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NO_x Control Technologies for the Cement Industry: Final Report

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NOX Control Technologies for the Cement Industry
FINAL REPORT

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1.0 INTRODUCTION

1.1 PURPOSE OF THIS DOCUMENT

The purpose of this document is to update the information in the document *Alternative Control Techniques Document - NO_x Emissions from Cement Manufacturing* (the 1994 ACT document).¹ This update incorporates comments received on the 1994 ACT document and provides more recent data on emission control technologies and their costs.

This report examines uncontrolled emissions from four kiln types (wet, long dry, preheater, precalciner). The report focuses on the current use, effectiveness, and cost of several control technologies applicable to all or some kiln types, including CemStar, low-NO_x burners, mid-kiln firing, and selective noncatalytic reduction via biosolids injection and NO_xOUT[®] technology.

1.2 METHODS

Data were collected for this report primarily through site visits at cement kiln facilities; contacts with control technology vendors, portland cement industry representatives, and state regulatory agencies; and a literature search. Additional information was obtained through seeking out useful sites on the internet.

1.3 ORGANIZATION

Chapter 2 presents a summary of the findings of this study. Chapter 3 provides a description of the portland cement industry. Chapter 4 examines uncontrolled NO_x emissions. Chapter 5 presents an update on selected NO_x control technologies. Chapter 6 presents an update on control costs and cost effectiveness.

1.4 REFERENCE FOR CHAPTER 1

1. U.S. Environmental Protection Agency. *Alternative Control Techniques Document - NO_x Emissions from Cement Manufacturing*. EPA-453/R-94-004. Research Triangle Park, NC. March 1994.

2.0 SUMMARY

This report addresses nitrogen oxides (NO_x) emissions from portland cement kilns and the current use, effectiveness, and cost of applicable control technologies. This chapter presents a summary of updated information on uncontrolled NO_x emissions from kilns and the applicability, effectiveness, and costs of NO_x control technologies. Information that is summarized in this chapter is presented in greater depth in subsequent chapters. Section 2.1 includes a summary of current uncontrolled NO_x emissions data from the four kiln types. Section 2.2 summarizes NO_x control technology emissions data. Section 2.3 presents a summary of updated control costs and cost effectiveness for these control technologies.

2.1 UNCONTROLLED NO_x EMISSIONS FROM CEMENT KILNS

In cement manufacturing, conditions favorable for formation of NO_x are reached routinely because of high process temperatures. Essentially all NO_x emissions associated with cement manufacturing are generated in cement kilns.

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

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

Often the raw material feed to the kiln contains a significant amount of 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, thermal NO_x formation provides the dominant mechanism for NO_x formation in cement manufacturing.

There are four different types of cement kilns used in the industry: wet kilns, long dry kilns, kilns with a preheater, and kilns with a preheater/precalciner. All cement kiln systems contain a rotary kiln. The wet, long dry, and most preheater kilns have only one fuel combustion zone; whereas, the newer preheater/precalciner kilns and preheater kilns with a riser duct have two fuel combustion zones. Some precalciner kilns have a third combustion zone. Since the typical temperatures in the combustion zones are different, the factors affecting NO_x formation are also somewhat different in the different kiln types. In the primary combustion zone at the hot end of a kiln, the high temperatures lead predominantly to thermal NO_x formation; whereas, in secondary combustion zones lower gas-phase temperatures suppress thermal NO_x formation.

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 should produce lower NO_x emissions per ton of clinker, the product of the rotary kiln.

EC/R obtained emissions data for cement kilns from state regulatory agencies in eight of the top ten states in terms of clinker capacity: California, Florida, Indiana, Michigan, Missouri, New York, Pennsylvania, and Texas. Table 2-1 presents a summary of the recent state emissions data alongside a summary of the estimates used in the 1994 ACT document and the current edition of AP-42.

TABLE 2-1. SUMMARY OF UPDATED UNCONTROLLED NO_x EMISSIONS DATA AND THE CORRESPONDING 1994 ACT DOCUMENT ESTIMATES

Cement kiln type	1994 ACT Document ¹		AP-42 ²	Recent State Data ³	
	Average (lb/ton of clinker)	Range (lb/ton of clinker)	(lb/ton of clinker)	Average rate (lb/ton of clinker)	Range of rates (lb/ton of clinker)
Wet kiln	9.7	3.6 to 19.5	7.4	6.2	1.9 - 13.4
Long dry kiln	8.6	6.1 to 10.5	6.0	4.5	2.5 - 7.1
Preheater kiln	5.9	2.5 to 11.7	4.8	1.7	0.4 - 3.7
Precalciner kiln	3.8	0.9 to 7.0	4.2	2.9	1.1 - 5.6

There is substantial spread in the reported NO_x emissions with significant overlap for different kiln types. The four different cement kiln types, however, do appear to have different levels of NO_x emissions and different characteristics influencing NO_x formation. Information used to calculate NO_x uncontrolled emission rates come from air emission tests at various cement manufacturing facilities in the United States. Twenty-two tests were used to calculate the AP-42 NO_x emission factors and all of the tests are over ten years old. In addition, the majority of these are short-term emissions tests, which do not capture the inherent variability of kiln NO_x emissions. As a result, the AP-42 NO_x emission factors have a quality rating of “D” (relatively low quality - limited data, or highly variable). When one reviews the original data summarized in the 1994 ACT document, it is clear that the average emission rates are not unduly influenced by outliers as evidenced by the fact that the average for each kiln type is nearly in the middle of the range. Because the data used in the calculation of the 1994 ACT document NO_x emission rates are newer, these average emission rates may be more representative of modern kilns than the factors presented in AP-42.⁴

Seven of the states that were contacted reported emissions in tons NO_x/year. Six of these states did not report production values, so kiln capacities⁵ were used to determine emission rates. The kilns were assumed to operate for an average of 8,000 hours/year at maximum production capacity. The resulting average emission rates are generally lower than the average emission

rates calculated in the 1994 ACT document or presented in AP-42. The lower numbers are probably a result of using kiln capacities rather than actual kiln production values. Because of the uncertainty surrounding the production values for the state data and because the AP-42 data have a “D” rating, the 1994 ACT document values for uncontrolled NO_x emissions from cement kilns are used in this document. However, it should be noted that the ranges in emissions and the average values for all three data sources generally support one another. Chapter 4 contains more detailed information on the uncontrolled NO_x emission values.

2.2 NO_x CONTROL TECHNOLOGY FOR CEMENT KILNS

NO_x control approaches applicable to the cement industry may be grouped in three categories: process modifications, where the emphasis is on increased energy efficiency and productivity; combustion control approaches, where the emphasis is on reducing NO_x formation; and NO_x reduction controls, which remove the NO_x formed in the combustion process.

2.2.1 Process Control Modifications

Process modifications 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. Process modifications are applicable to all kilns and 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 improve fuel efficiency, reduce operating costs, increase capacity and kiln operational stability. 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.

Continuous monitoring of oxygen and carbon monoxide 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 1430 to 1540 °C (2600 to 2800 °F) for completion of clinkering reactions and to maintain the quality of the cement produced.⁶ The corresponding gas-phase temperature is usually greater than 1700 °C (3100 °F).⁷ Maintaining the combustion zone temperature at the minimum necessary 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 oxygen in the exhaust, kiln operators typically strive for an oxygen level of 1 to 2 percent to guarantee the desired oxidizing conditions in the clinker 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 2 to 1 percent), NO_x emissions per unit time can be reduced by approximately 15 percent.^{8,9}

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 levels also results in increased productivity per unit of energy consumed and thus results in an indirect reduction of NO_x emissions per unit of clinker product.

Process modifications can be highly site specific and data from one site cannot be directly translated to other sites. Quite often a number of process modifications and combustion control measures are implemented simultaneously. Process modifications can reduce NO_x emissions in cement kilns without any specific NO_x control equipment. Some plants rely on process monitoring and control and process modifications as a means to maintain NO_x emissions within their allowable limits. Although process controls will reduce NO_x emissions in poorly operated kilns, for the purposes of this document, such approaches are considered necessary for proper kiln operation and are not specifically considered as NO_x control techniques, except as noted below for CemStar.

One process modification that can be quantified is the CemStar process, which can reduce NO_x emissions at any type of kiln by the addition of a small amount of steel slag to the raw kiln feed. 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 carbon dioxide emissions.¹⁰ CemStar is currently being used or is in the process of being incorporated at 11 cement facilities in the United States. 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 decrease NO_x emissions by 30% and can also increase production by 15 percent.¹⁰

2.2.2 Combustion Modifications

Combustion modifications are an efficient way to reduce the formation of thermal NO_x. The combustion modifications discussed in this report focus on staging the combustion to minimize the amount of combustion that must occur at the maximum temperatures. This can be accomplished by modifying the way oxygen or fuel is provided for combustion.

Low-NO_x burner systems are available for all kiln types and rely on the staged combustion of air. Technical literature and industry publications report NO_x reduction rates of 23 to 47 percent with the installation of low-NO_x burners, depending on the baseline emissions, type of kiln, type of low-NO_x burner, and operating conditions.^{11,12,13,14,15} In January 2000, the Portland Cement Association (PCA) and American Portland Cement Alliance (APCA) provided results of a survey of cement facilities where the respondents indicated 14% of the operating U.S. 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).^{16,17}

Staged combustion of fuel includes the use of preheaters/precalciners and mid-kiln firing. Mid-kiln firing of fuels is currently installed in 21 U.S. wet and long dry cement kilns, and whole tires are most frequently used for the mid-kiln fuel. Technical literature, industry publications, and state emissions data for several kilns that have used or tested mid-kiln firing demonstrate NO_x reductions ranging from 28 to over 50 percent.^{18,19,20,21,22,23,24} Use of tire derived supplemental fuel at a preheater/precalciner has been shown to decrease NO_x emissions by 30-40 percent.²⁵

2.2.3 NO_x Removal Control

NO_x removal controls destroy NO_x that is formed in the combustion process. Selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR) are two types of NO_x removal controls. Biosolids injection technology is not technically SNCR, but the chemistry and the principles of its operation are similar. For this reason it is discussed with the other NO_x removal controls.

SCR uses ammonia in the presence of a catalyst to selectively reduce NO_x emissions from exhaust gases. SCR technology has not been used on any cement kilns in the United States, although pilot plant trials and feasibility studies have been conducted in Europe.

SNCR relies on the reduction of NO_x in exhaust gases by ammonia or urea without using any catalyst and can achieve NO_x emission reductions of 30 to 70 percent. This approach avoids the problems related to catalyst fouling, as in SCR technology, but requires injection of the reagents in the kiln at a temperature between 870 to 1090 °C (1600 to 2000 °F). At these temperatures urea decomposes to produce ammonia which is responsible for NO_x reduction. Because of the temperature constraint, SNCR technology is only applicable to preheater and precalciner kilns. In principle, any of a number of nitrogen compounds may be used, 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. There have been two SNCR demonstration at full size kilns in the United States using the $\text{NO}_x\text{OUT}^{\text{®}}$ process.^{26,27} SNCR is currently operating on numerous kilns in Europe.²⁸

Biosolids injection technology is being used in one kiln in Southern California.^{29,30} At this facility, the biosolids (dewatered sewage sludge) are injected into the mixing chamber where the flue gas streams leaving the kiln and precalciner mix. The mixing chamber offers the benefits of good residence time in the appropriate temperature window and high mixing effectiveness. Biosolids injection is achieving a 50 percent NO_x emission reduction at this facility.

2.2.4 NO_x Control Efficiencies

An assortment of industry data, literature, and professional publications, as well as some of the state data described above, was used to develop an estimate of emissions from cement

kilns using NO_x control technologies. Table 2-2 presents a summary of updated control technology emission rates alongside the emission estimates used in the 1994 ACT document. The new emissions rates are all within or very close to the ranges established in the 1994 ACT document. CemStar, a relatively new process that involves adding steel slag to the feed mix in a long kiln, was not discussed in the 1994 ACT document. Emission rate reductions from the use of CemStar averaged 33 percent. New data on low-NO_x burners and mid-kiln firing tend to support the information presented in the 1994 ACT document. Both of these technologies have become more commonplace in controlling NO_x emissions from cement kilns and improved performance using mid-kiln firing technology has been obtained. Data were also obtained on two SNCR technologies, biosolids injection and NO_xOUT[®]. These technologies showed average emission reductions of 50 and 40 percent, respectively. Additional information on SCR was not obtained during the development of this report. Chapter 5 contains a more detailed discussion of the NO_x control technologies.

TABLE 2-2. COMPARISON OF 1994 ACT DOCUMENT AND CURRENT NO_x CONTROL TECHNOLOGY PERFORMANCE

	1994 ACT	Updated Emissions Data ³			
		Average Emission Reduction (%)	Range of Emission Reductions (%)	Average Emission Rate (lb NO _x /ton of clinker)	Range of Emission Rates Found (lb NO _x /ton of clinker)
Process Control Modifications	<25				
CemStar	n/a	33	23 to 40	6.0	3.2 to 11.2
Indirect firing with a low-NO _x burner	20 to 30	27	4 to 47	9.0 ^a	9.0 ^a
MKF (wet kilns only)	20 to 40	41	28 to 59	n/a	n/a
MKF (dry kilns only)	20 to 40	33	11 to 55	3.9	2.0 to 10
TDF in a precalciner ^b	not applicable	35	30 to 40	2.4 ^b	2.4 ^b
SNCR	30 to 70	BSI	50	NA	1.2 ^b
		NO _x -OUT	40	10 to 50	NA

n/a - not applicable

^a Only one facility reported emissions in lb NO_x/ton of clinker. The other data were reported in percent.

