, additionally, carbon monoxide in the process gas streams emitted by the kilns and precalciners. These concerns and potential impacts are discussed under Section 4 of this report to the extent that these issues needed to be specifically evaluated in considering application of any of the control technologies to Ellis County kilns. For example, the concentrations of sulfur dioxide in the gas streams of the Ellis County kilns are discussed in Section 4.1.1 in comparison to levels where selective catalytic reduction has been applied to electric utility boilers.

The potential impacts are summarized and compared in Table 1-17 below for all of the major control options considered in this report. To the extent that issues such as reagent release to the atmosphere (slip) or clogging and/or corrosion resulting from reagents or reactions in process and control equipment were concerns in applying control technologies in Ellis County, these issues are also discussed in Section 4 of this report. Table 1-17 summarizes and compares potential impacts to allow comparisons between technologies.

Table 1-17 Environmental and Other Impacts of Control Technologies				
Impact	Selective Catalytic Reduction	Selective Non-Catalytic Reduction	Oxidation Technologies	Kiln Modernizations
Process Chemistry Limits Application of Control Technology in Ellis County	Ellis County chemistry within limits [a]	Ellis County chemistry within limits [a]	Ellis County chemistry within limits [a]	Chemistry not a factor
Release of Additional Criteria Pollutants	Accelerated formation of $PM_{2.5}$ [b]	Accelerated formation of $PM_{2.5}$ [b]	Possible decrease in VOCs, scrubbers can produce co-control of SO_x and other pollutants [c]	Potential large decreases unless capacity increased [d]
Reagent Release to the Atmosphere	Possible ammonia slip < 5 ppm [e]	Possible ammonia slip < 10 ppm [e]	Reactive reagents unlikely to "slip"	No
Clogging and/or Corrosion Potential	Possible depending on location [f]	Possible depending on location [f]	Possible - scrubber & ducts design [g]	No
Formation of Solid or Hazardous Pollutants	Periodic removal of ammonia salt deposits [h]	Periodic removal of ammonia salt deposits [h]	No, potentially can decrease emissions of organics.	No
Formation of Wastewater Contaminants	No	No	Probably used onsite as fertilizer [i]	No

Explanation of notes in Table 1-17.

a The constituents in feed materials and gaseous pollutant concentrations have been evaluated by the experts for each control technology and determined to be within acceptable limits for deploying the control technology on Ellis County kilns.

b Presence of "slip" ammonia reagent is expected to form sulfate and nitrate fine particles closer to the stack and may cause increased opacity at the stack. However, this is not a “new” pollutant in that the precursor pollutants released by cement kilns will tend to form fine particles in the atmosphere using atmospheric ammonia. The excess ammonia from SCR and SNCR will cause formation to occur closer to the stack. Excess opacity with the raw mill off-line may be exacerbated using SNCR. This occurs in units that do not use SNCR and wet lime injection has been suggested as a control measure.

c Oxidation technologies can also oxidize hydrocarbons, particularly the higher temperature peroxide-based control technologies. These technologies have the potential to reduce VOC emissions. Oxidation technologies also require the use of a scrubber to remove oxidized pollutants and the scrubber can also be designed to control pollutants such as SO_2 and acid mists.

d The major “modernization” projects considered in this report were wet to dry kiln conversion and efficiency improvements for the older dry kiln at Holcim. Efficiency improvements result in substantial energy savings and emissions reductions. However, these options require large capital investments that may only be economically justified by production increases that could negate the efficiency improvements and emissions reductions.

e In preheater/calciner units, recent German experience suggests that most of the ammonia ends up in the raw meal during drying and grinding and is not released to the atmosphere. As discussed above under footnote “b”, this recycling of ammonia and ammonia salts may result in increased opacity when the raw mill is off-line.

f SCR is not likely to produce corrosive byproducts. The potential for clogging is discussed below as sulfate deposits.

g As the cement kiln exhaust gas steam is typically moist, oxidation products can become hydrated and acidic prior to removal in the scrubber. Depending on the reagent and injection location selected, this may require replacement of ductwork and components with more corrosion resistant materials.

h Periodic removal of deposits of ammonia salts (ammonium sulfate/chloride) may be required from equipment downstream of SCR and SNCR ammonia injection points. In preheater/calciner units, recent German experience suggests that most of the ammonia ends up in the raw meal during drying and grinding and is not released to the atmosphere. To the extent that ammonia salts form primarily in the raw mill, this limits potential downstream problems except when the raw mill is off-line.

i Scrubber waters rich in nitrates could be used on-site as fertilizer to promote plantings used to control wind erosion in and around quarry areas.

2.0 DEFINING PARAMETERS FOR CONTROL EVALUATION

This section of the report is taken from the EPA 2000 Report and is included, with minor editing by the ERG Team. This information is included to provide the Texas environmental communities with the comprehensive background information necessary to understand the parameters that dictate NO_x control options at cement kilns.

2.1 Overview of Portland Cement Manufacturing Process and NO_x Generation

Portland cement, a fine gray or white powder, is the generic term for the type of cement used in virtually all concrete, which is a mixture of aggregates (e.g., crushed stone, gravel, sand), water, and cement. The American Society for Testing and Materials (ASTM) defines Portland cement as "hydraulic cement (cement that not only hardens by reacting with water but also forms a water-resistant product) produced by pulverizing clinkers consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate as an inter ground addition."

In 2004, the Portland cement industry in the U.S. consisted of 114 facilities in 37 States (and two facilities in Puerto Rico). Approximately 90 million tons of Portland cement were produced in 2004, with California, Texas, Pennsylvania, Michigan, Missouri, and Alabama accounting for approximately 50 percent of the production (1).

Hydraulic Portland cement, the primary product of the cement industry, is made from clinker blended with gypsum. Clinker is produced by heating a mixture of limestone, clay, and other ingredients to incipient fusion at a high temperature. Limestone is the single largest ingredient required in the cement-making process, and most cement plants are located near large limestone deposits. Portland cement is used in almost all construction applications including homes, public buildings, roads, industrial plants, dams, bridges, and many other structures.

In the cement-making process, the solid raw materials are heated to their fusion temperature, typically 1400 to 1500 EC (2550 to 2750 EF), by burning various fuels such as coal. Portland cement has been defined as “a hydraulic cement produced by pulverizing Portland

cement clinker and usually containing calcium sulfate."(2) Portland-cement clinker has been defined as "a clinker, partially fused by pyroprocessing, consisting predominantly of crystalline hydraulic calcium silicates."(2) Burning an appropriately proportioned mixture of raw materials at a suitable temperature produces hard fused nodules called clinker, which are further ground to a desired fineness.

Five types of Portland cement are recognized in the United States which contain varying amounts of the basic clinker compounds given in Table 2-1. (3) Different types of cements are produced by starting with appropriate kiln feed composition, blending the clinker with the desired amount of calcium sulfate, and grinding the product mixture to appropriate fineness. Manufacture of cements of all of the various types involves the same basic high temperature fusion and clinkering process responsible for the NO_x emissions from cement kilns.

The five basic types of Portland cement recognized and produced in the United States are described below. (3,4) In addition, different varieties are prepared by using various blending formulations. (5)

Type I Portland cement is a normal, general-purpose cement suitable for all uses. It is used in general construction projects such as buildings, bridges, floors, pavements, and other precast concrete products. Type I is also known as regular cement and most commonly known as gray cement because of its color. White cement typically contains less ferric oxide and is used for special applications. There are other types of cements in general use such as oil-well cement, quick-setting cement, and others for special applications. Type IA Portland cement is similar to Type I with the addition of air-entraining properties.

Table 2-1. Basic Clinker Compounds (3)

Formula	Name
$2CaO\ SiO_2$	Dicalcium silicate
$3\ CaO\ Si\ O_2$	Tricalcium silicate
$3CaO\ AL_20_3$	Tricalcium aluminate
$4CaO\ A1_20_3\ Fe_20_3$	Tetracalcium aluminoferrite
MgO	Magnesium oxide in free state or combined in di- or tri-calcium silicate lattice.

Type II Portland cement generates less heat at a slower rate and has a moderate resistance to sulfate attack. Type II Portland cements are for use where moderate heat of hydration is required or for general concrete construction exposed to moderate sulfate action. Type IIA Portland cement is identical to Type II, with the exception of inclusion of an air-entraining admixture, and produces air-entrained concrete.

Type III Portland cement is a high-early-strength cement and causes concrete to set and gain strength rapidly. Type III is chemically and physically similar to Type I, except that its particles have been ground finer. It is made from raw materials with a lime to silica ratio higher than that of Type I cement. It contains a higher proportion of tricalcium silicate ($3CaO{\cdot}SiO_2$) than regular Portland cements. Type IIIA is an air-entraining, high-early-strength cement.

Type IV Portland cement has a low heat of hydration and develops strength at a slower rate than other cement types, making it ideal for use in dams and other massive concrete structures where there is little chance for heat to escape. Type IV Portland cement contains a lower percentage of tricalcium silicate ($3CaO{\cdot}SiO_2$) and tricalcium aluminate ($3CaO{\cdot}A1_2O_3$) than type I, thus lowering the heat evolution. Consequently, the percentage of dicalcium silicate is increased substantially and the percentage of tetracalcium aluminoferrite ($4CaO{\cdot}A1_2O_3{\cdot}Fe_2O_3$) may be increased or may stay the same.

Type V Portland cement is used only in concrete structure that will be exposed to severe sulfate action, principally where concrete is exposed to soil and groundwater with a high sulfate content. Type V Portland cements are those which, by their composition or processing, resist sulfates better than the other four types.

The use of air-entraining agents increases the resistance of the hardened concrete to scaling from alternate freezing and thawing. By adding these materials to the first three types of cements, IA, IIA, and IIIA varieties of cements are produced. Additional varieties of cements are produced for special applications by blending different ingredients: masonry cement, expansive cement, oil-well cement, etc. Masonry cements are commonly finely ground mixtures of Portland cement, limestone, and air-entraining agents. Granulated blast furnace slags and natural or artificial pozzolans are mixed and interground with Portland cement to prepare still other varieties such as blended types IP, IS, S, I(PM), and I(SM). (5)

2.1.1 Description of the Cement Industry

About 77.6 million metric tons of gray Portland and 274,000 metric tons of white cement were produced in a total of 198 cement kilns at 118 plants in the United States in 1998. (6) This was a 6.0 percent increase from the 1990 reported total production of 73.5 million metric tons. Cement industry annual clinker capacity steadily declined from the 1975 peak through 1990 and has steadily increased since the 1990 low. While the number of kilns has dropped sharply, average kiln size has increased. Since 1973 when average kiln size was 173,000 metric tons, average kiln size has now reached 393,000 metric tons. Although 42 cement companies produced clinker in 1998, the top 5 companies provided about 44.2 percent of the total finish grinding capacity. This is evidence of a high concentration of the U.S. production among a limited number of top producers. California and Texas are the two largest states in terms of clinker capacity with Pennsylvania, Missouri, and Alabama rounding out the top five. Fourteen states and the District of Columbia had no cement clinker-producing plants in 1998. (6)

The large majority of the cement plants (about 82.4 percent) in the United States are coal fired with about 2.8 percent using natural gas, and 0.9 percent using oil as the primary fuel. (6) The remaining 13.9 percent of the plants used other combinations, e.g. coal/waste as primary fuel. In 1998, 11 plants used waste as a primary fuel with 49 plants reporting waste as an alternate fuel.

Overview of Cement Manufacturing Process

The process of Portland cement manufacture consists of: (7)

- Quarrying and crushing the rock;
- Grinding the carefully proportioned materials to high fineness;
- Subjecting the raw mix to pyroprocessing in a rotary kiln; and
- Grinding the resulting clinker to a fine powder.

A layout of a typical wet process plant is shown in Figure 2-1, which also illustrates differences between the two primary types of cement processes: wet process and dry process. (7) Newer designs of dry process plants are equipped with innovations such as precalciners and/or suspension preheaters to increase the overall energy efficiency of the cement plant. (7) Figure 22 is an illustration of a preheater/calciner type of dry process system. (8)

The choice between the wet or dry process for cement manufacturing often depends upon the moisture content in the raw feed materials mined from quarries. If the moisture content of the feed materials is already very high (15 to 20 percent), a wet process may be attractive. The recent trend, however, has been toward the dry process with preheater/precalciner systems. In 1998, about 20.6 million metric tons of clinker were produced by the wet process with 57.4 million metric tons produced by a dry process. Within the dry process category, 14.2 million metric tons were produced by facilities equipped with a preheater system and 26.1 million metric tons were produced by facilities equipped with a precalciner system. (6)

The different steps involved in the cement manufacturing process are described in the following subsections.

Raw Materials and Kiln Feed Preparation

Calcium carbonate and the oxides of silicon, aluminum, and iron comprise the basic ingredients of cement raw mix. Because of the large requirement for calcium, the plants are generally located near the source of the calcareous material. The requisite silica and alumina may be derived from a clay, shale, or overburden from a limestone quarry. Such materials usually contain some of the required iron oxide, but many plants need to supplement the iron

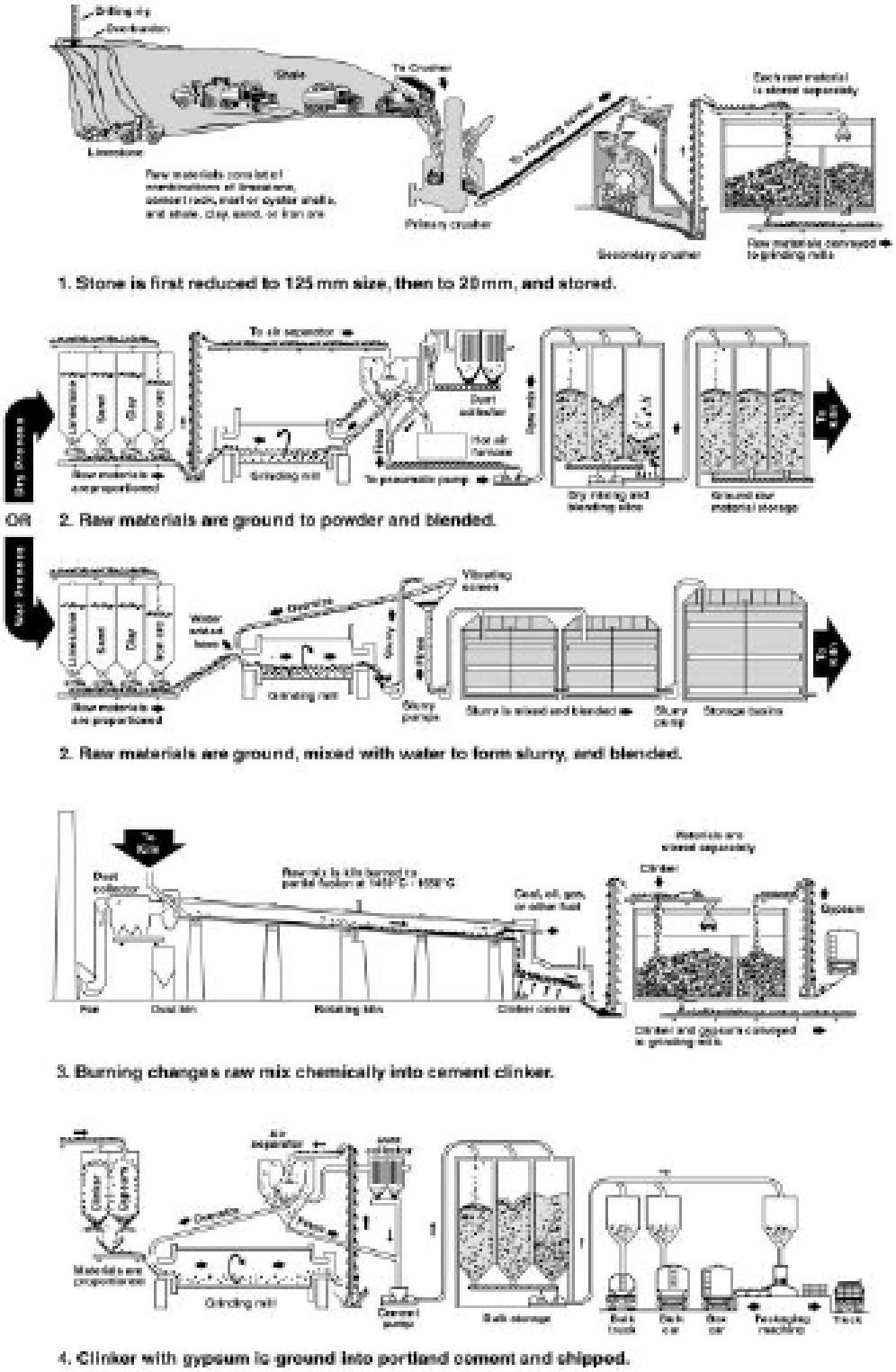


Figure 2-1. Typical Wet Process Cement Production

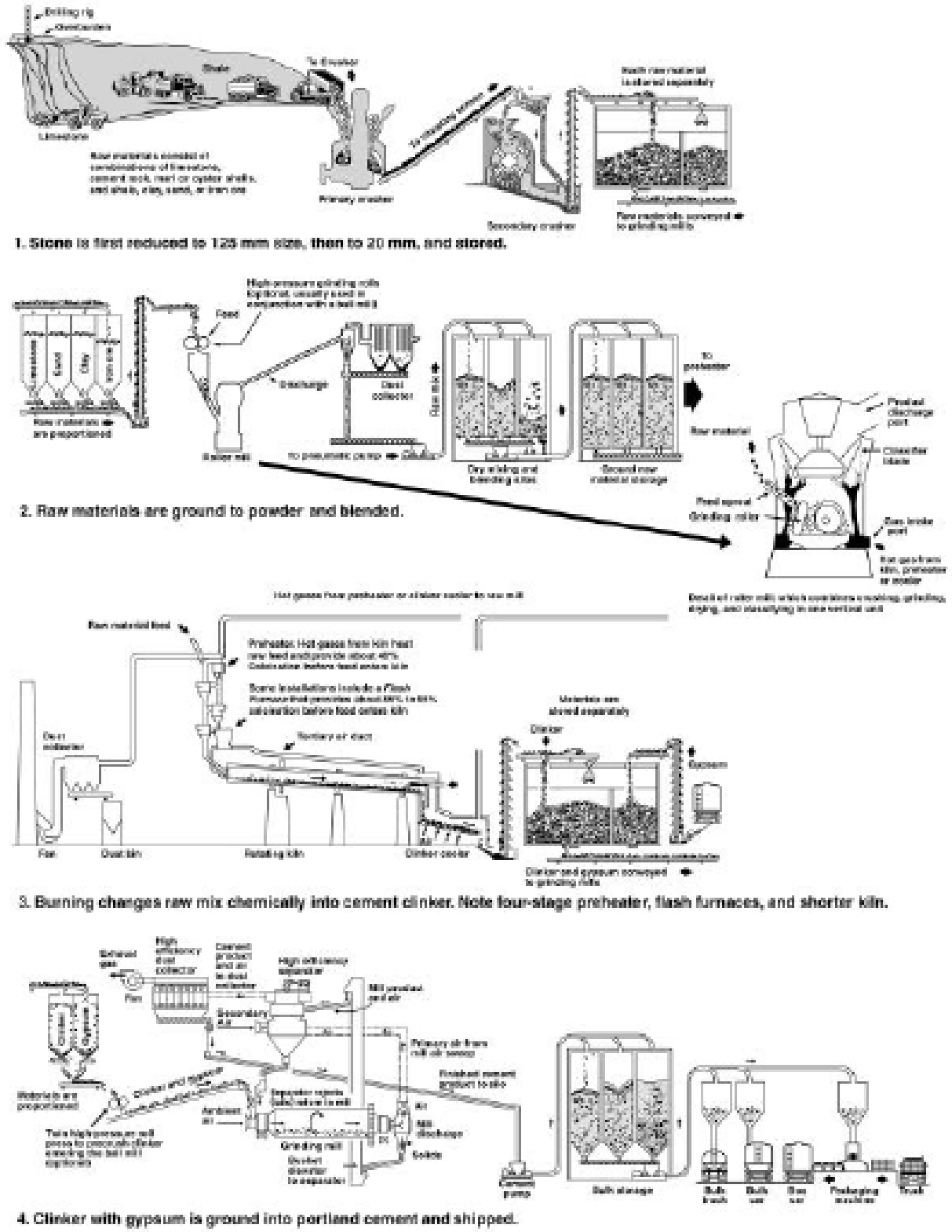


Figure 2-2. Typical Dry Process Cement Production with Calciner and Preheater

with mill scale, pyrite cinders, or iron ore. Silica may be supplemented by adding sand to the raw mix, whereas alumina can be furnished by bauxites and alumina-rich flint clays. (7) Industrial byproducts are becoming more widely used as raw materials for cement, e.g., slags contain carbonate-free lime, as well as substantial levels of silica and alumina. Fly ash from utility boilers can often be a suitable feed component, since it is already finely divided and provides silica and alumina.

The bulk of raw materials originates in the plant quarry. A primary jaw or roll crusher is frequently located within the quarry and reduces the quarried limestone or shale to about 100 mm top size. A secondary crusher, usually roll or hammer mills, typically gives a product of about 10 to 25 mm top size. Combination crusher-dryers can utilize exit gases from the kiln or clinker cooler to dry wet material during crushing. Each of the raw materials is stored separately and proportioned into the grinding mills separately using weigh feeders or volumetric measurements. Ball mills are used for both wet and dry processes to grind the material to a fineness such that only 15 to 30 wt% is retained on a 74-µm (200 mesh) sieve.

In the wet process the raw materials are ground with about 30 to 40 percent water, producing a well-homogenized mixture called slurry. Raw material for dry process plants is ground in closed-circuit ball mills with air separators, which may be adjusted for the desired fineness. Drying may be carried out in separate units, but most often is accomplished in the raw mill simultaneously with grinding. Waste heat can be utilized directly in the mill by coupling the raw mill to the kiln- and/or clinker cooler exhaust. For suspension preheater-type kilns, a roller mill utilizes the exit gas from the preheater to dry the material in suspension in the mill. A blending system provides the kiln with a homogeneous raw feed. In the wet process the mill slurry is blended in a series of continuously agitated tanks in which the composition, usually the calcium oxide content, is adjusted as required. These tanks may also serve as kiln feed tanks or the slurry may be pumped to large kiln feed basins. Dry process blending is usually accomplished in a silo with compressed air. (7)

Pyroprocessing

All cement clinker is produced in large rotary kiln systems. The rotary kiln is a refractory brick-lined cylindrical steel shell [3 to 8 m (10 to 25 ft) diameter, 50 to 230 m (150 to 750 ft) long] equipped with an electrical drive to rotate the kiln on its longitudinal axis at one to three rpm. It is a countercurrent heating device slightly inclined to the horizontal, so that material fed into the upper end travels slowly by gravity to be discharged into the clinker cooler at the lower, discharge end. The burners at the firing end, i.e., the lower or discharge end, produce a current of hot gases that heats the clinker, and the calcined and raw materials in succession, as it passes upward toward the feed end. Refractory bricks of magnesia or alumina combinations line the firing end. In the less heat-intensive midsection of the kiln, bricks of lower thermal conductivity are often used. Abrasion-resistant bricks or monolithic castable linings are used at the feed end. (7)

Pyroprocessing may be conveniently divided into four stages, as a function of location and temperature of the materials in the rotary kiln. (9)

1. Evaporation of uncombined water from raw materials, as material temperature increases to 100°C (212°F);

2. Dehydration, as the material temperature increases from 100ºC to approximately 430°C (800°F) to form dehydrated clay minerals composed of oxides of silicon, aluminum, and iron;

3. Calcination, during which carbon dioxide (CO_2) and CaO are formed from calcium carbonates, primarily between 900°C (1,650°F) and 982°C (1,800°F); and

4. Reaction, of the oxides in the burning zone of the rotary kiln, to form cement clinker at temperatures of approximately 1,510°C (2,750°F).

The duration and location of these stages in an actual kiln depend upon the type of process used, e.g., wet or dry, and the use of preheaters and precalciners as discussed in the following section.

It is desirable to cool the clinker rapidly as it leaves the burning zone. Heat recovery, preheating of combustion air, and fast clinker cooling are achieved by clinker coolers of the

reciprocating-grate, planetary, rotary, or shaft type. Most commonly used are grate coolers where the clinker is conveyed along the grate and subjected to cooling by ambient air, which passes through the clinker bed in cross-current heat exchange. The air is moved by a series of undergrate fans and becomes preheated to 370 to 1,000°C (700 to 1,830°F) at the hot end of cooler. A portion of the heated air serves as secondary combustion air in the kiln. Primary air is that portion of the combustion air needed to carry the fuel into the kiln and disperse the fuel. (7)

2.1.2 Kiln Types and Operation

There are four main types of kilns used in Portland cement manufacture:

- Long wet kilns;
- Long dry kilns;
- Dry kilns with preheaters; and
- Dry kilns with precalciners.

Wet kilns tend to be older units and are often located where the moisture content of feed materials from local sources (quarries) tends to be high. (10)

Long Wet Kilns

In a long wet-process kiln, the slurry introduced into the feed end first undergoes simultaneous heating and drying. The refractory lining is alternately heated by the gases when exposed and cooled by the slurry when immersed; thus, the lining serves to transfer heat as do the gases themselves. Large quantities of water must be evaporated; thus most wet kilns are equipped with chains suspended across the cross section of the kiln to maximize heat transfer from the gases to the slurry, or chain garlands that serve to recuperate heat and simultaneously convey the slurry. After most of the moisture has been evaporated, the nodules, which still contain combined water, move down the kiln and are gradually heated to about 550°C (1,022°F) where the calcination reactions commence. The calcined material further undergoes clinkering reactions. As the charge leaves the burning zone and begins to cool, clinker minerals crystallize from the melt, and the liquid phase solidifies. The granular clinker material drops into the clinker cooler for further cooling by air. (7)

Wet kilns typically represent an older cement technology with smaller capacity kilns. In the United States wet cement kiln capacities range from 77,000 to 1,179,000 metric tons/year with an average of 307,000 metric tons/year. (6)

Dry Process Kilns

The dry process utilizes a dry kiln feed rather than a slurry. Early dry process kilns were short, and the substantial quantities of waste heat in the exit gases from such kilns were frequently used in boilers to generate electric power, which often satisfied all electrical needs of the plant. In one modification, the kiln has been lengthened to nearly the length of wet-process kilns and chains were added. The chains serve almost exclusively a heat exchange function. Refractory heat-recuperative devices, such as crosses, lifters, and trefoils, have also been installed. So equipped, the long dry kiln is capable of better energy efficiency than wet kilns. Other than the need for evaporation of water, its operation is similar to that of a wet kiln. To improve the energy efficiency of the dry process, variations such as suspension preheaters and precalciners have been introduced as discussed in the next sections. (7)

Long dry process kilns are generally of a smaller capacity compared to long wet kilns. In the United States dry cement kiln capacities range from 50,000 to 590,000 metric tons/year with an average capacity of 265,000 metric tons/year. (6)

Dry Kilns With Preheaters

In dry kilns with suspension preheaters, the pulverized feed passes by gravity through a series of cyclones and riser ducts in a vertical arrangement, where it is separated and preheated several times, typically in a four-stage cyclone system. The partially (40 to 50 percent) calcined feed exits the preheater tower into the kiln at about 800 to 900°C (1,500 to 1,650°F). The kiln length required for completion of the cement formation is considerably shorter than that of conventional kilns, and heat exchange is very good. Suspension preheater kilns are very energy efficient compared to wet or long dry kilns. The intimate mixing of the hot gases and feed in the preheater riser ducts promotes condensation of alkalies and sulfur on the feed, which sometimes results in objectionable high alkali and sulfur contents in the clinker, or occasions buildups in the

preheater tower. To alleviate this problem, some of the kiln exit gases can bypass the preheater through a slipstream, or fewer cyclone stages can be used in the preheater with some sacrifice of efficiency.

Suspension preheater kilns represent a newer cement technology compared to the long dry kilns. They are also somewhat larger in production capacity than the conventional long rotary kilns. In the United States the preheater type kiln capacities range from 223,000 to 1,237,000 metric tons/year with an average capacity of 406,000 metric tons/year.

Dry Kilns With Precalciners

The success of preheater kiln systems, led to precalciner kiln systems. These units utilize a second burner to carry out calcination in a separate vessel attached to the preheater. The calciner utilizes preheated combustion air drawn from the clinker cooler or kiln exit gases and is equipped with a burner that typically burns about 60 percent of the total kiln fuel. Most often coal is used as a fuel in a calciner furnace; however, almost any fuel may be used including chipped tires. The raw material is calcined almost 95 percent, and the gases continue their upward movement through successive cyclone/riser duct preheater stages in the same manner as in an ordinary preheater. The precalciner system permits the use of smaller dimension kilns, since only actual clinkering is carried out in the rotary kiln. Energy efficiency is often even better than that of a preheater kiln, and the energy penalty for bypass of kiln exit gases is reduced since only about 40 percent of the fuel is being burned in the kiln. The burning process and the clinker cooling operations for the modern dry-process kilns are the same as for long wet kilns.

The precalciner technology is the most modern cement manufacturing technology and almost all of the newer cement plants are based on these designs. Precalciner kilns are also much larger in capacity than the conventional rotary kilns. The precalciner type kilns in the United States range from 449,000 to 1,580,000 metric tons/year with an average of 869,000 metric tons/year. Because of the new large precalciner plants replacing older and smaller plants, the overall average kiln capacity has been steadily increasing in the United States. It has increased from an average of 239,000 metric tons/year in 1980 to an average capacity of 393,000 metric tons/year in 1989.

Finish Grinding

The cooled clinker is conveyed to clinker storage. It is subsequently mixed with 4 to 6 percent gypsum and introduced directly into the finish mills. These are large, steel cylinders [2 to 5 m (7 to 16 ft) in diameter] containing a charge of steel balls, which rotate at about 15 to 20 rpm. Rarely, the desired size reduction may be accomplished in a roller mill, rather than in ball mills. Recently, the industry has also adopted the use of roller presses to precrush the clinker to smaller size prior to introduction to the finish mills. The roller press is more efficient than the crushing stage of the ball mill, and production capacities of finish grinding systems have been substantially increased and electrical energy requirements reduced by the incorporation of roller presses into finish circuits. The clinker and gypsum are ultimately ground to a fine, homogeneous powder. About 85 to 96 percent of the product is in particles less than 44 µm in diameter. This grinding may be accomplished by two different mill systems. In open-circuit milling, the material passes directly through the mill without any separation. A wide particle size distribution range is usually obtained with substantial amounts of very fine and rather coarse particles. Open circuit grinding is, however, rarely practiced in U.S. cement plants. In closed-circuit grinding, the mill product is carried to a cyclonic air separator in which the coarse particles are rejected from the product and returned to the mill for further grinding. (7)

Quality Control

Beginning at the quarry operation, quality of the end product is maintained by adjustments of composition, burning conditions, and finish grinding. Control checks are made for fineness of materials, chemical composition, and uniformity. Clinker burning is often monitored by the liter weight test (which involves weighing a portion of sized clinker), a free lime test, or may be checked by microscopic evaluation of the crystalline structure of the clinker compounds. Samples may be analyzed by wet chemistry, X-ray fluorescence, atomic absorption, or flame photometry. Standard cement samples are available from the National Institute of Standards and Technology. Fineness of the cement is most commonly measured by the air permeability method. Finally, standardized performance tests are conducted on the finished cement. (7)

2.1.3 Thermal Characteristics

Figure 2-3 provides a detailed look at the material and gas temperatures inside cement kilns. The concepts of high-grade heat and low-grade heat are well discussed by Weber. (11) Weber states, "The boundary between the main and the subsidiary thermal system is assumed always to correspond to a material temperature of 550°C, since decarbonation in the rotary kiln in general already begins at this temperature. A certain amount of heat whose temperature is below the gas temperature at the commencement of decarbonation will always be left over from the calcining zone. This heat is 'lower-grade' in the sense that, because of the low temperature, it cannot be further used for decarbonation or sintering, but only for preheating and drying."

In turn, Figure 2-4 provides a graphical look at the relationship between temperatures in the cement manufacturing process and the chemistry of cement clinker formation. Except for the process of drying the raw material slurry in wet kilns these profiles are essentially the same for both wet and dry process cement kilns. The only substantive difference is that the difference between the gas and material temperature in a preheater tower is less than in the back end of a wet kiln because of the more efficient heat transfer in the cyclones.

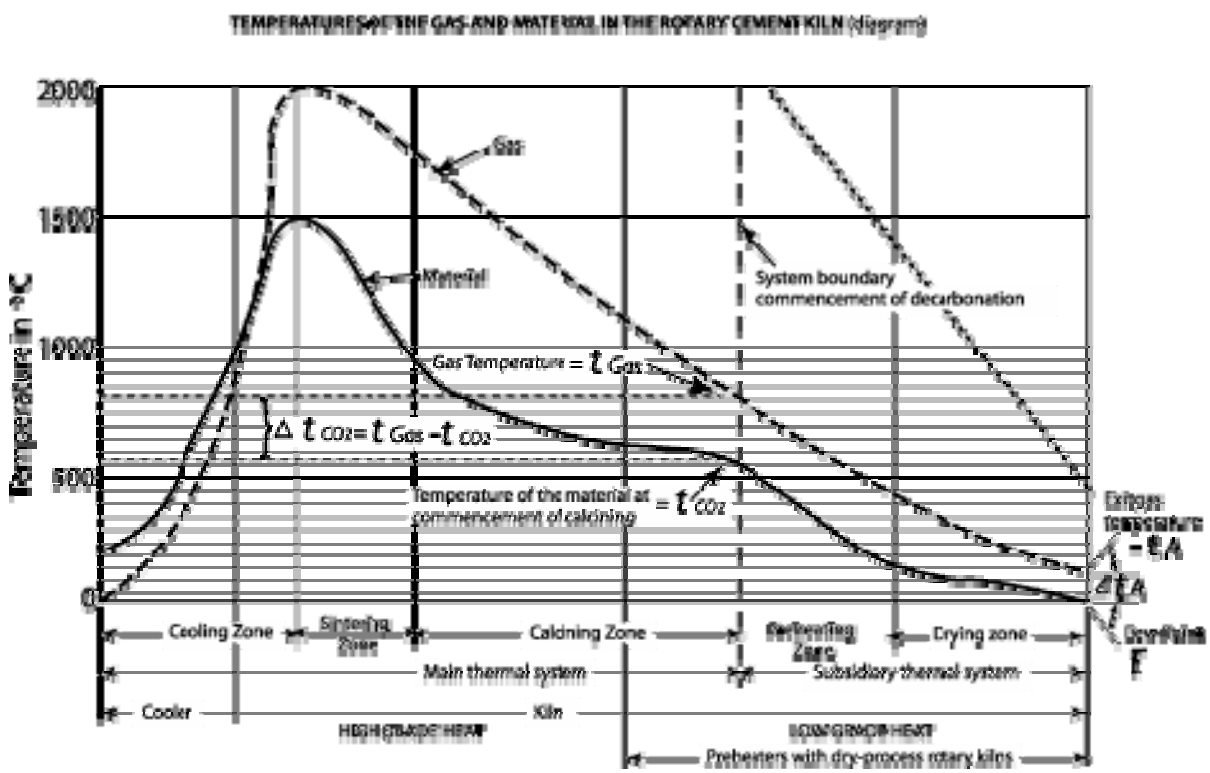


Figure 2-3. Temperature of the Gas and Material in the Rotary Cement Kiln 1

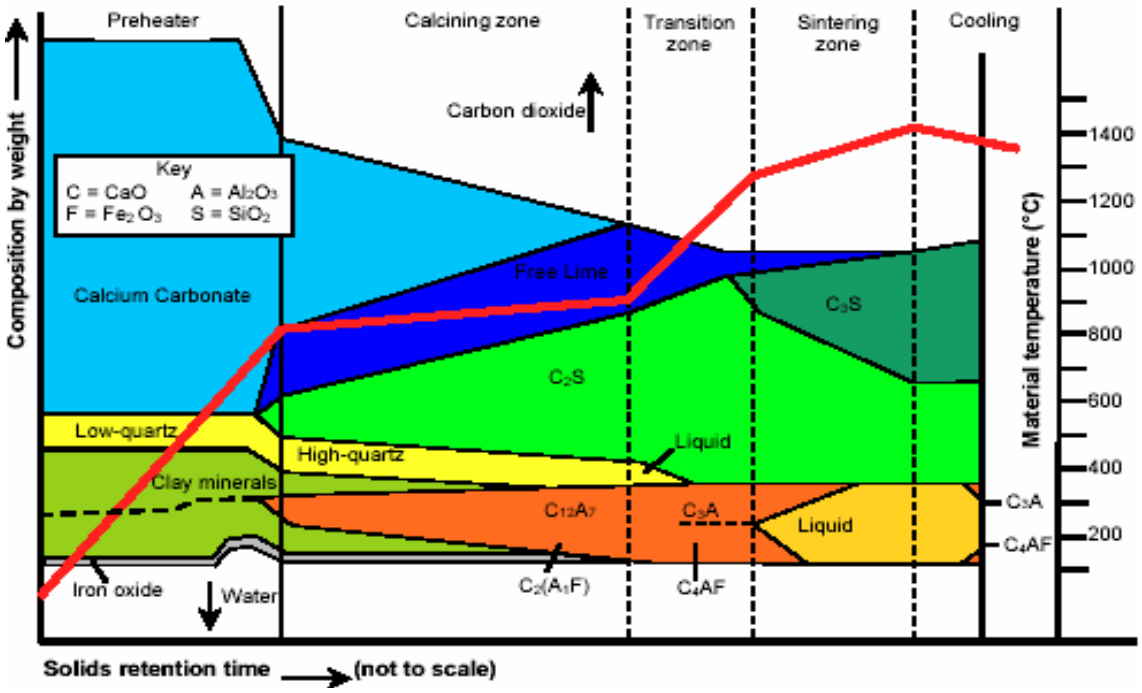


Figure 2-4. The Relationship Between Process Temperatures and the Chemistry of Cement Clinker Formation

2.1.4 Process Variables

The formation of clinker of suitable quality for manufacture of Portland cement depends on the characteristics of feed materials and the temperature profile of the pyroprocessing step. The most critical process variables are:

- Feed composition;
- Feed particle size;
- Feed moisture concentration;
- Feed mass flow rate;
- System heat losses; and
- Ambient air infiltration.

More than 30 raw materials (primarily calcium carbonate, aluminosilicates, silica and iron oxide) are known to be used in Portland cement manufacturing. (12) These materials are ground and mixed to create a feed that has the appropriate chemical and physical properties to produce clinker with the desired properties. Uniform feed composition and size ensure consistent quality and characteristics of the clinker produced.

Higher moisture contents require more heat input to maintain proper temperature profile in the kiln. Cement raw materials are received with an initial moisture content varying from one to more than 50 percent. In dry kilns, the moisture content is usually reduced to less than one percent before or during the grinding process (e.g., using drum dryers, air separators, or supplying supplemental heat to the raw mill). In the wet process, water is added to the raw mill during the grinding of the raw materials, thereby producing a slurry of approximately 65 percent solids. (12)

3.0 NO_X FORMATION IN CEMENT KILNS

This section of the report is taken from the EPA 2000 Report and is included, with minor editing by the ERG Team. This information is included to provide the Texas environmental communities with the comprehensive background information necessary to understand the parameters that dictate NO_x control options at cement kilns.

3.1 Overview of NO_x Formation Mechanisms

In cement manufacturing, conditions favorable for formation of nitrogen oxides (NO_x) are reached routinely because of the high process temperatures involved. Essentially, all of the NO_x emissions associated with cement manufacturing are generated in the cement kilns. Although, there are other heating operations in a cement plant, such as drying of raw feed or coal, often the heat from the kiln exhaust gases is used for these operations making their contribution to NO_x emissions negligible. In cement kilns, NO_x emissions are formed during fuel combustion by two primary mechanisms:

- Oxidation of the molecular nitrogen present in the combustion air which is termed thermal NO_x formation; and
- Oxidation of the nitrogen compounds present in the fuel, which is termed fuel NO_x formation.

Sometimes the raw material feed to the kiln may also contain nitrogen compounds, which may lead to feed NO_x formation similar to fuel NO_x formation. Because of the high temperatures involved in the burning or clinker formation step, the thermal NO_x formation provides the dominant mechanism for NO_x formation in cement manufacturing. The term NO_x includes both NO and NO_2 species, although NO_2 normally accounts for less than 10 percent of the NO_x emissions from a cement kiln exhaust stack. (13) The concentration and emission of NO_x are, however, typically expressed in equivalent NO_2 form.

3.1.1 Thermal NO_x Formation

Thermal NO_x is formed by the homogeneous reaction of oxygen and nitrogen in the gas phase at high temperatures. In the overall reaction mechanism proposed by Zeldovich, (14) the two important steps in NO_x formation are given as:

$$N2 + O \times NO_x + N \qquad kf = 2 \times 10^{14} \exp(-76500/RT)$$

$$N + O_2 \times NO_x + O \qquad kf = 6.3 \times 10^{9} \exp(-6300/RT)$$

where kf are the rate constants for the reactions shown. The high activation energy of reaction (4-1), 76.5 kcal/mol, means that this reaction is the most temperature sensitive. An equilibrium reaction of NO_x with O_2 further results in NO_2 formation.

The equilibrium concentrations of NO_x and NO_2 formed thus depend strongly upon the gas-phase temperature as well as the concentration of O_2 and N_2 in the gas phase. Table 3-1 shows the equilibrium concentrations of NO and NO_2 for two conditions. (15) First, the equilibrium concentrations of NO_x and NO_2 for N_2 and O_2 concentrations found in ambient air are shown. Secondly, Table 3-1 also shows the NO_x and NO_2 concentrations at flue gas conditions where the O_2 and N_2 concentrations are defined for this table as 3.3 percent O_2 and 76 percent N_2. The equilibrium NO_x concentrations for the flue gas conditions are lower than those for ambient conditions due to the lower O_2 concentration. The excess air used during fuel combustion can substantially affect NO_x formation by determining the amount of oxygen available for NO_x reaction. The cement kiln burning zones usually have about 5 to 10 percent excess air while higher excess air levels are not uncommon. Figure 3-1 shows the theoretical equilibrium concentrations of NO in the flue gas for different excess air levels. (13) As can be seen from this figure, over 1000 ppm of NO may possibly be formed at the typical kiln solids temperatures of 1430 to 1480°C (2600 to 2700°F) as the corresponding gas-phase temperatures are on the order of 1650°C (3000°F).

Table 3-1. Calculated Equilibrium Concentrations (In PPM) Of NO_x and NO_x In Air and Flue Gas (15)

Temperature		Air		Flue Gas	
K	°F	NO	NO_2	NO	NO_2
300	80	$3.4\ (10)^{-10}$	$2.1\ (10)^{-4}$	$1.1\ (10)^{-10}$	$3.3(10)^{-3}$
800	980	2.3	0.7	0.8	0.1
1440	2060	800	5.6	250	0.9

Fuel combustion in the kiln burning zone is the primary source of thermal NO_x, formation in cement kilns due to temperatures well above 1,400°C (2,550°F). In contrast, the fuel combustion temperature in a precalciner or in a kiln riser duct is well below 1,200°C (2,200°F), suppressing thermal NO_x formation. (16) Mainly fuel and feed NO_x may be formed in the secondary firing zone of preheater and precalciner kiln systems. Along with the combustion temperature, the gas-phase residence time and the available oxygen concentration in the high temperature kiln burning zone are important parameters. Longer residence times at the high temperatures will allow the NO to be formed in the equilibrium quantities. Greater amounts of oxygen in the combustion zone will of course lead to greater amounts of NO formation. Once formed, the decomposition of NO at lower temperatures, although thermodynamically favorable, is kinetically limited. Thus, strategies to reduce NO_x emissions need to be based upon reducing formation of $NO_{x,}$ which may be achieved by reducing combustion temperature, oxygen concentration in the high temperature combustion zone, and the gas residence time at high temperatures.

3.1.2 Fuel NO_x Formation

Fuel NO_x is formed by the conversion of nitrogen present in the fuel used. A recent survey of the cement industry by Portland Cement Association (PCA) indicates that almost 82 percent of the energy requirement of the cement industry is provided by coal. (17) Natural gas contributed about 3 percent of the energy demand, oil about one percent, and other fuels such as waste solvents provided about 14 percent of the energy. Both oil and natural gas have relatively low fuel bound nitrogen content, whereas coal may contain one to three percent of nitrogen by weight depending upon the source of coal. Waste-derived fuels (WDF) such as scrap tires, used motor oils, surplus printing inks, dry-cleaning solvents, paint thinners, sludge from the petroleum industry, agricultural wastes such as almond shells, and even municipal biosolids (dewatered

sewage sludge) are finding an increasing application in the cement kilns. (18) The nitrogen content in these fuels may be significant depending on the chemicals included in the waste mix being burned.

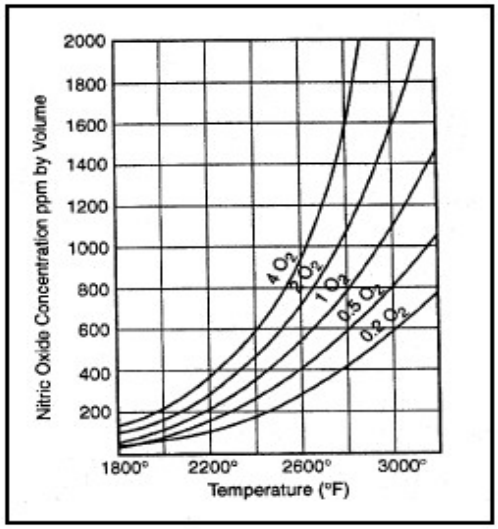


Figure 4-1. Theoretical equilibrium concentrations of NO in gas from combustion sustained in air.[1]

Figure 3-1. Theoretical Equilibrium Concentrations of NO_x

The maximum possible fuel NO_x formation may be estimated from the fuel nitrogen content by assuming 100 percent nitrogen conversion. The typical heat requirement for a wet process is estimated to be about 6 million Btu for a ton of clinker and the corresponding requirement for a dry process is estimated to be about 4.5 million Btu for a ton of clinker. Assuming an average heat requirement of 5.3 million Btu for a ton of clinker, and a coal heating value of 12,000 Btu/lb, about 442 lb. of coal will be required per ton of clinker produced. With a nitrogen content of one percent by weight, approximately 9.5 lb. of NO (14.5 lb. expressed as NO_2) would be produced per ton of clinker with 100 percent nitrogen conversion. Thus, even with only 10 percent conversion of coal nitrogen to NO_x, 1.5 lb. of fuel NO_x (expressed as NO_2) may be formed per ton of clinker when coal is used as a primary fuel.

The amount of fuel NO_x formed is difficult to identify separately from thermal NO_x as measurements indicate the overall NO_x formed. In general, however, thermal NO_x is assumed to be the dominant mechanism in cement kilns. (19) Typically, gas burners produce more intense and hot flames compared to the less intense "lazy" flames produced by coal burners. Thus, gas-fired kilns may be expected to produce greater thermal NO_x as compared to coal-fired kilns.

Coal, on the other hand, contains much greater amounts of fuel-bound nitrogen than natural gas, which has almost no fuel-bound nitrogen. The coal-fired kilns may thus be expected to produce more fuel NO_x than gas-fired kilns. A study of gas- and coal-fired kilns, however, clearly indicated that gas-fired, dry-process kilns typically produce almost three times more NO_x than the coal-fired, dry-process kilns. (19) This fact indicates the dominance of thermal NO in overall NO formation.

3.1.3 Feed NO_x Formation

Similar to coal, the raw materials used in cement production may contain a significant amount of nitrogen. In most cases, limestone is the major raw material, with the remainder of the raw mix being composed of clays, shales, sandstones, sands, and iron ores. Fly ash from coal-fired power plants is used as a raw material and may contain substantial amounts of nitrogen compounds, since it is usually derived from coal. Most of these raw material components are sedimentary minerals and they may contain small amounts of chemically bound nitrogen, presumably of organic origin. Various kiln feeds contain appreciable amounts of nitrogen, ranging from about 20 ppm up to as much as 1,000 ppm (as N). (20) The higher values (>100 ppm) are generally associated with minerals displaying noticeable kerogen contents. Since 100 ppm N in a kiln feed is equivalent to about one lb. NO_x per ton of clinker (if it all converted), NO_x emissions from the kiln feed may represent a major source of NO_x from cement kilns. Nevertheless, it is probably less important than thermal NO_x and fuel NO_x in most cases.

The same study indicated that conversion of feed nitrogen to NO_x occurs mainly in the 300 to 800°C (570 to 1,470°F) temperature range and depends upon the feed heating rate. (20) Rapid heating rates (~1,000°C flash heating) of the kiln feed mixtures were found to give much lower conversion efficiencies, whereas slow heating rates of kiln feed mixtures (~60°C/min) gave fairly high conversion of about 50 percent of bound nitrogen to NO_x. These results were explained by assuming that the organic nitrogen must vaporize from the sample prior to oxidation if high conversion efficiencies to NO_x are to be achieved. If heating rates are rapid, "cracking" of these volatile compounds may occur in situ, and this may result in conversion of the bound nitrogen directly to N_2 before it comes into contact with gaseous oxygen, thus reducing the fraction converted to NO_x. Such a hypothesis is also consistent with the observation

that, during coal combustion, the involatile or "char" nitrogen is converted to NO_x much less efficiently than the volatile nitrogen. (21)

3.1.4 Factors Affecting NO_x Emissions in Cement Manufacturing

There are four primary types of cement kilns used in the industry: wet kilns, long dry kilns, kilns with a preheater, and kilns with a preheater/precalciner. The wet and long dry kilns and some preheater kilns will have only one fuel combustion zone, whereas the newer preheater and precalciner kiln designs have two or three fuel combustion zones: kiln burning zone, riser duct and precalciner. Because the typical temperatures present in the combustion zones are different, the factors affecting NO_x formation are also somewhat different in different kiln types and are discussed in the following sections. In addition to the specific NO_x formation mechanisms, the energy efficiency of the cement-making process is also important as it determines the amount of heat input needed to produce a unit quantity of cement. A high thermal efficiency would lead to less consumption of heat and fuel, and would generally produce lower NO_x emissions.

NO_x Formation in the Kiln Burning Zone

In the kiln burning zone, thermal NO_x provides the primary mechanism for NO_x formation. Thermal NO_x formation depends upon the combustion zone temperature, the gasphase residence time and the oxygen concentration in the high temperature combustion zone. The flame temperature strongly depends upon the type of fuel burned. The temperature and intensity are generally greater for gas burners than coal burners. The oxygen concentration in the combustion zone depends upon the overall excess air used and on the source and proportion of primary and secondary combustion air. Less primary air may produce an initial high-temperature, fuel-rich combustion zone followed by a low-temperature fuel-lean combustion zone. Such a combination is likely to reduce NO_x formation.

The firing system used in the kiln affects the proportion of primary and secondary combustion air. Direct firing systems introduce a large proportion of combustion air with the fuel being burned. This produces two conflicting effects for NO_x emissions: higher oxygen

concentration or fuel lean combustion and lower gas temperature. Indirect firing systems on the other hand use only a small portion of combustion air to convey fuel and thus use less primary air. In general, direct fired systems may be expected to produce greater NO_x emissions compared to indirect fired systems. The flame shape and the theoretical flame temperature are important factors in thermal NO_x formation as these factors determine the hottest points in the flame. A long "lazy" flame will produce less NO than a short intense flame.

The flame shape depends on the fuel being burned as well as the proportion of air. For the same amount of primary air, gas burning may be expected to produce a shorter and more intense flame than coal burning. The lower the secondary air temperature and the greater the dust content in the secondary air, the lower the NO_x formation in the kiln burning zone. A large amount of water in the primary air (from a direct firing coal mill) and injection of cement kiln dust (CKD) in the burning zone (insufflation) may also reduce NO_x formation. With increasing excess air percentage, the NO_x formation in the kiln will increase, but only up to a certain point as an increasing excess air rate will reduce the secondary air temperature and, consequently, the flame temperature.

Process conditions that can affect NO_x emissions substantially are: temperature stability, stability of raw mix feed rate, burnability of raw mix, and alkali and sulfur control. Temperature stability is important to maintain the quality of clinker and is achieved by stable-flame conditions and energy efficiency. Clinker formation reactions require temperatures of 2,650 to 2,800°F (1,450 to 1,540°C) and an oxidizing environment. Sometimes natural gas or liquid waste derived fuel is used to control flame conditions and improve clinker quality. The excess air used during combustion has a substantial influence on NO_x emissions. Oxygen levels of 4 to 5 percent in kiln exhaust gases would correspond to high NO_x emissions, whereas oxygen levels of only 0.5 to 1.5 percent would mean lower NO_x emissions. Thus, NO_x emissions in a kiln may depend upon the care exercised by the operator in minimizing excess oxygen needed to maintain the quality of the clinker produced. All but one of the clinker formation reactions are exothermic and represent a dynamic process that requires constant operator adjustments which can vary NO_x formation.

The heating value of the fuel burned may also affect NO_x emissions. High heating value fuels, such as petroleum coke may require less combustion air and produce less NO_x per ton of clinker.

Different raw material compositions require different burning conditions to maintain the quality of clinker produced. Thus, similar types of kilns with different feed materials may produce different levels of NO_x emissions. The alkali content of finished cement needs to be below a certain acceptable level. Low alkali requirements may require higher kiln temperatures and longer residence times at high temperatures to volatilize the alkali present in the molten clinker. Raw materials with greater alkali content may need to be burned longer at higher temperatures to meet alkali requirements and thus may produce greater NO_x emissions. Increased volatilization of alkali results in increased alkali emissions in kiln exhaust gases. To control alkali emissions, a part of the kiln exhaust gases may be bypassed around a downstream unit, e.g., a precalciner. The bypassed gases are quenched to remove alkali and sent through a particulate matter collector. This alkali-rich particulate matter is removed from the process and disposed. The bypass of kiln exhaust gases typically involves a fuel penalty, e.g., about 20,000 Btu/tonne clinker for every one percent gas bypass. The additional heat requirement will contribute to increased NO_x emissions.

Wet kilns require about 33 percent more thermal energy than a dry kiln. This means a greater volume of exhaust gas from a wet kiln for the same production. On the other hand, the greater amount of combustion air will also mean a somewhat lower secondary air temperature. Based on these contradicting factors, one might expect the NO_x emissions from a wet process kiln to be similar to the dry and preheater kilns without riser duct firing.

NO_x Formation in Secondary Firing

In the secondary firing region of precalcining kilns, where temperatures range from 820 to 1100°C (1500 to 2000°F), the following reactions may take place:

$$\text{"N"} + O \rightarrow NO \qquad (4\text{-}3)$$
$$\text{"N"} + NO \rightarrow N2 + O \qquad (4\text{-}4)$$

where "N" means nitrogen originating from nitrogen compounds in the fuel. (13) Reaction (4-3) shows that NO formation in the secondary firing zone will depend upon the nitrogen content in the fuel and the oxygen level in the firing zone. Reaction (4-4) indicates that, if there is already NO present in the gas introduced into the secondary firing zone, a reduction of this NO may occur with the fuel nitrogen compounds acting as reducing agents. Accordingly, the net formation of NO in the secondary firing zone will also depend upon the initial NO concentration in the combustion gas. Finally, measurements have shown that the volatile content in the solid fuel and the temperature in the secondary firing zone also influence the NO formation in the secondary firing zone. (22) With increased volatile content in the fuel, the ratio of fuel nitrogen conversion into NO seems to decrease and, as the reaction rate of reaction (4-4) increases more rapidly with the temperature than that of reaction (4-3), an increase in the temperature of the secondary firing region may reduce-the net NO formation. (13)

3.1.5 Suspension Preheater (SP) Kilns with Riser Duct Firing

In many SP kiln systems 10 to 20 percent of the fuel is fired into the riser duct. The preheater systems are more energy efficient compared to long dry kilns. The increased energy efficiency and the reduction in the amount of fuel burned at the higher clinker burning temperature may be expected to reduce the NO_x emissions from preheater kilns when compared with the long dry and wet kilns. Measurements at several riser-duct fired kiln systems indicate that firing coarse fuel (e.g., tires) into the kiln riser duct will reduce NO_x emissions from the kiln systems. (23) This may be explained by the fact that a large part of the fuel falls directly down into the kiln charge, creating a reducing atmosphere in the kiln back-end where NO_x from the burning zone is reduced.

Conversely, when firing finely ground fuel into the kiln riser duct, the NO_x content in the exhaust gas may increase on passing through the riser duct. As the NO_x emissions from the kiln may also increase slightly due to an increased excess air rate, the total NO_x emissions from the kiln system may increase when starting up riser duct firing with finely ground fuel. (13)

3.1.6 Precalcining Kiln Systems

In precalcining kiln systems with a tertiary air duct, firing into the rotary kiln typically accounts for only 40 to 50 percent of the total heat consumption and the specific amount of combustion gases from the kiln burning zone is reduced proportionally. Precalciner kilns also typically require the least amount of energy per unit amount of clinker produced. The lower energy requirement and the substantial reduction in the proportion of the fuel burned at clinker burning temperatures may be expected to reduce the NO_x emissions from the precalciner kilns as compared to the preheater kilns. On the other hand, the NO_x concentration (in ppm) in the kiln gas may be considerably higher than in preheater kilns. This is probably due to the shorter material and longer gas retention times in the precalciner kiln burning zone combined with a very high secondary air temperature. (13)

When examining the contribution from the calciner firing to the emission of NO_x, two basically different types of precalcining kiln systems need to be considered:

- The in-line (ILC) type in which the kiln gas passes through the firing region of the precalciner; and
- The separate line (SLC) type in which the kiln exhaust gas bypasses the firing region of the precalciner.

ILC systems: In these systems, the fuel combustion in the calciner takes place in a mixture of the kiln exhaust gas and hot air from the cooler (tertiary air). Some of the nitrogen in the fuel reacts with NO from the kiln exhaust gas while another part reacts with oxygen to form NO. The result may be a net increase or a net reduction of NO in the calciner.

SLC systems: In these systems, the fuel combustion in the calciner takes place in pure hot air. In the case of oil firing, NO production in the calciner is negligible; but when using fuels containing fuel-bound nitrogen, up to 50 percent of the nitrogen compounds in the fuel may be converted into NO_x. The specific NO_x, production in an SLC calciner may be as high as 4 lb. NO_x per ton of clinker as measured in a calciner fired with petroleum coke which has a high nitrogen content and low volatile content. (13) The NO_x in the calciner exhaust gas is added to the NO_x in the gas from the rotary kiln which leaves this type of kiln system without being

reduced. When fired with solid fuels, SLC systems may therefore be expected to generate somewhat higher NO_x emissions than the ILC systems. (13) We should note, however, that some of the oxygen for combustion of the fuel in ILC systems passes through the burning zone, so the NO generated there may be higher (or lower due to lower temperatures) than for SLC systems.

3.1.7 Energy Efficiency of the Cement-Making Process

Since NO_x formation is directly related to fuel combustion, any reduction in the amount of fuel burned per unit amount of clinker produced should reduce NO_x emissions per unit clinker. Attempts to improve energy efficiency of the process by avoiding excessive clinker burning and utilizing waste heat effectively for preheating combustion air, coal, and raw mix is likely to reduce NO_x emissions. Improving heat transfer between hot gases and solid materials, e.g., by chain systems, will improve energy efficiency. The newer preheater and precalciner kiln designs provide very efficient preheating and precalcining of the raw mix with intimate gas-solids contact in cyclone towers. New cement kiln installations or renovations of older kilns thus predominantly involve precalciner designs for their energy efficiency. The inherent energy efficiency of these kiln designs is likely to produce lower NO_x emissions per unit amount of clinker as compared to the wet or long dry kilns.

4.0 OVERVIEW OF POTENTIALLY APPLICABLE CONTROL TECHNIQUES AND TECHNOLOGIES

Nitrogen oxides are formed by the oxidation of nitrogen during the fuel combustion process. The formation of thermal NO_x is a function of the flame temperature, flame turbulence, the amount of nitrogen and oxygen available for the thermal reaction, and the gas phase residence time at high temperature. To reduce the amount of thermal NO_x formed, one or more of these variables needs to be minimized. The formation of fuel and feed NO_x is not as well understood as the thermal NO_x formation. In general, however, the greater the concentration of nitrogen in the fuel and feed, the greater the fuel NO_x emissions. Therefore, reducing the amount of fuel and feed-bound nitrogen should reduce the contribution of the fuel and feed NO_x.

The typical NO_x emissions from a cement plant depend upon the type of the cement kiln. For any given type of kiln, the amount of NO_x formed is directly related to the amount of energy consumed in the cement-making process. Thus, measures that improve the energy efficiency of this process should reduce NO_x emissions in terms of lb. of NO_x/tonne clinker. With the rising costs of energy and the very competitive cement market, greater attention is being paid to increasing overall energy efficiency, such as through reduction of overburning of clinker and improvement in gas-solids heat transfer. Continuous emissions monitoring of CO, NO_x, and O_2 provide an indication of kiln conditions and also provide inputs for process control. Newer cement kiln designs are generally based on preheater/precalciner systems which provide very efficient gas-solids contact and greater energy efficiency. NO_x control approaches are evaluated below under four categories:

- High Temperature Emissions Controls;
- Combustion Optimization;
- Low Temperature Oxidation Emissions Controls; and
- Process Modifications.

This section of the report uses the EPA 2000 Report as the baseline for evaluating current control options for Ellis County kilns. The combustion and process optimization sections are included, with editing, from this report and describe the essential controls that have been considered and largely installed under the requirements of 30 TAC Chapter 117. Additions to sections for process modifications to improve energy efficiency through calciner modifications

and wet to dry conversions is discussed as site-specific options where applicable for Ellis County kilns. The section on oxidation controls is entirely new and was not considered in EPA 2000. The sections on SCR and SNCR consider EPA 2000 background information, but are written to reflect current status of these technologies and site-specific application to the Ellis County kilns. For the purposes of this report, *available* essentially means that the technology is commercially available and in use on similar types of cement kilns. *Transferable* means that the technology is commercially available and in use on similar process equipment and could reasonably be expected to work on the specified type of cement kiln. *Innovative* describes technologies that have not been successfully applied to a type of cement kiln, but in the judgment of the ERG Team could be expected to work on the type of cement kiln if correctly optimized through experimental application.

When discussing the transfer of technologies, comparisons are made between cement kilns, coal-fired utility boilers and refinery fluidized catalytic cracking units (FCCUs). While the emissions from these units vary widely, they are all capable of emitting thousands of tons of NO_x and SO_2 and typically use electrostatic precipitators (ESPs) to control particulate emissions that would also be thousands of tons per year prior to control. For the purposes of this discussion, a modern cement kiln producing one million tons per year of clinker would be roughly comparable to a coal-fired utility boiler of approximately 200 megawatts generating capacity and an FCCU of approximately 80,000 barrels per day. All of these units would have a typical air flow of approximately 300,000 cubic feet per minute. For comparison with the Ellis County kilns, a typical refinery of comparable air flow rate would tend to produce less NO_x and a utility boiler would typically produce more NO_x. The amount of SO_2 from these units would vary widely due to site specific operating conditions including fuels and feeds materials. The impact of SO_2 and particulate matter concentrations on the operation of SCR is discussed in depth below under Section 4.1.2. Other constituent pollutants in the gas stream are not considered to interfere with LoTox™ operation. Both SCR and LoTox™ have been demonstrated in units of comparable air flow to the Ellis County kilns.

4.1 High Temperature Emissions Controls

4.1.1 Selective Catalytic Reduction (SCR)

SCR is a process that uses ammonia in the presence of a catalyst to selectively reduce NO_x emissions from exhaust gases. This technology is widely used for NO_x abatement in other industries, such as coal-fired power stations and waste incinerators. The SCR process has been used extensively throughout the world to achieve a 90 percent reduction in NO_x emissions from fossil fuel fired boilers. In the United States SCR technology has successfully been used for gas turbines, internal combustion engines, and utility boilers.

In SCR, anhydrous ammonia, usually diluted with air or steam, or urea, is injected through a grid system into hot flue gases that are then passed through a catalyst bed to carry out NO_x reduction reactions. The two principal reactions are:

$$4\ NH_3 + 4\ NO + O_2 \text{ --- } 4\ N_2 + 6\ H_2O \text{ and}$$
$$4\ NH_3 + 2\ NO_2 + O_2 \text{ --- } 3\ N_2 + 6\ H_2O$$

The first reaction represents the predominant reaction since 90 to 95 percent of NO_x emissions in the flue gas are in the form of NO. A number of materials have been used for catalysts. Titanium dioxide (TiO_2) and vanadium pentoxide (V_2O_5) mixtures are most commonly used as catalysts due to their resistance to SO_x poisoning. Zeolite-based catalyst materials have also been developed capable of operating at higher temperatures than conventional metal-based catalysts. The catalyst is typically supported on ceramic materials, e.g., alumina in a honeycomb monolithic form. The active ingredients of the base metal (titania-vanadia) and zeolite catalysts often make up the bulk of the substrate material. The catalyst shape and reactor design vary depending upon the manufacturer.

The optimum temperature for the catalytic reactions depends upon the specific catalyst used and is usually in the range between 300 to 450ºC (570 to 840ºF). Without pre-heater and/or pre-calciner systems this temperature range may be higher than typical cement kiln flue gas temperatures, especially in plants using heat recovery systems or baghouses for particulate

collection. But it may be possible to reheat the exhaust using heat recovery systems. Of particular relevance, then, is the ability to use SCR at wet kilns.

Ammonia is typically injected to produce a NH_3: NO_x molar ratio of 1.05-1.1:1 to achieve NO_x conversion of 80 to 90 percent with an ammonia "slip" of about 10 ppm of un-reacted ammonia in the gases leaving the reactor. The NO_x destruction efficiency depends upon the temperature, NH_3: NO_x molar ratio, and the flue gas residence time (or the space velocity) used in the catalyst bed. The SCR reactor system can be designed for a desired NO_x reduction using appropriate reagent ratio, catalyst bed volume, and operating conditions. In general, the catalysts may be fouled or deactivated by the particulates present in the flue gas. In the case of cement plants, the presence of alkalis and lime, as well as sulfur dioxide, in the exhaust gases is also of concern. Recent developments, however, have led to sulfur tolerant SCR catalysts. In addition, soot blowers may be used to prevent dust accumulation on SCR catalysts.

In the cement industry, basically two SCR systems are being considered: low dust exhaust gas and high dust exhaust gas treatment. Low dust exhaust gas systems require reheating of the exhaust gases after de-dusting, resulting in additional cost. High dust systems are considered preferable for technical and economical reasons.