^b One facility in southern California provided emission reduction data for both biosolids injection technology and firing tire derived fuel in a precalciner.

2.3 CONTROL COSTS AND COST EFFECTIVENESS

Capital and annualized operating costs as well as cost effectiveness were determined for technologies for which detailed costs could be developed. Costs for low-NO_x burners and mid-kiln firing were developed for applicable model plants. Since there are limited cost data available for installations of CemStar and biosolids injection, and no U.S. installations of SNCR, the capital and annualized costs for these technologies were not developed for model plants for purposes of this report. Costs for SCR were developed in the 1994 ACT document and are presented again in this report. The SCR costs have not been updated or revised. All of the capital and annualized operating costs developed for this report are based on information provided by vendors, actual installations, and guidelines provided by the U.S. Environmental Protection Agency/Office of Air Quality Planning and Standards (EPA/OAQPS) Control Cost Manual.

The cost of a commercially available kiln process control system, based on existing installations, is approximately \$750,000. The resulting savings due to reduced energy and fuel requirements and increased refractory life were estimated to be about \$1.37/ton of clinker. Thus, for a kiln producing 300,000 tons/year of clinker, the reduced cost of producing cement is expected to recover process control installation costs in less than 2 years.

Costs for CemStar were estimated for a long wet kiln. Approximate capital investment in 1997 dollars was estimated at \$1,176,000 and annualized costs estimated to be \$220,000. Cost savings associated with CemStar due to the resulting production increase are estimated to be approximately \$63 per ton times the increase in production, which is usually 5 to 10 percent. The cost of CemStar could not be estimated on a variety of kilns because the amount of steel slag added is completely dependent on plant-specific variables.

Biosolids injection has been installed on one kiln. The total capital investment costs for this kiln were \$1.2 million with an annual operating cost of (\$322,000) per year (which includes tipping fees for the biosolids of \$5/ton). Costs for NO_xOUT[®] technology were obtained from the equipment vendor for two preheater/precalciner kilns. Total capital investment were \$1.06 million and \$1.2 million. The annualized costs for these kilns are \$560,000 and \$2,000,000 per year.

Cost analysis was performed for low-NO_x burners and mid-kiln firing on up to eight different model kilns. Models 1 and 2 were wet kilns with 30 and 50 tons of clinker per hour (ton/hour) respective capacities, models 3 and 4 were long dry kilns with 25 and 40 ton/hour respective capacities, models 5 and 6 were preheater kilns with 40 and 70 ton/hour respective capacities, and models 7 and 8 were precalciner kilns with 100 and 150 ton/hour respective capacities. The results of the cost analysis in 1997 dollars are summarized in Chapter 6.

Cost effectiveness was also estimated for each technology. A summary of the results is presented in Table 2-3. Greater detail on the cost analysis and cost effectiveness estimates is presented in Chapter 6.

TABLE 2-3. SUMMARY OF COST EFFECTIVENESS
(1997 Dollars/ton NO_x Reduced)

Technology		Range of Annual Cost Effectiveness	Average Annual Cost Effectiveness	Average Ozone Season Cost Effectiveness
CemStar		n/a	550	1,100
Low-NO _x Burners	Indirect-Fired Kilns	300 to 620	440	1,060
	Direct-Fired Kilns	760 to 1200	940	2,260
Mid-Kiln Firing		(460) to 730	55	130
Tire Derived Fuel at a Precalciner ^a		(1,900) ^b	(1,900) ^b	(4,500) ^b
Biosolids Injection		n/a	(310) ^b	(740) ^b
NO _x OUT [®]		1,000 to 2,500	1,750	2,160

N/A - not applicable

() - indicates a negative cost

^a The purchased equipment and total capital investment costs for a tire derived fuel installation on a precalciner are very similar to mid-kiln firing.

^b Represents a single installation.

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3.0 INDUSTRY DESCRIPTION

3.1 BACKGROUND

This chapter provides an overview of the cement industry, its annual production rates, and the various manufacturing processes used. Process and operating parameters most influential for NO_x formation in the various processes are discussed.

The cement industry is a vital industry for a modern society because cement is an essential ingredient in concrete. One need only mention reinforced-concrete walls and girders, tunnels, dams, and roads to realize the dependence of our society upon cement products. 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 °C (2550 to 2750 °F), 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.”¹ Portland-cement clinker has been defined as “a clinker, partially fused by pyroprocessing, consisting predominantly of crystalline hydraulic calcium silicates.”¹ 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 3-1.² 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.

3.2 TYPES OF CEMENT PRODUCED

The five basic types of portland cement recognized and produced in the United States are described below.^{2,3} In addition, different varieties are prepared by using various blending formulations.⁴

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 3-1. BASIC CLINKER COMPOUNDS²

Formula	Name
$2\text{CaO}\cdot\text{SiO}_2$	Dicalcium silicate
$3\text{CaO}\cdot\text{SiO}_2$	Tricalcium silicate
$3\text{CaO}\cdot\text{Al}_2\text{O}_3$	Tricalcium aluminate
$4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$	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 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. They contain a higher proportion of tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$) 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 ($3\text{CaO}\cdot\text{SiO}_2$) and tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$) than type I, thus lowering the heat evolution. Consequently, the percentage of dicalcium silicate is increased substantially and the percentage of tetracalcium aluminoferrite ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$) 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 cement 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).⁴

3.3 INDUSTRY CHARACTERIZATION

3.3.1 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 1998.⁵ This was a 6.0 percent increase from the 1990 reported total production of 73.5 million metric tons. As shown in Figure 3-1, 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 off 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. Table 3-2 provides a list of all companies along with their share of the total clinker production. Table 3-3 lists the clinker producing capacity in the United States by States. The locations of the operating kilns are shown in Figure 3-2. 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 1998.⁵

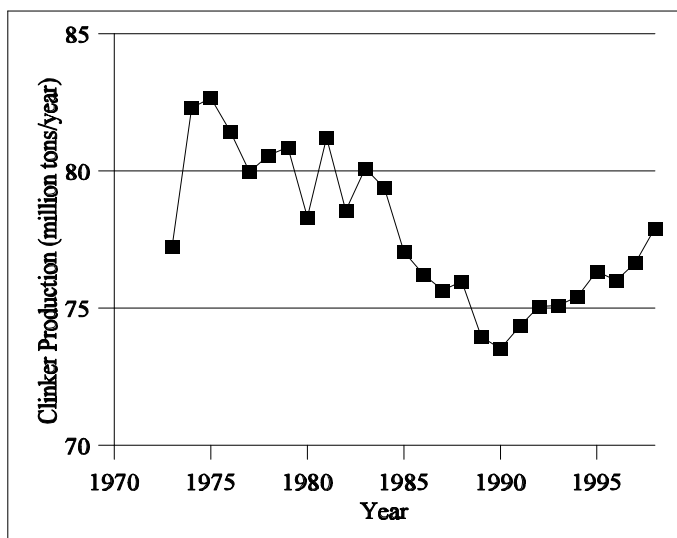


Figure 3-1. Annual clinker production.⁵

TABLE 3-2. UNITED STATES CEMENT COMPANY CAPACITIES IN 1998
(INCLUDES GRAY AND WHITE PLANTS)⁵

Rank	Clinker (10 ³ tons/year)	Percent Industry	Company Name
1	9371	12.0	Holnam Inc.
2	8297	10.6	Southdown Inc.
3	6459	8.3	Lafarge Corporation

TABLE 3-2. UNITED STATES CEMENT COMPANY CAPACITIES IN 1998 (continued)
(INCLUDES GRAY AND WHITE PLANTS) ⁵

Rank	Clinker (10 ³ tons/year)	Percent Industry	Company Name
4	4738	6.1	Ash Grove Cement Company
5	4367	5.6	Blue Circle Inc.
6	3972	5.1	Essroc Cement Corporation
7	3374	4.3	Lone Star Industries
8	3119	4.0	Lehigh Portland Cement
9	3096	4.0	Texas Industries
10	2965	3.8	California Portland Cement
11	2711	3.5	RC Cement Company, Inc.
12	1616	2.1	Centex
13	1580	2.0	Mitsubishi Cement Corporation
14	1457	1.9	Kaiser Cement Corporation
15	1387	1.8	Calaveras Cement Company
16	1358	1.7	Giant Cement Holding, Inc.
17	1075	1.4	Kosmos Cement Company
18	1047	1.3	St. Lawrence Cement Company
19	1003	1.3	Texas-Lehigh Cement Company
20	1003	1.3	Roanoke Cement Company
21	952	1.2	National Cement Company of Alabama
22	870	1.1	Sunbelt Cement Corporation
23	868	1.1	Capitol Cement Corporation
24	866	1.1	Pennsuco Cement Company
25	840	1.1	Allentown Cement Company Inc.
26	812	1.0	Dacotah Cement
27	788	1.0	Alamo Cement Company
28	768	1.0	North Texas Cement
29	763	1.0	Capitol Aggregates, Inc.
30	755	1.0	RMC Lonestar
31	639	0.8	Monarch Cement Company
32	567	0.7	Phoenix Cement Company
33	562	0.7	National Cement Company of California

TABLE 3-2. UNITED STATES CEMENT COMPANY CAPACITIES IN 1998 (continued)
(INCLUDES GRAY AND WHITE PLANTS) ⁵

Rank	Clinker (10 ³ tons/year)	Percent Industry	Company Name
34	545	0.7	Continental Cement Company, Inc.
35	545	0.7	Florida Crushed Stone
36	498	0.6	Dixon-Marquette
37	494	0.6	Rinker Portland Cement Corporation
38	492	0.6	Glens Falls Cement Company, Inc.
39	432	0.6	Rio Grande Cement Corporation
40	392	0.5	Dragon Products Company
41	294	0.4	Armstrong Cement & Supply Corporation
42	177	0.2	Royal Cement Company, Inc.

Total:	77914		

TABLE 3-3. UNITED STATES 1998 CLINKER CAPACITIES BY STATE
(INCLUDES GRAY AND WHITE PLANTS) ⁵

Clinker (10 ³ tons/year)	No. of Facilities Making Clinker	No. of Kilns	States
10461	10	18	California
8187	10	19	Texas
6809	10	21	Pennsylvania
4497	5	7	Missouri
4233	5	6	Alabama

TABLE 3-3. UNITED STATES 1998 CLINKER CAPACITIES BY STATE (continued)
(INCLUDES GRAY AND WHITE PLANTS) ⁵

Clinker (10 ³ tons/year)	No. of Facilities Making Clinker	No. of Kilns	States
4228	3	8	Michigan
3071	4	7	Florida
2745	3	4	New York
2670	4	8	Illinois
2632	4	8	Indiana
2630	3	7	South Carolina
2462	3	4	Iowa
1748	3	7	Oklahoma
1728	2	7	Arizona
1719	3	7	Maryland
1710	4	11	Kansas
1690	3	5	Colorado
1259	2	2	Utah
1127	2	3	Georgia
1104	2	3	Ohio
1060	2	3	Tennessee
1044	2	2	Washington
1003	1	1	Virginia
868	1	3	West Virginia
843	1	1	Nebraska
812	1	3	South Dakota
794	1	3	Arkansas
759	1	1	Oregon
726	1	1	Kentucky
623	2	3	Nevada

TABLE 3-3. UNITED STATES 1998 CLINKER CAPACITIES BY STATE (continued)
(INCLUDES GRAY AND WHITE PLANTS) ⁵

Clinker (10 ³ tons/year)	No. of Facilities Making Clinker	No. of Kilns	States
593	2	2	Montana
585	1	2	Wyoming
433	1	1	Mississippi
432	1	1	New Mexico
392	1	1	Maine
237	1	2	Idaho
77914	105	192	

There are no clinker producing plants in the following states:

Alaska	Connecticut	Delaware
Dist. of Columbia	Hawaii	Louisiana
Massachusetts	Minnesota	New Hampshire
New Jersey	North Carolina	North Dakota
Rhode Island	Vermont	Wisconsin