SCR may only be available as an applicable technology for dry kilns with preheat, as is described later herein. There are currently no installations of SCR units in any United States cement plants, however, a full-scale unit has been operating in Germany for over three years with SCR. As set forth in greater detail below, selective catalytic reduction has been installed and successfully operated at this one cement plant in Germany and SCR is now commonly used to control NO_x emissions from coal-fired power plants. This technology achieves NO_x emission reductions in the range of 80 to 90 percent or higher.

The experience of the German cement plant may be sufficient to demonstrate that the concerns regarding catalyst poisoning and fouling have been addressed with the development of a special catalyst specifically designed for the cement industry. In a typical design of a dry kiln with preheat, the SCR system could be located downstream of the pre-heater cyclones, prior to

the roller mill. The process exhaust temperature at the outlet of the pre-heater cyclones would be approximately 320°C (608°F), which is ideal for a SCR system.

Potential Advantages of SCR

The potential advantages of SCR are as follows:

- **SCR can potentially provide a high degree of NO_x removal.** Presently, guarantee levels on SCR systems being provided in the power industry are in the 90% to 94% range. Even on difficult applications such as coal-fired power plants, which have very dusty flue gases, NO_x control efficiencies of 90%+ are being guaranteed by vendors and being achieved.

- **SCR is an add-on or end-of-pipe control technology.** For dry kilns with preheat, the SCR system would be located downstream of the cement kiln and pre-heater furnace and cyclones and hence it would not interfere with or affect the cement manufacturing process. This would be a big advantage over the Selective Non-Catalytic Reduction (SNCR) process, which must be carried out in process conditions.

- **SCR can use urea ($CO(NH_2)_2$) rather than ammonia as the reducing agent.** To use urea, a conversion system is required. In a typical conversion system, urea is mixed with water and then heated. The process converts the urea to gaseous ammonia, which is then injected into the flue gas. This system is commonly used where there are safety concerns arising from the transport and storage of ammonia.

SCR at Coal-Fired Power Plants

Prior to 2001, there were approximately 12 coal-fired power plants in the United States utilizing SCR for NO_x control. According to the Electric Power Research Institute, there are now about 200 coal-fired power plants (totaling 100,000 megawatts of generating capacity) on-line utilizing SCR control. Most of the plants on which SCR has been installed are designed for, and have been achieving, 80% to 90% control of NO_x.

One possible problem mentioned with respect to utilizing SCR in cement plants is the technical feasibility of installing SCR in an environment where dust from the kiln could poison the catalyst, making SCR technically infeasible. On coal-fired power plants, the SCR catalyst is usually installed downstream of the boiler (between the economizer and the air pre-heater) prior

to the particulate control device. As a result, the catalyst is subject to the full dust loading from coal combustion, just as it would be at a cement plant. Typically, coal contains 6% to 20% ash on a dry basis. The high dust, high temperature characteristics of coal plant emissions thus are similar to those of cement kiln exhaust gases. The experience of the power industry with SCR on coal-fired power plants suggests that the catalyst poisoning and fouling concerns may be manageable.

SCR Experience in Cement Kilns

Differences in the nature of the cement kiln and coal fired power plant processes, the chemical composition of the ash and other factors mean that the success of SCR in controlling NO_x emissions from coal-fired power plants is not definitive evidence that the technology can be successfully applied at a cement plant. Among other things, dust from cement kilns is high in calcium, relative to coal dust, and calcium deactivates most conventional SCR catalysts. Also, the grain loading of cement kilns is likely to be different from that of coal-fired power plants, placing different stresses on the control device. As discussed in greater detail below, however, the recent successful use of SCR at a German cement plant demonstrates that these and other issues may have been resolved and that SCR is, under certain conditions, a technically feasible alternative for significantly reducing NO_x emissions from cement kilns.

The Solnhofen Portland-Zementwerke AG cement plant in southern Germany located between Munich and Nuremburg has been in successful operation with SCR since 2001. Lurgi, the engineering company who supplied the SCR system, addressed the problem of catalyst deactivation discussed above (caused by the high calcium content of cement plant ash) by developing a catalyst specifically for the cement industry. The catalyst can use ammonia or urea as a reagent. If urea is used, a conversion unit is used to convert the urea to ammonia prior to injection in the SCR system. These units, which are quite common, avoid the need to store ammonia on-site for use as a reagent.

As of the beginning of 2005, there was no evidence of catalyst poisoning or deactivation. The problem of fouling from the heavy dust loading has proven to be quite manageable with regular maintenance (i.e., cleaning of the catalyst with a vacuum cleaning system).

The SCR system is achieving NO_x emission reductions far in excess of those achievable using SNCR. Prior to installation of SCR, the Solnhofen plant, with SNCR, was achieving NO_x emissions of 700 to 800 mg/ Nm^3 (equivalent to 2.8 to 3.2 lb./tonne clinker). With SCR, the plant has been achieving approximately 200 mg of NO_x/Nm^3 (0.8 lb./tonne clinker). Based on an uncontrolled NO_x emission rate of 1050 mg/Nm^3 (4.2 lb./tonne clinker), the emission rate corresponds to a NO_x control efficiency of 80% for SCR compared with approximately 25-35% control efficiency for SNCR. It has been indicated, however, that the SCR system was capable of achieving a lower NO_x emission rate (they are not using all of their beds), but that they were operating at 200 mg/Nm^3 since German law only required a NO_x emission limit of 500 mg/Nm^3.(23a, 23b, 23c, 23d)

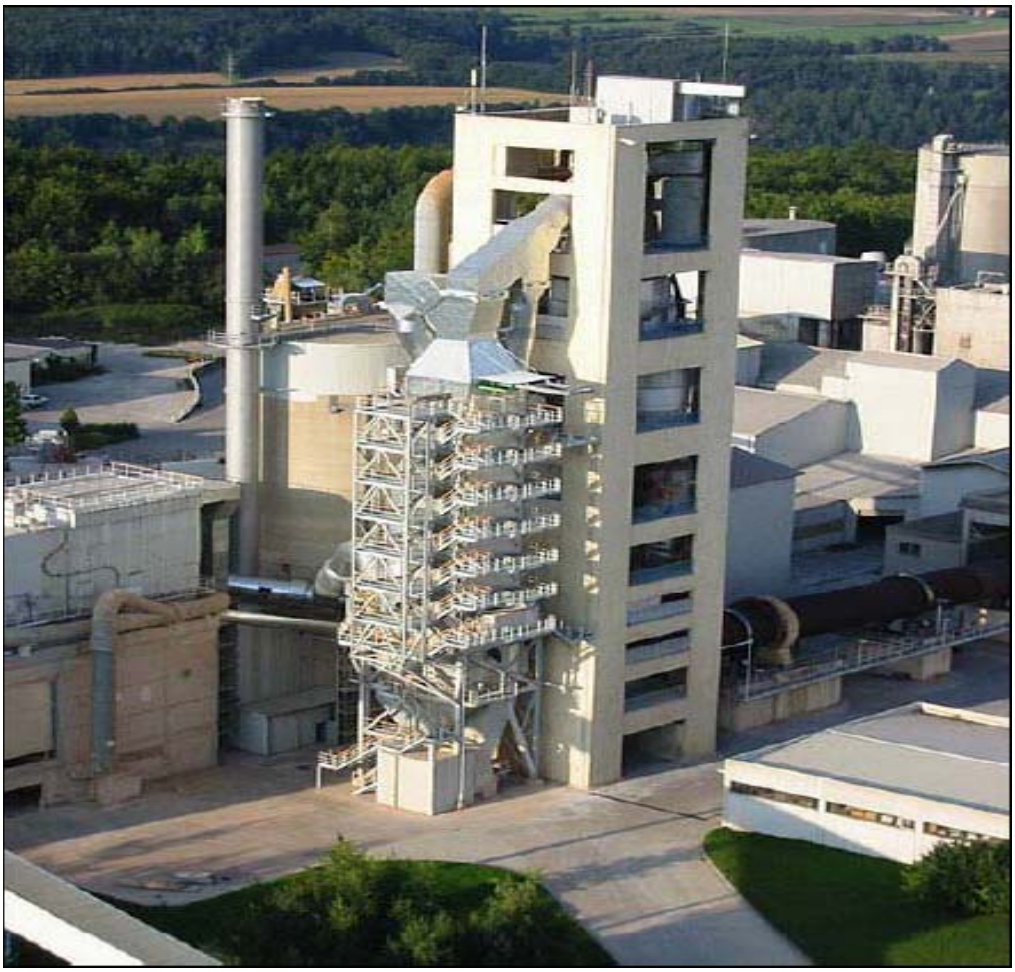


Figure 4-1.1 SCR on Preheater Tower at Solnhofen Zement, Germany

At approximately 500,000 tonnes per year of clinker, Solnhofen is smaller in capacity than the preheater/calciner units in Ellis County and larger than the wet kilns. With an uncontrolled NO_x emission rate of approximately 4.2 lb./ton, Solnhofen has a slightly higher emissions rate than the Holcim units and slightly lower than the Ash Grove kilns. The emissions rate is much higher than TXI #5 and much lower than the TXI wet kilns.

Site Specific Application of SCR to Ellis County Cement Kilns

SCR offers the possibility of significant NO_x reduction at the plants in Ellis County. As an "add on" technology, which can achieve 90% or greater NO_x reduction, with demonstrated performance at hundreds of coal fired power plants, SCR is a viable technology that is available for both dry and wet kilns. The economics of SCR are greatly influenced by the temperature of the flue gas at the point of installation. For the three dry precalciner kilns in Ellis County, a location in process with suitable temperatures is assumed and this leads to lower overall costs and cost effectiveness. For the wet kilns, a location downstream from the electrostatic precipitators (ESPs) is selected for installation, and reheat of the process gas is required. This substantially increases the overall cost and decreases the cost effectiveness of SCR in comparison to the dry kiln applications.

The technology has been available at only one cement plant, the Solnhofen Portland – Zementwerke AG dry kiln plant in Southern Germany, now in its fourth year of operation with SCR. While there are, at this time, no operating units in the U.S., the German experience leads one to assess the possibility that SCR can make a significant impact on NO_x reduction in Ellis County. In fact, the Midwest Regional Planning Organization has recently concluded that SCR is a reasonably available technology for controlling NO_x at cement plants (23e), and the possibility exists, with reheat, to utilize SCR at wet, as well as dry, kilns.

Applicability of SCR to Cement Kilns and Areas of Concern

Before examining site-specific data, it is important to first examine the areas of concern with respect to SCR, many of which have been raised in the literature (23f, 23g, 23h, 23i). This is necessary to see whether the data from the coal fired plants and from the one cement plant, is

sufficient to attempt to make even qualified statements with respect to existing facilities, even though some analyses now suggest that the German data indicates that these problems will not exist for the cement industry in the U.S. (23g). These concerns are delineated and discussed here. They include: catalyst deactivation due to catalyst poisoning; catalyst plugging and fouling due to high dust loading and deposits; reduction in NO_x control efficiency due to high sulfur levels; temperature related factors leading to lower NO_x removal efficiencies; NO_x concentration variability and ammonia slip; and undesirable by-product formation in the SCR causing adverse affects on downstream equipment.

Catalytic Deactivation Due to Catalyst Poisoning

Poisoning occurs when the contaminants in the gas being treated react with the catalyst, resulting in catalyst deactivation. It has been argued that the SCR catalyst in a cement plant will be subject to poisoning, principally from sodium (Na), potassium (K), and arsenic trioxide (As_2O_3). Phosphorus, chromium and lead compounds can also poison an SCR catalyst, but since these are expected to be present in lower concentrations at cement kilns, they are of lesser concern. However, the typical concentration of sodium oxide (Na_2O) in the particulate matter (PM) of certain coal-fired plants is greater than double the concentrations of Na_2O in the PM of the average cement plant, and the maximum concentration of Na_2O can be significantly greater than the maximum expected concentration of Na_2O in the PM of the average cement plant. Similarly, the concentration of As_2O_3 in the flue gas of the typical coal fired plant is well above the concentration of As_2O_3 in the expected flue gas from the average cement plant. Regarding the availability of catalyst poisons, an additional argument deals with the solubility of Na and K in the fly ash and the form of the fly-ash particles.

It is argued that in cement pre-heater pre-calciner kilns, materials such as sodium and potassium compounds may be present in relatively elevated concentrations on the surfaces of particles in "water soluble" form that can contact the surface of the SCR catalyst bed and thereby provide an opportunity to poison the V_2O_5 "active ingredient" in the SCR bed. Conversely, it is argued, in coal-fired boilers, the sodium and potassium are, to a major extent, trapped within a glass-like fly-ash particle. It is widely known however that fly-ash particles from coal-fired boilers are in the form of tiny spheres (cenospheres) and that during the combustion of the coal,

the particles are actually liquid and the spheres are formed as tiny bubbles by evolved gases trying to escape. Boilers are designed to cool the molten particles to a solid state such that they can be easily removed from boiler tubes. However, depending on the temperature of the fly ash and its chemical composition, some of the fly ash will deposit in various sections of the boiler. The deposits that form at the back-end of the boiler (on the economizer and air heater) are called "low-temperature deposits". Low temperature deposits are usually characterized by low pH (highly acidic); many contain hydrated salts, and for most bituminous coals are water-soluble. Therefore, coal-fired boilers have fly-ash deposits in the economizer section of the boiler that are water-soluble. However, deactivation has not been found to occur. In addition, SCR systems have been installed on oil-fired boilers despite the relatively higher levels of water-soluble alkaline metals found in the fly ash from such boilers.

Catalyst Plugging and Fouling Due To High Dust Loading and Depositing of "Sticky" Materials

Catalyst plugging and fouling involves the accumulation of dust that blocks access to the pores of the catalyst. It is argued that high dust loadings could plug or foul the SCR catalyst beds. However, the Solnhofen SCR system has operated at a dust loading of 80 g/Nm^3, a relatively high dust loading. The level of NO_x removal shows that high dust loading can be managed to avoid catalyst plugging and fouling while maintaining high levels of control. Related to the plugging and fouling issues, it is argued that "sticky deposits" in the pre-heater exhaust gas could foul and plug the SCR catalyst. Specifically, certain cement kiln operations could be prone to producing sticky deposits at exactly the temperature ranges in which SCR systems operate. Sticky deposits are a widespread problem occurring throughout the world on cement kiln induced draft (I.D.) fans. In many plants it is an extremely hard, layered, brick-like build-up that is associated with impingement of particulate at high velocity against the rotating parts of the fan impeller.

While the presence of alkali in the cement kiln system is a factor in the build-up, the mechanical aspect (namely, impact velocity) is more critical to the formation of build-up. The recommendation for avoiding build-up is to select a fan that minimizes the gas/dust velocity at the inlet of the fan rotor. Alternatives include using double inlet fans or using larger diameter, lower RPM (revolutions per minute) fans. Sticky deposits or build-up developing on other parts

of the cement kiln system are not common. Thus, the sticky deposit problem appears to be related solely to the I.D. fan and is due to the high impact velocity of the dust particles mostly on the fan. This problem should not affect an SCR catalyst that is subject to comparatively low gas velocities in comparison to an I.D. fan.

For instance, gas velocities through an SCR system are typically less than 6.2 meters per second (1220 ft./min.), whereas peripheral gas speed at the kiln I.D. fan rotor inlet is approximately 15,000 ft./min. Possible problems relating to thermal sintering and catalyst erosion have been addressed by advances in catalyst technology and proper system design. The problem of thermal sintering has been avoided by the incorporation of tungsten in the catalyst formulation and also by providing a bypass around the SCR system so that the catalyst is not exposed to high temperature excursions. Hardening the leading edge of the catalyst and also arranging the catalyst bed so that the airflow is parallel to the catalyst channels have addressed catalyst erosion.

Reduction in NO_x Control Efficiency Due to High Sulfur Levels

In general, operational histories of SCR installations at coal fired plants and the one cement plant indicate that NO_x reductions are being achieved in a reliable manner. The reason that many of the older units are not achieving NO_x removals greater than 80% is that the plants were not designed to achieve such high removal efficiencies. Great advances in the application of SCR technology have taken place. Present day SCR systems are typically achieving NO_x reduction efficiencies of 90% or greater. It is argued that when only a low NO_x reduction is required, the catalyst manufacturer can use a catalyst with a lower vanadium oxide content which will reduce the oxidation of SO_2 to SO_3 and thereby avoid the potential for $CaSO_4$ masking. However, the Solnhofen SCR system is achieving a high degree of NO_x control.

It is argued that high SO_3 concentrations could lead to catalyst deactivation and other serious problems relating to SO_2 oxidation. A high SO_3 concentration (10 -20 ppmv) when coupled with the high calcium level in the cement kiln flue gas could purportedly cause deactivation of the SCR catalyst due to the masking effect of calcium sulfate ($CaSO_4$). In addition, any SO_3 that does not react with the calcium could react with any unused NH_3 to form

ammonium sulfate (AS) or ammonium bisulfate (ABS) that could cause fouling of downstream equipment. Sulfur in the raw mix can be in several forms, namely: calcium sulfate, magnesium sulfate, and sulfides such as pyrites or organically bound sulfur. Only the volatile sulfur compounds (namely: the sulfides and organically bound sulfur) are oxidized and released in the pre-heater as SO_2. With respect to these concerns, the success of SCR systems at a number of coal-fired boilers show that SCR systems can be designed for high calcium and high sulfur flue gases and the SCR catalyst suppliers have indicated that $CaSO_4$ formation does not pose a major concern, as they assert that the SO_3 generated in the process is captured by the large amount of free lime in the gas stream. SO_2 oxidation by the catalyst will then have no negative impact on the amount of SO_3 formed and subsequently captured. There is also concern regarding the possible formation of ammonium salts, which can form in SCR systems at temperatures below 580 to 590°F. However, this problem can be avoided by ensuring that the SCR inlet temperature is always 600F or greater.

Temperature Related Factors Leading to Lower NO_x Removal Efficiencies

Several temperature-related factors have been identified as important to successful operation of an SCR system. These are: (1) an acceptable normal operating temperature; (2) an even temperature distribution; and (3) avoiding temperature extremes (which may lead to catalyst deactivation or sintering). Low temperatures can lead to lower NO_x reduction efficiencies and/or higher catalyst activity (leading to possible SO_2 oxidation) and to possible ABS/AS formation in the catalyst pores. Concerns regarding a slightly lower than desirable inlet temperature, however, can be resolved by installing equipment to ensure a desired temperature of 600°F or greater going into the SCR system. Such control systems are commonly used on boiler air supply systems and economizer bypass ducts. Note that the SCR reactor should also have an automatically activated bypass duct around the SCR reactor, so that in the event of high temperature fluctuations (greater than approximately 800°F), automatically controlled dampers would send the hot flue gas to a reactor bypass duct, thus preventing any damage to the SCR catalyst. Therefore, temperature issues, whether involving normal operating temperatures or temperature fluctuations, should be correctable with simple process reconfigurations.

NO_x Concentration Variability and NH_3 Slip

It has been argued that unlike a coal-boiler SCR application, an SCR system applied to a cement kiln will be faced with highly variable inlet NO_x loadings and that elevated NH_3 slip levels are possible, which, coupled with possibly higher sulfur oxide levels, represent a serious risk. However, in an SCR system, the injected NH_3 is adsorbed onto the surface of the catalyst. Thus, there is a reservoir of unused NH_3 on the surface of the catalyst that is available to handle sudden peaks in inlet NO_x concentrations and thereby enable SCR systems to control fluctuating levels of NO_x. SCR systems do not have to overfeed ammonia to handle surges in inlet NO_x concentration and so tend to have very low NH_3 slip levels.

Coal-fired boilers have been operating SCR systems successfully for years despite considerable NO_x fluctuations in their flue gases. SCR suppliers typically guarantee a NH_3 slip of no more than 2 ppmv for any coal-fired boiler SCR application. In addition, the Solnhofen plant is a cement kiln with all of the inherent variability and has nevertheless been achieving a high degree of NO_x control with a low ammonia slip level. Data at Solnhofen indicates that the SCR inlet NO_x concentration varies considerably, from less than 1000 mg/Nm^3 to 2030 mg/Nm^3 while the outlet NO_x concentration varies from approximately 300 to 726 mg/Nm^3, but maintains an average outlet NO_x concentration of less than 500 mg/Nm^3. At these variable conditions, however, NH_3 slip has been maintained in the 1-2 ppmv range.

Undesirable Byproduct Formation in the SCR Causing Adverse Effects on Downstream Equipment

Concerns have been raised regarding the generation and release of SO_3 that could cause corrosion of downstream equipment, or that the SO_3 may react with unused NH_3 to form ammonium salts (ABS and AS), which could plug or corrode downstream equipment. In addition it is argued that ammonium salts could increase condensable particulate matter levels, making it difficult for a facility to meet its particulate matter emission limit. In SCR systems with SO_3, NH_3 and moisture present, ammonium salts will form at temperatures below 580-590°F. The best way to prevent their formation is to continuously control the SCR inlet temperature such that it is always 600°F or greater. Regarding the possible release of SO_3, catalyst manufacturers report that the SO_3 gas is totally captured by conversion to particulate

calcium sulfates and sulfites as it is contacted by free lime upstream, within, and downstream of the SCR catalyst. Thus, the formation of undesirable byproducts should be inherently controlled by the free lime in the system and can be further controlled by controlling the SCR inlet temperature.

General Conclusions

The experience of coal-fired power plants and the one cement plant with SCR offers the following lessons. First, the success of coal-fired power plants shows that catalyst deactivation from alkali poisoning is not expected to be a significant problem for cement kiln applications. Second, the success of SCR systems on a number of coal-fired boilers reveals that even when flue gases have significant levels of both calcium oxide (CaO) and sulfur dioxide (SO_2), the condition can be handled in SCR systems without the occurrence of pore masking from calcium sulfate ($CaSO_4$) formation. Third, the power plant experience shows that SCR systems can be designed to achieve at least 85% NO_x reduction despite extremely large gas flow rates with significant NO_x variability and relatively high particulate loadings. Last, the power plant experience shows that equipment can be designed and operated such that the flue gas entering the SCR catalyst will always be in the proper temperature range. For wet kiln applications, this can lead to a requirement for significant gas re-heat.

Site-Specific Analyses

The follow sub-sections are specific to TXI, Holcim, and Ash Grove. In what follows, the additional NO_x associated with gas re-heat, if required, has not been added, as the level of additional NO_x would be below 10 tons per year and 85% of that would be removed.

SCR at the TXI Kilns

To consider SCR at the TXI facilities, one must perform separate analyses for Kiln 5 (the dry kiln with pre-heater/pre-calciner, as found at the Solnhofen plant) and Kilns 1-4 (the long wet kilns, which usually operate as kilns 1 and 4 in tandem, or 2 and 3 in tandem). Neither the alkali percentages, the sulfur fuel percentages nor the stack concentrations (extrapolated to

uncontrolled for TXI #5) would be considered high for SCR utilization in coal-fired power plants (see Confidential Attachment – TXI).

With respect to the dry kiln (TXI 5), it would be expected that an SCR system would be installed downstream of the pre-heater, where the temperature would be in the range required. With respect to process economics, this temperature is assumed to be 700°F (the temperature utilized in all the cases at all the plants studied). With respect to this particular kiln, the present data indicates a low NO_x level in the 150-ppm range. For conservatism, it is therefore assumed that an SCR system for this kiln would operate at an 80% reduction efficiency, as opposed to a significantly higher level (85%) to be expected at the other kilns at TXI and at the other facilities in Ellis County.

The economic analysis for this case is found in the confidential attachments. It is found that the cost effectiveness, based on NO_x removed ($/ton NO_x removed) is approximately $2,200/ton. With respect to cost effectiveness based on metric tonnes of clinker produced ($/tonne clinker), the cost is approximately $0.87/tonne.

The wet kilns have been economically modeled based on a number of possible scenarios. The reported stack gas temperature 160°C (320°F) was utilized in the reheat calculations (to 700 ºF at the SCR inlet) in all cases, and natural gas, at $12.00/therm is utilized. Three different scenarios were studied. In the first scenario, one SCR system serves kilns 1 and 4 consistent with TXI's operation (85% of the time). In the second scenario, one SCR system serves kilns 2 and 3 again consistent with TXI's operation (15% of the time). In the third scenario, one SCR system serves all four wet kilns with piping and controls to match the normal operating scenarios. These three scenarios were again modeled based on the possibility that TXI might introduce mid-kiln firing as a method of NO_x control in its four wet kilns. Therefore, a total of six economic analyses for the TXI wet kilns are found in the confidential attachment.

For the scenario without mid-kiln firing in kilns 1 and 4, the cost effectiveness based on NO_x removal ($/ton NO_x removed) is approximately $5,500/ton. The cost effectiveness based on metric tonnes of clinker produced ($/tonne clinker) is approximately $8.90/tonne. These estimates are based on the assumption that mid-kiln firing is in place as required under the

existing Texas regulations. Mid-kiln firing is currently required at Ash Grove, but has not been installed due to permit issues. Assuming mid-kiln firing avoids possible double counting of the emissions reductions achieved by mid-kiln firing.

The scenarios involved with kilns 2 and 3 with SCR lead to what must be considered unacceptable economics, since capital cost is essentially equal to that for kilns 1 and 4, but operation (both from the standpoints of NO_x removed and clinker produced) is only 15% of the total. Therefore, without mid-kiln firing, the economics yields a cost effectiveness based on NO_x removal of approximately $96,000/ton, while the cost effectiveness based on clinker produced is in the $13.50/tonne range. Mid-kiln firing is also assumed for kilns 2 and 3.

Based on economies of scale, utilizing one large SCR unit to service all four kilns (the model assumes a capacity equivalent to approximately 3 kilns in operation at any time) should lead to the most cost effective manner of control. With mid-kiln firing, the cost effectiveness based on NO_x removal is approximately $5,300/ton, while the cost effectiveness based on clinker produced is about $5.90/tonne.

It is clear that while the reheat required in the wet kilns significantly increases the costs associated with NO_x control with the utilization of SCR, the cost effectiveness is best when one SCR unit is installed for all four wet kilns. For the dry kiln, the economics is, of course, significantly better and assuming space for the catalyst beds and ancillary equipment is available, SCR must be seriously considered.

SCR at the Holcim Kilns

To consider SCR at the Holcim facilities, separate analyses are performed for each of the two dry units. Each is equipped with precalciners and preheaters, but Holcim 2 is a newer, more efficient unit, emitting 26% less NO_x (in mg/m^3). The temperature after the preheater for both Holcim 1 and 2 is expected to be adequate (i.e. 700°F), so no reheat would be required, and 85% NO_x removal is assumed. Neither the alkali percentages, the sulfur fuel percentages, nor the stack concentrations extrapolated to uncontrolled would be considered high for SCR utilization

in coal-fired power plants (see Confidential Attachment – Holcim). The utilization of SCR is, therefore, not precluded.

The annual cost spreadsheets are found in the confidential attachments for each cement plant. The cost effectiveness based on NO_x removal ($/ton NO_x removed) for Holcim 1 is approximately $1,950/ton. The cost effectiveness based on metric tonnes of clinker produced ($/tonne clinker) is about $2.00/tonne.

For Holcim 2, which is more efficient, the NO_x removed is less (since less NO_x is produced) and the clinker production is greater. Therefore, the cost efficiency based on NO_x removal is slightly greater for Holcim 2, at approximately $2,000/ton, and the cost effectiveness based on tonnes of clinker produced is approximately $1.70/tonne.

SCR at the Ash Grove Kilns

Ash Grove has three wet kilns with mid-kiln firing: Ash Grove 1, Ash Grove 2 and Ash Grove 3. Data indicate nearly identical operating conditions and NO_x emission levels (in the 350 ppm to 400 ppm range). Neither the alkali percentages, the sulfur fuel percentages nor the stack concentrations would be considered high for SCR utilization in coal-fired power plants (see Confidential Attachment – Ash Grove). In addition, Ash Grove reports temperatures at the air pollution control device (APCD) inlets of 330°F to 370°F. Assuming the installations of SCR between the APCDs and the stacks, these temperatures indicate that Ash Grove can install SCR at each of their kilns with reheat required, and 85% NO_x removal can be expected.

Four scenarios are presented, that of the installation of an SCR at each of the three wet kilns, the fourth being the installation of one SCR for all three units. For Ash Grove 1, the cost effectiveness based on NO_x removal ($/ton NO_x removed) is about $5,800/ton (all reheat at $12.00/therm). The cost effectiveness based on clinker produced ($/tonne clinker) is approximately $9.20/tonne.

For Ash Grove 2, the cost effectiveness based on NO_x removal is approximately $5,800/ton. The cost effectiveness based on clinker produced is about $9.90/tonne.

For Ash Grove 3, the cost effectiveness based on NO_x removal is approximately \$6,100/ton. The cost effectiveness based on clinker produced is approximately \$10.60/tonne clinker.

If space is available and operation is not impeded, one SCR unit can be installed to service all three kilns. In this case, the cost effectiveness based on NO_x removal improves to about \$4,600/ton. The cost effectiveness based on clinker production improves to approximately \$7.70/tonne.

It is clear that if space is available for one SCR unit and its ancillary equipment, in order to serve all three kilns, the economics is far more favorable than if three SCRs are installed. SCR, therefore, for these wet kilns is an available technology at 85% NO_x control, albeit at a high cost/tonne of clinker removed.

Table 4-1.1. Summary of Modeling Results for SCR on Ellis County Kilns – Performance Results

Existing Unit	Control Technology	Emissions Rate tpy before	Emissions Rate tpy after (a)	Controlled Emissions Rate ppm	Controlled Emission Rate lb./tonne clinker	Control Efficiency %	Reduction tpy
Ash Grove #1- wet	SCR	702	301.6	60	0.84	85%	400.4
Ash Grove #2- wet	SCR	750	322.2	58	0.89	85%	427.8
Ash Grove #3- wet	SCR	764	328.3	53	0.91	85%	435.7
Ash Grove #1,2,&3 (c)	SCR	2205	947.4	57	0.88	85%	1,257.6
TXI #1 and #4–wet (b)	SCR	838	155.3	109	0.85	85%	478.0
TXI #2 and #3–wet (b)	SCR	121	52	109	0.51	85%	69.0
TXI #1,2,3,4 –wet (c)	SCR	1802	774.2	109	0.85	85%	1,027.8
TXI#5 – dry	SCR	1710	734.7	29	0.30	80%	975.3
Holcim #1 – dry	SCR	2222	954.7	108	0.56	85%	1,267.3
Holcim #2 – dry	SCR	1778	763.9	80	0.45	85%	1,014.1

(a) NO_x emission rate after SCR does not reflect SCR efficiency reduction due to adjustment by the ozone season factor of 0.671 (NO_x reduction is modeled to occur only during the ozone season).
(b) The results for TXI 1 & 4 and #2 & #3 are average per kiln – for example, total emissions reductions for controlling both TXI #1 & #4 are double the value listed in the table.
(c) A large single SCR was modeled for the Ash Grove and TXI wet kilns with the capacity of 3 wet kilns.
(d) Models assume mid-kiln firing installed at TXI as required under current SIP.

Table 4-1.2. Summary of Modeling Results for SCR on Ellis County Kilns – Economic Results

Existing Unit	Control Technology	Capital Cost	Annual Cost	Cost Effectiveness $/ton NO_x	Energy Penalty or Benefit	Emissions Penalty or Benefit	Burden Cost $/tonne clinker
Ash Grove #1- wet (e)	SCR	$5.0MM	$2.3 MM	$5,800	(a)	(b)	$9.20
Ash Grove #2- wet (e)	SCR	$5.2MM	$2.5MM	$5,800	(a)	(b)	$9.90
Ash Grove #3- wet (e)	SCR	$5.3MM	$2.7MM	$6,100	(a)	(b)	$10.60
Ash Grove #1,2,&3(d)	SCR	$11.8MM	$5.7 MM	$4,600	(a)	(b)	$7.70
TXI #1 & #4–wet (c,e)	SCR	$5.7MM	$2.6MM	$5,500	(a)	(b)	$8.90
TXI #2 & #3–wet (c,e)	SCR	$5.7MM	$0.6MM	$96,000	(a)	(b)	$13.50
TXI #1,2,3,4 –wet (d,e)	SCR	$11.2MM	$5.4MM	$5,300	(a)	(b)	$5.90
TXI#5 – dry	SCR	$8.4MM	$2.2MM	$2,200	(a)		$0.87
Holcim #1 – dry	SCR	$7.5MM	$2.4MM	$1,900	(a)		$2.00
Holcim #2 – dry	SCR	$6.7MM	$2.0MM	$2,000	(a)		$1.70

(a) Increased fan power due to pressure drop across catalyst bed included in the models
(b) Increase in NO_x from gas reheat occurs, but is controlled by the SCR
(c) The results for TXI #1 & #4 and #2 & #3 are average per kiln – for example, total capital costs for controlling both TXI #1 & #4 are double the value listed in the table.
(d) A large single SCR was modeled for the Ash Grove and TXI wet kilns with the capacity of 3 wet kilns.
(e) Costs for wet kilns include cost of RTO to reheat flue gas.

4.1.2 Selective Noncatalytic Reduction (SNCR)

This control technique relies on the reduction of NO_x in exhaust gases by ammonia or urea, without using any catalyst, with the same reactions as in the case of the SCR process. Because of low capital and maintenance costs associated with this technology vis-à-vis other end-of-pipe technologies like SCR and oxidative methods, it is likely to command attention in the near future within the industry. This approach combines a low initial capital cost and avoids the problem related to catalyst fouling and replacement associated with SCR technology. SNCR requires injection of the reagents in the kiln at a temperature between 870 to 1,090°C (1,600 to 2,000°F). In principle, any of a number of nitrogen compounds may be used as SNCR reagents (e.g., cyanuric acid, pyridine, and ammonium acetate). However, for reasons of cost, safety, simplicity, and by-product formation, ammonia and urea have been used in most of the SNCR applications. The selection of reagents is process and temperature specific. At higher temperatures, urea decomposes to produce ammonia, which is responsible for NO_x reduction. In cement kiln applications, ammonia typically has performed best as the reducing reagent.

Because no catalyst is used to increase the reaction rate, the temperature window is critical for conducting this reaction. At higher temperatures, the rate of a competing reaction for the direct oxidation of ammonia, which actually forms additional NO_x, becomes significant. At lower temperatures, the rates of NO_x reduction reactions become too slow resulting in too much unreacted ammonia being released to the atmosphere (i.e., ammonia slip). The effective temperature window range can be lowered to about 700°C (1,300°F) by the addition of hydrogen along with the reducing agent. (24) Addition of hydrogen can promote SNCR reactions (enhanced SNCR), but high levels of sulfur oxides may interfere with this reaction (Recent evidence tends to call into question this tentative conclusion). Nalco Fuel Tech, the producer of the SNCR technology NOxOUT®, has also introduced NOxOUT® PLUS which is said to broaden the operating temperature window and to reduce ammonia slip and CO and NO_2 formation.

In a conventional long kiln, the appropriate temperature window is in the middle of a kiln. Until quite recently, because of the rotating nature of a long kiln, continuous injection of ammonia- or urea-based reagents had not been considered possible. The technology developed

for mid-kiln firing of containerized solid fuels allows injection of a certain amount of material once during the kiln revolution. Injection of solid ammonium or urea salts in this manner had not been used because of the assumption of rapid decomposition of such salts. Therefore, SNCR technology had not been thought applicable to date for long dry or wet kilns. There is some limited evidence from Europe, suggesting that injection of urea into long wet kilns may have promise(25). Urea injection was reportedly continued over a four month period with satisfactory results at a wet kiln in France. The publicized information does not, however, give detailed data needed to evaluate this test. The test does not stipulate:

- Location of reagent injection,
- Titration rate for reagent,
- Reagents tried and their performance (only urea is mentioned),
- NOx reduction rate vs. titration rate,
- NOx reduction rate vs. temperature,
- Average NOx emissions rates for controlled and uncontrolled operation,
- Operating costs,
- Other NOx control measures employed at the kiln, and
- A physical description of the kiln and information on feed and production materials. (25)

Without this type of detailed information, it is difficult to draw any definitive conclusions about the potential for application to wet kilns in Ellis County.

In addition, Fuel Tech Inc. is currently evaluating dry dust or pellet injection methods for direct injection into kilns. (26) The possibility of injection of ammonia or solid urea inside automobile tires that are injected into the kiln has still to be evaluated. With the known ability of mixing air fans to induce turbulence in the system, mixing combustion gases containing NO_x with ammonia, either generated from urea or from ammonium salts, may also offer possibilities. Chain gas temperatures generally are in the range of 1500-1600ºF (815-871ºC). The mid-kiln injection systems are usually down kiln somewhat from this point, which means that they will be higher than this in gas temperature. There is a good possibility that the correct temperature range can be achieved if mixing is induced and volatilization or decomposition of the urea can be delayed by inserting it in a solid form in a carrier such as a tire. This option needs to be explored. It will clearly be necessary to mix the NO_x with the reagent before the latter has an opportunity for decomposition. Inducing turbulence is presently conceived as a key element in this strategy.

In preheater/precalciner type cement kilns, the temperatures at the cooler end of the rotating kiln, in the riser duct, and in the lower section of the cyclone preheater tower are likely to be in the temperature window appropriate for SNCR. Such kilns are therefore good candidates for application of SNCR technology.

The NO_x reduction efficiency of SNCR depends upon the temperature, oxygen, carbon monoxide, and residence time, as well as the ammonia and NO_x concentrations in the flue gas. Injection of ammonia at a NH_3:3 NO_x proportion of 1 to 1.5 will reduce NO_x emissions between 60 to 80 percent. Using a molar ratio of 0.5 will give NO_x reductions of approximately 40 percent. (27) Work done by the German equipment supplier Polysius (28) has shown that the optimum temperature for reduction of NO_x by ammonia is about 950ºC (1,740ºF), while for urea, the temperature increases to about 1,000ºC (1,830ºF). Ammonia is also somewhat more efficient, as shown in Figure 4-1.2. below.

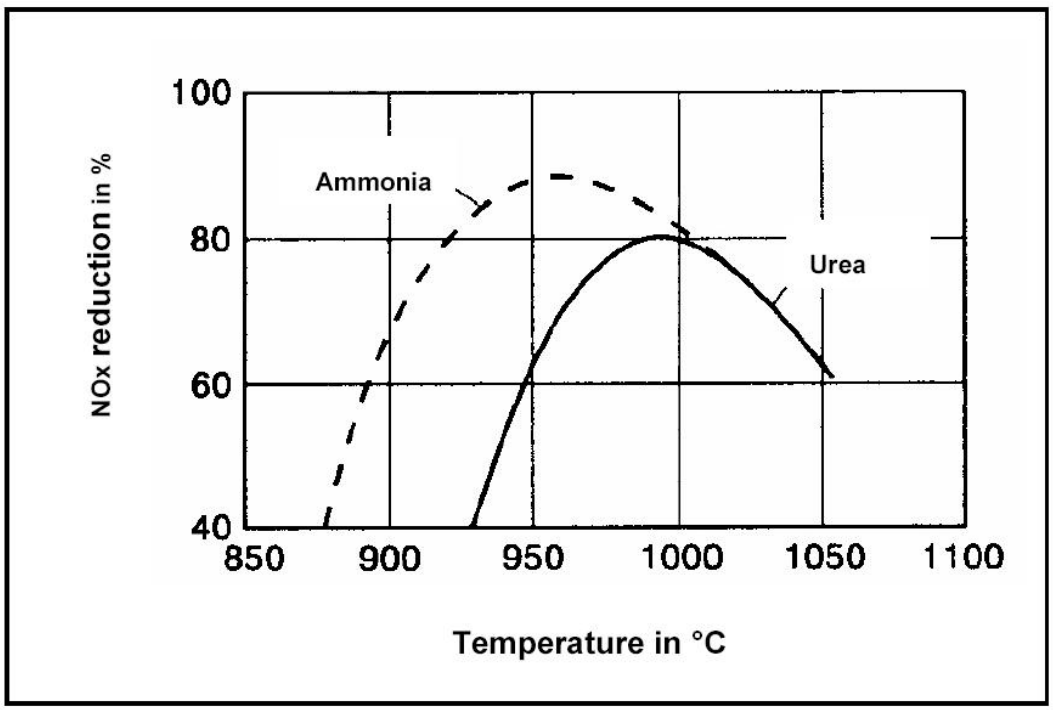


Figure 4-1.2. Dependence of NO_x Reduction on Temperature for Ammonia and Urea

Actual SNCR results with ammonia (19% aqueous solution) at one US plant employing a calciner are given in Table 4-1.3. It can be seen that the reduction was remarkably good, considering that ammonia was never added at greater than a stoichiometric equivalent to NO_x

Due in part to the fact that no excess ammonia was introduced into the system, no ammonia slip was demonstrated. The ammonia emissions were undetectable.

Table 4-1.3. Summary of Test Results for SNCR Test

Run #	Molar Ratio NH_3:NO	NO_x Reduction %	Average NO_x Before lb./hr	Average NO_x During SNCR lb./hr
1	0.918	65.49%	325.47	112.31
2	0.533	36.71%	322.90	204.35
3	0.425	44.93%	345.52	190.27
4	0.331	16.90%	282.70	234.91
5	0.465	15.49%	290.18	245.25
6	0.286	12.95%	269.35	234.47
7	0.534	45.06%	269.35	147.97
8	0.552	31.91%	281.71	191.81
Long term	0.368	47.78%	329.83	172.24

These results were very good. The temperature and oxygen concentrations were nearly optimum for the SNCR system. The carbon monoxide levels were somewhat higher than has been considered optimum, but according to Brouwer et al. (29), CO may promote the reaction at the lower end of the temperature range, because of the temperature increase due to the heat given off by the reaction of CO with OH radicals. Among other SNCR tests recently performed, tests have been carried out at a preheater plant and four calciner plants. Some of these tests were carried out using ammonia, and others using urea. At the preheater plant, both ammonia and urea were tested, injecting the reagents into the kiln riser duct. Ammonia proved to be considerably more effective than urea, in keeping with the Polysius plot given above.

Despite these successes, reagent consumption can be significantly higher with greater ammonia slip in SNCR systems as compared to SCR systems. Operating experience has identified several concerns with both ammonia and urea-based SNCR processes. The most frequently reported is the buildup of ammonium bisulfite or bisulfate scale, which is significant for sulfur-containing fuels. SNCR processes also appear to convert some NO_x to N_2O. (30) The rate of N_2O formation is a weak function of both the reactant and the NO concentration. However, N_2O formation seems to be inherently more prevalent in systems using urea than those using ammonia. (31)

The NO_x destruction efficiency also depends upon the flue gas residence time in the appropriate temperature window. Unlike an SCR system where the reaction temperature is controlled in a dedicated reactor, an SNCR system relies on the existing gas temperature profile to provide an adequate residence time for a desired NO_x destruction. Maximum achievable NO_x reduction in a cement kiln may thus depend upon the gas temperature profile.

The SNCR process was demonstrated in Europe in a preheater type kiln. Both ammonia- and urea-based reagents were investigated. The reagents were injected in the gas duct as shown in Figure 4-1.3. (32) With a molar ratio of reagent to NO_2 of 1:1, about 70 percent reduction in NO_x emissions was observed with ammonia-based reagent and about 35 percent NO_x reduction was obtained with urea. (32) With this reagent ratio, there was no major increase in ammonia emissions in exhaust gases over the background level of ammonia emissions generated by kiln feed material. Greater NO_x reductions were observed with more than stoichiometric amount of reagent, although there was increasing ammonia 'slip' in the exhaust gases.

Figure 4-1.3. Application of SNCR at Holcim

Albert Scheuer, of the Research Institute of the Cement Industry in Düsseldorf, Germany, reported on 148 SNCR trials carried out on five different kilns. Three kiln systems had cyclone preheaters and two had grate preheaters. A 25% molar concentration of NH_3 in water was the main reagent tested, with some additional testing done with ammonium sulfate solutions and

with urea solutions. Scheuer reported that NO reductions with the NH_3/water solution ranged from 15% to 75% and that temperature appeared to be one of the main determinants of the effectiveness of the reagent. Maximum NO reduction occurred at 980°C (1796°F). NH_3 escape occurred when temperatures were less than 900°C (1652°F) and when the NO concentration fluctuated. NH_3 utilization decreased significantly with increasing NH_3:NO molar ratio and with decreasing NO concentration in the exhaust gases, indicating that SNCR appears to be a less promising methodology at low NO emissions rates. (33,34)

SNCR is presently being used in 18 cement kilns in Europe. Fifteen kilns are in Germany, two are in Sweden, and one is in Switzerland. These kilns are either suspension preheater kilns or precalciner kilns. The names and locations of these installations have not been found in any of the European references that discuss these installations. The most common reagent used is 25% ammonia water. (35) NO_x reduction rates vary from 10 to 50 percent with NH_3/NO_2 molar ratio of 0.5 to 0.9, NO_x emissions at these reductions are 2.4 to 3.8 lb./tonne clinker. Two dry process cyclone preheater/precalciner kilns in Sweden achieve 80 to 85 percent reduction (1.0 lb./tonne clinker) at a NH_3/NO_2 molar ratio of 1.0 to 1.1. (35) One reason for the remarkable results in these kilns is the use of multiple injection points (12 in all) that ensure long enough retention time for the reaction to take place. The optimum temperature is said to be 900-1,100ºC (1,650-2,010ºF) in good agreement with other authors. These results suggest that some SNCR tests may have been carried out under lower-than-optimum temperatures.

F. L. Smidth and Company tested SNCR on a preheater/precalciner kiln. (36) Ammonia was injected into the lower cyclone of the preheater tower where temperatures are favorable for the reduction reactions to occur. NO_x emissions reductions during this experiment averaged 40 percent, but NO_x reductions of over 90 percent were obtained when the ammonia injection rate was 10 to 20 percent in excess of stoichiometric.

In North America, SNCR has been tested on at least nine kilns. In some of the earlier work, NOxOUT® technology was tested under ten different operating conditions at a preheater/precalciner kiln in Seattle, Washington during October 1993. NO_x emissions were effectively reduced from 3.5 to 6.0 lb. NO_x/tonne clinker to less than one lb. NO_x/tonne clinker. (37,38) Another test of NOxOUT® technology was conducted during October 1998 in

Davenport, Iowa. This test found NO_x reductions of 10 to 20 percent from a baseline of approximately 350 pounds NO_x/hour, although higher levels of reduction are thought to be achievable when the baseline is higher. (39) An evaluation of NOxOUT® technology was conducted in 1994 for a long dry kiln in Southern California, but the study concluded that application of the NOxOUT® technology at the subject kiln was technically infeasible. (40) The details of this testing are not known.

Biosolids Injection (BSI). The Mitsubishi Cement Corporation's Cushenbury plant in Lucerne Valley, CA, uses biosolids injection technology (BSI) to achieve SNCR of NO_x. The BSI process was developed by the Cement Industry Environmental Consortium (CIEC). The founding participants in the CIEC are Southdown, Inc., Riverside Cement Company, Mitsubishi Cement Corporation, California Department of Commerce (now Trade & Commerce Agency), and the San Bernardino County Air Pollution Control District (now Mojave Desert Air Quality Management District). This technology is covered under U.S. Patent No. 5,586,510 issued December 24, 1996. (33)

The basic principle is to utilize the naturally occurring ammonia content of dewatered biosolids as the reagent. The dewatered biosolids are obtained from wastewater treatment plants. Since the biosolids are mechanically dewatered without heat input, the solids content varies between 16 and 30 percent (moisture content of 84 to 70%). Depending on the moisture content, the net Btu content (after evaporating the moisture) of the biosolids varies between -750 and +2200 Btu/lb. Since the biosolids heating value is relatively small, the net effect on kiln fuel combustion is expected to be small. (41)

The same conditions that affect NO_x reduction performance in SNCR affect BSI performance: temperature (927°C / 1,700°F is optimal), residence time (> 0.5 seconds is desirable), inlet NO_x concentration, inlet CO concentration, and NH_3/ NO_x molar ratio. Another key issue is mixing effectiveness, which affects the extent of contact and, hence, reaction between NH_3 and NO_x. The BSI technology is applicable to preheater/precalciner kilns because the temperature window for BSI (927°C / 1700°F) occurs in a location where it is feasible to inject biosolids. (41)

The biosolids are injected into the mixing chamber where the flue gas stream leaves the kiln and precalciner mix. The mixing chamber offers the benefits of good residence time in the appropriate temperature window (927°C / 1700°F) and high mixing effectiveness. (41)

At the Cushenbury plant, BSI underwent long-term testing and eventual adoption in 1994 and 1995. The kiln is fueled with coal (85 percent) and tires (15 percent). The plant began using tire-derived fuel (TDF) in mid-1993, so it is difficult to isolate the effects of TDF or BSI on NO_x emissions. The company estimates that the use of TDF reduces NO_x emissions from the kiln by 30 to 40 percent. (42) Before the SNCR technology was adopted, the company estimated NO_x emissions averaged 2.4 lb./tonne clinker; afterwards, the average fell to 1.2 lb./tonne clinker, a 50 percent reduction. The effects of BSI on CO emissions varies between a large increase and no change at all, but in all cases it has remained below 500 ppm. BSI has not caused any significant changes in either metal HAP or organic HAP emissions. Using the SNCR biosolids technology, the kiln also reduced its fuel consumption by 5 percent. (41)

NOxOUT®. An SNCR process using aqueous urea was developed by Electric Power Research Institute (EPRI) and is now marketed by Nalco Fuel Tech, Inc., under the trade name NOxOUT®. In the urea reaction with NO, one mole of urea reacts with two moles of NO to complete the reaction to nitrogen, carbon dioxide and water. Normalized Stoichiometric Ratio (NSR) is used to express the reagent feed rate relative to the reaction stoichiometry. The NSR takes into account the 2:1 mole ratio of the NO:urea reaction as the "normalized" ratio. If 50% of the urea reacts to reduce NO to nitrogen, reduction of 100% NO_x occurs at NSR=2; 80% reduction at NSR=1.6; 50% reduction at NSR=1.0, etc. Performance improves with increased turbulence or mixing, residence time, and more favorable temperature conditions. A higher NO_x baseline generally leads to a higher percentage of NO_x reduction. (26)

Urea is safer to handle than anhydrous ammonia. Both ammonia and urea need to be injected in a similar temperature window, which is 870 to 1090°C (1600 to 2000°F). The Polysius results earlier noted, however, appear to suggest that the ammonia optimum may be lower than the urea optimum. Proprietary additives have been developed by Nalco to widen the temperature window. (43) One modification of the urea-based SNCR system is the addition of methanol injection downstream of the urea injection point to improve overall NO_x removal.

Nalco also introduced an improved NOxOUT® PLUS, which is said to further broaden the operating temperature window and to reduce ammonia slip and CO and NO_2 formation.

The Ash Grove plant in Seattle is a preheater/precalciner kiln with average processing rates of 160 tons dry feed/hour producing approximately 100 tonnes clinker/hour. NOxOUT® was tested on this kiln under varying conditions, including the use of different fuel types (natural gas and coal), heat input to the calciner (5 to 9 percent), and preheater O_2 (1.8 to 2.9 percent). (It is probably necessary to point out that this calciner is an example of the so-called "air through" unit which employs no tertiary air duct; all air for combustion in the calciner must be furnished through the kiln. As of the present time, this heat input is in the range of 20-30% of the total. The baseline NO_x levels varied from 350 to 550 lbs. NO_x/hour. When NOxOUT® was used, NO_x emission reductions varied significantly depending on the conditions, with a maximum reduction of 90 percent (less than 100 lbs. NO_x/hour). Typical reductions were greater than 50%. (38)

NOxOUT® was tested for one week in October of 1998 on the preheater/precalciner kiln at the Lafarge-Davenport Plant. Operating conditions were unstable most of that week and only five hours of testing produced results that could provide a reasonable indication of what may be achievable with NOxOUT®. The baseline NO_x rate was approximately 350 lbs. NO_x/hour. Using NOxOUT®, emission reductions of 10 to 20 percent were achieved. (39) Operating conditions such as residence time, temperature, and the use of coal at this kiln were contrasted to conditions at the Ash Grove kiln that achieved greater reductions to explain why NOxOUT® may achieve better results on some kilns than others.

Nalco also has conducted a number of demonstrations and commercial projects in preheater/precalciner cement kilns. The fuels have included coal, and coal in combination with No. 6 heavy fuel oil, waste oil, and/or tire chips. The clinker capacity on these kilns ranged from approximately 1,000 metric tons to 3,200 metric tons per day. The results of two tests with average NO_x reductions of approximately 50%, were featured in a recent report (see Table 4-1.4). (26)

Table 4-1.4. Emissions Reductions From Two Kilns Using NOxOUT®

	Baseline NO_x Emissions (ppm)	NO_x Emissions with NOxOUT® (ppm)	Percent Reduction (%)
Kiln A, Test 1	412	203	51
Kiln A, Test 2	389	185	53
Kiln B	525	284	46

Site-Specific Analyses

SNCR at Holcim

Holcim Kiln #1

Holcim carried out trial SNCR tests on both of their precalciner kilns in Midlothian, TX. For the injection in line 1, (the older unit) the optimum location was identified to be on the riser duct, after the precalciner and before the bottom stage cyclone. This location would address NO_x formed both in the kiln (principally presumably thermal NO_x) and in the calciner (principally presumably fuel NO_x). The reports do not indicate the temperature, oxygen, or carbon monoxide concentrations of the flue gas, considered very important for optimum efficiency. There is therefore no basis for concluding that conditions had been optimized. With this condition, it proved possible to obtain about 50% removal of NO_x at a molar ratio of ammonia to NO_x of 0.75. This is not considered to be as good as obtained in the Florida kiln indicated earlier, nor for some of the Northern European kilns. However, the removal efficiency appears to be in good agreement with the data cited earlier, where a molar ratio of 0.5 is cited as achieving 40% removal, while a molar ratio of 1.0 is said to achieve 60% removal. While the conditions may not have been optimized, the results are considered acceptable compared to performance at other similar kilns. Experience at other kilns indicates further optimization may result in better performance at Holcim #1 than was achieved during the initial trial period.

Holcim Kiln #2

For the Kiln #2 system, the injection point was on the riser duct after tertiary air input and before the Pyroclon (calciner). This differs from the location for the Kiln #1 system, where the

injection point is post-calciner. This difference implies that the gases from the calciner were treated in the Kiln #1 system, but no SNCR was applied to calciner exhaust gases in the Kiln #2 system. Experience to date suggests that with normal bituminous coal fuel, roughly 70% of the system NO_x may be generated in the kiln, and 30% in the calciner as a general rule of thumb. To the extent that this supposition is justified, it appears as though an SNCR injection location that does not treat gases from the calciner may be omitting treatment of about 30% of the NO_x. In addition, the injection location for this kiln system may be experiencing a temperature decrease from the cooler tertiary air. Any residual carbon monoxide from the kiln exit gases was probably oxidized by the high O_2 content at this location, further compromising the results. If this is the case, further erosion of the efficiency of the SNCR system may be occurring.

As a result, with a molar ratio of 0.75, the efficiency of removal of NO_x was only 35%. This cannot be considered satisfactory. It proved possible to increase the NO_x removal to as high as 80%, but this was with a molar ratio of about 2.0. At this molar ratio, ammonia slip and detached plumes were severe. In addition, the plant reported a buildup of ammonium sulfate/ammonium bisulfate in the top preheater stage forming under conditions of high ammonia injection. They claim that this buildup had the potential to assume catastrophic dimensions, but was removed before this occurred.

It does not appear likely that the location for NO_x removal on Kiln #2 was optimized. The lack of any data on temperature, oxygen, and/or carbon monoxide suggests that these data were not collected. It was discovered during the Florida test that optimization of these parameters was important to the success of the experiment. We believe that if the conditions are properly optimized using the necessary temperature, oxygen, and CO data, that better results are achievable at Holcim#2.

<u>SNCR at TXI</u>

TXI Kiln #5

This kiln is already achieving very good NO_x control without employing any end of pipe technologies. It appears that the kiln is running at about 1.9 lb. NO_2/tonne clinker at present –

this may be the lowest value for any Portland cement kiln in the country. The application of SNCR may be worth consideration for further reduction of NO_x. It should be recognized, however, that 35% removal may be the best achievable, and even this level may not be achievable without optimization of the location in the preheater tower for temperature, oxygen, and CO. SNCR becomes less effective at lower NO_x concentration and European experience indicates that 200 mg/m^3 or approximately 100 ppm may be a lower limit for efficient application of SNCR at cement kilns. As earlier indicated, TXI has a high level of relatively nonvolatile organic carbon, a high level of total Kjeldahl nitrogen (unfortunately, the temperature profile of nitrogen release from the feed at TXI is not known), and an apparently relatively easy burning mix. All these factors mitigate in the direction of lower uncontrolled NO_x numbers.

TXI Wet Kilns

The ERG Team has estimated that the TXI wet kilns are currently operating at over 8 lb. NO_2/tonne clinker. The Texas Code (Chapter 117) requires mid-kiln injection or meeting an emissions limitation of 4.0 lbs./tonne clinker. For the purposes of modeling SNCR and other control techniques on the TXI wet kilns, a 30% reduction in NO_x emissions is assumed to result in emissions similar to the Ash Grove wet kilns when the mid-kiln firing is installed. The ERG Team understands that TXI is waiting for permit approval to convert the wet kilns to mid-kiln firing with tire injection. As discussed above, the lack of available alternative NO_x controls for wet kilns leads the ERG Team to a recommendation of trying innovative or experimental techniques involving some SNCR injection involving urea or another reagent in tires. This experimentation would determine if mixing and the proper form of ammonia might travel into the proper temperature range of the kiln to be effective. These ideas will have to be verified or disproved with experimentation. For the purposes of cost modeling, a 35% efficiency is assumed to be achievable through a mid-kiln injection of a SNCR reagent.

<u>SNCR at Ash Grove</u>

Ash Grove Wet Kilns

The Ash Grove wet kilns are already using mid-kiln firing and are emitting approximately 5.0 lbs./tonne clinker. Mid-kiln firing is traditionally regarded as the most

effective wet kiln method for controlling NO_x. As discussed above, it may be worthwhile considering a modification of traditional SNCR here, in which the urea is introduced inside whole tires, and mixing air is used to promote reaction with NO_x before the urea is decomposed. This is innovative and speculative, and requires testing to verify, but it should be quite inexpensive and cost effective for a plant already employing mid-kiln firing. Attempting an innovative control method for wet kilns based on SNCR seems to be a worthwhile option since other control options have not been applied to wet kilns. SCR and LoTOx^{TM} appear to be transferable from other applications but have high costs associated with reheating the flue gas in the case of SCR and installing a spray tower in the case of LoTOx^{TM}. As mentioned in evaluating TXI #5, there appears to be the potential for some NO_x reduction to be occurring from the materials already being fed to this kiln. With other mid-kiln injection in long kilns, NO_x reduction has occurred through feeding nitrogen containing sands at mid-kiln. It might be possible to introduce another material high in non-volatile carbon and/or TKN nitrogen at mid-kiln to see whether the foregoing explanation for the low NO_x from the TXI kilns is valid. Again, this would not be expensive as an experimental investigation. Similar to the TXI wet kilns, for the cost models, it was assumed that one of these experimental techniques could result in 35% NO_x reduction and that the costs would be similar to the costs of installing SNCR on a utility boiler.

Table 4-1.5. Summary of Modeling Results for SNCR on Ellis County Kilns – Performance Results

Existing Unit	Control Technology	Emissions Rate tpy before	Emissions Rate tpy after (a)	Controlled Emissions Rate ppm	Controlled Emission Rate lb./tonne clinker	Control Efficiency %	Reduction tpy
Ash Grove #1- wet	SNCR	702	537.1	200	3.6	35%	164.9
Ash Grove #2- wet	SNCR	750	573.9	200	3.9	35%	176.1
Ash Grove #3- wet	SNCR	764	584.6	200	3.9	35%	179.4
TXI #1 and #4–wet (b)	SNCR	838	641.2	250	3.7	35%	196.8
TXI #2 and #3–wet (b)	SNCR	121	92.6	250	3.7	35%	28.4
TXI#5 – dry	SNCR	1710	1,308.4	100	1.0	35%	401.6
Holcim #1 – dry	SNCR	2222	1,476.5	190	1.9	50%	745.5
Holcim #2 – dry	SNCR	1778	1,181.5	150	1.5	50%	596.5

(a) NO_x emission rate after SNCR does not reflect SNCR efficiency reduction due to adjustment by the ozone season factor of 0.671 (NO_x reduction is modeled to occur only during the ozone season).
(b) The results for TXI 1 & 4 and #2 & #3 are average per kiln – for example, total emissions reductions for controlling both TXI #1 & #4 are double the value listed in the table.
Models assume mid-kiln firing installed at TXI as required under current SIP.

Table 4-1.6. Summary of Modeling Results for SNCR on Ellis County Kilns – Economic Results

Existing Unit	Control Technology	Capital Cost	Annual Cost	Cost Effectiveness $/ton NO_x	Energy Penalty or Benefit	Emissions Penalty or Benefit	Burden Cost $/tonne clinker
Ash Grove #1- wet	SNCR	$1.2 MM	$0.4MM	$2,500	(a)	(b)	$1.70
Ash Grove #2- wet	SNCR	$1.3MM	$0.4MM	$2,400	(a)	(b)	$1.70
Ash Grove #3- wet	SNCR	$1.4MM	$0.4MM	$2,400	(a)	(b)	$1.70
TXI #1 and #4–wet (c)	SNCR	$1.4MM	$0.5MM	$2,400	(a)	(b)	$1.60
TXI #2 and #3–wet (c)	SNCR	$1.4MM	$0.3MM	$13,000	(a)	(b)	$5.00
TXI#5 – dry	SNCR	$2.3MM	$1.0MM	$2,900	(a)		$0.45
Holcim #1 – dry	SNCR	$2.3MM	$1.1MM	$1,500	(a)		$1.00
Holcim #2 – dry	SNCR	$2.3MM	$1.0MM	$1,700	(a)		$0.90

(a) SNCR should not have energy impacts.
(b) Ammonia slip can be significant for SNCR when not properly optimized.
(c) The results for TXI 1 & 4 and #2 & #3 are average per kiln – for example, total capital costs for controlling both TXI #1 & #4 are double the value listed in the table.

4.2 Combustion Optimization

This section of the report is taken from the EPA 2000 Report and is included, with minor editing by the ERG Team. This information is included to provide the Texas environmental communities with the comprehensive background information necessary to understand the parameters that dictate NO_x control options at cement kilns. Combustion optimization is largely in place in the Ellis County kilns, with the exception of the TXI wet kilns that are awaiting permits for mid-kiln firing to comply with the requirements of 30 TAC Chapter 117.

Combustion optimization is generally applicable to all types of kilns and is an efficient way to reduce the formation of thermal NO_x. The combustion modifications discussed in this section focus on staging the combustion to minimize combustion at the maximum temperatures. This can be accomplished by modifying the way oxygen or fuel is provided for combustion. For the purposes of this report, the level of emissions reduction contained in 30 TAC Chapter 117 is the level associated with combustion and process optimization. As such, the techniques below have largely been already required and implemented at the Ellis County cement plants. However, the differing performance of the kilns may indicate that more combustion and process optimization could be implemented as part of the effort to reach higher NO_x emissions reductions levels.

4.2.1 Staged Combustion of Air

Staging of combustion air allows combustion of fuel to proceed in two distinct zones. In the first zone, the initial combustion is conducted in a fuel-rich, oxygen-poor flame zone. This zone provides the high temperatures necessary for completion of the clinkering reactions, but the lack of available oxygen minimizes the formation of thermal and fuel NO_x. The lack of sufficient oxygen leads to only partial combustion of the fuel.

In the second, fuel-lean zone, additional (secondary) combustion air is added to complete the combustion process. However, the temperature in this second zone is much lower than the first zone because of mixing with the cooler secondary air, so the formation of NO_x is minimized in spite of the excess available oxygen. This staged approach can be used for combustion of all fossil fuels. Staged combustion is typically achieved by using only a part of the combustion air (primary air) for fuel injection in the flame zone, with remaining secondary air being injected in the subsequent cooler zone.

For effective staging of combustion air to reduce NO_x emissions, cement plants must have indirect-fired kilns. In a direct-fired cement kiln, air used for conveying pulverized coal from a coal mill, i.e., primary air, is typically 17 to 20 percent of the total combustion air. The amount of primary air may be reduced by separating the coal mill air from coal. A cement kiln using less than 10 percent of primary air is an indirect-fired kiln. Conversion of a direct-fired kiln to an indirect-fired kiln involves adding particle separation equipment such as a cyclone or a baghouse and a fan to provide the primary air used to transport the powdered coal from storage to the kiln. An indirect-firing system increases overall energy efficiency by allowing a greater proportion of hot clinker cooler air to be used as secondary combustion air.

4.2.2 Flue Gas Recirculation

In addition to changing the combustion air distribution, the oxygen content of the primary air may be reduced to produce a fuel-rich combustion zone by recycling a portion of the flue gas into the primary combustion zone. (44) The recycled flue gas may be premixed with the primary

combustion air or may be injected directly into the flame zone. Direct injection allows more precise control of the amount and location of the flue gas recirculation (FGR). In order for FGR to reduce NO_x formation, recycled flue gas must enter the flame zone. The FGR also reduces the peak flame temperature by heating the inert combustion products contained in the recycled flue gas.

The use of FGR may not be a viable method of reducing NO_x in a full-size cement kiln burning zone. FGR's effectiveness relies on cooling the flame and generating an oxygen-deficient (reducing) atmosphere for combustion to reduce NO_x formation, conditions that may not be compatible with cement kiln operation. High flame temperature and an oxidizing atmosphere are process requirements to produce a quality clinker product. A cement kiln differs from a utility boiler and other combustion devices because minimum temperatures and an oxidizing atmosphere are required to initiate chemical reactions in a cement kiln in addition to providing the required heat (Btu/tonne clinker). Reduced flame temperatures and reducing conditions in the burning zone of a cement kiln may not be compatible with the production of cement clinker. (33)

Coupling a low-NO_x step burner with flue gas recirculation has been shown to reduce NO_x emissions further in a cement kiln. (45) The additional NO_x reduction attributable to FGR was estimated to be about 15 to 38 percent depending upon the proportion of FGR used. (45) Incorporation of FGR in a cement kiln also results in somewhat increased power consumption and reduced kiln output.