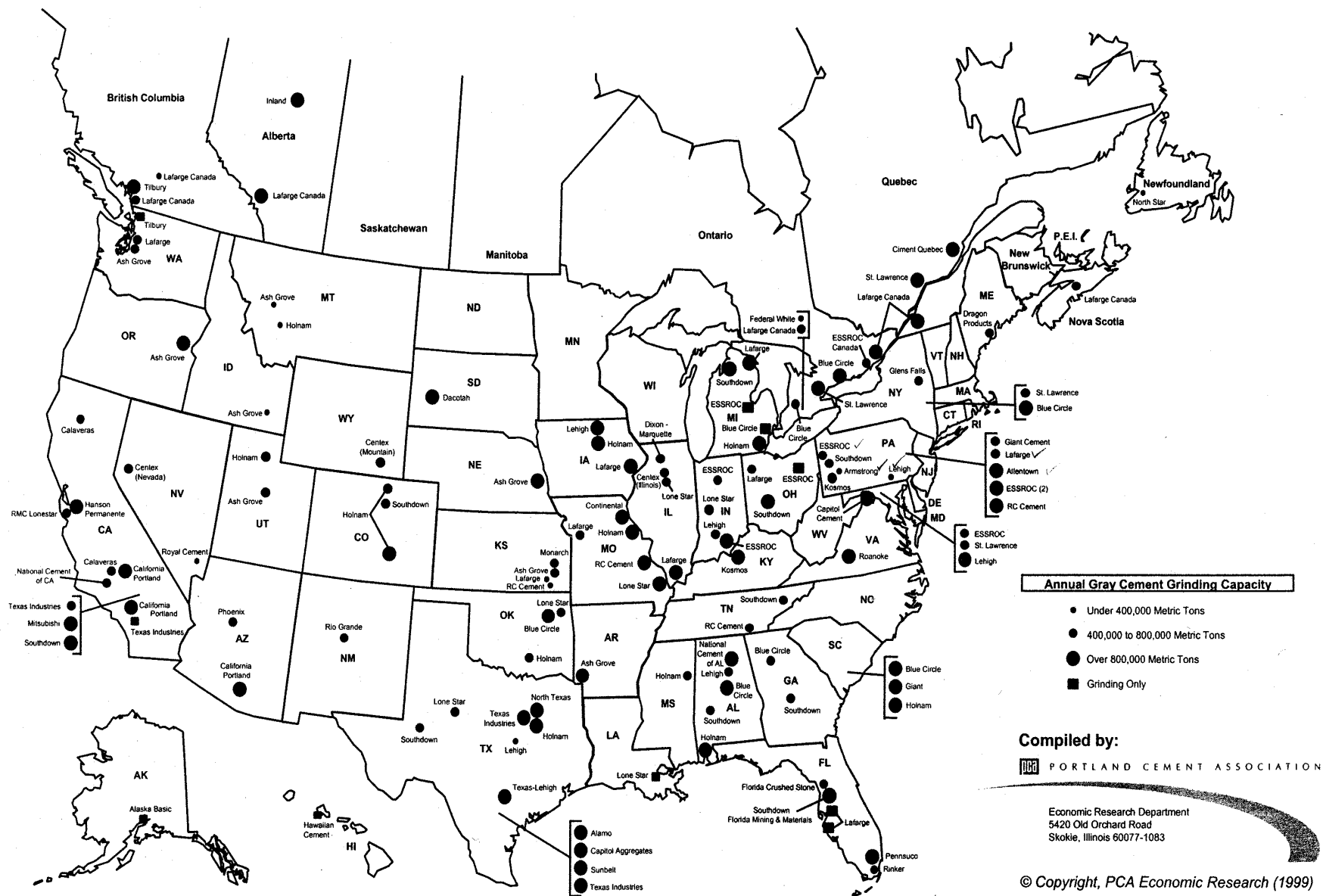


Figure 3-2. United States and Canadian Portland Cement Locations
(December 31, 1998)

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.⁵ 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.

3.3.2 Overview of Cement Manufacturing Process

The process of portland cement manufacture consists of:⁶

- 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 plant is shown in Figure 3-3 which also illustrates differences between the two primary types of cement processes: wet process and dry process.⁶ 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.⁶ Figure 3-4 is an illustration of a preheater/precalciner type of dry process system.⁷

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.⁵

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

3.3.3 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 with mill scale, pyrite cinders, or iron ore. Silica may be supplemented by adding sand to the

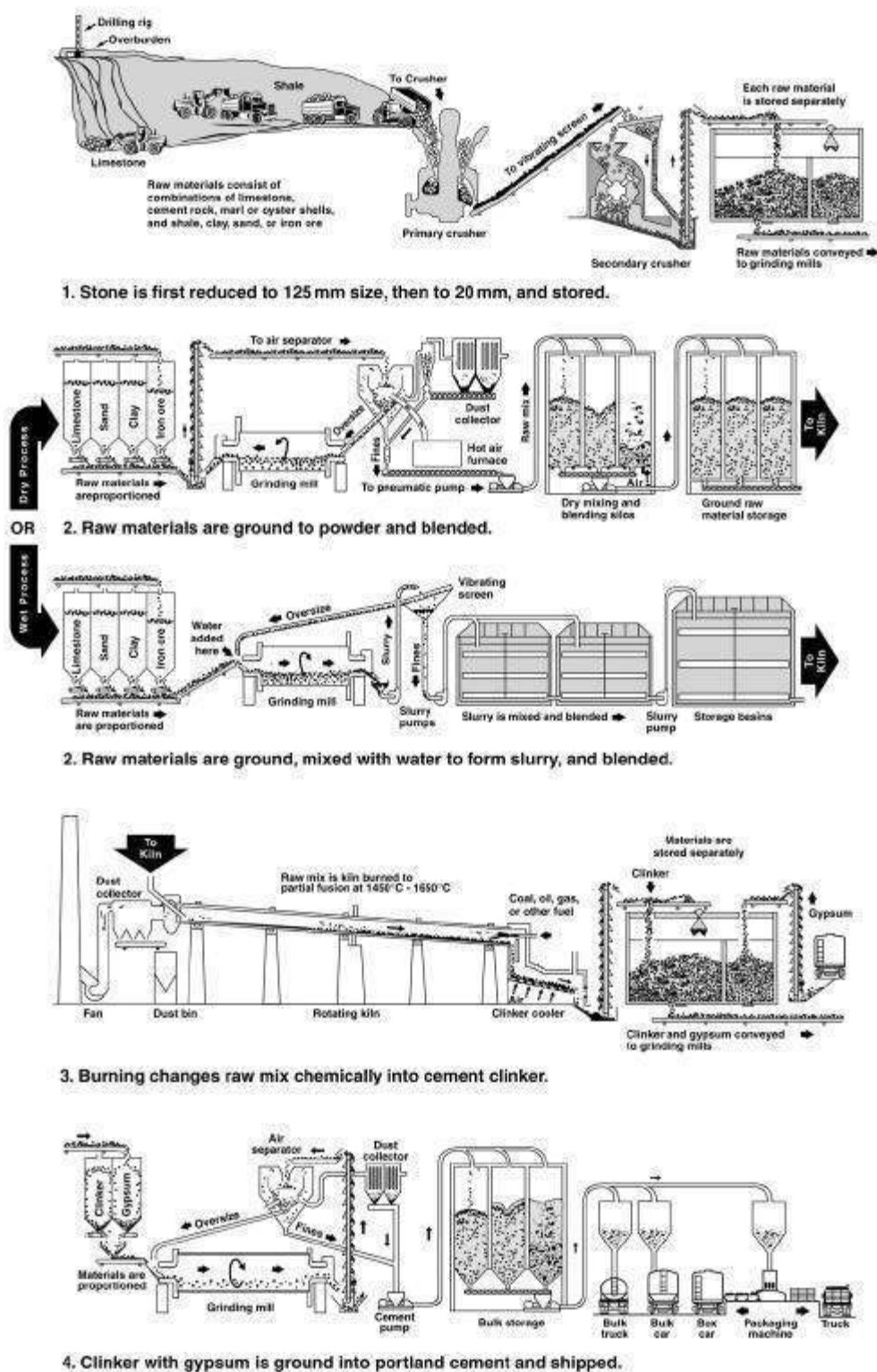
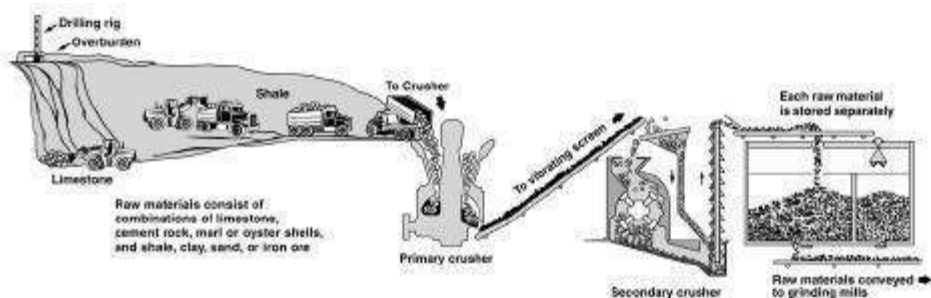
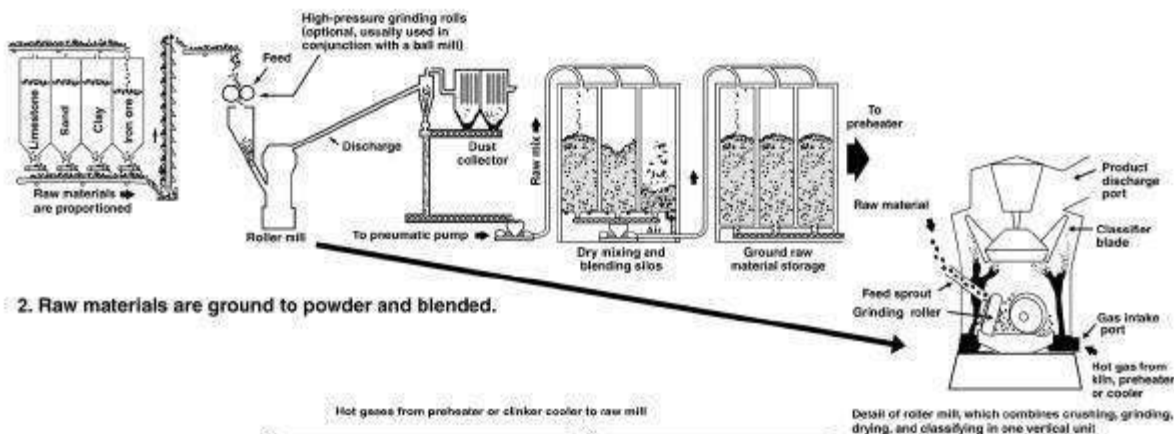


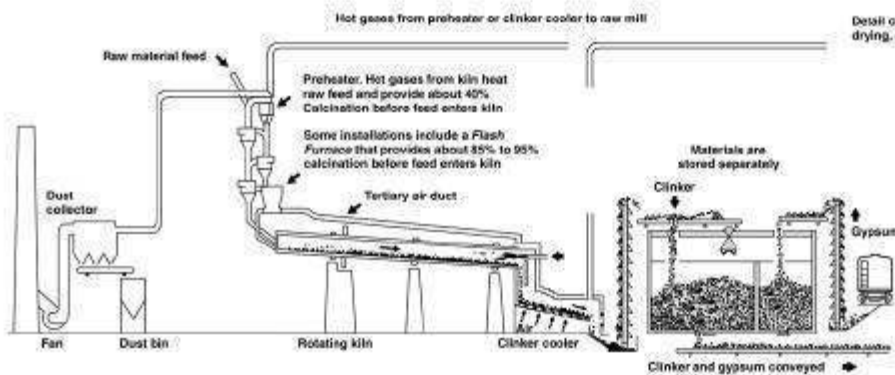
Figure 3-3. Steps in the manufacture of portland cement. ⁷



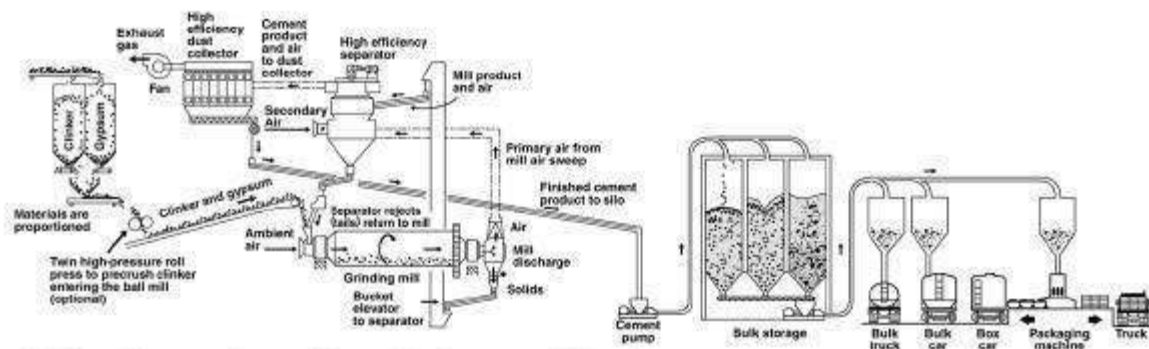
1. Stone is first reduced to 125 mm size, then to 20 mm, and stored.