4.2.3 Low-NO_x Burners

Some cement kiln burners, specifically marketed as low- NO_x, burners, typically use 5 to 7 percent primary air (46,47) and thus can be used only on indirect-fired kiln systems. Low-NO_x burners can be installed on any type of kiln. Low-NO_x burners are designed to reduce flame turbulence, delay fuel/air mixing, and establish fuel-rich zones for initial combustion. The longer, less intense flames resulting from the staged combustion lower flame temperatures and reduce thermal NO_x formation. Some of the burner designs produce a low pressure zone at the burner center by injecting fuel at high velocities along the burner edges. Such a low pressure

zone tends to recirculate hot combustion gas which is retrieved through an internal reverse flow zone around the extension of the burner centerline. The recirculated combustion gas is deficient in oxygen, thus producing a similar effect as FGR. Combustion of the fuel in the first stage thus takes place in an oxygen-deficient zone before the fuel is diluted in the secondary air. Installing such a burner reduces NO_x emissions from the kiln-burning zone by up to 30 percent. (46,48,49)

Low- NO_x burners have been used by the cement industry for twenty years. (50) Many suppliers offer low-NO_x burners and most of these systems focus on lowering the NO_x formation in the calciner by air or fuel staging, by reburning, or by high temperature combustion. (51) Test data from several different low-NO_x burners are now available. Thomsen, Jensen, and Schomburg reported on tests of a F.L. Smidth in-line calciner low-NO_x system in a preheater/precalciner kiln where different percentages of coal were added to the reduction zone of the precalciner (the remaining coal was added to the oxidizing zone). (51) When 100 percent of the coal was added to the reduction zone of the precalciner, the NO_x content at the preheater exit was reduced by 44 percent relative to when zero coal was added (see Table 4-2.1).

Table 4-2.1. NO_x Emissions from a Precalciner Equipped with a Low-NOx Burner

Percent Coal Added to Reduction Zone[a] (lb. NO_x/tonne clinker)	Nox Emissions[b] (lb. NO_x/tonne clinker)	Percent Reduction[c] (%)
0	2.8	-
50	1.9	31
100	1.6	44

[a]The remaining percentage of the coal was added to the oxidizing zone.
[b]Emission measurements were taken at the preheater exit.
[c]Percent reductions are relative to emissions when zero percent of the coal was added; the original measurements were in kg NO_x/tonne clinker to the hundredth place - the percent reductions were calculated using the original measurements, which results in slightly different values than when lb. NO_x/tonne clinker are used.

Steinbiß, Bauer, and Breidenstein reported emissions changes for five kilns before and after the installation of Pyro-Jet low-NO_x burners (see Table 4-2.2). (50) The emission reductions ranged from 15 to 33 percent. Information on kiln-type was not provided.

Table 4-2.2. NO_x Emissions Before and After Installation of Pyro-Jet Low-NO_x Burners

Kiln	Before Installation (ppm)	After Installation (ppm)	Percent Reduction (%)
A	970	650	33
B	not given	not given	30
C	650	460	29
D	900	730	19
E	not given	not given	15

There are two new data sources on emissions reductions from the use of Rotaflam® low-NO_x burners. The Pillard Combustion Equipment and Control Systems published data on four kilns, comparing NO_x emissions with a 3 channel burner to emissions when a Rotaflam® burner was used (see Table 4-2.3). (52) The emission reductions ranged from 23 to 47 percent. Information on kiln-type was not provided.

Table 4-2.3. NO_x Emissions with 3 Channel and Rotaflam® Low-NO_x Burners

Kiln	With 3 Channel Burner (ppm)	With Rotaflam® Burner (ppm)	Percent Reduction (%)
A	774	409	47
B	865	664	23
C	484	350	28
D	487	336	31

Emissions data are also available before and after a Rotaflam® low-NO_x burner was installed on a long-wet kiln (see Table 4-2.4). (53) The average emissions decreased 14 percent.

Table 4-2.4. Emissions Before and After Installation of a Rotaflam® Burner on a Wet Kiln

Year	Average Emissions (lb. NO_x/tonne clinker)	Percent Reduction[a] (%)
1990	277	-
1992[b]	288	-
1993	269	-
1994	275	-
1995 (Rotaflam® installed)	239	14

[a] Percent reduction is relative to the 1990, 1992-1994 average NO_x emissions, 277.25 lb. NOx/hr.
[b] 1991 data were not provided.

The Fuller Company low NO_x In-Line Calciner was installed in an RMC Lonestar kiln, which reported 30-40 percent reductions in the amount of thermally formed NO_x after installation. (54)

In January 2000, the PCA provided results of a survey of cement facilities where the respondents indicated 14% of the operating U.S. kilns (22 kilns) have already installed a low-NO_x burner (81% of the facilities representing 81% of the operating U.S. kilns responded to the survey). The remaining 139 kilns that are represented by the survey have not installed low- NO_x burners. (55,56)

4.2.4 Staged Combustion of Fuel

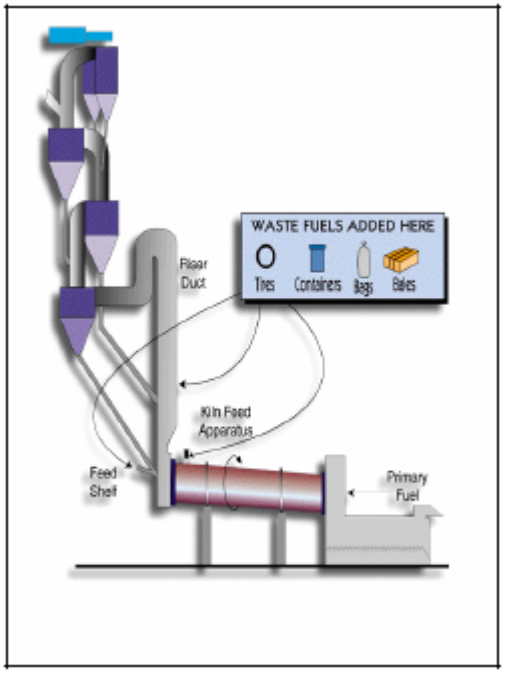
In conventional long (wet or dry) rotary kilns, all heat required for the cement-making process is supplied in the primary kiln burning zone, where the combustion occurs at the hottest temperature in the kiln. In the cement-making process, the preheating and calcination of the raw materials requires a large amount of heat but are typically at a temperature of 600 to 900°C (1,100 to 1,650 °F) which is much lower than the kiln's clinker-burning temperature of 1,200 to 1480 °C (2,200 to 2,700 °F). (57) In the secondary combustion method, part of the fuel is burned at a much lower temperature in a secondary firing zone to complete the preheating and calcination of the raw materials.

4.2.5 Preheater/Precalciner and Tire Derived Fuel

This concept of a secondary firing zone is the basis of the preheater/precalciner cement kiln design. Almost all new cement kilns have a preheater/precalciner-type design. In the preheater kilns, the primary emphasis is on efficient heat recovery from kiln exhaust gases (see Figures 4-2.1 and 4-2.2). (58) However, up to 15 to 20 percent of the fuel may be fired in the riser duct in preheater designs. (58)

Precalciner systems typically employ a tower of four-stage cyclones for efficient gas-solids contact, which improves the energy efficiency of the overall process (see Figure 4-2.2).

(58) In a typical precalciner kiln almost 40 to 50 percent of the fuel is burned at a lower (calcination) temperature which reduces the thermal NO_x formation considerably.



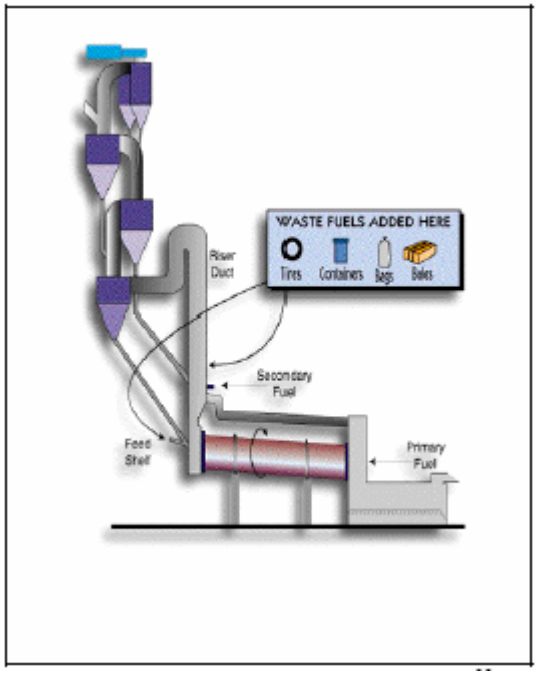


Figure 4-2.1. Schematic of Preheater (58) **Figure 4-2.2. Schematic of Precalciner (58)**

Tire-derived fuel can also be added to the feed end of a preheater or precalciner kiln. The Mitsubishi Cement Company's Cushenbury Plant in Lucerne Valley, CA began using whole waste tires as a fuel supplement in 1993. The waste tires are delivered in enclosed container trucks and dumped into the plant's automated handling system. A live bottom hopper and singulator place the waste tires on a conveyor system. This conveyor system transports the tires to the feed end of the kiln and drops the tire into an airlock system that allows the waste tire to fall onto the feed plate inside the kiln at a rate of five to six tires per minute.

Currently, 8,000 to 9,000 tires are burned per day, totaling about 13 percent of the fuel. Tires have a fuel content of approximately 14,000 Btu/lb. and a sulfur content that is roughly the same as the coal that would be used. The steel belting in the waste tires supplements the iron requirements and approximately two percent of the iron in the final product comes from the tires. The addition of waste tires reduces NO_x emissions from the kiln by 30 to 40 percent, and there is no significant change in toxic, hydrocarbon, or metal emissions. (59,60,61)

4.2.6 Low- NO_x Precalciners

Most of the major cement kiln suppliers are now offering "low NO_x" precalciner designs for new kilns. These designs typically inject a portion of the fuel into the feed end of the kiln, countercurrent to the exhaust gas flow.(62) This fuel is burned in a substoichiometric O_2 environment to create a strongly reducing atmosphere (relatively high concentrations of CO) by following the simplified reactions:

$$NO + C \rightarrow N + CO$$

and

$$NO + CO \rightarrow N + CO_2$$

This reducing atmosphere inhibits the formation of fuel NO_x and destroys a portion of the NO_x formed in the kiln burning zone. In some designs, additional fuel is then added, again with insufficient O_2 for complete combustion, to create another reducing zone. Several precalciner kilns in the US have recently been retrofitted with these "low NO_x" precalciners and preliminary information indicates a noticeable reduction in NO_x per ton of clinker. (33) Up to 46 percent reduction of NO_x emissions has been reported without causing excessive coating difficulties in the kiln. (62)

Nitrogen present in the fuel may also participate in the reduction of NO_x. The primary NO_x formation mechanism in the secondary firing is the fuel NO_x formation that depends upon the nitrogen content of the fuel used. In order for the above reactions to proceed at reasonable rates the temperature in the reduction zone should be maintained between 1000 and 1200°C (1830 to 2190°F). These temperatures may lead to coating difficulties, particularly if the fuel used is coal with high ash content. (63)

It is not possible to use "staged combustion" on preheater kilns that are firing fuel in the riser since in staged combustion it is necessary to add the fuel in an oxygen deficient atmosphere and then supply additional combustion air to fully combust the fuel. Preheater kilns do not have tertiary air ducts to supply the additional combustion air. The air for combustion of the

secondary fuel must come through the kiln, which precludes introducing the secondary fuel into an atmosphere with insufficient oxygen for complete combustion. (33)

Emissions reductions have also been found when tire derived fuel was burned in a precalciner. In one case, when 47 percent of the coal fired in the calciner was substituted with tire-derived-fuel, a reduction in NO_x emissions of about 29 percent was observed. (64)

4.2.7 Mid-Kiln Firing

The concept of staged combustion of fuels may also be used in conventional wet and long-dry kilns by injecting solid fuel into the calcining zone of a rotating long kiln using a specially designed feed injection mechanism. (65) This system is known as mid-kiln firing (MKF) and allows part of the fuel to be burned at a material calcination temperature of 600 to 900°C (1100 to 1650°F) which is much lower than the clinker burning temperature of 1200 to 1480°C (2200 to 2700°F). (57)

To maintain continuity in the heat input, solid and slow burning fuels (such as tires) are most amenable for MKF. The Cadence feed fork MKF technology was first introduced in 1989. It can be installed during an annual maintenance shutdown. It is comprised of three primary components: (1) a staging arm or 'feed fork' that picks up the fuel modules and positions them for entry into the kiln, (2) two pivoting doors that open to allow the fuel modules to drop into the kiln, and (3) a drop tube that extends through the side wall of the kiln. In addition to these basic components, feed fork technology also requires a delivery system, which positions the fuel modules so they can be picked up by the feed fork and a mechanism for opening the doors so the fuel modules can enter the kiln. (66) Due to the rotation of the kiln, fuel can be conveniently injected only once per revolution from the top.

Although most feed forks today are dedicated to whole tires, one facility uses baled industrial waste as a fuel, and many others are investigating a variety of energy containing waste materials from carpet scrap to pharmaceutical waste. These energy-bearing waste materials can be containerized or dimensionalized into discrete fuel modules to be fed to the kiln using the feed fork. (66)

Inserting whole tires into mid-kiln locations can give precalciner stability to the kiln. The operators have two points of control to assist in stabilizing kiln operation. Tires burn for 15 to 20 minutes within the kiln after entry. This is deduced from observations of the rate of change in kiln exit oxygen levels after entry of tires begins. With proper instrumentation, control of the kiln can be improved by adding solid fuels midkiln. (67)

Mid-kiln firing of tires or other waste-derived fuels does not reduce the final product quality; in fact, many of Cadence's cement kiln partners have reported an improvement in the clinker burnability and mineralogy. The enhanced control has shown to impart better formation of clinker. Reductions in cement fineness have been shown while maintaining similar seven-day strengths. Several facilities also have reported an extended life of the refractory in the burn zone. (66,67)

By adding fuel in the main flame at mid-kiln, MKF changes both the flame temperature and flame length. These changes may reduce thermal NO_x formation by burning part of the fuel at a lower temperature and by creating reducing conditions at the solid waste injection point, which may destroy some of the NO_x, formed upstream in the kiln burning zone. MKF may also produce additional fuel NO_x depending upon the nitrogen content of the fuel. (68) However, as discussed in section 5.1.3, fuel NO_x is unimportant relative to thermal NO_x formation. Additionally the discontinuous fuel feed from MFK can result in increased CO emissions especially if hazardous wastes are used. To control CO emissions, the kiln may have to have increased combustion air, which can decrease production capacity. (69)

According to literature from Cadence, in tests of its feed fork technology, one kiln reduced NO_x emissions by 38%, overall particulate emissions by 14%, metal emissions by 30%, SO_2 emissions by 36%, and net emissions of all hydrocarbons by 29%. (66,67) In the research conducted for this report, test data were compiled for seven dry kilns and three wet kilns with MKF technology. In nine tests on the dry kilns, the average reduction in NO_x emissions was 33%, with a range from 11% to 55%. In three tests on the wet kilns, the average reduction in NO_x emissions was 40%, with a range from 28% to 59% (see Table 4-2.5). (69,70,71,72,73) It

should be noted that the three kilns that are known to have CEMS all reported emissions reductions of 45 percent or more.

Table 4-2.5. Emissions From Kilns With Mid-Kiln Firing

	Emissions (lb. NO_x/tonne clinker)	Percent Reduction (%)	Emissions Based on CEMS Data
Dry Kilns[a]			
A[40]	not given	13.6	unknown
B[40]	not given	11.1	unknown
C[24,44]	not given	45.1	yes
C[40]	not given	55.3	yes
D[21,41]	2.7	not given	unknown
E[22,42]	10.2	13.9	unknown
F[40]	not given	46.6	unknown
F[40]	not given	50.4	unknown
F[40]	not given	28.3	unknown
Average (Dry Kilns)	6.4	33.3	
Wet Kilns			
G[23,43]	not given	59.0	yes
H[40]	not given	35.0	unknown
I[40]	not given	27.6	unknown
Average (Wet Kilns)	n/a	40.5	
Average (Dry & Wet Kilns)	6.4	35.1	

[a] There was more than one test at some kilns.

Waste-derived fuels with high heating values represent an economical source of energy for the cement industry and its consumption has been increasing during the past decade.[12] Midkiln firing is a proven technology and so far at least 21 long kilns in the U.S. and nearly 40 kilns worldwide have been modified to allow mid-kiln firing of solid and hazardous waste. (66,74)

4.3 Lower Temperature Oxidation Based Technologies

Oxidation technologies were not evaluated in the EPA 2000 Report. One of these technologies, LoTOx™, is currently being installed in refineries at fluidized catalytic cracking units (FCCUs). The temperatures, gas flow rates and other characteristics of FCCUs are similar

enough to cement plants that these technologies should be considered as candidates for evaluation as transferable technologies to application at cement kilns.

4.3.1 Introduction

Oxidation technologies for flue gas NO_x control developed in recent years have become commercially successful and economically viable as an alternative to ammonia and urea based technologies using reduction chemistry to remove NO_x. Commercially available technologies such as Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR), which reduce NO_x to nitrogen using ammonia or urea as an active chemical are optimized to specific temperature windows and have similar reagent costs for the varying ammonia based reagents. Oxidation technologies can work in other temperature regimes and use different reagents that are not linked to ammonia costs and, thereby, provide important control options to ammonia-based NO_x reduction technologies.

Oxidation technologies convert lower nitrogen oxides such as nitric oxide (NO) and nitrogen dioxide (NO_2) to higher nitrogen oxides such as nitrogen sesquioxide (N_2O_3) and nitrogen pentoxide (N_2O_5). These higher nitrogen oxides are highly water soluble and are efficiently scrubbed out with water as nitric and nitrous acids or with caustic solution as nitrite or nitrate salts. NO_x removal in excess of 90% has been achieved using oxidation technology on NO_x sources with high sulfur content, acid gases, high particulates and processes with highly variable load conditions. Generally these technologies work at relatively low temperatures (100-950ºF) and some of these technologies are likely most cost effective for use on plants with existing scrubbers. But may also prove to be cost effective options due to their potential application in lower temperature windows which can avoid expensive options like gas reheat. These technologies are used for NO_x control for a variety of NO_x emission sources but are not known to have been used to date on a cement kiln.

4.3.2 LoTOx™

General description. The LoTOx™ System uses ozone as the oxidizing agent, which selectively oxidizes relatively insoluble NO_x to higher oxides of nitrogen. These higher oxides

are readily soluble and easily removed in a wet scrubber. The patented system, which can be installed as a stand-alone or retrofit design, provides sufficient residence time under maximum load conditions to allow complete reaction of the ozone. The system's small and adaptable footprint, as well as its ability to produce ozone on demand, provides control of the installation to maximize NO_x control and minimize capital and operating costs. The LoTOx™ System is very selective for NO_x removal, oxidizing only the NO_x and therefore efficiently using the treatment chemical, ozone, without causing any significant SO_x oxidation and without affecting the performance of the downstream SO_x scrubber.

Figure 4-3.1. is an overall process diagram of the LoTOx™ System.

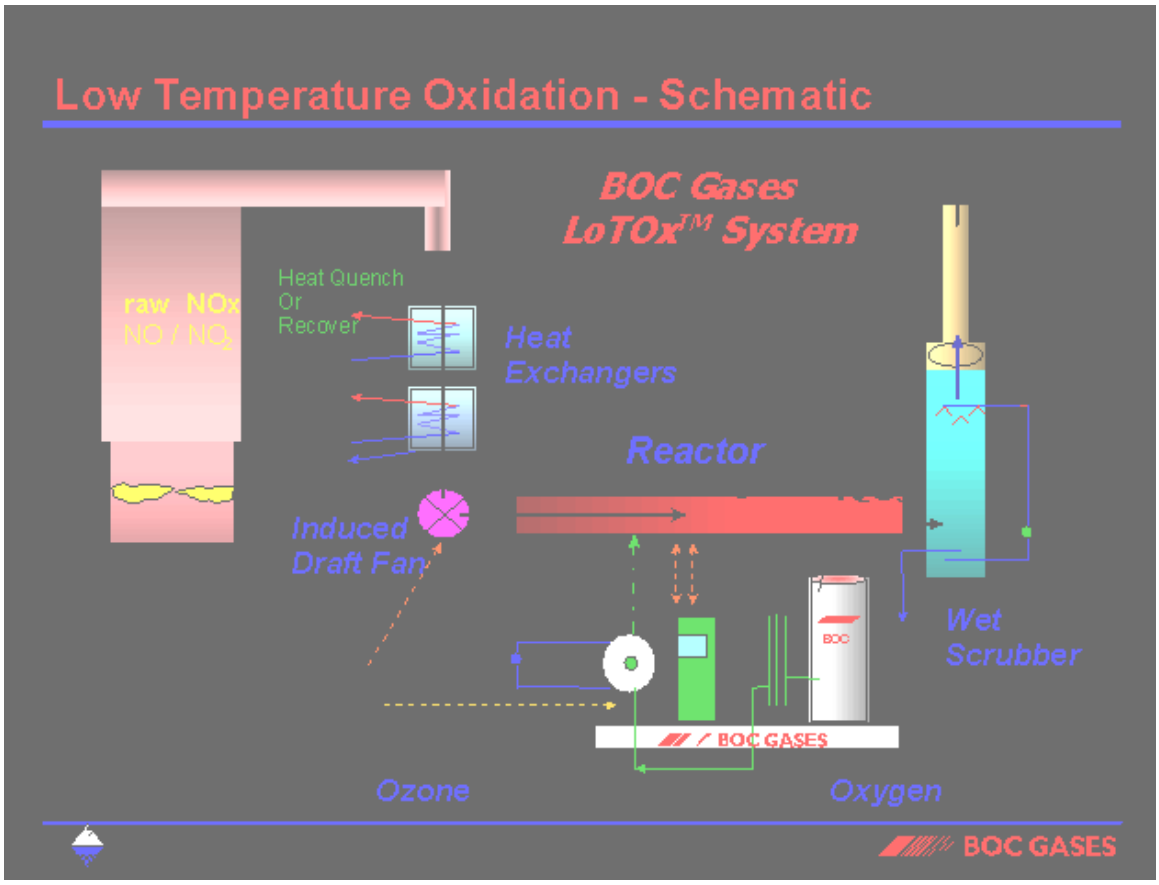


Figure 4-3.1. Overall Process Diagram of the LoTOx™ System

Figure 4-3.2. provides another example of a LoTOx™ system where the ozone injection is included in the scrubber.

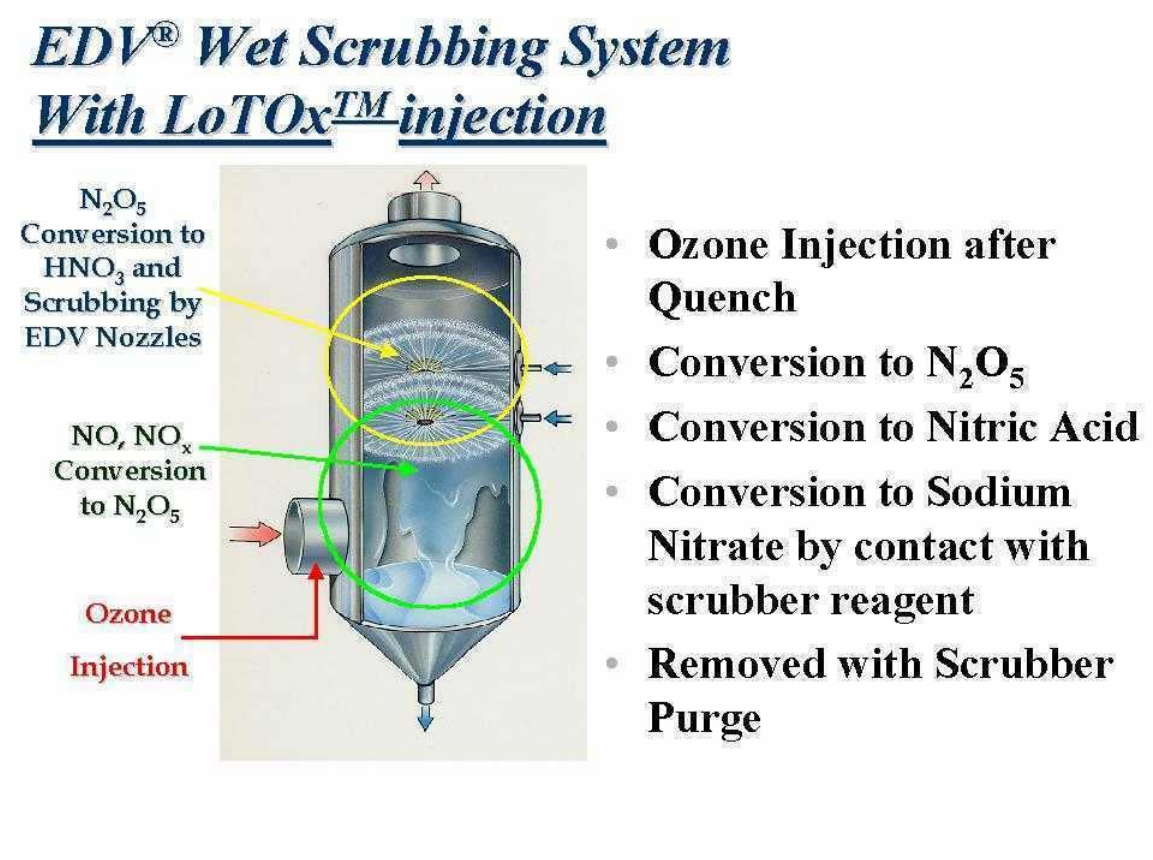


Figure 4-3.2. EDV Wet Scrubbing System with LoTOx^{TM} Injection

Potential applicability. The large gas volumes, high moisture levels and large quantities of dilution air needed to reach the operating temperature range in some systems may limit the applicability of the LoTOx^{TM} system.

Advantages. Table 4-3.1 provides an overview comparing the LoTOx^{TM} process with SNCR and SCR technologies.

Table 4-3.1. Comparison Of Common Post Combustion NO_x Abatement Technologies For NO_x Emissions Control

	SNCR	SCR	LoTOx™
Mode of Treatment	Reduction	Reduction	Oxidation
Active Chemical	NH_3 / Urea	NH_3 / Urea	Ozone
Gas Temperature Required °F	1650 - 2000	500 - 900	150 – 250
Pressure Required, psig	0+	0++	0+
Placement in Exhaust System	Near Combustion Chamber	Between Air Pre-Heater and Economizer (boiler)	Tail End
Catalyst Bed	No	Yes	No
Gas Phase Reaction Duct	Yes	No	Yes
Scrubber	Optional	Optional	Yes
NO_x Reduction Achieved	40 - 70 Percent	60 - 95 Percent	90 - 95 Percent
Slip of Active Agent	NH_3 – Yes	NH_3- Yes	Ozone - No
CO Emissions After Treatment	May Increase	May Increase	No Effect
SO_x Emissions After Treatment	Little Effect – Maybe H_2S	Little Effect - Maybe H_2S	No Effect or Significantly Reduced
Gas Temperature Outside Operating Range - Overshoot	More NO_x Emissions Through NH_3 Oxidation	More NO_x Emissions Through NH_3 Oxidation, Ammonia Slip	Increased O_3 Consumption for the Time Period of Overshoot
Gas Temperature Outside Operating Range - Undershoot	More NO_x Emissions Through Reduced Reduction by NH_3	More NO_x Emissions Through Reduced Reduction by NH_3, Ammonia Slip	No Effect

An additional advantage is the control of SO_x emissions that would likely be achieved if the LoTOx™ system were added to any system that currently does not have a wet scrubber if joint control of SO_x and NO_x is required. Lower cost spray towers that do not appreciably control SO_x can be installed at lower cost than flue gas desulfurization scrubbers. The cost models for application of LoTOx™ at wet kilns are based on installing simple spray towers that do not control SO_x.

Disadvantages. It is likely that for most applications, the LoTOx™ option would be an add-on to existing APCD systems. Because of high electrical power usage, costs are reported to be high. Electricity and oxygen costs alone are estimated to be greater than $1,600/ton of NO_x controlled.

Additional nitrate captured in the existing sulfate scrubber could impact the quality of the plant's artificial gypsum although, with a typical dewatering system, this should not be a problem because of the much higher solubility of the nitrates relative to sulfates. High nitrate wastewater could be used by local farmers as fertilizer or could be used at the plant to fertilize grass areas as well as water/fertilize in quarry reclamation areas. Lowering the exit gas temperature and adding moisture may result in problems with condensation in the stack.

Emissions performance. There are three primary process variables which impact the NO_x control capabilities of the LoTOx™ process: temperature of the flue gas (T), residence time of the flue gas in the reactor duct (RT) and amount of ozone (O_3 Factor) injected into the reactor duct. Based on the results of LoTOx™ demonstration testing, the most efficient control parameters for a full scale system on the Quemetco, Inc., furnace are a temperature of 175 °F or less, a residence time of four seconds, and an ozone injection factor of 80 to 90. The O_3 Factor represents the O_3 to NO_x ratio at the inlet to the reaction duct. The presented data uses O_3 Factor for the sake of clarity and to provide meaningful data while maintaining confidentiality of proprietary intellectual information. Figure 4-3.3. depicts the performance conditions of the LoTOx™ process for the design conditions of RT = 4 seconds, T = 175 °F and O_3 Factor = 70 to 90. Under these design conditions the NO_x removal achieved ranges from 80 percent at an O_3 Factor of 70 to 95 percent at an O_3 Factor of 90.

This technology should be considered transferable in nature. It has not been used on a cement kiln but it has been used on similar large sources. Discussions with this technology's vendors reveals that existing SO_x and CO levels at the cement plants in Midlothian should not be a factor in the use of this technology. Applications or tests have already been performed at CO and SO_x levels well above those seen in any of these cement plants.

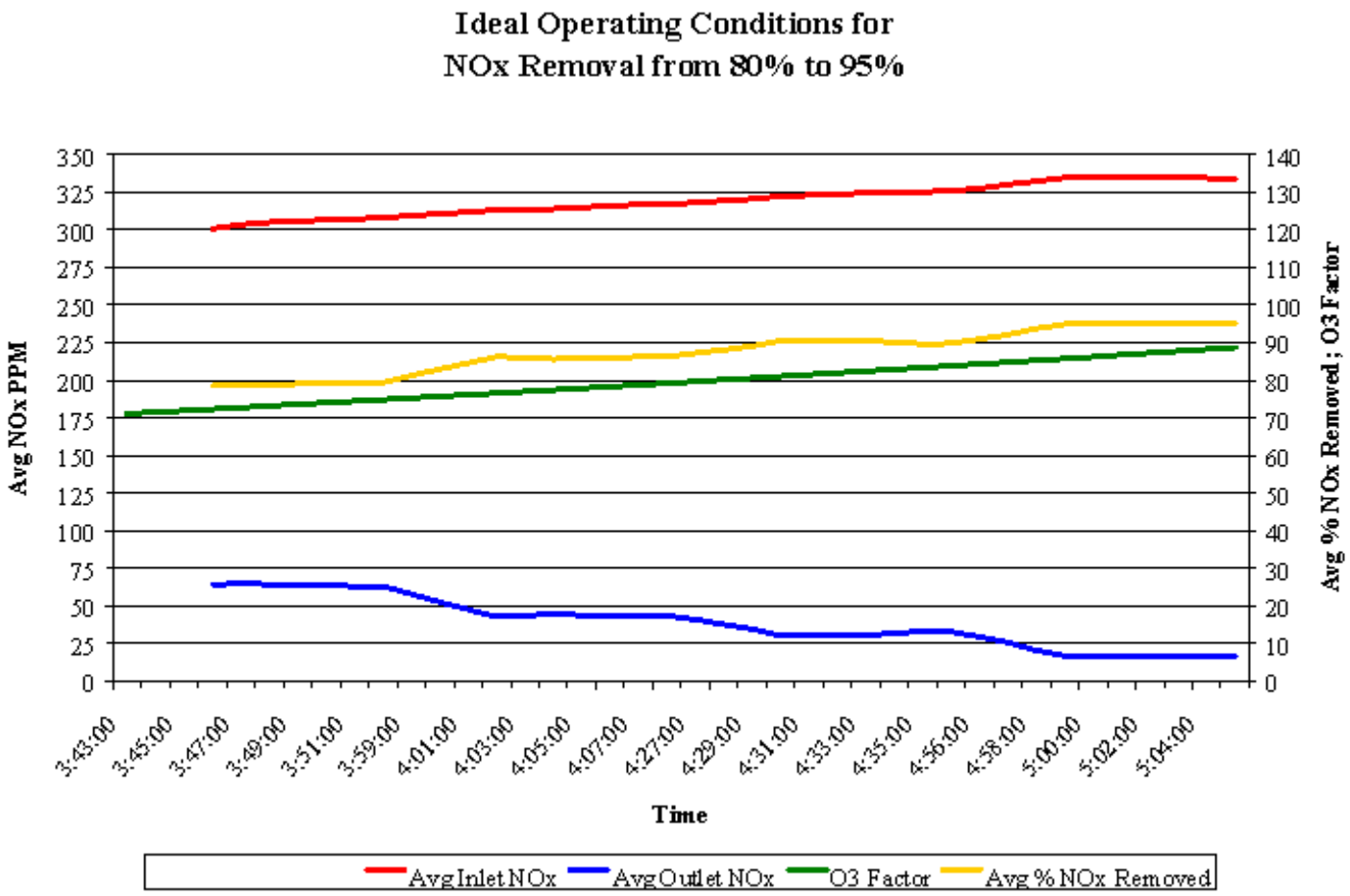


Figure 4-3.3. Ideal Operating Conditions for NO_x Removal from 80% to 95%

Cost. Ohio Coal Development Office (OCDO) provided 65 percent of the capital to install a $6.3 million LoTOx™ unit at the Medical College of Ohio. The project includes two processes: LoTOx™ for NO_x and particulate material control and Rapid Absorption Process (RAP, another BOC licensed process) for sulfur dioxide control. The controls are for 25 megawatt capacity boilers burning Ohio coal containing 3 percent sulfur. According to the BOC Company literature, the unit is designed to remove about 90 percent of the NO_x in emission gases. The RAP process uses a slurry of lime injected into the flue gas to capture SO_2 and a fabric filter (baghouse) to remove the calcium sulfate particles. Cost effectiveness has been estimated to be in the range of $1,700 to $1,950 per ton NO_x removed. (54)

In June 2001, BOC announced that they had installed, started up and commissioned a LoTOx™ unit at J & L Specialty Steel's Midland, PA plant. Details of the installation are not

published in any detail. However, Robert Ferrell, BOC Vice President of Business Development, said, "We were able to modify the system to achieve a higher level of control than was originally anticipated. We have been able to reduce NO_x emissions by more than 95 percent." No costs or capacity numbers were available.

A subsequent search of EPA's RBLC27 Database indicates that at least two other plants in the U.S. are using (or are planning to use) BOC's LoTOx™ process in their facilities. These plants are Lion Oil Company in El Dorado, AR and Marathon-Ashland Oil in Texas City, TX. Both plants use (or will use) the LoTOx™ on their Fluidized-Bed Catalytic Cracking Units (FCCU) for NO_x control. Operating conditions and performance results are not available.

Another article, written by a BOC employee, stated, "The capital (recovery) and operating costs for the (LoTOx™) system have been evaluated for various system sizes and (they) fall well within the costs per ton of NO_x removed typical for post-combustion treatment technologies in non-utility applications." Unfortunately, this information is not very helpful for determining cost for the cement industry since a paper published by NESCAUM gives the cost effectiveness range for NO_x removal from $390 to $5,450 per ton NO_x. Cost effectiveness is heavily dependent on each individual facility's situation. This includes their existing control equipment, extent of modifications necessary to install new control equipment, and the degree of DRE required to achieve the desired results.

Based on the data available, capital costs for adding LoTOx™ to a system that does not have a wet scrubber such as the wet kilns in Midlothian are likely to be much more costly than the kilns that already have wet scrubbers. Vendor information was used to calculate costs associated with the application of LoTOx™ to the cement plants in Midlothian. Estimated costs associated with the precalciner kilns which already have scrubber systems in place are $2,300-$2,600/ton of NO_x controlled. Estimated costs associated with the wet kilns which do not have scrubber systems in place are $3,000-$3,700/ton of NO_x controlled. The costs for the wet kilns include installation of a spray tower to remove the soluble NO_x oxidation products produced by the LoTOx™ system. (74a, 74b, 74c, 74d, 74e, 74f, 74g, 74h, 74i, 74j, 74k, 74l, 74m, 74n)

4.3.3 Hydrogen Peroxide

General description. There are several methods for controlling NO_x emissions. Gas scrubbing is one of the most common forms of NO_x treatment, with sodium hydroxide being the conventional scrubbing medium. However, the absorbed NO_x is converted to nitrite and nitrate, which may present wastewater disposal problems. Scrubbing solutions containing hydrogen peroxide are also effective at removing NO_x, and can afford benefits not available with NaOH. For example, H_2O_2 adds no contaminants to the scrubbing solution and so allows commercial products to be recovered from the process, e.g., nitric acid or nitrate salts (for use as fertilizer). In its simplest application, H_2O_2 (0.5-1 wt.%) and nitric acid (35-45 wt.%) are used to scrub both nitric oxide (NO) and nitrogen dioxide (NO_2) -- the chief components of NO_x from many industrial sources. The reactions are rapid at moderate temperatures (30-80 °C), with about 1.7 and 0.37 lb. H_2O_2 required per lb. NO and NO_2, respectively. The chemistry controlling the process is outlined below:

$$3NO_2 + H_2O <==> 2HNO_3 + NO$$
$$NO + HNO_3 + H_2O \text{ ----> } 3HNO_2$$
$$HNO_2 + H_2O_2 \text{ ----> } HNO_3 + H_2O$$

There are several other processes that also use hydrogen peroxide to remove NO_x. The Kanto Denka process employs a scrubbing solution containing 0.2% hydrogen peroxide and 10% nitric acid while the Nikon process uses a 10% sodium hydroxide solution containing 3.5% hydrogen peroxide. A fourth process, the Ozawa process, scrubs NO_x by spraying a hydrogen peroxide solution into the exhaust gas stream. The liquid is then separated from the gas stream, and the nitric acid formed is neutralized with potassium hydroxide. The excess potassium nitrate is crystallized out, and the solution reused after recharging with hydrogen. In addition to the methods cited above in which NO_x is oxidized to nitric acid or nitrate salts, a series of Japanese patents describe processes and equipment for reducing NO_x to nitrogen using hydrogen peroxide and ammonia. The processes are efficient but must be carried out at higher temperatures than the processes cited earlier.

The injection of hydrogen peroxide (H_2O_2) into hot flue gases to prevent emissions of nitrogen oxides (NO_x) has been demonstrated at the pilot scale at a boiler at Kennedy Space Center (KSC). That project was an outgrowth of research funded by the Gulf Coast Hazardous Substance Research Center from the years 1993-1996. The H_2O_2 is injected into hot boiler flue gases to oxidize the NO into NO_2, HNO_2 and HNO_3, which can then be removed in a wet or dry scrubber (see Figure 4-3.4). (74o)

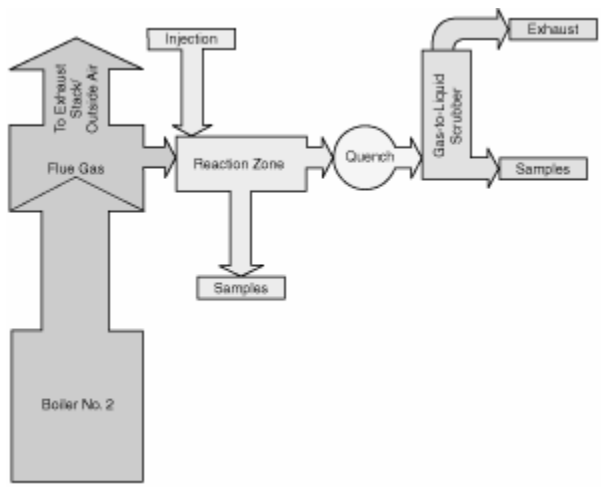
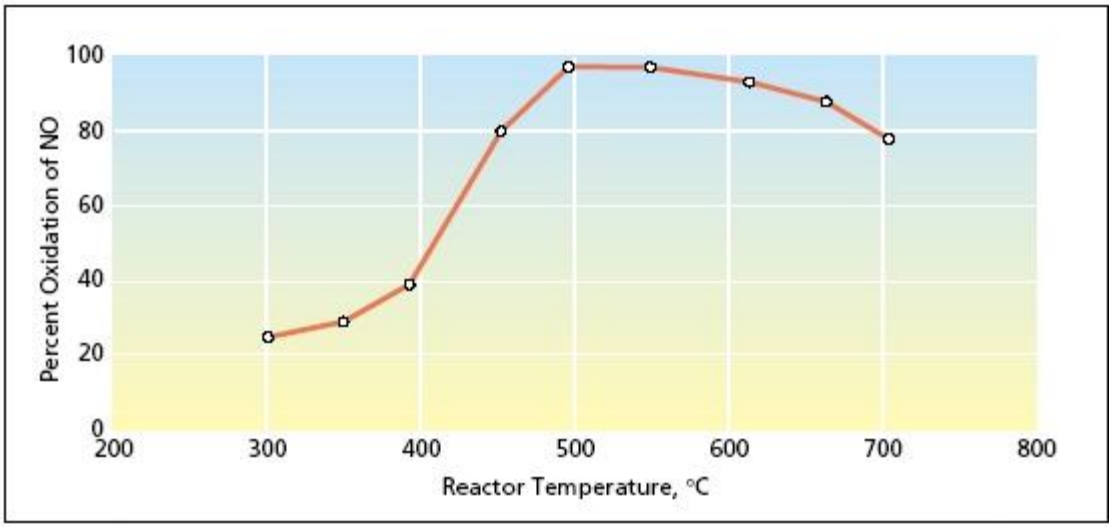


Figure 4-3.4. Conceptual Design of Hydrogen Peroxide NO_x Control System

In one of several sets of experiments to demonstrate the feasibility of the method, the optimum temperature for conversion of NO to HNO_2, HNO_3, and NO_2 by use of injected H_2O_2 was found to be about 500 °C (see Figure 4-3.5).

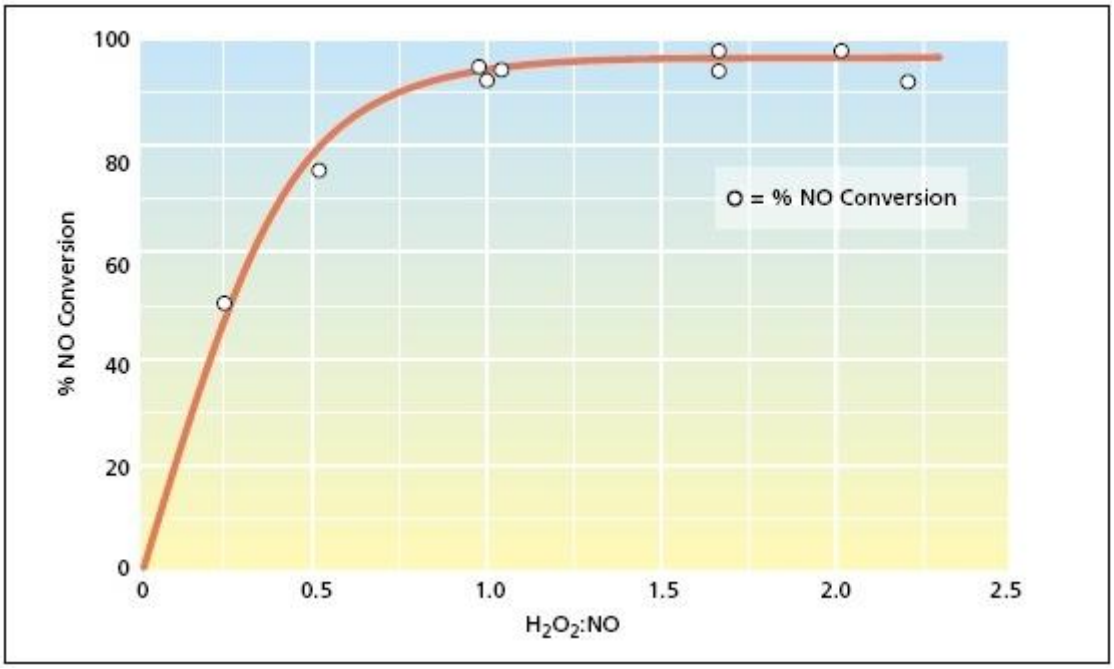


The conversion of NO by oxidation to other species was measured as a function of reactor temperature. The reactor inlet conditions for the points shown here were 400 ppm NO and 400 ppm H_2O_2 for a molar ratio of 1:1.

Figure 4-3.5. Effect of Temperature on Peroxide Oxidation of NO

In a study performed under guidelines of the EPA, EPRI compared the economics of SCR and the experimental H_2O_2-injection/scrubbing method for a design base case and a variety of alternative cases. This study illustrated the tradeoff between capital and operating costs for the two methods. The single largest factor in determining the total cost of one method relative to the other method was found to be the H_2O_2:NO molar ratio. At the H_2O_2:NO molar ratio of 1.92, which was previously demonstrated in the laboratory, the H_2O_2-injection/scrubbing method was shown to be uneconomical. However, it was also concluded that the molar ratio in a full-size coal-fired power plant could be lower than that found in the laboratory, and that on the basis of all the assumptions of the study, at an H_2O_2:NO molar ratio of 1.37, the H_2O_2 injection/scrubbing method could be an economically feasible alternative to SCR.

Pilot-scale tests run at Kennedy Space Center demonstrated the feasibility and competitiveness of this new technology. The H_2O_2 to NO molar ratio, at 500 °C shown to achieve a NO conversion efficiency of greater than 90 percent was 1:1, which is significantly lower than the required 1.37:1 (See Figure 4-3.6). (74l)



The outlet concentration of the O was significantly reduced when the H_2O_2 was injected. At 500 °C, 400 ppm NO, and various inlet concentrations of H_2O_2 (represented as the molar ratios), 90 percent conversion of NO was achieved at the reactor outlet for a molar ration of 1:1.

Figure 4-3.6. Effect of Molar Ratio on Peroxide Oxidation of NO

Potential applicability. This option is a solution that may have particular applicability to kilns with existing scrubber systems. Data suggests it may work over a wide range of temperatures depending on the specific version of this technology that is implemented. For the high temperature version of this process, injection of the hydrogen peroxide into the upper portion of the preheater tower of a precalciner kiln at the appropriate temperature may be possible.

Advantages. The biggest advantage of this technology may be a relatively low capital investment for plants with existing scrubbers. An additional advantage is that there are indications that hydrogen peroxide based scrubbers may also enhance SO_x scrubbing and may lower hydrocarbon emission depending on the operating temperature, reagent system and retention time of the system.

An additional advantage of this technology is that it operates in a unique temperature window that is slightly below the temperatures commonly used for SCR. The optimal technology for any specific cement kiln process may be the technology that installs best in the

existing temperature windows of the process with the least potential adverse impact on downstream processes and equipment. Prices of ammonia-based reagents fluctuate with natural gas prices and are currently relatively high. Cement plants may elect to use more than one NO_x control technology to take advantage of changes in the market for reagents. Hydrogen peroxide currently appears to be a more cost effective reagent than ammonia-based reagents.

Disadvantages. For plants without scrubbers, add on systems are required. An additional factor is that the cost of hydrogen peroxide has risen significantly in recent years with increased natural gas prices and fluctuating supplies. Hydrogen peroxide has become a major commodity chemical as a bleaching agent for paper production free of chlorine. Recent production capacity increases appear to be stabilizing prices.

Additional nitrate captured in the existing sulfate scrubber could impact the quality of the plant's artificial gypsum although, with a typical dewatering system, this should not be a problem because of the much higher solubility of the nitrates relative to sulfates. High nitrate wastewater could be used by local farmers as fertilizer or could be used at the plant to fertilize grass areas as well as water/fertilize in quarry reclamation areas.

Emissions performance. At 500 °C and with a molar ratio of 1:1 H_2O_2/NO_x removal efficiencies of greater than 80% appear to be achievable. Scrubber efficiency data for the wet low temperature process was not available. Either of these technologies should be considered investigative in nature. Application of this technology would clearly be an innovative approach that does not have a history of commercial application compared to SCR, SNCR or LoTOx^{TM}. Testing in a cement plant application would clearly be required to determine performance and process impacts.

Cost. Assuming a cost of $0.50/lb. of hydrogen peroxide the reagent cost would be approximately $739/ton of NO_2 removed (depending on the existing oxidation state of the NO in the system). This might be offset to some extent by the sale of solutions of nitrate salts as fertilizer. This cost appears to be favorable relative to the electrical and oxygen costs of the LoTOx^{TM} that exceed $1,600/ton of NO_x controlled. It is also favorable to the current ammonia cost of about $1,200/ton of NO_x controlled using SNCR.

4.3.4 OXONE (Dupont – potassium monopersulfate)

General description. Scrubbing with strong aqueous oxidants promises to be less expensive than competing post-combustion methods for NO_x removal such as selective catalytic reduction (SCR) and thermal NO_x removal. The goal of a project by Yusuf G. Adewuyi at North Carolina A&T State University is to develop an innovative and cost-effective aqueous scrubber for the simultaneous removal and destruction of oxides using strong oxidizing agents such as oxone. Oxone ($2KHSO_5.KHSO_4.K_2SO_4$) is a triple salt of potassium and may be regarded as a mono-substituted derivative of hydrogen peroxide. However, it has an oxidation potential greater than that of hydrogen peroxide (E HSO_5^-/HSO_4^- = 1.82 eV compared to E H_2O_2/H_2O = 1.77 eV). The aqueous absorption and kinetics of oxidation of nitrogen oxides (NO_x) and SO_2 by OXONE in a bubble column operated as batch or continuous OXONE was presented at an AIChE meeting in October of 2005. Table 4-3.2 provides a breakdown of the chemical constituents of the Oxone reagent. (74p)

Table 4-3.2. Oxone Constituents

Material	CAS Number	%
"Oxone" Monopersulfate Compound	70693-62-8	
Potassium Peroxymonosulphate	10058-23-8	34-43
Potassium Bisulfate	7646-93-7	18-23
Potassium Sulfate	7778-80-5	23-29
Potassium Peroxydisulfate	7727-21-1	2-3
Sodium Carbonate	497-19-8	0-20
Magnesium Carbonate	546-93-0	1-2

Potential applicability. Applicability is similar to the wet low temperature hydrogen peroxide option.

Advantages. Advantages are similar to the hydrogen peroxide option. Costs may be lower.

Disadvantages. This is an experimental technology. Additional nitrate captured in the existing sulfate scrubber could impact the quality of the plant's artificial gypsum although with a typical dewatering system this should not be a problem because of the much higher solubility of the nitrates relative to sulfates. High nitrate wastewater could be used by local farmers as fertilizer or could be used at the plant to fertilize grass areas as well as water/fertilize in quarry reclamation areas.

Emissions performance. As an experimental technology performance is not clear but is likely to be similar to the hydrogen peroxide technology. This technology should be considered investigative in nature.

Cost. Oxone is a commercial product manufactured by Dupont. Inquiries to Dupont about cost have not been responded to at this time.

4.3.5 Sodium Acetate Process

General description. This process involves absorption and subsequent reaction of NO_x in the aqueous phase. Direct absorption involves a reaction chain that achieves both SO_x and NO_x removal. One form involves an SO_2 reaction step, a subsequent NO reaction, and a termination step that produces gypsum. Table 4-3.3 shows the different steps involved in the process.

Table 4-3.3. Reaction Steps and Pathway Equations for the Sodium Acetate Direct Absorption Process For Simultaneous NO_x And SO_x Removal (OECD, 1983).

Absorption and Gypsum Formation
Absorption $SO_2 + 2CH_3COONa + H_2O \rightarrow Na_2SO_3 + 2CH_3COOH$ $2NO + 5Na_2SO_3 + 4CH_3COOH \rightarrow 2NH(NaSO_3)_2 + Na_2SO_4 + 4CH_3COONa + H_2O$
Gypsum formation $Na_2SO_4 + Ca(OH)_2 + 2CH_3COOH \rightarrow CaSO_4$ $.2H_2O + 2CH_3COONa$
Imide Treatment Step
Hydrolysis $NH(NaSO_3)_2 + 2H_2O \rightarrow NH_4HSO_4 + Na_2SO_4$ Release of NH_3 $NH_4HSO_4 + Ca(OH)_2 \rightarrow NH_3 + CaSO_4_2H_2O$ Nitrogen gas formation $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$

Potential applicability. Applicability is likely to be similar to the wet low temperature hydrogen peroxide process.

Advantages. The advantage of this process is its ability to eliminate gaseous NO_x and SO_x simultaneously. For plants with existing SO_x scrubbers the application may be as simple as adding selected reagents to the recirculating scrubber solution and subsequent scrubber treatment tanks. For plants with cooling towers the option of adding the reagents to the cooling tower water feed may be functional.

Disadvantages. SO_x is required in adequate quantities to maintain the chain-reaction mechanism. Also, this process turns an air-pollution problem into a wastewater problem. Additional nitrate captured in the existing sulfate scrubber could impact the quality of the plant's artificial gypsum although with a typical dewatering system this should not be a problem because of the much higher solubility of the nitrates relative to sulfates. High nitrate wastewater could be used by local farmers as fertilizer or could be used at the plant to fertilize grass areas as well as water/fertilize in quarry reclamation areas.

Emissions performance. Unknown. Data for application of this technology to cement kilns and similar emission sources was not found in the literature. This technology should be considered investigative in nature.

Cost. Costs are not clear at this time but may be lower than the hydrogen peroxide option.

4.3.6 Potential Applicability of Oxidation Technology to Ash Grove Plant

General Discussion. The Ash Grove plant has three wet process kilns without any existing wet scrubber system. That would require them to place a complete oxidation system in place as an add-on technology including the scrubber or alternatively just a spray tower after the existing ESPs. Assuming that all of the available options would have a similar capital cost for a spray tower/scrubber system careful evaluation of the alternative reagent systems is warranted.

A trial system for evaluating the reagent systems may be warranted. As an example, three one-month trials using alternative reagents in a skid-mounted scrubber could be performed prior to scaling up to a full system. It may be possible to combine the gas flows from the three kiln systems into a single flow to minimize the cost of the scrubber system.

Because of the high moisture levels in the gasses from wet kilns it may be necessary to bypass a portion of the stack gasses around the spray tower/scrubber for use as reheat gas after the spray tower/scrubber to prevent condensation problems in the stack. To the extent that such a strategy is required the efficiency of the NO_x removal would be proportionately impacted.

Conclusions. SCR at the Ellis County wet kilns would require reheat of the exhaust gas. This suggests that further investigation of the oxidation technologies is likely to be a cost effective option. As these technologies would require a scrubber, consideration of the benefits of control of sulfur oxides should also be considered in evaluating scrubber options. The cost modeling for oxidation technologies is based on a simple spray tower that does not control sulfur oxides. However, additional air quality benefits, including reduction in fine PM precursors would occur should a source choose to install flue gas desulfurization. A combination of midkiln

combustion, midkiln SNCR and a low temperature oxidation technology may provide exceptional NO_x control at the most effective aggregate cost per ton of NO_x controlled for wet kilns.

4.3.7 Potential Applicability of Oxidation Technology to Holcim Plant

General Discussion. The Holcim Plant has two large precalciner kiln systems with existing scrubbers. An oxidative control technology for these kiln lines has significant potential to provide NO_x control using the existing scrubber system.

A variety of low temperature oxidation reagent systems could be tested for efficiency in the existing wet scrubber system. It should also be relatively simple to set up a temporary system to test the high temperature hydrogen peroxide control option in a manner similar to the set up that was used to test SNCR. The critical factor in the successful use of the high temperature hydrogen peroxide control technology will be determining the best location for injection. Careful gas phase temperature measurements and modeling should help determine the optimum location.

Conclusions. It may be possible to add a hydrogen peroxide injection system to the preheater tower at the correct location with a relatively low capital expenditure. By combining SNCR and the high temperature hydrogen peroxide system, an effective control system could be put in place at a minimal capital expenditure that would then allow the plant to use more or less of the hydrogen peroxide and ammonia reagents based on their current costs – thus optimizing the long term cost per ton of NO_x control.

4.3.8 Potential Applicability of Oxidation Technology to TXI Plant

General Discussion. The TXI plant has 4 wet process kilns without any existing wet scrubber system. That would require them to place a complete oxidation system in place as an add-on technology including the scrubber for these systems. Assuming that all of the control options would have a similar capital cost for a spray tower/scrubber system careful evaluation of the alternative reagent systems is warranted.

A trial system for evaluating the reagent systems may be warranted. As an example, three one-month trials using alternative reagents in a skid-mounted scrubber could be performed prior to scaling up to a full system. It may be possible to combine the gas flows from the kiln systems into a single flow to minimize the cost of the scrubber system.

Because of the high moisture levels in the gasses from wet kilns it may be necessary to bypass a portion of the stack gasses around the spray tower/scrubber for use as reheat gas after the spray tower/scrubber to prevent condensation problems in the stack. To the extent that such a strategy is required the efficiency of the NO_x removal would be proportionately impacted.

TXI also has a large modern precalciner kiln with a scrubber system on-site. An oxidative control technology for the precalciner kiln has significant potential to provide NO_x control using the existing scrubber system. A variety of low temperature oxidation reagent systems could be tested for efficiency in the existing wet scrubber system. It should also be relatively simple to set up a temporary system to test the high temperature hydrogen peroxide control option. The critical factor in the successful use of the high temperature hydrogen peroxide control technology will be determining the best location for injection. Careful gas phase temperature measurements and modeling should help determine the optimum location.

For TXI the added benefit of the high temperature hydrogen peroxide control technology might be the added control of hydrocarbons. There is the real potential that at the temperatures, which the hydrogen peroxide system operates at, those hydrocarbons will also be oxidized. Because these hydrocarbons may be evolved from the raw feed at a lower temperature this is not a certainty but, if it were to occur, the potential does exist for such a system to replace the existing catalytic control system. In that event, the savings on natural gas costs would be substantial.

Conclusions. For the precalciner the addition of the high temperature hydrogen peroxide oxidation control technology to the preheater tower has significant potential. In addition to controlling NO_x emissions this oxidation technology has the potential to control hydrocarbon emissions and eliminate the need for the existing catalytic control system and the associated

operating costs. These potential cost savings could more than offset the cost of the hydrogen peroxide and capital investment for this kiln line to achieve even greater NO_x control than its already relatively low levels. Tests of this technology should be able to be conducted with minimal investment. Alternatively tests of various wet scrubber reagent systems could also be conducted in the existing SO_x scrubber system.

In the wet kilns, because of the reheat costs, further investigation of the low temperature oxidation technologies is likely to be the most cost effective and is therefore recommended for further investigation. Combination of midkiln combustion, midkiln SNCR and a low temperature oxidation technology may provide exceptional NO_x control at the most effective aggregate cost per ton of NO_x controlled for these kilns.

Table 4-3.4. Summary of Modeling Results for LoTOx™ on Ellis County Kilns – Performance Results

Existing Unit	Control Technology	Emissions Rate tpy before	Emissions Rate tpy after (a)	Controlled Emissions Rate ppm	Controlled Emission Rate lb./tonne clinker	Control Efficiency %	Reduction tpy
Ash Grove #1- wet	LoTOx™	702	301.6	60	0.84	85%	400.4
Ash Grove #2- wet	LoTOx™	750	322.2	58	0.89	85%	427.8
Ash Grove #3- wet	LoTOx™	764	328.3	53	0.91	85%	435.7
TXI #1 and #4–wet (b)	LoTOx™	1197	514.3	109	1.21	85%	682.7
TXI #2 and #3–wet (b)	LoTOx™	121	52	109	0.49	85%	69.0
TXI#5 – dry	LoTOx™	1710	734.7	29	0.30	80%	975.3
Holcim #1 – dry	LoTOx™	2222	954.7	73	0.38	85%	1,267.3
Holcim #2 – dry	LoTOx™	1778	763.9	53	0.30	85%	1,014.1

(a) NO_x emission rate after SCR does not reflect SCR efficiency reduction due to adjustment by the ozone season factor of 0.671 (NOx reduction is modeled to occur only during the ozone season).
(b) The results for TXI #1 & #4 and #2 & #3 are average per kiln – for example, total emissions reductions for controlling both TXI #1 & #4 are double the value listed in the table.
(c) Models assume mid-kiln firing installed at TXI as required under current SIP.

Table 4-3.5. Summary of Modeling Results for LoTOx™ on Ellis County Kilns – Economic Results

Existing Unit	Control Technology	Capital Cost	Annual Cost	Cost Effectiveness $/ton NO_x	Energy Penalty or Benefit	Burden Cost $/tonne clinker
Ash Grove #1- wet (c}	LoTOx™	$4.8 MM	$1.4 MM	$3,400	(a)	$5.00
Ash Grove #2- wet (c}	LoTOx™	$5.2MM	$1.5MM	$3,500	(a)	$5.40
Ash Grove #3- wet (c}	LoTOx™	$5.8MM	$1.6MM	$3,700	(a)	$5.70
TXI #1 & #4–wet (b,c)	LoTOx™	$5.4MM	$1.6MM	$3,300	(a)	$4.70
TXI #2 & #3–wet (b,c)	LoTOx™	$2.8MM	$0.5MM	$11,000	(a)	$10.50
TXI#5 – dry	LoTOx™	$5.2MM	$2.4MM	$2,600	(a)	$0.90
Holcim #1 – dry	LoTOx™	$6.7MM	$3.1MM	$2,400	(a)	$2.35
Holcim #2 – dry	LoTOx™	$5.4MM	$2.5MM	$2,300	(a)	$1.90

(a) Increased fan power due to pressure drop across scrubber included in the models
(b) The results for TXI 1 & 4 and #2 & #3 are average per kiln – for example, total capital costs for controlling both TXI #1 & #4 are double the value listed in the table.
(c) Costs for wet kilns include addition of spray tower to scrub oxidation products.

4.4 Process Modification

Process modifications are applicable to any type of kiln and are usually done to reduce heat consumption, to improve clinker quality, and to increase the lifetime of the equipment (such as the refractory lining) by stabilizing process parameters. Reduction of emissions, such as NO_x, SO_x, and dust, are secondary effects of these modifications. Smooth and stable kiln operation close to design values for process parameters is beneficial for all kiln emissions. Process modifications can include many elements, such as instruction and training of the kiln operators, homogenizing raw material, ensuring uniform coal dosing, improving the cooler's operation, and installing new equipment. Process modifications are primarily done to reduce operating costs, increase capacity, and improve product quality. Adopting process modifications usually results in a reduction of operating costs for a kiln. The savings result from reduced fuel and refractory consumption, lower maintenance costs, and higher productivity, among other factors. (35)

This section describes process modifications that improve fuel efficiency and kiln operational stability with an emphasis on reducing NO_x formation. Since NO_x formation is directly related to the amount of energy consumed in cement-making, improving fuel efficiency and productivity will reduce NO_x emissions.

4.4.1 Combustion Zone Control of Temperature and Excess Air

Continuous monitoring of O_2 and CO emissions in the cement kiln exhaust gases indicates the amount of excess air. At a given excess air level, NO_x emissions increase as the temperature of the combustion zone increases. A typical kiln combustion zone solids temperature range is about 1,430 to 1,540 °C (2,600 to 2,800 °F) for completion of clinkering reactions and to maintain the quality of the cement produced. (75) The corresponding gas-phase temperature is usually greater than 1,700 °C (3,100 °F). (76) Maintaining the combustion zone temperature at a necessary minimum value would minimize both the process energy requirement and the NO_x emissions.

Along with the appropriate temperature, it is also necessary to maintain an oxidizing atmosphere in the clinker burning zone to ensure the quality of the clinker produced. Although a kiln could be operated with as little as 0.5 percent kiln exhaust oxygen level, typically the kiln operators strive for an oxygen level of one to two percent to guarantee the desired oxidizing conditions in the kiln burning zone. An experimental test on a cement kiln showed that by reducing excess air from 10 to 5 percent (i.e., reducing exhaust oxygen levels from two to one percent) NO_x emissions per unit time can be reduced by approximately 15 percent. (77,78)

With state-of-the-art continuous emissions monitoring systems (CEMS) and feedback control, excess air can be accurately controlled to maintain a level that promotes optimum combustion and burning conditions in addition to lowering NO_x emissions. Reducing excess air level also results in increased productivity per unit amount of energy consumed and thus results in an indirect reduction of NO_x emissions per unit amount of clinker product.

4.4.2 Feed Mix Composition

Heat requirements for producing clinker are dependent on the composition of the raw feed which varies among cement plants. Experiments have demonstrated that by improving the burnability of the raw feed, the heat requirement of clinker can be reduced by 15 percent. (79) If the raw feed composition can be formulated to require less heat input per ton of clinker, less fuel

is burned and less NO_x per unit product is produced. This approach of changing the feed composition may, however, be highly site specific and may not be applicable at all locations.

Reduction of Alkali Content of Raw Feed. The alkali content of finished cement generally needs to be below a certain acceptable level. Low alkali requirements need higher kiln temperatures and longer residence times at high temperatures to volatilize the alkali present in the semi-molten clinker. Raw materials with greater alkali content need to be burned longer at higher temperatures to meet alkali requirements and thus may produce greater NO_x emissions. Increased volatilization of alkali also results in increased alkali emissions in kiln exhaust gases. To control alkali emissions, a part of the kiln exhaust gases may be bypassed around a downstream unit, e.g., a precalciner. The bypassed gases are quenched to remove alkali and sent through a particulate collector. The bypass of kiln exhaust gases typically involves a fuel penalty, e.g., about 20,000 Btu/tonne clinker for every one percent gas bypass. The additional heat requirement may also contribute to increased NO_x emissions; thus, reducing the alkali content of the raw feed mix may contribute to a reduction in the NO_x emissions.

4.4.3 CemStar Process

Another feed modification that can reduce NO_x emissions is the addition of a small amount of steel slag to the raw kiln feed. This patented technique is known as the CemStar Process and was developed by TXI Industries. Steel slag has a low melting temperature and is chemically very similar to clinker. Since many of the chemical reactions required to convert steel slag to clinker have already taken place in a steel furnace, the fuel needed to convert steel slag into clinker is low. The decreased need for limestone calcination per unit product and improved thermal efficiency of the process both contribute to reduced thermal NO_x and CO_2 emissions. (80)

Eleven facilities are using or in the process of incorporating CemStar. (81) CemStar requires little extra equipment and the addition of steel slag to the feed mix can result in a reduction or elimination of the need for some mineral sources, such as shale or clay. This process can also increase production by 15 percent. (80)

According to the Entellect Environmental Services "Evaluation of the Effects of the CemStar Process on a Wet Process Cement Kiln" report, the CemStar process reduces the kiln material temperature in the region of the flame by an average of 200°F (from 2,610°F to 2,405°F); the lower gas temperature of the flame results in lower NO_x emissions. (82) Another test of CemStar technology found an average reduction in burn zone temperature of 160°F, a six percent reduction. (82) The amount of NO_x emissions reductions achievable with CemStar varies by kiln type but ranges from over 20 to 60 percent. (80) Short- and long-term tests of CemStar were conducted at two different types of TXI cement kilns in 1999. Short-term tests (two days) on a preheater/precalciner kiln found NO_x emissions reductions in lbs. NO_x/tonne clinker of 44 percent when operated at maximum capacity, and between 9 and 30 percent when operated at normal capacity, depending on the quality of the raw feed mix (see Table 4-4.1).