2. Raw materials are ground to powder and blended.



3. Burning changes raw mix chemically into cement clinker. Note four-stage preheater, flash furnaces, and shorter kiln.



4. Clinker with gypsum is ground into portland cement and shipped.

Figure 3-4. Preheater/precalciner cement kiln.⁷

raw mix, whereas alumina can be furnished by bauxites and alumina-rich flint clays.⁶ 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, 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- μ m (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 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.⁶

3.3.4 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) dia, 50 to 230 m (150 to 750 ft) long] equipped with an electrical drive to rotate the kiln on its longitudinal axis at 1 to 3 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, alumina, or chrome-magnesite 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.⁶

Pyroprocessing may be conveniently divided into four stages, as a function of location and temperature of the materials in the rotary kiln.⁸

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 100°C to approximately 430°C (800°F) to form oxides of silicon, aluminum, and iron;
3. Calcination, during which carbon dioxide (CO₂) and CaO are formed from calcium carbonates, primarily between 900°C (1650°F) and 982°C (1800°F); and
4. Reaction, of the oxides in the burning zone of the rotary kiln, to form cement clinker at temperatures of approximately 1510°C (2750°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 800 °C (700 to 1500 °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.⁶

3.3.4.1 Wet Process 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 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. 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 (1022°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.⁶

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.⁵

3.3.4.2 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 precalciner have been introduced as discussed in the next sections.⁶

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.⁵

3.3.4.3 Suspension Preheaters. In systems with suspension preheaters, the dry, pulverized feed passes by gravity through a series of cyclones 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 (1500 to 1650 °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 preheaters promotes condensation of alkalis and sulfur on the feed which sometimes results in objectionable high alkali and sulfur contents in the clinker. To alleviate this problem, some of the kiln exit gases can bypass the preheater through a slip stream or fewer cyclone stages can be used in the preheater with some sacrifice of efficiency.⁶

Suspension preheater kilns represent a newer cement technology compared to the long dry kilns. They are also somewhat larger in production capacity than the long conventional 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.⁵

3.3.4.4 Precalciner Systems. 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 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 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 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.⁶

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.⁵ 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 1989.⁵

3.3.5 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, that rotate at about 15 to 20 rpm. The clinker and gypsum are 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.⁶

3.3.6 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 monitored by the liter weight test weighing a portion of sized clinker, a free lime test, or 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.⁶

3.3.7 Emission Control Systems

All cement plants are equipped with particulate collection devices to remove cement kiln dust (CKD) from the kiln exhaust gases and clinker dust from clinker cooler exhaust gases. Several small dust collectors are also installed at various dust emission points throughout the

plant such as material transfer points and grinding operations. The collected CKD is usually recycled with the feed or injected at different points in the kiln depending upon the quality and source of the CKD. None of the cement plants in the United States uses any flue gas treatment for reducing NO_x emissions.

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4.0 UNCONTROLLED NO_x EMISSIONS

4.1 MECHANISMS OF NO_x FORMATION IN CEMENT MANUFACTURING

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.

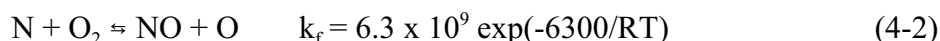
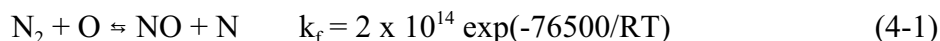
In cement kilns, NO_x emissions are formed during fuel combustion by two primary mechanisms:

- 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 NO₂ species, although NO₂ normally accounts for less than 10 percent of the NO_x emissions from a cement kiln exhaust stack.¹ The concentration and emission of NO_x are, however, typically expressed in equivalent NO₂ form.

4.1.1 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,² the two important steps in NO formation are given as:



where k_f 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 with O₂ further results in NO₂ formation.

The equilibrium concentrations of NO and NO₂ formed thus depend strongly upon the gas-phase temperature as well as the concentration of O₂ and N₂ in the gas phase. Table 4-1 shows the equilibrium concentrations of NO and NO₂ for two conditions.³ First, the equilibrium concentrations of NO and NO₂ for N₂ and O₂ concentrations found in ambient air are shown. Secondly, Table 4-1 also shows the NO and NO₂ concentrations at flue gas conditions where the O₂ and N₂ concentrations are defined for this table as 3.3 percent O₂ and 76 percent N₂. The equilibrium NO concentrations for the flue gas conditions are lower than those for ambient conditions due to the lower O₂ concentration. The excess air used during fuel combustion can substantially affect NO formation by determining the amount of oxygen available for NO reaction. The cement kiln burning zones usually have about 5 to 10 percent excess air while higher excess air levels are not uncommon. Figure 4-1 shows the theoretical equilibrium concentrations of NO in the flue gas for different excess air levels.¹ 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 4-1. CALCULATED EQUILIBRIUM CONCENTRATIONS (in ppm)
OF NO AND NO₂ IN AIR AND FLUE GAS ³

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 1400 °C (2550 °F). In contrast, the fuel combustion temperature in a precalciner or in a kiln riser duct is well below 1200 °C (2200 °F), suppressing thermal NO_x formation.⁴ 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.

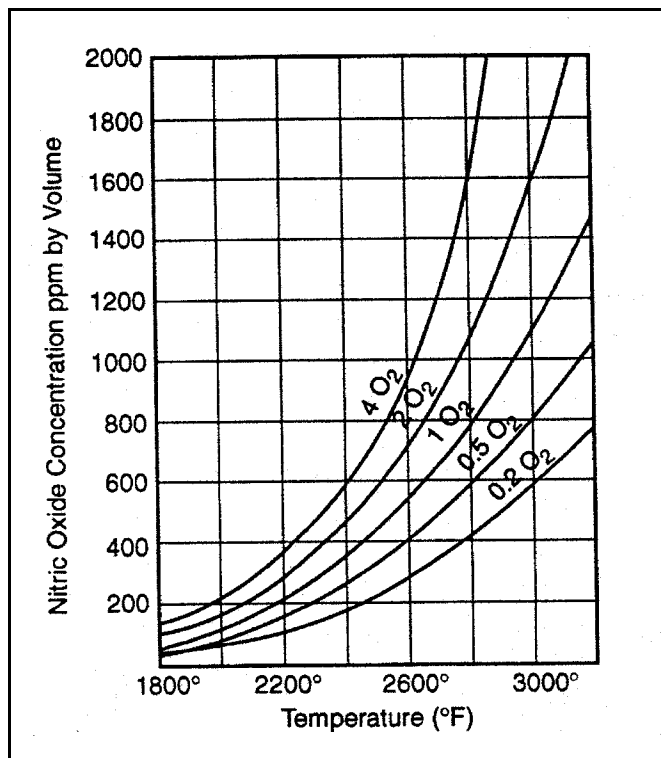


Figure 4-1. Theoretical equilibrium concentrations of NO in gas from combustion sustained in air.¹

4.1.2 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.⁵ Natural gas contributed about 3 percent of the energy demand, oil about 1 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 1 to 3 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.⁶ The nitrogen content in these fuels may be significant depending on the chemicals included in the waste mix being burned.

The maximum possible fuel NO_x formation may be estimated from the fuel nitrogen content by assuming 100 percent nitrogen conversion. As discussed in section 4.3, 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 1 percent by weight, approximately 9.5 lb of NO (14.5 lb expressed as NO₂) 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 NO₂) 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.⁷ 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.⁷ This fact indicates the dominance of thermal NO_x in overall NO_x formation.

4.1.3 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. Since most of these raw material components are sedimentary minerals, 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 1000 ppm (as N).⁸ 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 1 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 1470 °F) temperature range and depends upon the feed heating rate.⁸ Rapid heating rates (~1000 °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 . 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.⁹

4.2 FACTORS AFFECTING NO_x EMISSIONS IN CEMENT MANUFACTURING

Chapter 3 identified four different 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 typically 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.

4.2.1 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 gas-phase 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 majority of kilns in the United States are direct fired.

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 2650 to 2800°F (1450 to 1540°C)¹⁰ 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, 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/ton of clinker for every 1 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.

4.2.2 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:



where "N" means nitrogen originating from nitrogen compounds in the fuel.¹ 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.¹¹ 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_x formation.¹

4.2.2.1 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.¹² 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.¹

4.2.2.2 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.¹

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.¹ 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.¹

4.2.3 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 less NO_x emissions per unit amount of clinker as compared to the wet or long dry kilns.

4.3 AVAILABLE DATA FOR UNCONTROLLED NO_x EMISSIONS FROM CEMENT MANUFACTURING FACILITIES

The four types of cement kilns discussed in the last section exhibit different combustion characteristics as well as energy efficiencies and heat requirements. The available NO_x emissions data are therefore generally grouped by these cement kiln types.

In January 1995, EPA published a revised AP-42 section for Portland Cement Manufacturing.¹³ The revised NO_x emission factors adopted for the AP-42 document for the same four kiln types mentioned above are: 7.4 lb/ton of clinker for wet process kilns, 6.0 lb/ton of clinker for dry process kilns, 4.8 lb/ton of clinker for kilns with preheaters, and 4.2 lb/ton of

clinker for kilns with precalciners. These emission factors were developed from 23 references. All 23 references are over ten years old and primarily represent short-term compliance tests.

Each AP-42 emission factor is given a rating from A through E, with A being the best. Two steps are involved in factor rating determination. The first step is an appraisal of data quality, the reliability of the basic emission data that will be used to develop the factor. The second step is an appraisal of the ability of the factor to stand as a national annual average emission factor for that source activity. All of the AP-42 NO_x emission factors have a "D" rating which is below average. A "D" rating means the factors were developed from A-, B-, and/or C - rated test data from a small number of facilities, and there may be reason to suspect that these facilities do not represent a random sample of the industry.¹ There also may be evidence of variability with the source population.

During preparation of the 1994 ACT document, NO_x emissions data were collected from major cement companies in the United States. Out of 51 cement kilns providing NO_x emissions data, 22 were from wet kilns, 10 were from long dry kilns, 10 were from preheater kilns, and 9 were from precalciner type cement kilns. Table 4-2 presents the NO_x emissions data along with the kiln types and fuels burned.

As seen from Table 4-2, in general, wet kilns were found to produce the highest NO_x emissions ranging from 3.6 to 19.5 lb NO_x/ton of clinker with an average of 9.7 lb NO_x/ton of clinker. Wet kilns also consume the most energy among different cement kiln types. The energy consumption of wet kilns was found to be in the range of 4.9 to 8.8 MM Btu/ton of clinker with an average of 6.0 MM Btu/ton. Wet kilns burning gas were found to produce greater NO_x emissions as compared to those burning coal. Also in some cases, high secondary combustion air temperatures were present with high NO_x emission rates. Twelve of the wet kilns reported burning WDFs² in significant quantities. Five of these kilns used "mid-kiln" firing of the solid and liquid waste fuel and the other seven kilns injected liquid waste in the hot kiln burning zone.

¹ A = Tests are performed by a sound methodology and are reported in enough detail for adequate validation.

B = Tests are performed by a generally sound methodology, but lacking enough detail for adequate validation.

C = Tests are based on an unproven or new methodology, or are lacking a significant amount of background information.

D = Tests are based on a generally unacceptable method, but the method may provide an order-of-magnitude value for the source.

² Waste Derived fuels can include scrap tires.

TABLE 4-2. NO_x EMISSIONS DATA USED TO DEVELOP 1994 ACT DOCUMENT

Location	Kiln #	Kiln type	Capacity (tons/hr)	Fuel burned	Heat in MM Btu/ton	NO _x emissions (lb/ton clinker)	Method and date of data	Reference
1. Ash Grove Cement Co.								
Foreman, AR	1	Wet	36	42% - Coal 42% - LWDF 16% - SWDF	6.86	13.51	CEM Jul-92	14
	2	Wet	36	As above	7.1	18.34	CEM Jul-92	14
	3	Wet	54	As above	7.05	15.65	CEM Jul-92	14
Chanute, KS	1 & 2	Wet		30% - Coal 7.1% - Coke 61.6% - WDF 1.3% - Gas	6.56	9	CEM 7/10/92 7/18/92	14
Durkee, OR	1	Four-stage Preheater	68.2	100% - Coal during tests 95% - Gas Currently	3.88 during test 3.72 currently	5.06	CEM Method 7 9/15/85	14
Nephi, UT	1	Precalciner	80	100% - Coal	3.6	3.43	Nov-82	14
						4.51	Jul-88	
						1.31	Apr-92	

CEM = Continuous emissions monitor; WDF - waste derived fuel; LWDF - liquid waste derived fuel; SWDF - solid waste derived fuel; either WDF or SWDF can include waste tires

TABLE 4-2. NO_x EMISSIONS DATA USED TO DEVELOP 1994 ACT DOCUMENT (continued)

Location	Kiln #	Kiln type	Capacity (tons/hr)	Fuel burned	Heat in MM Btu/ton	NO _x emissions (lb/ton clinker)	Method and date of data	Reference
2. Blue Circle Inc.								
Calera, AL	1	Dry	38	100% - Coal	3.8	9.58	CEM	15
Atlanta, GA	1	Dry	38.5	50% - Coal 50% - Coke	3.95	10.47	CEM	15
Ravena, NY	1	Wet	106.3	40% - Coal 60% - Coke	4.9	9.38	CEM	15
Tulsa, OK	1	Dry	38.5	100% - Coal	4	7.5	CEM	15
Harleyville, SC	1	Preheater	85	100% - Coal	3.5	5.87	CEM	15
3. California Portland Cement Inc.								
Rillito, AZ	1	Long Dry	17	71% - Coal 28% - Gas 1% - Coke	5	7.2 - 11.0 (9.1)	EPA Method 7E - CEM Jun-91	16
	2	Long Dry	17	54.2% - Coal 44.8% - Gas 1% - Coke	5	7.2 - 11.0 (9.1)	EPA Method 7E - CEM Jun-91	16
	3	Long Dry	17	66.8% - Coal 31.8% - Gas 1.2% - Coke	5	7.2 - 11.0 (9.1)	EPA Method 7E - CEM Jun-91	16

CEM = Continuous emissions monitor; WDF - waste derived fuel; LWDF - liquid waste derived fuel; SWDF - solid waste derived fuel; either WDF or SWDF can include waste tires

TABLE 4-2. NO_x EMISSIONS DATA USED TO DEVELOP 1994 ACT DOCUMENT (continued)

Location	Kiln #	Kiln type	Capacity (tons/hr)	Fuel burned	Heat in MM Btu/ton	NO _x emissions (lb/ton clinker)	Method and date of data	Reference
Mojave, CA	4	Precalciner	125	64% - Coal 23.8% - Gas 3.6% - Coke 3.8% - Used oil 5.7% - Tires	3.4	3.6 - 6.6 (5.1)	EPA Method 7E - CEM Jun-Aug-91	16
	1	Precalciner	130	90.8% - Coal 4.7% - Oil 4.5% - Gas	3.1	3.9	CARB 100 Compliance Test May-92	16
4. CBR Cement Corporation								
Redding, CA	1	Preheater	85	80% - Coal 20% - Tires	3.1	2.5	CEM Jul-92	17
5. Holnam, Inc.								
Theodore, AL	1	Precalciner	193.8			4	EPA Method 7E 9/24/91	18
Florence, CO	3	Wet	60			5.8	EPA Method 7E 10/24/91	18

CEM = Continuous emissions monitor; WDF - waste derived fuel; LWDF - liquid waste derived fuel; SWDF - solid waste derived fuel; either WDF or SWDF can include waste tires

TABLE 4-2. NO_x EMISSIONS DATA USED TO DEVELOP 1994 ACT DOCUMENT (continued)

Location	Kiln #	Kiln type	Capacity (tons/hr)	Fuel burned	Heat in MM Btu/ton	NO _x emissions (lb/ton clinker)	Method and date of data	Reference
Fort Collins, CO	1	One-stage preheater	61.7			8.1	CEM Jan-Jun-92	18
Artesia, MS	1	Wet	62.5			12.5	CEM 7/16/92	18
Clarksville, MO	1	Wet	170			6.8	CEM	18
Three Forks, MT	1	Wet	37.7			11.6	EPA Method 7 2/10/86	18
Ada, OK	1	Wet	40			15.9	KVB System Jun-92	18
	2	Wet	40			19.5	KVB System Jun-92	
Holly Hill, SC	1	Wet	60			5.7	CEM 6/28/92	18
	2	Wet	102			5.3	CEM 7/9/92	

CEM = Continuous emissions monitor; WDF - waste derived fuel; LWDF - liquid waste derived fuel; SWDF - solid waste derived fuel; either WDF or SWDF can include waste tires

TABLE 4-2. NO_x EMISSIONS DATA USED TO DEVELOP 1994 ACT DOCUMENT (continued)

Location	Kiln #	Kiln type	Capacity (tons/hr)	Fuel burned	Heat in MM Btu/ton	NO _x emissions (lb/ton clinker)	Method and date of data	Reference
Morgan, UT	1	Wet	22			6.61	EPA Method 7E 11/21/91	18
	2	Wet	22			5.46	EPA Method 7E 11/27/91	18
Seattle, WA	1	Wet	56.2			8.12	EPA Method 7E 10/15/90	18
6. Lafarge Corporation								
Demopolis, AL	1	Preheater	98	70% - Coal 30% - WDF Gas - Preheat	3.2	4.8	EPA Method 7E 9/5/8/91	19
Davenport, IA	1	Preheater- Precalciner	108.3	100% - Coal	3.2	217 lb/hr 2.61	EPA Method 7 9/21/82	20
						204.4 lb/hr 2.07	6/6/84	20

CEM = Continuous emissions monitor; WDF - waste derived fuel; LWDF - liquid waste derived fuel; SWDF - solid waste derived fuel; either WDF or SWDF can include waste tires

TABLE 4-2. NO_x EMISSIONS DATA USED TO DEVELOP 1994 ACT DOCUMENT (continued)

Location	Kiln #	Kiln type	Capacity (tons/hr)	Fuel burned	Heat in MM Btu/ton	NO _x emissions (lb/ton clinker)	Method and date of data	Reference
Fredonia, KS	1	Wet	17	100% - Coal	5.98	~200 ppm 4/11/89	EPA Method 7E	21
					6.17	~550 ppm 9/17/91		21
	2	Wet	28.5	100% - Coal	5.85	~500 ppm 9/18/91		21
Alpena, MI	1	Dry	70	78% - Coal 22% - WDF	5	957 ppm avg	CEM 8/7/92	22
	2	Dry	45	100% - Coal	4.6	393 ppm avg	CEM 8/7/92	22
Sugar Creek, MO	1 & 2	Dry	66.7	71.4% - Coal 23.8% - Coke 4.8% - Gas	4.52	6.1	EPA Method 7E 9/19/91	23
Paulding, OH	1 & 2	Wet	30	45.3% - Coal 2.5% - Coke 52.2% - WDF	5.3	3.6	EPA Method 7E 5/25/82	24

CEM = Continuous emissions monitor; WDF - waste derived fuel; LWDF - liquid waste derived fuel; SWDF - solid waste derived fuel; either WDF or SWDF can include waste tires

TABLE 4-2. NO_x EMISSIONS DATA USED TO DEVELOP 1994 ACT DOCUMENT (continued)

Location	Kiln #	Kiln type	Capacity (tons/hr)	Fuel burned	Heat in MM Btu/ton	NO _x emissions (lb/ton clinker)	Method and date of data	Reference
Whitehall, PA	3	Four-stage preheater	36	70% - Coal 30% - Coke	3.3	4.24	EPA Method 7E Dec-91	25
				90% - Coal 10% - Tire		3.2		25
				80% - Coal 20% - Tire		3.3		25
				70% - Coal 30% - Tire		4.1		25
New Braunfels, TX	1	Preheater- Precalciner	122	50.2% - Coal 40.7% - Coke 9.1% - Gas	3	4.15	EPA Method 7E 3/90-5/90	26
7. Lehigh Portland Cement Co.								
Leeds, AL	1	Preheater	83	89% - Coal 11% - Gas	3.76	3.46 - Mill off 2.24 - Mill on	5/23/91 5/21/91	27
Cementon, NY	1	Wet	77	100% - Coal	5.25	5.9	5/22/90	27
Buda, TX	1	Precalciner	138	95% - Coal 5% - Gas	3.63	3.8	6/30/86	27

CEM = Continuous emissions monitor; WDF - waste derived fuel; LWDF - liquid waste derived fuel; SWDF - solid waste derived fuel; either WDF or SWDF can include waste tires

TABLE 4-2. NO_x EMISSIONS DATA USED TO DEVELOP 1994 ACT DOCUMENT (continued)

Location	Kiln #	Kiln type	Capacity (tons/hr)	Fuel burned	Heat in MM Btu/ton	NO _x emissions (lb/ton clinker)	Method and date of data	Reference
Waco, TX	1	Wet	10	68% - Gas 32% - Coke	8.8	17.1	12/5/85	27
8. Lone Star Industries								
Oglesby, IL	1	Dry	64.6			8	CEM 5/92-6/92	28
						7.2	EPA Method 7 12/13/83	28
Greencastle, IN	1	Wet	91.7			5	CEM	28
Cape Girardeau, MO	1	Precalciner	139.4			1.4 (178 ppm)	CEM 4/13/92	28
	1	Precalciner	139.4			0.9 (115 ppm)	CEM 4/15/92	28
	1	Precalciner	139.4			1.5 (182 ppm)	CEM 6/25/92	28
Sweetwater, TX	3	Preheater	20.8			11.68	EPA Method 7 Apr-May 1991	28

CEM = Continuous emissions monitor; WDF - waste derived fuel; LWDF - liquid waste derived fuel; SWDF - solid waste derived fuel; either WDF or SWDF can include waste tires

TABLE 4-2. NO_x EMISSIONS DATA USED TO DEVELOP 1994 ACT DOCUMENT (continued)

Location	Kiln #	Kiln type	Capacity (tons/hr)	Fuel burned	Heat in MM Btu/ton	NO _x emissions (lb/ton clinker)	Method and date of data	Reference
9. Southdown, Inc.								
Brooksville, FL	1	Preheater	80	100% - Coal	3.2	3	CEM Feb-92	29
Fairborn, OH	1	Preheater	85	80% - Coal 20% - LWDF	3.9	11	CEM Dec-91	29
Knoxville, TN	1	Preheater- Precalciner	80	75% - Coal 12% - LWDF 13% - SWDF	3.6	7	CEM Jan-91	29

CEM = Continuous emissions monitor; WDF - waste derived fuel; LWDF - liquid waste derived fuel; SWDF - solid waste derived fuel; either WDF or SWDF can include waste tires

The kilns with mid-kiln firing reported much greater NO_x emissions ranging from 9 to 18.3 lb/ton of clinker, whereas other waste-fuel burning wet kilns reported much lower NO_x emissions ranging from 3.6 to 8.1 lb NO_x/ton of clinker. NO_x emissions data from these kilns prior to introducing waste fuels, however, were not available to directly assess the effect of waste fuel burning on NO_x emissions.

The long dry kilns consume significantly less energy than wet kilns (about 4.5 MM Btu/ton on average) and produce less NO_x emissions in the range of 6.1 to 10.5 lb NO_x/ton of clinker with an average of 8.6 lb NO_x/ton of clinker. The wet and long dry kilns are similar in terms of structure and firing of fuels. The difference in the NO_x emission rates may thus be attributed to the difference in the energy consumption rates in these two types of kilns.

The preheater kilns reported NO_x emissions in the range of 2.5 to 11.7 lb NO_x/ton of clinker with an average of 5.9 lb NO_x/ton of clinker. The high values of 8.1 and 11.7 were incidentally found in gas burning kilns. As expected, the energy consumption of preheater kilns was much lower, about 3.8 MM Btu/ton. In addition, combustion of a part of the fuel at a lower preheating temperature is expected to reduce the NO_x emissions as compared to burning all the fuel in the hot kiln burning zone. These two factors account for the lower NO_x emissions in preheater kilns as compared to wet or long dry kilns.

The precalciner kilns produced the least NO_x emissions ranging from 0.9 to 7.0 with an average of 3.8 lb NO_x/ton of clinker. These kilns are the most energy efficient with an average energy consumption of 3.3 MM Btu/ton of clinker. Precalciner kilns have lower NO_x emission rates because they burn more fuel at the calcining temperature.

There have been many changes in the six years since the 1994 ACT document was published. One of the most interesting from an emissions estimation perspective is the increased use of continuous emissions monitors (CEM) on cement kilns. In January 2000, the PCA and PCA provided results of a survey of cement facilities where the respondents indicated 46% of the operating U.S. kilns (74 kilns) have already installed a CEMS (81% of the facilities representing 81% of the operating U.S. kilns responded to the survey). The remaining 87 kilns that are represented by the survey have not installed a CEMS.^{30,31} CEMS record NO_x measurements at closely spaced intervals. These measurements are accumulated and averaged by a process control computer at preset time intervals. CEMS data provide a better estimation of average NO_x emissions from cement kilns than do short-term tests because of the high degree of variability in NO_x emissions and autocorrelation between sequential NO_x measurements.³²

Eight state air pollution control agencies were asked to provide NO_x emissions data for their kilns. These data were supplemented with additional test data, and industry literature to determine average uncontrolled emission rates for the four kiln types.³³ These most recent data are summarized in Table 4-3. The emissions data from the state agencies are primarily from CEMS and are the reported annual emissions for the facilities. Most of the states did not report production values (because they tend to be confidential) so kiln capacities⁵ were used to

determine emission rates. The kilns were also assumed to operate for an average of 8,000 hours per year. In addition, most of the state agencies did not provide additional information on any NO_x control measures that may have been implemented (e.g., low-NO_x burners). The resulting average emission rates are generally lower than the average emission rates calculated in 1994 or presented in AP-42. The lower numbers are probably a result of using kiln capacities rather than actual kiln production values but may also be a result of assumptions regarding the installation of NO_x control devices (approximately 14% of the operating U.S. kilns have installed low-NO_x burners - see section 5.2.1.2).^{30,31}

TABLE 4-3. SUMMARY OF ADDITIONAL NO_x EMISSION DATA
FOR DIFFERENT KILN TYPES

Cement kiln type	Average rate (lb/ton of clinker)	Range of rates (lb/ton of clinker)	Number of Data Points
Wet kiln	6.2	1.9 - 13.4	10
Long dry kiln	4.5	2.5 - 7.1	6
Preheater kiln	1.7	0.4 - 3.7	6
Precalciner kiln	2.9	1.1 - 5.6	12

All of the literature and data gathered indicate substantial spread in the reported NO_x emissions with significant overlap for different kiln types. Table 4-4 compares the NO_x emission rates from the 1994 ACT document, AP-42, and the data recently collected from the State air agencies. The four different cement kiln types, however, do appear to have different levels of NO_x emissions and different characteristics influencing NO_x formation. As shown, the rates calculated from the State data are generally lower than the values calculated during development of the 1994 ACT document. The new data are not necessarily more representative than the 1994 ACT document data. The lower rates derived from the new data probably result from the assumptions made regarding kiln production and level of NO_x control. It should be noted that the lower emission rates derived from the new data for preheater kilns relative to precalciner kilns is contrary to expectation and could be due to the lack of data points for preheater kilns. The AP-42 factors are also lower than the 1994 ACT document rates but are primarily based on short term emission tests, which do not capture the inherent variability of kiln NO_x emissions, and the data are all over 10 years old. When one reviews the original data summarized in the 1994 ACT document, the maximum or minimum NO_x emission rate for a specific kiln type is about equally greater or less than the calculated average. Because the data used to calculate the 1994 ACT document NO_x emission rates are newer, these average emission rates may be more representative of modern kilns than the factors presented in AP-42.³⁴

TABLE 4-4. COMPARISON OF EMISSION RATES

Kiln Type	Emission Rate (lb NO _x /ton clinker)		
	1994 ACT	AP-42	New Data
Wet	9.7	7.4	6.2
Long dry	8.6	6.0	4.5
Preheater	5.9	4.8	1.7
Precalciner	3.8	4.2	2.9

The emission data compiled for the 1994 ACT document will be used in estimating uncontrolled emissions from typical cement kilns because these data are newer and include more CEMS data than the data used in AP-42; the NO_x emission rates derived in AP-42 have a “D” quality rating (based on number of tests and variability of emissions from the process); and the data collected from the state agencies are less certain because of lack of production data. These data are presented in Table 4-5. This table also includes the heat input requirement for the different cement kiln types which indicates a good correlation with the NO_x emission rates.