Table 4-4.1. Results of Short-Term Cemstar Tests on a Preheater/Precalciner Kiln

	Poor Quality Feed Mix (lb. NO_x/tonne clinker)	Percent Reduction[a] (%)	Ideal Quality Feed Mix (lb. NO_x/tonne clinker)	Percent Reduction[a] (%)
Without CemStar	4.98	-	5.59	
With CemStar at normal feed rate[b]	4.51	9	3.89	30
With CemStar at maximum feed rate[c]	(no test)	-	3.15	44

[a] Percent reductions are relative to the emission rate without CemStar.
[b] The normal feed rate is 170 - 180 tons per hour of dry feed.
[c] The maximum feed rate is 195 tons per hour of dry feed.

Andover Technologies also reported on short-term and long-term tests of a wet kiln using CemStar Technology. The short-term tests (one day) found emission reductions of 36 to 55 percent in lbs. NO_x/tonne clinker, and the long-term tests (approximately two and a half months) found reductions of 24 percent (see Table 4-4.2). (80)

Kilns with lower initial baseline NO_x emissions would have less NO_x reduction with CemStar than those with higher baseline emissions. Wet and long-dry kilns would have greater NO_x reductions with CemStar because more energy is used per ton of clinker produced than preheater/precalciner kilns. Wet kilns may achieve the greatest NO_x reductions with CemStar because the addition of steel slag would reduce the amount of water needed to create the slurry and consequently decrease the amount of heat needed to dry it. (80)

Table 4-4.2. Results of Cemstar Tests on a Wet Kiln

	Test 1 (lb. NO_x/tonne clinker)	Test 2 (lb. NO_x/tonne clinker)	Percent Reduction[a] (%)
Short-Term Test			
Without CemStar	17.53	24.7	-
With CemStar	11.24	no 2nd test	Test 1 = 36 Test 2 = 55
Long-Term Test			
Without CemStar	5.23	no 2nd test	-
With CemStar		no 2nd test	24

[a] Percent reductions are relative to the emission rate without CemStar.

4.4.4 Kiln Fuel

Changing the primary kiln fuel from natural gas to coal can reduce the flame temperatures significantly, resulting in lower thermal NO_x emissions. (83,84) Although nitrogen present in coal may provide greater fuel NO_x contribution, switching the fuel burned in kilns from natural gas to coal has been shown to provide substantial reduction in the total NO_x emissions in one experimental study. (83) In the dry process kilns tested in this study the average NO_x emissions decreased from 20.4 lb./tonne clinker to 6.2 lb./tonne clinker when the fuel was changed from natural gas to coal. A number of cement kilns have already made the switch from natural gas to coal and currently 87 percent of cement kilns in the United States use coal as the primary fuel. (85)

When natural gas (with no nitrogen in the fuel) is used in the burning zone of a cement kiln, the NO_x emissions are significantly higher than when coal is used. There may be additional environmental impacts when coal is burned as opposed to natural gas (e.g., sulfur dioxide and sulfate emissions may increase). Although switching to a lower nitrogen fuel in a precalciner may reduce NO_x, the fuel nitrogen content in the burning zone has little or no effect on NO_x generation. Some researchers have found no relationship between fuel nitrogen content and the NO_x emissions from a cement kiln. (86)

Switching to a fuel with a higher heating value and lower nitrogen content may reduce NO_x emissions in a cement kiln, e.g., petroleum coke has a lower nitrogen content per million Btu than coal. Petroleum coke is also more uniform in terms of heat value, lower in volatile matter content and burns with a lower flame temperature. However, some claim that petroleum coke cannot be burned alone because it does not provide enough volatile matter. (87)

4.4.5 Increasing Thermal Efficiency

The thermal efficiency of the cement-making process has improved substantially as energy costs have increased and new technology has been developed. Although there are a variety of cement process technologies used in the US, the kilns in this study are all either 1960's wet kiln technologies that are not energy efficient or modern dry process kilns with preheat and precalcination that represent the most energy efficient process for making Portland cement. Both Holcim #2 and TXI #5 are new and energy efficient units. Holcim #1 began operation in 1987 and is slightly less efficient and could potentially be upgraded by options such as calciner modification discussed below. In addition, there are interim steps that improve the efficiency of wet process to semi-wet or semi-dry process. However, the main opportunity for substantial reductions in NO_x emissions in Ellis County from energy improvements comes from closing the wet process units and replacing them with modern, dry-process production.

Calciner Modifications

A study for the Department of Energy (88) evaluates use of low pressure drop cyclones for suspension preheaters. Worrell reports, "Cyclones are a basic component of plants with pre-heating systems. The installation of newer cyclones in a plant with lower pressure losses will reduce the power consumption of the kiln exhaust gas fan system. Depending on the efficiency of the fan, 0.6-0.7 kWh/ton clinker can be saved for each 50 mm W.C. (water column) the pressure loss is reduced. For most older kilns this amounts to savings of 0.6-1.0 kWh/ton (89). Fujimoto (1994) discussed a Lehigh Cement plant retrofit in which low-pressure drop cyclones were installed in their Mason City, Iowa plant and saved 4 kWh/ton clinker (90). Installation of the cyclones can be expensive, however, since it may often entail the rebuilding or modification of the preheater tower, and the costs are very site specific. Also, new cyclone systems may

increase overall dust loading and increase dust carryover from the preheater tower. However, if an inline raw mill follows it, the dust carryover problem becomes less of an issue. A cost of $2.7/annual ton clinker is assumed for a low pressure drop cyclone system."

The only candidate for a calciner upgrade among the Ellis County kilns is Holcim #1. This process line represents a slightly older version of the technology than Holcim #2 or TXI #5. Low-NO_x and low energy consumption performance is largely inherent in the design and Holcim #1 would appear to be the unit that could best benefit from this upgrade. Cost modeling has been provided based on the assumption that this unit could move to a level of performance similar to TXI #5 after the upgrade. The expert panel reviewed the current performance of the Holcim kilns in comparison to TXI #5. Although Holcim #2 and TXI #5 were both built near the year 2000, TXI #5 has typical NO_x emissions that are substantially lower than Holcim #2. It was the judgment of the expert panel that an intrinsic low- NO_x redesign of Holcim #1 should produce performance more similar to that of TXI #5 than Holcim #2. These results are provided in Table 4-4.5.

Semi-Wet Upgrades to Wet Kilns

Hendriks and Worrell (91) report that conversion from a wet to a semi-wet process can save between 0.8 and 1.6 GJ/tonne clinker. There is a penalty of increased electrical energy use of approximately 3 to 5 kWh associated with this conversion.

Worrell (88) also reviews this option and describes it as a filter press system. "In the wet process the slurry typically contains 36% water (range of 24-48%). A filter press can be installed in a wet process kiln in order to reduce the moisture content to about 20% of the slurry and obtain a paste ready for extrusion into pellets (92). In the U.S. several plants have tried slurry filters, but have not been very successful. Currently, there seem to be no plants in the U.S. using this technology (93). Additional electricity consumption is 3-5 kWh/ton clinker (94). In this analysis it is assumed that energy use increases by 4 kWh/ton clinker to reduce the moisture content to 20%. The corresponding fuel savings are 1.0 MBtu/ton (94). Jaccard and Willis (1996) estimate the conversion cost to run $1.6/annual ton clinker capacity with increased operation costs of $0.1/ton clinker (95)."

Semi-Dry/Semi-Wet Upgrades to Wet Kilns

Hendriks and Worrell (91) report that conversion from a wet to a semi-dry process can save approximately 2.0 GJ/tonne clinker. They report a "small" increase in electrical energy use associated with this conversion of approximately 3 to 5 kWh.

Buzzi-Unicem operates a semi-dry/semi-wet system in Greencastle, IN, which had been converted from a large wet kiln system. While anticipated increases in production capacity were achieved, predicted improvements in thermal efficiency were not fully realized. Actual thermal efficiency improvement was only about 15%. Capital cost for this type of conversion are likely to be in the range of $75-85/tonne. Significant NO_x improvements have been observed in this conversion although not to the levels predicted by the vendor. Even with a 50% increase in production total NO_x emissions have been significantly reduced.

Because kiln conversion economics are significantly impacted by the size of the existing kiln the conversion of any of the wet kilns at TXI or Ash Grove is not considered a feasible alternative for further analysis.

Replacement of Wet Kilns with Dry

Worrell evaluates conversion of a wet kiln to a dry preheat/precalciner process (88). This conversion is essentially a reconstruction of the main kiln and processing areas with a new, modern dry plant. Worrell reports "If economically feasible a wet process kiln can be converted to a state-of-the art dry process production facility that includes either a multi-stage preheater, or a pre-heater/pre-calciner. Average specific fuel consumption in U.S. wet kilns is estimated at 6.0 MBtu/ton clinker. Studies of several kiln conversions in the U.S. in the 1980s found fuel savings of 2.9 MBtu/ton or less (96). In Hranice (Czech Republic) a 1,050 tonne per day wet process plant was converted to a dry kiln plant with a new kiln specific fuel consumption of 2.7 MBtu/ton clinker (97). Fuel savings of 2.7 MBtu/ton clinker and an increase in power use of about 9 kWh/ton clinker (98) are assumed. The cost of converting a wet plant to a dry process

plant may be high, as it involves the full reconstruction of an existing facility. Costs may vary between $50/annual ton clinker capacity and $100/annual ton clinker capacity (99,100)."

This option is also discussed by Hendriks (91). Hendriks gives a cost of approximately $133/tonne of annual capacity as the cost of building the new dry process plant. Hendriks estimates that about 2.2 GJ/tonne of energy can be saved. Increased energy use of about 10kWh/tonne is required for operation of the preheat/precalcination tower. These models do not consider any lost revenues that may be associated with wet to dry conversion. Certain types of cement, such as oilfield cement, are typically produced by wet kilns. This means that a plant that converts from a wet to dry process may lose some revenues. Companies that operate wet kilns and companies that operate preheat/calciner kilns are likely to have differences of opinion about the magnitude of difference in cement quality. This cost impact depends on the amount of materials sold by a particular plant and may include subjective criteria regarding cement qualities that cannot be quantified as part of this project.

Wet to Dry Conversion of Ellis County Kilns

On average, dry preheat/precalciner kilns emit substantially less NO_x per tonne of cement produced and require less energy per tonne of cement produced. Both in terms of energy use and NO_x emissions rates, the wet process units are often nearly double the modern dry process units. The cost modeling presumed that the wet kilns could obtain a value approximately that of high performing modern kilns and that would result in an approximate 65% decrease in NO_x emissions. A substantial energy savings was predicted to result in fuel savings in the cost models (see Confidential Attachment Wet to Dry Conversions).

The economics of wet kilns compared to dry kilns are very complex and involve issues such as lower production capacity of wet kilns, use of waste fuels and quality of cement products. However, as the energy costs of wet production are higher than for modern dry process units, there is a point at which the higher costs of pollution controls that may result from the final determinations of this study would trigger a decision to close the wet kilns and replace them with dry. Stating this another way, it is likely that at a certain cost of pollution controls in terms of dollars per tonne of clinker produced, the economics of the wet process including higher

fuel costs and higher pollution control costs would reach a point where replacement of the wet units with larger dry process units would be the reasonable alternative for a cement plant to continue operations at that site.

It is likely that any new kilns built to replace the wet kilns in Ellis County would include increased production capacity in the economic justification. However, for purposes of control cost modeling, the units need to replace the existing capacity for the evaluations to make sense in the context of our control option evaluations. For this reason, two dry process kiln replacement scenarios were modeled. One involved replacing the three wet kilns at Ash Grove with one new dry process unit and the second involved replacing the four wet kilns at TXI with one new dry process unit. The capacity of the new units was modeled as essentially equal to the capacity of the existing wet units combined. It is likely that Ash Grove and perhaps TXI would replace the existing kilns with a new dry preheat/precalcination process typical of current generation dry process plants with approximately twice (over two million tons per year of clinker) the capacity of the existing wet kilns (under one million tons per year of clinker) and the added production capacity would be an important part in cost justification of the expense of the new dry process unit.

The modeling, summarized in Table 4-4.4, shows an annualized cost of approximately $11 per tonne clinker for the replacement dry process units. This cost includes an annual benefit of approximately $4.0 to $4.5 million in reduced fuel costs. An increased annual cost of electricity of approximately $0.5 million results from the additional fan power required to move air through the preheat and precalcination tower. This information indicates that energy savings are very significant, but are not sufficient for a company to justify replacement of the wet kilns. Annual operating costs (capitalization of the new equipment) are reduced by nearly one third to approximately $9 million dollars by energy savings; however, even with the current high costs of energy this would not by itself justify replacement of the wet kilns.

The current use of alternative fuels complicates this analysis. The fuel savings are based on an assumption that the energy for the current wet kilns is all based on coal. Lower cost alternative fuels lessen the economic benefit of the increased energy efficiency. Preserving these alternative fuel programs may be important economic considerations in company analyses of wet

to dry conversions and the overall economics of cement production on a dollars per tonne clinker basis. The realistic assumption that larger modern units of a size similar to TXI #5 are needed to achieve the energy efficiency desired and using increased production to offset the high cost of these projects both impact fuel economics. If it is assumed that the current amounts of alternative fuels are permitted to be used in a new larger kiln, the amount of coal predicted to be reduced would still be reflected in the overall reduction in fuel use.

Conversion of the Ellis County wet kilns to dry process would result in year-round emissions reductions for NO_x, SO_2, particulate matter and hazardous air pollutants. The modern dry process unit would have updated controls that would result in potentially large emissions reductions for SO_2 and other air quality benefits for the region including reduction in fine PM precursors.

Table 4-4.3. Summary of Modeling Results for Wet to Dry Conversion of Ellis County Kilns – Performance Results

Existing Unit	Replacement Unit	Emissions Rate tpy before	Emissions Rate tpy after (a)	Controlled Emissions Rate ppm	Controlled Emission Rate lb./tonne clinker	Control Efficiency %	Reduction tpy
Ash Grove #1- wet	Ash Grove #4 - dry	2,200	772	180	1.99	65%	1,428
Ash Grove #2- wet							
Ash Grove #3- wet							
TXI #1 –wet	TXI #6 – dry	1,800	630	180	1.94	65%	1170
TXI #2 –wet							
TXI #3 –wet							
TXI #4 –wet							

Table 4-4.4. Summary of Modeling Results for Wet to Dry Conversion of Ellis County Kilns – Economic Results

Existing Unit	Replacement Unit	Capital Cost	Annual Cost	Cost Effectiveness $/ton NO_x	Energy Penalty or Benefit*	Emissions Penalty or Benefit**	Burden Cost $/tonne clinker
Ash Grove #1- wet	Ash Grove #4 - dry	$169 M	$9.3 M	$6,500	-$4.4 M	-1,428 tpy	$10.94
Ash Grove #2- wet							
Ash Grove #3- wet							
TXI #1 -wet	TXI #6 - dry	$143 M	$7.9 M	$6,700	-$3.7 M	-1,170 tpy	$10.94
TXI #2 -wet							
TXI #3 -wet							
TXI #4 -wet							

* Large benefit in fuel efficiency partly offset by increased electrical use in tower
** Large benefit in reduced fuel – does not account for increased emissions at power plant for power used in tower.

Table 4-4.5. Summary of Modeling Results for Calciner Upgrade for Ellis County Kilns – Economic Results

Control Technology	Control Technology Status	Emissions Rate Before Control tpy	Emissions Rate Before Control $lbsNO_x$//tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate $lbNO_x$/tonne	Cost Effectiveness \$/ton NO_x	Burden Cost \$/tonne clinker
Holcim #1	Available	2,222	3.76	40%	888.8	2.2	\$2,795	\$2.70

40% for new low-NO_x calciner based on TXI #5 performance.
Cost effectiveness for calciner upgrade calculated by ratio of burden costs using SCR data.
Calciner upgrade is not a seasonal ozone measure – emissions benefit is for full year.

4.5 Performance of Current NO_x Control Techniques and Technologies in the Cement Industry

4.5.1 Comparison of Current Performance of NO_x Control Technologies

Table 4-5.1 is a spreadsheet that is too large for inclusion as a table in the body of this report. This table compares the performance of different technologies against a standard performance criterion of pounds of NO_x per tonne (lbs./tonne) of clinker produced. Only information on complete references is included in this table. When sufficient information could be located to identify the plant and calculate performance of the control technology in lbs./tonne clinker, the information was included in this table. There are additional, less complete references to performance in this report that could not be included in this table because insufficient information was available to compare performance.

4.5.2 Summary of Current Regulations

This report focuses on evaluating the NO_x control measures for Portland cement manufacturing that go beyond current 30 TAC Chapter 117 requirements. In the US, it appears that several areas of the country are in a similar position to Texas in that they are currently evaluating more stringent active controls of NO_x for ozone attainment under the 8-hour standard. While active NO_x controls may be required under New Source Review requirements, current State SIP requirements are less stringent. ERG reviewed and summarized current US NO_x control requirements for cement kilns and this summary is presented in Attachment D as Table D-1. This review showed that four states had performance standards that were similar in stringency to Texas (Maryland, Illinois, Indiana and Michigan). Five states (Pennsylvania, South

Carolina, Tennessee, Ohio and Alabama) had technology based standards that were similar in stringency to the option under Texas regulations to comply by installing a technology such as mid-kiln injection instead of meeting a specific performance standard. Kentucky and California's South Coast Air Quality Management District has standards that appear to be less stringent than Texas. New York uses a case-by-case approach so that the stringency of the regulation is not clear. States are currently considering more stringent measures to comply with the NO_x SIP Call and with projected noncompliance with the 8-hour ozone standard. Both the State of Georgia and the Great Lakes States are considering more stringent control requirements of cement kilns; these measures are discussed below.

Control requirements in Europe are generally moderately stringent emissions limitations based on a performance requirement such as 500 mg/m^3. These requirements have prompted use of SNCR (recent documents report as many as 50 installations), but generally are not stringent enough to require higher performing technologies. One exception is Sweden, that has a very stringent performance requirement of 200 mg/m^3 (approximately 98 ppm). There are currently two cement plants in Europe capable of meeting this 200 mg/m^3 limit. The Solnhofen Portlandzementwerke in Germany (using SCR) and Scancem Slite in Sweden (using SNCR with multi-point injection). European control requirements are presented in Tables 4-5.1 and 4-5.2

Japan has a national standard for NO_x from cement plants and divides the emissions limits into those that apply to plants built before 1975 and those built after 1975. For pre-1975 plants the NO_x standard is 480 ppmv and for those built after, the standard is 250 ppmv. The 250 ppmv standard is very similar to the German standard of 500 mg/m^3. For the purposes of evaluating the particulate matter standards table, a US standard of 0.02 grains per dry standard cubic foot would be equivalent to a European standard of 50 mg/Nm^3.

As noted above, the US is somewhat behind Europe in requiring active controls on Portland cement manufacturing plants. Communications between TCEQ and EPA Region 6 indicate that recent BACT determinations typically require 1.95 lbs./tonne clinker (2.15 lbs./tonne) and SNCR. Other recent US studies include planning studies for compliance with the 8-hour ozone standard.

Two recent documents that recommend measures beyond current 30 TAC Chapter 117 requirements are the Midwest Regional Planning Organization's "Identification and Evaluation of Candidate Control Measures, April, 2005" and the "Fall Line Air Quality Study. November, 2004". Both of these studies are evaluations of potential measures to reduce ozone and recommend consideration of SCR for control of cement kilns. The Fall Line Study was conducted for the State of Georgia and recommends SCR for wet kilns as well as dry process kilns and provides estimates of cost effectiveness per ton of NO_x controlled. The Midwest RPO Study also discusses the potential for control of wet kilns with SCR, particularly for low-dust applications (after pollution controls) and mentions the high cost of gas reheat as a limitation in application of this technology. SCR costs are only estimated for long dry and dry preheat/precalcination process kilns. The cost information from these two studies is summarized in Tables 4-5.3 and 4-5.4.

Table 4-5.1. National SO_2 and NO_x Emission Limits for the Production of Cement Within the European Union (EU 15), in mg/Nm^3, Around 2000

Country	Data Based on	New/Modified or Existing Plant	SO_2 Normal Situation	SO_2 S-rich Raw Materials	NO_x	PCDD/Fs* ng TEQ/Nm^3
Austria	Na (a)	New/modified Existing	200 200	400 400	500 1000	
Belgium	P	New/modified Existing	1000 1000		1800 1800	
Denmark	P (a)	Existing	5/250/450 (b)	No limit	1200/2500/850 (c)	no limit
Finland	P (d)	Existing	150–400		1200–1800	
France	Na	New/modified Existing	500 500 (e)	1200/1800 (f) 1200/1800 (e)(f)	1200/1500/1800 (g) 1200/1500/1800 (g)	
Germany	Na	New/modified Existing	400 400	400 400	500 800	
Greece						
Ireland	Na	New/modified Existing	400 400	700 700	1300 1300	n.a. n.a.
Italy	Na/P	New/modified Existing	600		1800	10000 (h) 10000 (h)
Luxembourg	P	Existing	100 (i)		80(j)	0.1 (k)
Netherlands	P	Existing	(l)		1300(j)	0.1
Portugal	Na	New/modified Existing	400	1300		0.1 0.1
Spain	Na	New/modified Existing	2400/6000 (m) 600 (n) 2400/6000 (m) 600 (n)	2400/6000 (m) 1800 (n) 2400/6000 (m) 1800 (n)	1300-1800 (n)	
Sweden	P	Existing	-	<200	<200	0.1
UK	Na (o)	New/modified Existing	200 (p)(q)	600-2500 (r)	900 (p) 500-1200 (q)(s)	

Source: EIPPC Cement BREF (2000). Based on Cembureau report (1997) and information provided by experts of the Technical Working Group set up in order to support the production of the BREF

* Polychlorinated dibenzo dioxins and furans (total emitted quantity in nano g/ Norm m^3).

Na = National law; R=Regional law; P=Typical permit; in mg/ Norm m^3.

a) Daily averages and reference condition of 273 K, 101.3 kPa, dry gas and 10% O_2.

b) 5 for semi-dry process, 250 for wet process and 450 for wet process with wet scrubber and heat recovery. Limits under discussion.

c) 1200 for semi-dry process, 2500 for wet process and 850 for wet process with wet scrubber and heat recovery. Limits under discussion.

d) Monthly averages, reference condition of 10% O_2 and dry gas.

e) Existing plant must meet limit for new plant by 2001.

f) 1200 mg/Nm^3 if ≥ 200 kg/h; 1800 mg/Nm3 if < 200 kg/h.

g) 1200 mg/Nm^3 for dry process with heat recuperation, 1500 mg/Nm^3 for semi dry and semi wet processes, and 1800 mg/Nm^3 for wet and dry processes without heat recuperation.

h) General rule for any kind of industrial emission.

i) Half hour average.

j) Daily average value.

k) 6 hour average.

l) 90 kg/h as daily average, maximum 375 tonne/year.

m) Current limits.

n) Limits under discussion.

o) IPC Guidance Note S2 3.01.

p) 'Benchmark releases'.

q) Benchmark releases are, in particular, not applicable to existing plant but are a factor in considering appropriate limits.

r) Limit values reflect the actual levels of releases. Daily averages and reference condition of dry gas and actual O_2 content.

s) Actual releases, daily averages, not all plants currently have limits.

Table 4-5.2. National Emissions Standards for PM of the European Union Countries for Cement Manufacturing in mg/Nm3

Country	Data Based on	New/Modified or Existing Plant	Kiln Stack	Clinker Cooling	Cement Grinding	Other Point Sources
Austria	Na (a)	New/modified	50	50	50	50
		Existing	50	50	50	50
Belgium	P	New/modified	50	50	50	
		Existing	50 - 150	50 - 400	50 - 150	50 – 300
Denmark	P	Existing	50 (b)	50 (b)	50 (b)	50 (b)
Finland	P	New/modified	50	50	30 – 50	30 – 50
		Existing	50 (c)	50	30 - 50	30 – 50
France	Na	New/modified	50	100	50	30
		Existing	50 (d)	100 (d)	50 (e)	30
Germany	Na	New/modified	50	50	50	50
		Existing	50	50	50	50
Greece	Na/R	New/modified	100	100	100	
		Existing	150	150	150	
Ireland	Na	New/modified	50	100	75	50
		Existing	50	100	75	50
Italy	Na/P	Existing	50	50	50	50
Luxembourg	P	Existing	30 (f)			
Netherlands	P	Existing	15 (f)	10 (f)	10 (f)	10(f)
Portugal	Na	New/modified	50	100	75	50
		Existing	100	100	75	50
Spain	Na	New/modified		170/100 (g) 100 (h)	300/250 (g) 75 (h)	300/250 (g) 50 (h)
		Existing	400/250 (g) 100 (h)	170/100 (g) 100 (h)	300/250 (g) 75 (h)	300/250 (g) 50 (h)
Sweden	P	Existing	50 (i)	50	50	20
UK	Na (j)	New/modified	40 (k)	50 (k)	40 (k)	50 (k)
		Existing	(l)	(l)	(l)	(l)

Na= National law; R= Regional law; P= Typical permit
a) Daily averages and reference condition of 273 K, 101.3 kPa, dry gas and 10% O_2.
b) Limits under discussion. Reference condition of 273 K, 101.3 kPa, dry gas and 10% O_2.
c) Existing plant must meet 50 mg/Nm^3 by January 1, 2001. Monthly averages and reference condition of 10% and dry gas.
d) Existing plant with emission < 150 mg/Nm^3 must meet limit for new plant by 2001.
e) Existing plant must meet limit for new plant by 2001.
f) Daily average values.
g) Current limits.
h) Limits under discussion.
i) Daily average value. A limit value of 90 mg/Nm^3, including start/stop and CO-trips, applies for monthly averages.
j) IPC Guidance Note S2 3.01.
k) "Benchmark releases."
l) Benchmark releases are, in particular, not applicable to existing plant but are a factor in considering appropriate limits.
[Based on [Cembureau report, 1997] and information provided by the Technical Working Group of the European Commission BREF Report (2000)].

Table 4-5.3. Midwest RPO – LADCO Study
(Large Preheater Kiln SCR 1,200,000 tpy clinker 2,880 tpy uncontrolled emissions)

	70% Removal Efficiency		90% Removal Efficiency	
	Low Capital Cost	High Capital Cost	Low Capital Cost	High Capital Cost
Total Capital Investment – TCI	$1,760,296	$14,668,188	$1,760,296	$14,668,188
Total Annual Cost	$1,305,377	$3,040,107	$1,305,377	$3,040,107
Pollutant Removal - tpy	2,016	2,016	2,592	2,592
Cost Per Ton of NO_x Removed	$648	$1,508	$504	$1,173

Table 4-5.4. Fall Line Air Quality Study (Georgia)

Medusa Cement (Houston)	In-process fuel use – coal	SNCR	$1,726	
	Cement manufacturing dry	Mid-kiln firing	$62	
	Cement manufacturing wet	Mid-kiln firing	$62	
		SCR	$3,947	Mid-kiln

In summary, current US emissions limitations indicate that 1.95 lbs./tonne clinker using SNCR is currently considered BACT for dry kilns. In order to meet 8-hour ozone standards, several areas of the country are looking at requiring more stringent NO_x controls on Portland cement plants and at least two areas are looking at requiring SCR. Experience in Europe indicates that emissions levels of approximately 200 mg/m^3 (98 ppm) and less than 1.0 lb./tonne clinker are being achieved at two dry precalciner kilns, one using SNCR and one using SCR.

4.5.3 Summary of European Experiences

In Europe, many cement plants have adopted general primary measures, such as process control optimization, use of modern, gravimetric solid fuel feed systems, optimized cooler connections and use of power management systems. These measures are usually taken to improve clinker quality and lower production costs but they also reduce energy use and air emissions.[1]

In March 2000, the European Integrated Pollution Prevention and Control (IPPC) Bureau issued a report on Best Available Techniques for European cement kilns. (35) The report collected emissions data from several sources. Emission rates for European kilns included in this

study range from less than 0.8 to 12 lb. NO_x/tonne clinker. A set of German kiln emission measurements presented in the European report found NO_x emissions for a cyclone preheater with heat recovery of 1.2 to 6.2 lb./tonne clinker, for a cyclone preheater without heat recovery of 1.6 to 7.0 lb./tonne clinker, and for a grate preheater of 1.6 to 8.2 lb./tonne clinker. These rates are similar to the averages for preheater and precalciner kilns found by EC/R in the new data presented in Chapter 4 (1.7 and 2.7 lb./tonne clinker respectively), but are less than those reported in the ACT document (5.9 and 3.8 lb./tonne clinker respectively). (35)

Table 4-5.5 presents a summary of NO_x control device applicability, reduction efficiency, and reported average emissions from the IPPC Bureau report on BAT for European cement kilns. (35) There are no emissions data in the IPPC report for kilns with CemStar technology or midkiln firing. For low-NO_x burners, the IPPC report found a lower average NO_x emissions rate (1.6 lb./tonne clinker) than EC/R found in the new State data (8.98 lb./tonne clinker). Both the IPPC report and the 1994 ACT document had estimated reduction efficiencies for low- NO_x burners of up to 30 percent. The reduction efficiencies in the IPPC report for SNCR (10 to 85 percent) and SCR (85 to 95 percent) are close to but slightly greater than those reported in the 1994 ACT document (30 to 70 percent and 80 to 90 percent respectively). (35)

Table 4-5.5. NO_x Control Techniques Summary From European Best Available Techniques Report (35)

Technique	Kiln Systems Applicability	Reduction Efficiency	Reported Emissions	
			mg/Nm^3 [a]	kg/tonne [b] (lb./ton)
Flame cooling	All	0 to 50%	400	0.8 (1.6)
Low-NO_x burner	All	0 to 30%		
Staged combustion	Preheater and Precalciner	10 to 50%	<500 to 1000	< 1.0 to 2.0 (2.0 to 4.0)
Mid-kiln firing	Wet and long dry	20 to 40%	no info	no info
SNCR	Preheater and Precalciner	10 to 85%	200 to 800	0.4 to 1.6 (0.8 to 3.2)
SCR - data from pilot plants only	Possibly all	85 to 95%	100 to 200	0.2 to 0.4 (0.4 to 0.8)

[a] Normally referring to daily averages, dry gas, 273 K, 101.3 kPa and 10% O_2.
[b] kg/tonne clinker is based on 2000 m^3/tonne clinker.

The IPPC report concludes that BAT for reducing NO_x emissions are a combination of general primary measures, primary measures to control NO_x emissions, staged combustion and SNCR. The BAT emission level associated with the use of these techniques is 0.4 to 1.0 lb./tonne clinker (200-500 mg NO_x/m^3 (as NO_2)). This emission level could be seen in context of the current reported emission range of 0.4 to 6.0 lb./tonne clinker (<200-3000 mg NO_x/m^3), and that the majority of kilns in the European Union is said to be able to achieve less than 2.4 lb./tonne clinker (1200 mg/m^3) with primary measures. (35)

While there was support for the above concluded BAT to control NO_x emissions, there was an opposing view that the BAT emission level associated with the use of these techniques is 1.0 to 1.6 lb./tonne clinker (500-800 mg NO_x/m^3 (as NO_2)). There was also a view that selective catalytic reduction is BAT with an associated emission level of 0.2 to 0.4 lb./tonne clinker (100-200 mg NO_x/m^3 (as NO_2)). (35)

5.0 CHEMISTRY OF ELLIS COUNTY MATERIALS AND IMPACTS ON CONTROL DETERMINATIONS

In order to evaluate the characteristics of feed material and their potential impacts on controls, the expert panel worked together to select the parameters they determined necessary for their evaluations. During the team's site visits, it was determined which of these parameters could be supplied by the companies, and which would need to be obtained through chemical analyses. The expert panel assisted TCEQ in preparing an information request for the parameters that could be obtained from the plants and a sampling protocol for the additional chemical analyses that would be required. The additional testing that was required is discussed below under analytical results.

5.1 Analytical Results

Analysis was conducted to determine the chemical, mineral and elemental composition of limestone and other raw materials used in clinker production in Ellis County. Total organic carbon, total sulfur, various forms of sulfur including sulfite and sulfate, chloride, and total Kjeldahl nitrogen content were determined. Three samples of each type (dry powder, wet slurry, slag) were collected from representative operating kiln sites using Ellis County limestone feed material. Analyses were chosen based on the need to identify composition that was expected to affect NO_x emissions or control option performance.

Total organic carbon results are determined using a technique known as differential scanning calorimetry (DSC). Analyses are carried out in gas with a composition of 20% carbon dioxide, 3% oxygen, and 77% nitrogen similar to the basic constituents of kiln flue gas. This causes an oxidative pyrolysis, which closely parallels actual kiln conditions. The formation of char residues is very unlikely for this testing method. Several samples were also analyzed by an alternative technique that gradually heats the material electrically from an external source using nitrogen as the carrier gas. The results reflect a pyrolysis regimen and provide additional supplemental data on the temperature profile at which carbon is released.