TABLE 4-5. NO_x EMISSION FACTORS FOR DIFFERENT KILN TYPES

Cement kiln type	Heat input requirement (MM Btu/ton of clinker)	Average NO _x emission rate (lb/ton of clinker)	Range of NO _x emissions (lb/ton of clinker)
Wet kiln	6.0	9.7	3.6-19.5
Long dry kiln	4.5	8.6	6.1-10.5
Preheater kiln	3.8	5.9	2.5-11.7
Precalciner kiln	3.3	3.8	0.9-7.0

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5.0 NO_x CONTROL TECHNIQUES

As discussed in Chapter 4, nitrogen oxides (NO_x) 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 as shown in Table 4-6. 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/ton of 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 over-burning of clinker and improvement in gas-solids heat transfer. Continuous emissions monitoring of CO, NO_x, and O₂ 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 applicable to the cement industry may be grouped in three categories:

1. Process modifications where the emphasis is on increased energy efficiency and productivity (section 5.1);
2. Combustion control approaches where the emphasis is on reducing NO_x formation (section 5.2); and
3. NO_x reduction controls which remove the NO_x formed in the combustion process (section 5.3).

Section 5.4 provides a discussion of the technologies supporting the recent selection of Best Available Techniques (BAT) for NO_x control at European cement kilns. Section 5.5 gives a summary of the applicable NO_x control technologies, and section 5.6 provides the references for this entire chapter.

5.1 PROCESS CONTROL 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.¹

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.

5.1.1 Combustion Zone Control of Temperature and Excess Air

Continuous monitoring of O₂ 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 1430 to 1540 °C (2600 to 2800 °F) for completion of clinkering reactions and to maintain the quality of the cement produced.² The corresponding gas-phase temperature is usually greater than 1700 °C (3100 °F).³ 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 1 to 2 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 2 to 1 percent) NO_x emissions per unit time can be reduced by approximately 15 percent.^{4,5}

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.

5.1.2 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.⁶ 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.

5.1.2.1 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/ton of clinker for every 1 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.

5.1.2.2 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 CO₂ emissions.⁷

Eleven facilities are using or in the process of incorporating CemStar.⁸ 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.⁷

According to the 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 2610°F to 2405°F); the lower gas temperature of the flame results in lower NO_x emissions.⁹ Another test

of CemStar technology found an average reduction in burn zone temperature of 160° F, a six percent reduction.⁹ The amount of NO_x emissions reductions achievable with CemStar varies by kiln type but ranges from over 20 to 60 percent.⁷ 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/ton of 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 5-1).

TABLE 5-1. RESULTS OF SHORT-TERM CEMSTAR TESTS ON A PREHEATER/PRECALCINER KILN

	Poor Quality Feed Mix (lb NO _x /ton of clinker)	Percent Reduction ^a (%)	Ideal Quality Feed Mix (lb NO _x /ton of 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/ton of clinker, and the long-term tests (approximately two and a half months) found reductions of 24 percent (see Table 5-2).⁷

Kilns with lower initial baseline NO_x emissions would have less NO_x reductions 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.⁷

TABLE 5-2. RESULTS OF CEMSTAR TESTS ON A WET KILN

	Test 1 (lb NOX/ton of clinker)	Test 2 (lb NOX/ton of clinker)	Percent Reduction ^a (%)
<i>Short-Term Test</i>			
Without CemStar	17.53	24.7	-
With CemStar	11.24	no 2 nd test	test 1 = 36 test 2 = 55
<i>Long-Term Test</i>			
Without CemStar	5.23	no 2 nd test	-
With CemStar	4.00	no 2 nd test	24

^a Percent reductions are relative to the emissions rate without CemStar during the same test period.

5.1.3 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.^{10,11} 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.¹⁰ In the dry process kilns tested in this study the average NO_x emissions decreased from 20.4 lb/ton of clinker to 6.2 lb/ton of 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.¹²

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 sulphate 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.¹³

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, petroleum coke cannot be burned alone because it does not provide enough volatile matter.¹⁴

5.1.4 Increasing Thermal Efficiency

The thermal efficiency of the cement-making process may be increased by improving gas/solids heat transfer, e.g., using an efficient chain system, increasing heat recovery from clinker cooler, and by minimizing infiltration of cold ambient air leaking into the kiln. Heat recovery from a clinker cooler may be improved by increasing the proportion of secondary air. Recycling cement kiln dust from the dust collectors would reduce the energy requirement per ton of a clinker. By increasing the thermal efficiency, NO_x emissions are reduced per ton of clinker produced.

5.2 COMBUSTION MODIFICATION

Combustion modifications are generally applicable to all types of kilns and are 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.

5.2.1 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.

5.2.1.1 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.¹⁵ 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 the providing the required heat (Btu/ton of 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.¹³

Coupling a low- NO_x step burner with flue gas recirculation has been shown to reduce NO_x emissions further in a cement kiln.¹⁶ The additional NO_x reduction attributable to FGR was estimated to be about 15 to 38 percent depending upon the proportion of FGR used.¹⁶ Incorporation of FGR in a cement kiln also results in somewhat increased power consumption and reduced kiln output.

5.2.1.2 Low- NO_x Burners

Some cement kiln burners, specifically marketed as low- NO_x burners, typically use 5 to 7 percent primary air^{17,18} 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

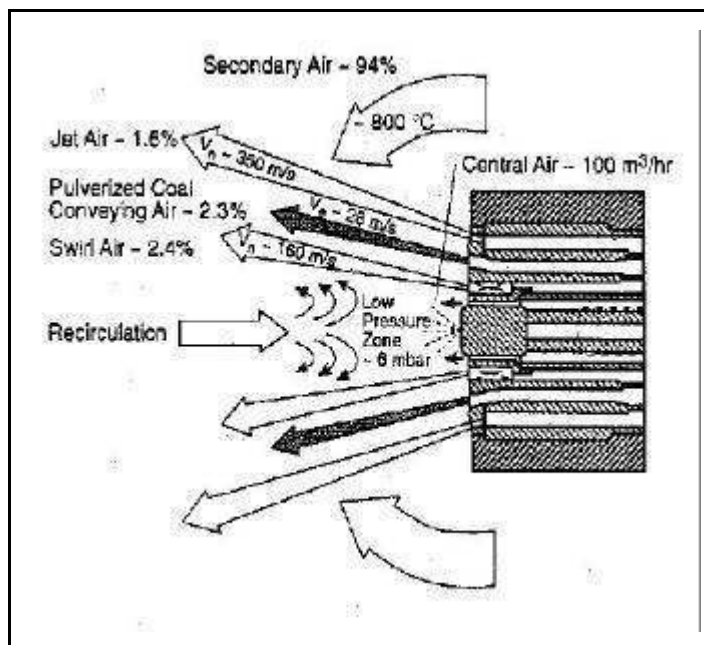


Figure 5-1. Schematic of low- NO_x burner.¹⁷

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, as shown in Figure 5-1,¹⁷ 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.^{17,19,20}

Low-NO_x burners have been used by the cement industry for twenty years.²¹ 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.²² 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).²² 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 5-3).

TABLE 5-3. NO_x EMISSIONS FROM A PRECALCINER EQUIPPED WITH A LOW-NO_x BURNER

Percent Coal Added to Reduction Zone ^a (lb NO _x /ton of clinker)	NO _x Emissions ^b (lb NO _x /ton of clinker)	Percent Reduction ^b (%)
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/ton of 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/ton of 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 5-4).²¹ The emission reductions ranged from 15 to 33 percent. Information on kiln-type was not provided.

TABLE 5-4. 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 5-5).²³ The emission reductions ranged from 23 to 47 percent. Information on kiln-type was not provided.

TABLE 5-5. 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 5-6).²⁴ The average emissions decreased 14 percent.

TABLE 5-6. EMISSIONS BEFORE AND AFTER INSTALLATION OF A ROTAFLAM® BURNER ON A WET KILN

Year	Average Emissions (lb NO _x /ton of 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 NO_x/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.²⁵

In January 2000, the PCA and 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.^{26,27}

5.2.2 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 (1100 to 1650 °F) which is much lower than the kiln's clinker-burning temperature of 1200 to 1480 °C (2200 to 2700 °F).²⁸ 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.

5.2.2.1 Preheater/Precalciner and Tire Derived Fuel

This concept of a secondary firing zone is the basis of the preheater/precalfiner cement kiln design. Almost all new cement kilns have a preheater/precalfiner-type designs. In the preheater kilns, the primary emphasis is on efficient heat recovery from kiln exhaust gases (see

Figure 5-2).²⁹ However, up to 15 to 20 percent of the fuel may be fired in the riser duct in preheater designs.²⁹

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 5-3).²⁹ 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.

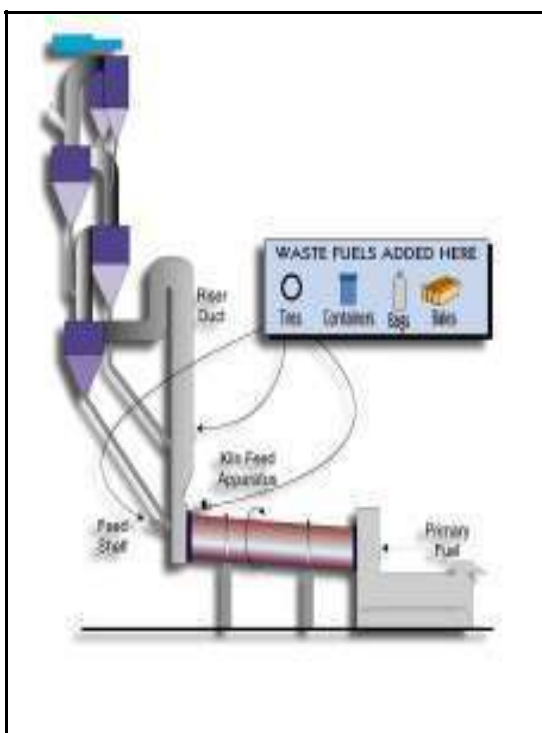


Figure 5-2. Schematic of preheater.²⁹

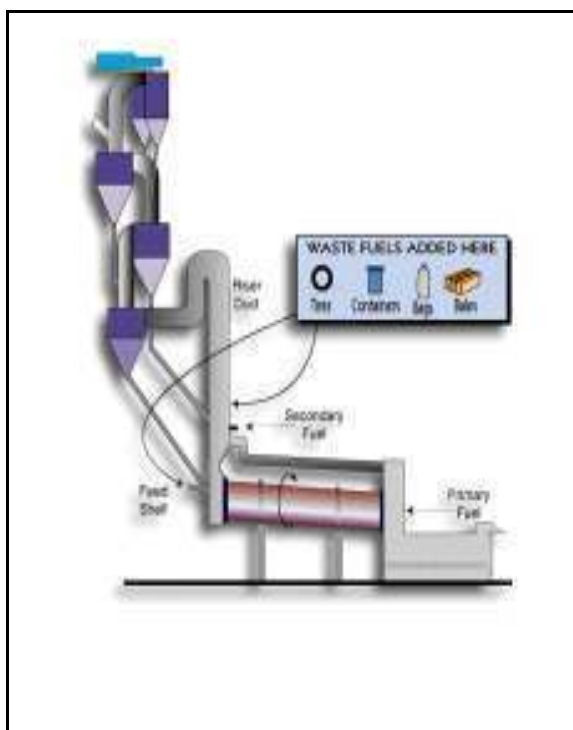


Figure 5-3. Schematic of precalciner.²⁹

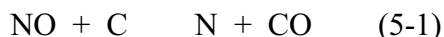
Tire-derived fuel can also be added to the feed end of a preheater or precalciner kiln. The Mitsubishi Cement Company's Cushenbury Plant in Lucerne Valley, CA began using whole waste tires as a fuel supplement in 1993. The waste tires are delivered in enclosed container trucks and dumped into the plant's 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 2 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.^{30,31,32}