Total Kjeldahl Nitrogen (TKN) is a measure of organic nitrogen and ammonia in any form found in the samples. Total nitrogen results are determined by a heated digestion of the

samples. The ammoniacal nitrogen is the most volatile form of nitrogen. The TKN test does not measure nitrite or nitrate. Since nitrate and nitrite nitrogen would not react with NO_x they are of little interest for the feed evaluation.

There are some distinct differences among the feed types that are independent of the incinerator site or treatment. Slag is a manufactured feed material that aids burnability and so would be expected to reduce thermal NOx generation. It also has lower content of some of the key chemicals of concern for emissions control or new control technology application. For instance, nitrogen and total sulfur in slag is less than the amount found in wet slurry or dry powder, sulfate in slag and slurry less than sulfate in dry powder, and pyritic sulfur in slag is present at lower concentrations than pyritic sulfur in all other feed types. As a percent of total mass, organic sulfur tends to be higher in slag than other feed materials. There is a caveat: The methodology used by the laboratory lumps organic sulfur with simple sulfide (non pyrite). The sulfate in feed tends to be relatively constant compared to other compounds tested in the feed material. Site specific results of kiln feed sample chemical analysis are summarized in confidential attachments for each kiln site (Appendix A, B, and C, and Tables 1 through 5). Results are summarized in the remainder of this section.

5.1.1 Organic Carbon

One set of kiln feed materials had higher organic content than all others. Organic carbon in these dry feed materials is much greater than in all other feed material. Organic carbon in wet slurry from the same site is also higher than the organic carbon in other slurry feed materials. One kiln dry feed material had higher total organic carbon than the others in this sample set. The highest carbon containing feed material also contained higher organic nitrogen. This site also demonstrated lower NO_x emissions than other sites. Results for feed sample carbon analysis from this site are provided in confidential data Appendix A.

The lowest organic carbon content was found in dry powder limestone feed from a different site and supplier. The organic content in these feed materials is quite variable, Total nitrogen was also lower in samples from the same site. This site demonstrates higher NO_x

emission than other comparable sites. Results of percent carbon analysis in feed are shown in confidential data Appendix B.

Most of the organic material in the dry feed is released between 350 and 500 ºC indicating high molecular weight organic or pure carbon material. It was noted in the DSC data that some of the samples began generating heat at temperatures below 150 ºC, while others only began above 200 ºC. The higher temperatures required to liberate the carbon are a function of the volatility (molecular weight) of the carbonaceous material. It is not known whether this has any effect on NO_x emissions, but could influence VOC emissions. However, NO_x emissions were lower from the site supplying samples containing higher molecular weight carbon compounds. Efforts to control VOC emission should take into account the resulting oxidative conditions that do not favor reduction of NO_x.

The pattern of organic combustion determined by DSC appears to be fairly similar for all samples, except of course the slags. Much of the exothermic activity at 400-450 ºC for all kiln feeds is probably attributable to pyrite oxidation. In preheater or calciner kilns, this may be occurring in Stage 2 of the preheater. Whether this has any impact on NO_x emissions is questionable. It is possible, of course, that nascent, freshly formed SO_2 may reduce NO_2.

The results for total heat generated during carbon analysis by the alternative nitrogen purged technique appear to be higher for samples containing higher molecular weight carbon. The heat release results for these higher carbon containing samples show characteristics indicating considerable amounts of char, as evidenced by the lower heating results vis-à-vis the DSC results on samples analyzed using both approaches. If this char is produced in the kiln, it may serve as a reducing agent for NO_x assuming it was available in the hot zone of the process, or it may be oxidized to CO which itself may be acting as a reducing agent. The additional carbon could be a partial explanation for the very low NO_x emissions at this site.

5.1.2 Total Kjeldahl Nitrogen

The high carbon content feed also has the highest Total Kjeldahl Nitrogen (TKN) content. Dry powder feed from this site contains slightly more Total Kjeldahl Nitrogen (TKN)

than similar dry feed materials from other sites. While the ratio of %carbon to TKN feed materials is approximately the same for all samples, the total carbon and TKN in wet slurry from sites generating higher NO_x is less than that found in sites using dry powder limestone feed that generate lower NO_x emissions. Results sorted by TKN values are shown in separate tables in confidential Appendices A-4, B-4, and C-4. Assuming the TKN nitrogen is the nonvolatile nitrogen component of the feed, it is likely to be organic based and that nitrogen and carbon are released in the process from the feed at approximately the same time. Such nitrogen release could act as a source of ammoniacal nitrogen at high temperatures, which could establish a quasi-"SNCR/SCR" reductive path for NO, particularly in the presence of iron based catalysts, which at that point in the process have not yet been converted to the ferrite phase of cement clinker, and so may exert a catalytic action. This is admittedly unproven.

5.1.3 Total Sulfur

Total Sulfur and speciated sulfur results are shown in Appendices A, B, and C, and confidential Tables A-4 through C-4. Total sulfur in samples with higher carbon and nitrogen is generally higher than total sulfur from other kiln sites. Total sulfite in dry feed material follows the same trend with the highest carbon containing material also showing the highest sulfur as sulfite. Pyritic sulfur content in high organic samples trends higher than other kiln sites.

5.1.4 Summary of Analytical Results

As discussed above, the results of the testing conducted at the three Ellis County plants to characterize feed materials are considered confidential business information and are, therefore, reported in confidential attachments to this report. The table below summarizes testing results. All feed material is averaged together for the results below and the slag samples are omitted. Averaging the results from the three plants provides protection of confidentiality. As the slag material was understood to be obtained from only one source, this information could not be presented in a manner that protected confidentiality. Table 5-1.1 presents the results for both wet and dry feed materials averaged together, as there are only two plants running wet and two running dry, reporting the results of the averages of two plants' data does not protect confidentiality.

Table 5-1.1. Summary of Analytical Results on Feed Materials

	Carbon Evolution Temp. range, °C	Total DH, J/g	Organic %	Organic Sulfur %	Pyritic Sulfur %	Sulfate %	Sulfite %	Sulfur %	Chloride (Water Soluble) %	Kjeldahl Nitrogen mg/kg
mean	NA	161.01	0.320	0.110	0.295	0.099	0.035	0.539	0.003	236.27
std. deviation	NA	51.73	0.1028	0.0346	0.0696	0.0296	0.0207	0.0782	0.0012	93.73
range	115-630	NA	NA	NA	NA	NA	NA	NA	NA	NA

5.2 Data from Plant Surveys

The other source of data on the composition of feed materials was an information request that the expert panel assisted TCEQ in preparing and forwarding to the plants. This information was also requested to be treated as confidential by the plants. As discussed above, data from all three plants was averaged to protect confidentiality. Although other data were requested and obtained, when less than all three plants reported a parameter, that parameter was not included in Table 5.2.1 to protect confidentiality.

Table 5-2.1. Summary of Plant Reports on Feed Materials

	Feed Composition (% wt typical)				Kiln Feed			Size	Sulfur
	Limestone	Shale	Silica	Other	Lime Saturation Factor	Silica Ratio	Alkali	% + 200 mesh	weight %
mean	88.1%	3.8%	5.8%	2.4%	100.9%	2.985	0.4927	29.5%	1.3%
std. deviation	0.0078	0.0359	0.0238	0.0076	0.0494	0.3066	0.1153	0.2948	0.0023

5.3 Conclusions

Total carbon nitrogen and sulfur content seem to be major factors in the difference between kiln feed materials. TKN can impact NO_x emissions by oxidation to NO, but also as a component that may reduce NO formed in the burning zone, by a reaction similar to SNCR or SCR. We do not know the temperature profile of organic nitrogen generation from these feeds, only that nitrate or nitrite nitrogen is not reflected in the values. However, process emissions tests from the site providing highest carbon organic nitrogen and sulfur also show the lowest uncontrolled NO_x release. Other sites use dry powder feed material contains slightly lower levels

of TKN but do not show the organic carbon or nitrogen content found in the lower NO_x emitting site.

Feed nitrogen under high carbon loading may be released into a reducing environment and need not generate NO. The temperatures required for organic carbon and nitrogen release are too cold for authentic SNCR, and the process doesn't have the right catalysts for SCR. However, the low NO emissions at the site with the higher carbon in feed limestone suggest that these latter reactions may be occurring. One possible conclusion from the feed analysis information is a reaction under reducing conditions, similar to SNCR or SCR, as follows:

$$CO + NO \Longrightarrow CO_2 + N$$

$$12NH_3 \text{ (from TKN in feed)} + 8NO + 5\ O_2 \Longrightarrow 10N_2 + 18H_2O$$

While this site may not have the right temperature/oxygen/CO conditions in the tower for SNCR to be maximally effective, there seems to be some combination of chemistry and process conditions occurring that reduces the NO_x emissions. Further evidence of this possibility can be found in a paper from Zement-Kalk-Gips (German cement journal) written by M. Ono and co-workers, Japan, the authors show the effects of certain iron compounds in catalyzing the reaction of carbon monoxide with NO at temperatures below those usual in SNCR (the reference for this report has not been located).

It is possible that the calciner design and process conditions at the site with the lowest NO_x emissions may be better in general or that its design may produce the right conditions for reduced NO_x emissions with the higher carbon/higher organic nitrogen containing feed. Several additional feed analyses (e.g. temperature related nitrogen release, speciated metals analysis) coupled with measurement of gases in kiln emissions are necessary to validate this conclusion.

SO_2 is a high-temperature scavenger for high oxygen radicals like OH and O, and may thereby help reduce NO_x. Feed material containing higher carbon and a higher level of sulfur than other kiln feed materials may contribute to the reducing environment and lower NO_x emissions. The “organic sulfur” found in samples also includes sulfide (nonpyritic) sulfur.

Sulfite is not usually present in materials taken directly from ore deposits. There is more sulfite in the feed at the lower NO_x emission site than in the other feed from the other sites. This may reflect the return kiln dust and its sulfite content, which in turn may reflect the effect of oxygen upstream of the dust collector. If the available O_2 is lower in the kiln process gas this may also reduce low temperature formation of NO.

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Attachment A
ERG SUMMARY OF EPA 2000 NO_x CONTROLS FOR CEMENT KILNS

Attachment A – Table A-1

Table A-1. Summary of EPA Reported NO_x Control Technologies for Cement Kilns – EPA 2000

NO_x Control Strategies		Applicability	NO_x Reduction Efficiency (%)	Estimated Costs	Number of Installations
Process modifications	Excess air and temperature optimization (using CO and O_2 CEMS and feedback control)	All kiln types	15[a]	Capital cost = ~$750,000[s]	Unknown
	Reduce alkali content of feed where feasible	All kiln types	Not available	Not available	Unknown
	CemStar (addition of steel slag)	All kiln types although higher NO_x reductions expected from wet and long-dry kilns due to greater heat input offsets	9 - 60[b]	Capital cost = $200,000 - $500,000[t] Annual costs are highly site-specific (e.g., slag injection rate, potential cost savings due to increased production)	11
	Fuel switching (natural gas to coal)	All kiln types	70[c]	Not available	~ 87% of existing kilns use coal
	Improving thermal efficiency	All kiln types	Not available	Not available	Unknown
Combustion modification	Staged air combustion - staged fuel combustion	All kiln types (most effective with indirect fired kilns)	Not available	Not available	Unknown
	Staged air combustion - flue gas recirculation	May not be suitable for cement kilns. Incorporation of FGR in a cement kiln also results in somewhat increased power consumption and reduced kiln output.	Not available	Not available	Unknown
	Staged air combustion - flue gas recirculation w/low-NO_x burner		15 - 38[d]	Not available	Unknown
	Staged air combustion - Low-NO_x burner	All kiln types (burners that use 5-7% excess air are only for indirect-fired kilns)	44[e] 15 - 33[f] 23 - 47[g] 14[h]	Capital cost = $511,000 - $966,000[u] Annual cost = $136,000 - $204,000[u]	~ 22 existing kilns use low-NO_x burners

Attachment A – Table A-1 (continued)

NO_x Control Strategies		Applicability	NO_x Reduction Efficiency (%)	Estimated Costs	Number of Installations
Combustion modification (cont.)	Staged fuel combustion - Tire-derived fuel (TDF)	All kiln types	30 - 40[i]		Unknown. Approximately 53,300,000 tires are burned in cement kilns annually http://www.epa.gov/epaoswer/non-hw/muncpl/tires/tdf.htm#cement
	Staged fuel combustion - Low-NO_x precalciner	Not applicable to preheater kilns that f ire fuel in the riser	$\leq$46[j]	Not available	Unknown
	Staged fuel combustion - Mid-kiln firing	Wet and long-dry kilns	38[k] 11 - 55[l] 28 - 59[m]	Capital cost = ~ $3,000,000[v] Annual cost = ($370,000) - $189,000[v]	21 long kilns (US), 40 kilns (worldwide)
Post-formation removal	Selective catalytic reduction (SCR)	No cement kilns had SCR at the time of the EPA Study prior to 2000.		Not available in 2000.	No installations were reported on cement kilns in EPA 2000.
	Selective non-catalytic reduction (SNCR)	Best application is for preheater/ precalciner kilns. Generally not applicable to long-dry or wet kilns	71 -98[n] 10-20[o]	Not available	2 kilns (US), 18 in Europe
	Biosolids (SNCR)	Preheater/precalciner kilns	Not available	Capital cost = $240,000[w] Annual cost = ($322,000)[w]	Unknown
	NOxOUT (SNCR)	Preheater/precalciner kilns	> 50 - 90[p] 10 - 20[q] 46 - 53[r]	Capital cost = ~$1,200,000[x] Annual cost = $560,000 - $2,000,000[x]	None
	Low Temperature Oxidation (LoTOx™, Hydrogen Peroxide, OXONE (Dupont) & Sodium Acetate)	Oxidation technologies were not discussed or considered in the EPA 2000 report.	Not considered	Not considered	Oxidation technologies were not discussed or considered in the EPA 2000 report.

[a]Results based on experimental test on one kiln.
[b]Results derived from short- and long-term tests on two different kiln types.
[c]Results based on emission tests of dry kilns.
[d]Results based on a single 1988 study. The percent reduction depends on degree of flue gas recirculation.
[e]Results based on emission tests of a preheater/precalciner kiln.
[f]Results based on emission tests of five kilns.
[g]Results based on emission tests of four kilns.

Attachment A – Table A-1 (continued)

[h]Emission test of one kiln.
[i]Results based on tests conducted at one California facility.
[j]Results based on a test conducted by the Portland Cement Association.
[k]Results based on one study.
[l]Results based on testing of seven dry kilns.
[m]Results based on testing of three wet kilns.
[n]Based on emission tests of a preheater/precalciner kiln at one facility.
[o]Results based on emission test at one facility
[p]Results based on emission tests of a single kiln.
[q]Results based on a emission tests of a single kiln (operating conditions during most of the test were unstable).
[r]Results based on emission test of two kilns.
[s]Estimate for a commercially available process control system.
[t]Cost estimates obtained from Texas Industries (TXI).
[u]Costs derived for retrofitting low-NO_x burners to eight model kilns with clinker production capacities ranging from 25 to 150 tons of clinker per hour.
[v]Costs derived for retrofitting low-NO_x burners to four model kilns with clinker production capacities ranging from 25 to 50 tons of clinker per hour. Annual costs reflect the fuel credit associated with using tire-derived fuel.
[w]Costs based on a clinker production rate of 215 tons per hour.
[x]Costs based on two preheater/precalciner kilns with a clinker production rates of 92 tons per hour and 133 tons per hour.

ATTACHMENT B
SAMPLING PLAN

Sample Acquisition and Handling

Clean, clear, pre-labeled, one (1) liter sample bottles were shipped to each Kiln site on August 23, 2005 via Federal Express. The nine (9) samples returned on August 25 in good condition from Texas Industries Inc. included three wet slurry, three dry powder and three slag samples. The six (6) samples returned from Ash Grove Cement on August 26 included three (3) wet slurry and (3) slag samples. The 6 samples returned from Holcium on August 31 included three (3) samples from line 1 and 3 samples from line 2.

All were samples returned to ERG's analytical laboratory with chain of custody and security seals. ERG consulted with three cement kiln experts, F. MacGregor Miller, Gabriel Miller, and David Gossman on the analyses required to determine key features of the kiln feed chemistry important to NO_x emissions and control. Recommendations were sought from the experts on laboratories experienced in each analysis. Three laboratories were ultimately selected on the basis of expertise and price. Table 1 summarizes the analyses requested for each sample.

ERG repackaged samples for distribution to the specialty analysis laboratories scheduled to perform feed material composition analysis. Repackaged samples were give unique identification numbers to keep Kiln identity anonymous to the analysis laboratories.

Table B-1. Feed Chemical Composition

Plant Name	Samples Received	Sample Type	Total Sulfur	Sulfate	Sulfite	Pyritic Sulfur	Organic Sulfur	Chloride	Nitrogen (TKN)	VOCs
Texas Industries Inc (TXI)	3	Wet Slurry	X	X	X	X	X	X	X	X
Texas Industries Inc (TXI)	3	Dry Powder	X	X	X	X	X	X	X	X
Texas Industries Inc (TXI)	3	Slag	X	X	X	X	X	X	X	X
Holcim US Inc	0	Dry Power Line 1	X	X	X	X	X	X	X	X
Holcim US Inc	0	Dry Power Line 2	X	X	X	X	X	X	X	X
Ash Grove Cement Inc	3	Wet Slurry	X	X	X	X	X	X	X	X
Ash Grove Cement Inc	3	Slag	X	X	X	X	X	X	X	X

ATTACHMENT C
ERG Report on LoTOx™ Application to Refineries

ERG Report - Refinery Application of Low Temperature Oxidation Emissions Controls

LoTOx™

LoTOx™ is a trademark of the BOC Group Inc. for an end-of-pipe process that uses ozone to oxidize insoluble species of NO_x, such as NO and NO_2, to highly soluble species, primarily N_2O_5. N_2O_5 then reacts with moisture in the flue gas to form nitric acid (HNO_3) and is removed from the gas in a wet gas scrubber. LoTOx™ is a developing technology for NO_x control, and there are currently only about three commercial applications of LoTOx™. Another three installations are planned in the next two years. LoTOx™ has been demonstrated using slipstream testing at ten types of facilities, including a smelting plant, a glass furnace, a lead furnace, a petroleum coke and high sulfur coal fired boiler, a chemical plant, a steel pickling bath process, a gas-fired boiler, a composite fuel fired boiler, a petroleum refinery fluid catalytic cracking unit (FCCU), and a lignite-fired boiler. No cement plants have tested LoTOx™.

In the LoTOx™ process, ozone is formed from oxygen using a corona-discharge ozone generator. The resulting concentration of ozone is between 7 and 15 weight percent (1). The ozone/oxygen mixture is injected into the flue gas stream as it enters either a wet gas scrubber or a reaction vessel adjacent to a wet gas scrubber. The ratio of ozone to NO_x is 0.2-2.8:1, and varies with factors such as flue gas temperature and residence time. The principal reactions for NO_x oxidation are:

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$2\ NO_2 + O_3 \rightarrow N_2O_5 + O_2$$
$$N_2O_5 + H_2O \rightarrow 2\ HNO_3$$

The maximum temperature for the oxidation reactions is 325 °F (163 °C), while the optimal temperature is generally less than 300 °F (149 °C). The NO_x oxidation reactions become unstable over 325 °F. Trials at a coal-fired power plant and a steel pickling process found the optimal temperature was in the range of 160 to 250 °F (1). A trial at a battery lead recovery furnace found the optimal temperature was 175 °F or less, although the temperature could be increased up to 225 °F without sacrificing NO_x removal, but at the cost of increased ozone demand (2). A trial at Marathon Ashland Petroleum's (MAP) Texas City refinery FCCU found the optimal temperature was 140 to 150 °F (3). These temperatures are lower than typical cement kiln flue gas temperatures. In addition to cooling using heat recovery systems, quenching with water is typically used to lower the gas temperature to the adiabatic saturation temperature.

After NO_x is oxidized to N_2O_5, it is absorbed from the flue gas by water spray in a wet gas scrubber. The relative solubility of N_2O_5 compared to other flue gas species is presented below.

Relative Solubility of Flue Gas Components

Species	Relative Solubility at 25 °C
NO	1
NO_2	20
SO_2	2000
N_2O_5	>>2000
HNO_3	Mixes with water in all proportions

Ferrell 2003, p. 4

N_2O_5 reacts immediately and irreversibly with water to form nitric acid. The nitric acid then is neutralized with caustic or lime in the scrubber liquor to form sodium or calcium nitrates.

Potential Advantages of LoTOx™

The potential advantages of LoTOx™ are as follows.

LoTOx™ can provide a high degree of NO_x removal. Based on slipstream testing, 70 to 90 percent NO_x removal is typical, with greater than 95 percent NO_x removal achievable.

LoTOx™ can respond quickly to variable NO_x emissions. Since ozone is produced on demand, changes in NO_x load can be met without loss of NO_x removal efficiency. Swings in NO_x concentration by 100 percent or more over the course of minutes have been accommodated using combined feed-forward/feed-back control schemes (Ferrell 2000, pp. 8-9; Ferrell 2003, pp. 13-14). Although most LoTOx™ trials have been for combustion processes (90:10 NO to NO_2 ratio), the steel pickling process had variable NO to NO_2 ratios, with NO_2 sometimes higher than NO. Ozone production was decreased since less ozone was required to oxidize NO_x to N_2O_5, while NO_x removal was maintained above 95 percent (1).

LoTOx™ does not emit excess reactant. Unlike SCR and SNCR, which can emit excess ammonia, the ozone that does not react with NO_x in the LoTOx™ process is scavenged by sulfite in the scrubber solution. A trial at a lead furnace examined the potential for unreacted ozone to be emitted from the process. It was found that the ozone addition had to be increased by a factor of eight over what was required for NO_x removal to cause 0.6 ppm of ozone to be measured in the stack gas (2).

LoTOx™ is highly selective for NO_x. Although ozone can oxidize SO_2 and CO, the presence of SO_2 and CO does not impact NO_x removal. This is due to the faster reaction rates for NO_x oxidation compared to oxidation of other gas species.

Relative Reaction Rates of Flue Gas Components with Ozone

Species	Relative Reaction Rates
$NO + O_3 \rightarrow NO_2 + O_2$	62,500
$2\ NO_2 + O_3 \rightarrow N_2O_5 + O_2$	125
$SO_2 + O_3 \rightarrow SO_3 + O_2$	5
$CO + O_3 \rightarrow CO_2 + O_2$	1

Ferrell 2003, p. 3

LoTOx™ does not interfere with other pollution control technologies. The trial at MAP's Texas City refinery FCCU indicated LoTOx™ does not have a negative impact on SO_2 scrubbing efficiency. The scrubber maintained SO_2 removal in excess of 99 percent during the LoTOx™ trial (3).

Areas of Concern

Wet Gas Scrubber Required

A wet gas scrubber is necessary to take advantage of the increased solubility of N_2O_5 over NO and NO_2. For cement plants with an existing wet gas scrubber for SO_2 and particulate matter removal, LoTOx™ can be installed as an upstream retrofit. For plants that do not require a scrubber for SO_2 or particulate matter removal, installing a scrubber for NO_x removal only may not be cost effective.

Gas Temperature

Cement kiln flue gases typically have temperatures greater than the LoTOx™ maximum temperature of 325 °F. If the flue gas temperature is greater than 325 °F after useful heat has been recovered, quenching with water is required prior to ozone injection. BOC indicates that water quenching can be used on gas streams with temperatures up to 650 °F and moisture contents of 30 to 35 percent.

Nitrates in Wastewater

Sodium nitrate is typically the primary byproduct of the LoTOx™ process. This may be a concern for treatment and/or discharge of the wastewater. MAP examined the possible problems of increased nitrates in the study at the Texas City refinery (3). Regarding sodium toxicity, MAP found that the contribution of sodium nitrate from LoTOx™ was small compared to sodium sulfate from SO_2 scrubbing. Regarding wastewater treatment impacts, monovalent cations, such as sodium, can have a destabilizing effect on bioflocculation by displacing divalent cations, such as calcium or magnesium. This can lead to decreased biofloc settling and increased suspended solids. This problem does not occur if the monovalent to divalent cation ratio is maintained at 2:1 or less (by addition of divalent cations if necessary). In addition, nitrogen gas produced by denitrification in the secondary clarifier sludge bed can cause the bed to rise, increasing suspended solids. In this case, a holding tank can be installed to shift the denitrification reactions out of the secondary clarifier.

Cost

BOC indicates NO_x removal of 70 percent or greater must be required for LoTOx™ to be cost effective. In ERG's experience, the estimated cost effectiveness for LoTOx™ installations at refineries has ranged from approximately 2,500 to 10,000 dollars per ton of NO_x (as NO_2) removed. In general, the cost per ton of NO_x removed was lower for units with high NO_x removal (greater than 85 percent), due to economy of scale. Similarly, the annual operating cost was at least 50 percent of the total annualized cost for those units with the lowest cost per ton of NO_x removed. The costs of oxygen and electricity for the ozone generator accounted for 80 to 90 percent of the annual operating costs.

For a 200 MW coal-fired power plant, BOC estimated the cost to be only 1,696 dollars per ton of NO_x removed (1). This application was designed for 95 percent NO_x removal, and the annual mass of NO_x removed was 4 to 46 times larger than the refinery applications.

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ATTACHMENT D
SUMMARY OF CURRENT US REGULATIONS FOR NOx

Table D-1. Summary of US NO_x Control Regulations for Cement Kilns – EPA 2004								
State	Effective Date	Source Type	Description	Emission Limit	Applicability	Avg. Time	Test/CEM	Rule
NY	5/1/03	NOx Budget Trading Program	EGUs ≥ 15 MW; non EGUs ≥ 250mmBtu/hr; Portland Cement Plants ≥ 250mmBTU/hr	Allowances & Trading Program	All statewide	Ozone season	CEM	Part 204
	05/31/95	Portland cement kilns	Sources with PTE 25 TPY in NYC and lower Orange county metro areas; PTE 100 TPY elsewhere in State	Analysis of RACT controls; select control; NY approves RACT emission limit & submits to EPA as a SIP revision				Part 220 RACT
MD	11/24/03	Cement kilns	Capacity no more than 600,000 TPY	0.5 tons per hour		30 day rolling avg	CEM	COMAR 26.11.09.08
	11/24/03		Capacity greater than 600,000 TPY	0.9 tons per hour		30 day rolling avg	CEM	COMAR 26.11.09.08
	05/1/03	Non-trading source	Cement Kilns	Long wet-6.0 lb./T of clinker;long dry-5.1;preheater/precalciner or pre-calciner-2.8			CEM	26.11.29.15
PA	Proposed	Cement	Kilns	LNB or mid-kiln firing or alt. that achieves 30% reduction	Statewide	Season	CEM	Chapter 145-Subchapter C-proposed
AL	04/06/01	Cement kilns	Long dry -12 TPH; Long wet -10TPH;Preheater-16TPH ; Precalciner & PH/PC-22 TPH	LNB or mid-kiln firing or equivalent controls	Various counties	Ozone season		335-3-8-.01
KY	08/15/01	Cement kilns	Process rates at least(TPH)-long dry-12;long wet-10;preheater-16;PH/PC-22	6.6 lbs./T of clinker	Statewide	30 day rolling avg-ozone season	CEM	401 KAR 51:170

Table D-1. Summary of US NO_x Control Regulations for Cement Kilns – EPA 2004

SC	05/31/04	Cement kilns	Process rates at least(TPH)-long dry-12;long wet-10;preheater-16;PH/PC-22 or NOx>1 TPD	LNB or mid-kiln firing or similar controls	All Statewide	ozone season	CEM or annual source test	61-62.99 Subpart B
		Early Action Compact (EAC)	Cement kilns	LNB or equivalent capable of achieving 30% reduction				Reg 61-62.5;Standard No.5.2
TN	05/31/04	Cement kilns	Process rates(TPH) at least-long dry-12;long wet-10;preheater-16;PH/PC-22	LNB or mid-kiln firing or similar controls or RACT	Statewide	ozone season		1200-3-27-.04
IL	05/30/04	Cement kilns	Long dry kilns at least 12 TPH	5.1 lb./T or 30% reduction or LNB or mid kiln firing	Statewide	Ozone season	Annual stack test	Part 217; Subpart T
	05/30/04	Cement kilns	Long wet kilns at least 10 TPH	6.0 lb./T or same as above	Statewide	Ozone season	Annual stack test	Part 217; Subpart T
	05/30/04	Cement kilns	Preheater kilns at least 16 TPH	3.8 lb./T or same as above	Statewide	Ozone season	Annual stack test	Part 217; Subpart T
	05/30/04	Cement kilns	Preheater/precalciner kilns at least 22 TPH	2.8 lb./T or same as above	Statewide	Ozone season	Annual stack test	Part 217; Subpart T
IN	08/04/97	Emission limits	Cement kilns - long dry-at least 20 TPH	Daily – 10.8 lb./T; Rolling 30 day - 6.0 lb./T	Clark, Floyd Cos;may avg among plants statewide under same owner	ozone season	CEM	326 IAC 10-1-4
	08/04/97		Preheater kilns at least 20 TPH	Daily - 5.9 lb./T; Rolling 30 day – 4.4 lb./T	Same as above	ozone season	CEM	326 IAC 10-1-4

Table D-1. Summary of US NO_x Control Regulations for Cement Kilns – EPA 2004

	03/01/04	Reduction - certain categories	Cement kilns - long dry at least 12 TPH;long wet- 10 TPH	5.1, 6.0 lb./T or LNB or mid kiln firing or 30%control	Statewide	ozone season	CEM unless LNB or mid-kiln	326 IAC 10-3
	03/01/04		Preheater kilns at least 16 TPH;precalciner and PH/PC - 22 TPH	3.8, 2.8 lb./T; same as above	Statewide	ozone season	same as above	326 IAC 10-3
MI	12/04/02	Non SIP Call	Cement kilns	LNB or mid-kiln or 25% red from 1995	Statewide	ozone season		336.1801
	12/04/02	Cement kilns	Long dry -12 TPH; Long wet - 10TPH;Preheater-16TPH	LNB or mid-kiln or long wet - 6.0 lbs./T; long dry - 5.1 lbs./T	Fine grid	ozone season	Annual stack test or CEM	336.1816
	12/04/02	Cement kilns	Precalciner & PH/PC-22 TPH	Preheater - 3.8 Lb/T; PH/PC-2.8 lb./T or 30%red	Fine grid	ozone season		336.1816
OH	04/30/04	Cement kilns	Long dry -12 TPH; Long wet - 10TPH;Preheater-16TPH	LNB or mid-kiln firing or similar controls	Statewide	ozone season	Annual stack test or CEM	3745-14-11
	04/30/04	Cement kilns	Precalciner & PH/PC-22 TPH	LNB or mid-kiln firing or similar controls	Statewide	ozone season	Annual stack test or CEM	3745-14-11
TX *	03/27/03	Cement kilns	Wet kilns	6.0 lb./T of clinker	Bexar, Hays, Comal and McLennan Cos	30 day rolling avg	CEM or PEMS	Chap.117; Sec.265
	03/27/03	Cement kilns	Wet kilns	4.0 lb./T	Ellis Co.	30 day rolling avg	CEM or PEMS	Chap.117; Sec.265
	03/27/03	Cement kilns	Long dry kilns	5.1 lb./T	Bexar, Hays, Comal and McLennan Counties	30 day rolling avg	CEM or PEMS	Chap.117; Sec.265

Table D-1. Summary of US NO_x Control Regulations for Cement Kilns – EPA 2004

	03/27/03	Cement kilns	Preheater kilns	3.8 lb./T	Above counties	30 day rolling avg	CEM or PEMS	Chap.117; Sec.265
	03/27/03	Cement kilns	Preheater/precalciner or precalciner kilns	2.8 lb./T	Above counties	30 day rolling avg	CEM or PEMS	Chap.117; Sec.265
SCAQMD	07/01/86	Cement kilns	Any gray cement kiln	11.6 lbs./T; 6.4 lbs./T	Districtwide	24 cons. Hrs/30 consecutive days		Rule 1112

TPH refers to tons of clinker per hour of cement production.
* Texas has the option of complying with the following technical standard:
Each long wet or long dry kiln for which the following controls are installed and operated during kiln operation is not required to meet the NOx emission limits of subsection (a) of this section, provided that each owner or operator choosing this option submits written notification of this choice to the executive director, the appropriate regional office, and any local air pollution control program with jurisdiction before the appropriate compliance date in §117.524 of this title:
(1) a low-NOx burner and either:
(A) mid-kiln firing; or
(B) some other form of secondary combustion achieving equivalent levels of NOx reductions; or alternatively;
(2) other additions or changes to the kiln system achieving at least a 30% reduction in NOx emissions, provided the additions or changes are approved by the executive director with concurrence from EPA.
(d) Each preheater or precalciner kiln for which either a low-NOx burner or a low-NOx precalciner is installed and operated during kiln operation is not required to meet the NOx emission limits of subsection (a) of this section. Each owner or operator choosing this option shall submit written notification of this choice to the executive director, the appropriate regional office, and any local air pollution control program with jurisdiction before the appropriate compliance date in §117.524 of this title.

ERG reviewed US EPA's Summary of State / Local NOx Regulations for Stationary Sources and selected and reviewed those control measures that apply to cement kilns to create this table. This file is locate at : www.epa.gov/ttn/naaqs/ozone/ozonetech/**statenox**regs518.pdf