5.2.2.2 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, as illustrated in Figure 5-4.³³ This fuel is burned in a sub-stoichiometric O₂ environment to create a strongly reducing atmosphere (relatively high concentrations of CO) by following the simplified reactions:



and



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 O₂ 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.¹³ Up to 46 percent reduction of NO_x emissions have been reported without causing excessive coating difficulties in the kiln.³³

As discussed in Section 4.2.2, 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 which depends upon the nitrogen content of the fuel used. In order for the above reactions (5-1) and (5-2) 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.³⁴

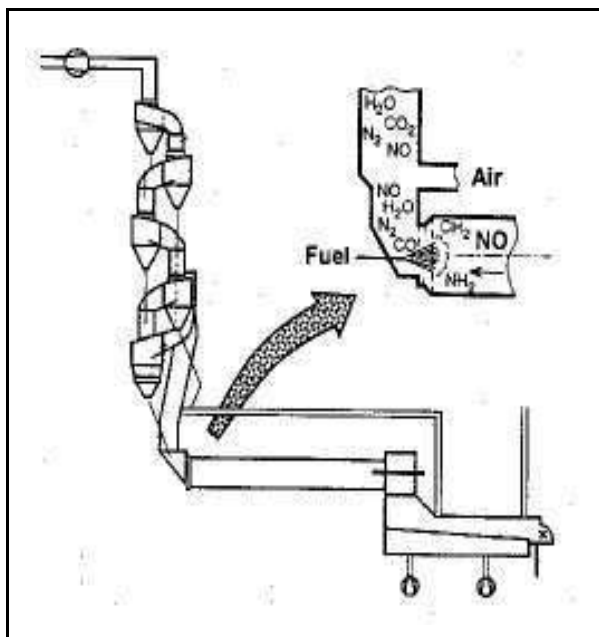


Figure 5-4. Reduction of NO_x emissions from precalcining kiln system by fuel injection in the rotary kiln gas outlet.³³

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.¹³

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.³⁵

5.2.2.3 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.³⁶ 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).²⁸

To maintain a 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 models 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.³⁷ Due to the rotation of the kiln, fuel can be conveniently injected only once per revolution from the top, as shown in Figures 5-5²⁹ and 5-6.³⁸

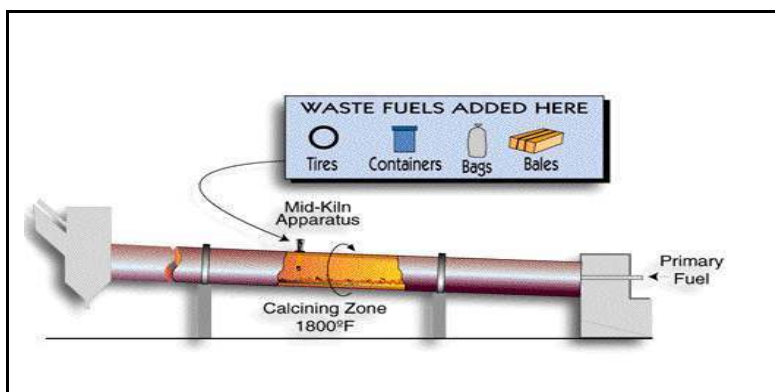


Figure 5-5. Schematic of mid-kiln firing.²⁹

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 dementionalized into discrete fuel modules to be fed to the kiln using the feed fork.³⁷

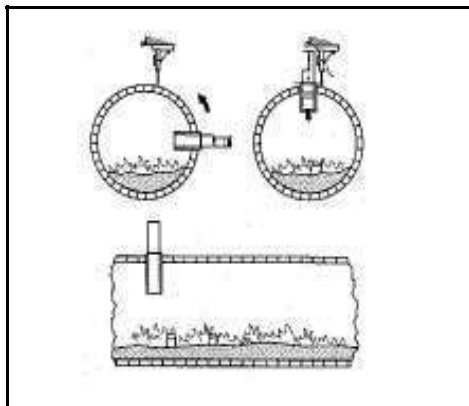


Figure 5-6. Schematic of fuel injection in kiln.³⁸

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 mid-kiln.³⁹

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.^{37,39}

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.³⁸ 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.⁴⁰

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%.^{37,39} 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 40%, with a range from 28% to 59% (see Table 5-7).^{40,41,42,43,44} It should be noted that the three kilns that are known to have CEMS all reported emissions reductions of 45 percent or more.

TABLE 5-7. EMISSIONS FROM KILNS WITH MID-KILN FIRING

	Emissions (lb NO _x /ton of 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 Mid-kiln 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.^{37, 45}

5.3 NO_x REMOVAL CONTROLS

NO_x removal controls are intended to destroy NO_x that is formed in the combustion process. Selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR) are described; however, SCR has not been demonstrated on any cement kilns in the United States at

this time. There have been two demonstrations of SNCR in the United States and there are 18 actual full-scale installations of SNCR for cement kilns in Europe. Biosolids injection technology is not technically SNCR, but the chemistry and the principles of its operation are similar. For this reason it is discussed with the other NO_x removal controls.

5.3.1 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 in Japan to achieve a 90 percent reduction in NO_x emissions from fossil fuel-fired boilers.⁴⁶ In the United States SCR technology has successfully been used for gas turbines, internal combustion engines, and utility boilers.⁴⁶

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



and



Equation (5-3) 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 (TiO₂) and vanadium pentoxide (V₂O₅) mixtures are most commonly used as catalysts due to their resistance to SO_x poisoning.^{47,48} Zeolite-based catalyst materials have also been developed capable of operating at higher temperatures than conventional metal based catalysts.⁴⁸ 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 300 to 450 °C (570 to 840 °F). This temperature 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.

Ammonia is typically injected to produce a NH₃: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 unreacted ammonia in the gases leaving the reactor.⁴⁹ The NO_x destruction efficiency depends upon the temperature, NH₃: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 alkalies and lime as well as sulfur dioxide in the exhaust gases is also of concern. Because of fouling problems, the SCR system must be installed after the particulate collection device. Recent developments have led to sulfur tolerant SCR catalysts which limit SO_2 oxidation to less than 1 percent.⁵⁰ 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 dedusting, resulting in additional cost. High dust systems are considered preferable for technical and economical reasons.¹ Up to now SCR has only been tested on preheater and semi-dry kiln systems, but it might be applicable to other kiln systems as well.¹

Pilot plant trials on small portions (three percent) of the exhaust gas have shown promising results in Austria, Germany, Italy, and Sweden. There are at least three suppliers in Europe that offer full scale SCR to the cement industry with performance levels of 100 to 200 mg/m^3 (approximately 0.2 to 0.4 lb/ton of clinker).¹ A full-scale SCR demonstration plant is being built in Germany with governmental financial support; a full-scale SCR plant is also under consideration in Austria.¹

There are currently no installations of SCR units in any United States cement plants. In 1976, Hitachi Zosen, an SCR manufacturer, conducted three pilot test programs to evaluate SCR on cement kilns.³ During these tests, two suspension preheater kilns and a wet process kiln were tested for 5,400 hours each. Electrostatic precipitators were used to remove particulates before the flue gas entered the SCR unit. Also, a heat recovery system equipped with supplemental fuel firing was provided to raise the flue gas temperatures to the required reaction temperatures. Slipstreams of about 3,000 scfm were treated with initial NO_x removal efficiencies of 98 percent. However, after 5,400 hours of operation, NO_x removal efficiencies dropped to about 75 percent due to catalyst coating.

Full-scale production runs will have to be carried out in order to remove the technical and economic uncertainties related to upscaling of the SCR technique. The main uncertainties are related to the high dust concentration in the gases (up to 500 g/Nm^3 , approximately 1.0 lb/ton of clinker), the catalyst dust removal techniques, lifetime of catalysts, and total investment costs.¹ Feasibility studies have been carried out in Austria, Germany, the Netherlands, and Sweden. The estimated costs vary considerably, with the production costs and lifetime of the catalyst being major variables.¹ Based on the experience in other industries, NO_x reductions in the range of 80 to 90 percent are considered possible, regardless of kiln type.⁴⁶ However, further studies are needed to demonstrate the specific NO_x reduction in the cement kiln exhaust gas environment.

5.3.2 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 (5-3) and (5-4) as in the case of the SCR process. This approach avoids the problems related to catalyst fouling, as in SCR technology, but requires injection of the reagents in the kiln at a temperature between 870 to 1090 °C (1600 to 2000 °F). At these temperatures urea decomposes to produce ammonia which is responsible for NO_x reduction. In principle, any of a number of nitrogen compounds may be used, 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.

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 NO_x becomes significant. At lower temperatures, the rates of NO_x reduction reactions become too slow resulting in too much unreacted ammonia slip. The effective temperature window range can be lowered to about 700 °C (1300 °F) by the addition of hydrogen along with the reducing agent.⁵¹ Nalco Fuel Tech, the producer of the SNCR technology $\text{NO}_x\text{OUT}^{\text{®}}$, has also introduced $\text{NO}_x\text{OUT}^{\text{®}}$ 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. Because of the rotating nature of a long kiln, continuous injection of ammonia- or urea-based reagents is presently not 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 has not been used because of the rapid decomposition of such salts. Therefore, SNCR technology has not been applicable for long dry or wet kilns. However, Fuel Tech Inc. is currently evaluating dry dust or pellet injection methods for direct injection into kilns.⁵²

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, residence time, as well as ammonia and NO_x concentrations in the flue gas. Injection of ammonia at a $\text{NH}_3:3\text{NO}_x$ 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.⁴⁷ The 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 scale which is significant for sulfur-containing fuels. SNCR processes also appear to convert some NO to

N_2O .⁵³ 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.⁵⁴

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 bottom gas duct as shown in Figure 5-7.⁵⁵ 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.⁵⁵ 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.

Scheuer, of the Research Institute of the Cement Industry in Dusseldorf, 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 less promising at low NO emissions rates.^{13,56}

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 most common reagent used is 25% ammonia water.¹

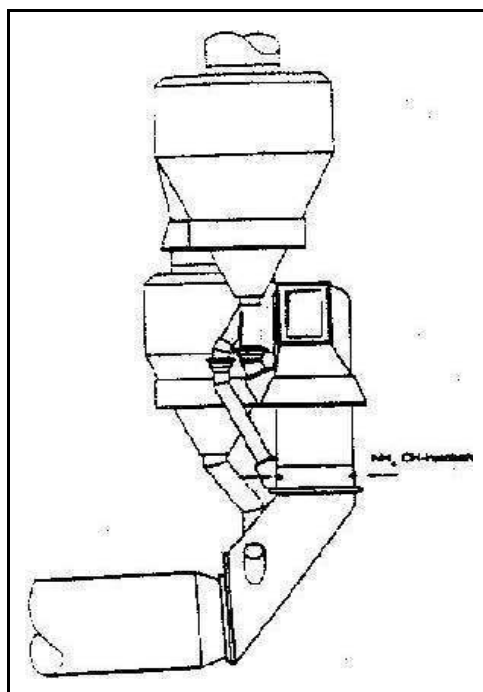


Figure 5-7. Application of SNCR in preheater kiln.

NO_x reduction rates vary from 10 to 50 percent with NH₃/NO₂ molar ratio of 0.5 to 0.9, NO_x emissions at these reductions are 2.4 to 3.8 lb/ton of clinker. Two dry process cyclone preheater/precalciner kilns in Sweden achieve 80 to 85 percent reduction (1.0 lb/ton of clinker) at a NH₃/NO₂ molar ratio of 1.0 to 1.1.¹

F. L. Smidth and Company tested SNCR on a preheater/precalciner kiln.³ 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 the United States, SNCR has been tested on two kilns. NO_xOUT[®] 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/ton of clinker to less than 1 lb NO_x/ton of clinker.^{57, 58} Another test of NO_xOUT[®] 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.⁵⁹ An evaluation of NO_xOUT[®] technology was conducted in 1994 for a long dry kiln in Southern California, but the study concluded that application of the NO_xOUT[®] technology at the subject kiln was technically infeasible.⁶⁰

5.3.2.1 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, 1996.¹³

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.⁶¹

The same conditions that affect NO_x reduction performance in SNCR affect BSI performance: temperature (927°C / 1700°F is optimal), residence time (> 0.5 seconds is desirable), inlet NO_x concentration, inlet CO concentration, and NH₃/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.⁶¹

The biosolids are injected into the mixing chamber where the flue gas stream leaving 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.⁶¹

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.⁶² Before the SNCR technology was adopted, the company estimated NO_x emissions averaged 2.4 pounds/ton of clinker; afterwards, the average fell to 1.2 lb/ton of 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.⁶¹

5.3.2.2 $\text{NO}_x\text{OUT}^\circ$

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 of $\text{NO}_x\text{OUT}^\circ$. 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 $\text{NSR}=2$; 80% reduction at $\text{NSR}=1.6$; 50% reduction at $\text{NSR}=1.0$, 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.⁵²

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). Proprietary additives have been developed by Nalco to widen the temperature window.⁶³ 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 $\text{NO}_x\text{OUT}^\circ\text{ PLUS}$, 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 tons clinker/hour. $\text{NO}_x\text{OUT}^\circ$ 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 O₂ (1.8 to 2.9 percent). The baseline NO_x levels varied from 350 to 550 lbs NO_x/hour. When NO_xOUT[®] 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%.⁵⁸

NO_xOUT[®] 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 NO_xOUT[®]. The baseline NO_x rate was approximately 350 lbs NO_x/hour. Using NO_xOUT[®], emission reductions of 10 to 20 percent were achieved.⁵⁹ 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 NO_xOUT[®] 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 1000 metric tons to 3200 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 5-8).⁵²

TABLE 5-8. EMISSION REDUCTIONS FROM TWO KILNS USING NO_xOUT[®]

	Baseline NO _x Emissions (ppm)	NO _x Emissions with NO _x OUT [®] (ppm)	Percent Reduction (%)
Kiln A, Test 1	412	203	51
Kiln A, Test 2	389	185	53
Kiln B	525	284	46

5.4 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 the 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.¹ 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/ton of 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/ton of clinker, for a cyclone preheater without heat recovery of 1.6 to 7.0 lb/ton of clinker, and for a grate preheater of 1.6 to 8.2 lb /ton of 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/ton of clinker respectively), but are less than those reported in the ACT document (5.9 and 3.8 lb/ton of clinker respectively).¹

Table 5-9 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.¹ There are no emissions data in the IPPC report for kilns with CemStar technology or mid-kiln firing. For low-NO_x burners, the IPPC report found a lower average NO_x emissions rate (1.6 lb/ton of clinker) than EC/R found in the new State data (8.98 lb/ton of 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).

TABLE 5-9. NO_x CONTROL TECHNIQUES SUMMARY FROM EUROPEAN BEST AVAILABLE TECHNIQUES REPORT¹

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% O₂.

^b kg/tonne clinker is based on 2000 m³/tonne of 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/ton of clinker (200-500 mg NO_x/m³ (as NO₂)). This emission level could be seen in context of the current reported emission range of 0.4 to 6.0 lb/ton of clinker (<200-3000 mg NO_x/m³), and that the majority of kilns in the European Union is said to be able to achieve less than 2.4 lb/ton of clinker (1200 mg/m³) with primary measures.¹

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/ton of clinker (500-800 mg NO_x/m³ (as NO₂)). There was also a view that selective catalytic reduction is BAT with an associated emission level of 0.2 to 0.4 lb/ton of clinker (100-200 mg NO_x/m³ (as NO₂)).¹

5.5 SUMMARY OF APPLICABLE NO_x CONTROL TECHNOLOGIES

Table 5-10 presents NO_x control techniques and the types of kilns on which they are applicable.

TABLE 5-10. NO_x CONTROL TECHNIQUES AND APPLICABLE TYPES OF CEMENT KILNS

NO _x Control Technique	Applicable Kiln Type			
	Wet	Long-Dry	Preheater	Precalciner
Process Control Systems	yes	yes	yes	yes
CemStar	yes	yes	yes	yes
Low-NO _x Burner ^a	yes	yes	yes	yes
Mid-Kiln Firing	yes	yes	no	no
Tire Derived Fuel ^b	yes	yes	yes	yes
SNCR	no	no	yes	yes

^a Low-NO_x burners can only be used on kilns that have indirect firing.

^b Tire derived fuel can be introduced mid-kiln in a wet or long-dry kiln, or at the feed end of a preheater or precalciner kiln.

Table 5-11 presents a comparison between the NO_x reductions identified in the 1994 ACT document and updated emissions data for various control technologies.

TABLE 5-11. COMPARISON OF 1994 ACT NO_x EMISSIONS REDUCTIONS
WITH NEWLY AVAILABLE EMISSIONS DATA

	1994 ACT ⁶⁴	Updated Emissions Data ⁶⁵			
	Possible NO _x Emission Reduction (%)	Average Emission Reduction (%) ^a	Range of Emission Reductions (%)	Average Emission Rate (lb NO _x /ton of clinker) ^a	Range of Emission Rates (lb NO _x /ton of clinker)
Process Control Modifications	<25				
CemStar	n/a	33	23 to 40	6.0	3.2 to 11.2
Indirect firing with a low-NO _x burner	20 to 30	27	4 to 47	9.0 ^b	9.0 ^b
MKF (wet kilns only)	20 to 40 ^c	41	28 to 59 ^d	n/a	n/a
MKF (dry kilns only)	20 to 40 ^c	33	11 to 55	3.9	2.0 to 10
TDF in a Precalciner ^e		35	30 to 40	2.4	2.4
SNCR	30 to 70	BSI ^e	50	1.2	1.2
		NO _x - OUT ^f	40	10 to 50	

n/a - not applicable

^a The average emission reduction and average emission rate were calculated using a simple (not weighted) average of the available data.

^b There was only one source that provided emission rate data for low-NO_x burners; the rest of the kilns with low-NO_x burners only provided percent reductions.

^c The 1994 ACT document provide one range of possible emission reductions for MKF at both wet and dry kilns.

^d At the time the kiln with the 59 percent emission reduction installed MKF, it also added a Linkman control system; the next largest percent emission reduction at a wet kiln from MKF was 35.0.

^e One facility in southern California provided emission reduction data for both biosolids injection (BSI) technology and firing tire derived fuel (TDF) in a precalciner.

^f The average emissions reduction for NO_xOUT[®] was estimated from the three tests/demonstrations described in 5.3.2.2.

Monitoring the temperature and excess air in the combustion zone as discussed in Section 5.1.1 provides optimum kiln operating conditions, which increase the energy efficiency and

productivity of the cement-making process while minimizing NO_x emissions. The NO_x reduction effect of other process modifications discussed in Section 5.1 is usually difficult to isolate from other factors. These measures can be highly site specific and data from one site cannot be directly translated to other sites. Quite often a number of process modifications and combustion control measures are implemented simultaneously. Process modifications can reduce NO_x emissions in cement kilns without any specific NO_x control equipment. Some plants rely on process monitoring and control and process modifications as a means to maintain NO_x emissions within their allowable limits.

The CemStar process described in Section 5.1.2.2 is being used or incorporated by 11 facilities in the United States. Several long-term and short-term tests of CemStar have found average NO_x emission reductions of 33 percent.

Combustion modifications to reduce NO_x emissions include the staged combustion of air and of fuel. Low-NO_x burner systems described in Section 5.2.1.2 rely on the staged combustion of air. Technical literature and industry publications report NO_x reduction rates of 4 to 47 percent with the installation of low-NO_x burners, depending on the baseline emissions, type of kiln, type of low-NO_x burner, and operating conditions.

As described in Section 5.2.2, staged combustion of fuel includes the use of preheaters/precalciners and mid-kiln firing. Mid-kiln firing of fuels is practiced in over 20 U.S. cement kilns and whole tires are most frequently used for the mid-kiln fuel. Data are available for several kilns that have used or tested mid-kiln firing demonstrating NO_x reductions ranging from 11 to over 59 percent.

The NO_x removal controls discussed in Section 5.3 include selective catalytic reduction, and selective noncatalytic reduction (biosolids injection and NO_xOUT). SCR technology has not been used on any cement kilns in the U.S., although pilot plant trials and feasibility studies have been conducted in Europe. The principles of SNCR technology are applicable to preheater/precalciner kilns. It is believed that SNCR would be difficult, if not impossible, to be used in wet and long dry process kilns due to problems in obtaining the right temperature and retention time. Two SNCR technologies, biosolids injection and NO_xOUT[®], have demonstrated NO_x emission reductions in cement kilns. Biosolids injection is being used on one kiln in Southern California and NO_xOUT has been demonstrated on two kilns in the U.S. SNCR technology is widely practiced in Europe.

5.6 REFERENCES

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6.0 COSTS OF NO_x CONTROL TECHNIQUES

This chapter presents the cost estimates for the NO_x emission control techniques discussed in Chapter 5. Section 6.1 presents the cost methodology used to develop capital and annual operating costs for these techniques. Based upon the distribution of the type of kilns used in the cement industry and their typical capacities, model plants were developed to perform cost calculations. Section 6.2 presents costs of selected incombustion and postcombustion control approaches. The cost effectiveness of different control approaches is discussed in Section 6.3. All costs presented in this chapter are in 1997 dollars.

6.1 COST CALCULATION METHODOLOGY

The cost calculation methodology is dependent upon the definition of model plants and the guidance provided by EPA in the OAQPS Control Cost Manual.¹ The definition of the model plants, calculation of capital costs and annual operating costs is presented in this section.

6.1.1 Model Plants

As discussed in Chapter 3, existing cement kilns in the United States may be grouped in four types: wet, long dry, preheater, and precalciner types. Coal is the most common fuel used in all types of kilns.² Several types of waste-derived fuels are being used in the portland cement industry to replace coal and reduce NO_x emissions. As seen from data presented in Chapter 4, the NO_x emissions from individual kilns expressed as lb NO_x/ton of clinker do not seem to depend on the kiln capacity. Therefore, only two capacities of the kilns of a given type are used to define model plants for each of the kiln types. Each of the four kiln types has typical energy consumption and NO_x emission rates as shown in Table 6-1 describing model plant parameters. The model plant kilns were assumed to be in continuous-duty operation and were assumed to operate 8,000 hours per year which allows scheduled downtime for maintenance operations.³ Although waste-derived fuels are finding increasing applications in cement kilns, coal provided more than 82 percent of the energy requirement of the cement industry.² Model plants were assumed to use 100 percent coal as a fuel and where available, a percentage of coal and waste-derived fuels (i.e., for mid-kiln firing 85% coal and 15% tire-derived fuel were used).

6.1.2 Capital Cost Estimation

The total capital investment is the sum of the direct cost (which is the purchased equipment costs and direct installation costs), indirect installation costs, contingency costs, sales taxes, freight, and production downtime. The purchased equipment costs (PECs) used in this chapter for each control technology are based on cost information provided by vendors or from data provided by existing facilities. Table 6-2 provides a list of various cost elements included in the capital costs. Where installation costs were not provided by vendors, direct and indirect installation costs were developed using the factors 45 and 33 percent, respectively, of PEC, per guidelines in the EPA OAQPS Control Cost Manual.¹ A contingency factor of 20 percent was

TABLE 6-1. CEMENT KILN MODEL PLANTS FOR COST CALCULATIONS

Model no.	Kiln type	Capacity (tons clinker/hr)	Heat input rate (MM Btu/ton clinker)	Uncontrolled NO _x emissions		Gas flow rate at stack location (dry std ft ³ /min)
				(lb/ton clinker)	(lb/hr)	
1	Wet	30	6.0	9.7	291	59,100
2	Wet	50	6.0	9.7	485	98,500
3	Long dry	25	4.5	8.6	215	38,500
4	Long dry	40	4.5	8.6	344	61,500
5	Preheater	40	3.8	5.9	236	53,200
6	Preheater	70	3.8	5.9	413	93,000
7	Precalciner	100	3.3	3.4	340	118,500
8	Precalciner	150	3.3	3.4	510	176,000

Average stack gas temperature ~150°C (300°F).

Average stack gas moisture content ~12%.

Average particulate loading in stack gas ~0.01 grains/dry std ft³.

added to the vendor costs in all cases to cover contingencies as listed in Table 6-2.¹ The capital costs of in-combustion approaches such as low NO_x burners and postcombustion approaches such as selective noncatalytic reduction are related to the clinker production capacity of the kiln as well as the energy requirement of the kiln per unit amount of clinker production.

6.1.3 Annual Operating Costs

Annual operating costs are composed of the direct operating costs of materials and labor for maintenance, operation, utilities, material replacement and disposal and the indirect operating charges, including plant overhead, general administration, and capital recovery charges.

Table 6-3 lists the typical values used for these costs. A brief description is provided below for each component of the direct annual operating costs used in the cost evaluation.

6.1.3.1 Utilities. The utility requirements for the control techniques consist of electricity and/or compressed air to power control instrumentation and auxiliary equipment and the energy requirements for vaporization and injection of ammonia for SCR systems. The cost for electricity and compressed air is considered to be negligible relative to the other operating costs.

The credit applied (tipping fee) for burning tires is an average value.⁴ Tire tipping fees are highly variable showing a large regional variation and large fluctuations in the market. The average tipping fee used in this analysis is within the 1997 range of \$20 to \$200 credit/ton of

tires provided by Waste News.⁵ A direct access of the Waste News - Current Commodity Pricing demonstrated a range in tipping fee credits of \$140 to \$75 in New York; \$125 to \$65 in Miami, Florida; \$100 to \$75 in Atlanta, Georgia; \$150 to \$75 in Houston, Texas; \$85 to \$75 in Chicago, Illinois; \$85 to \$20 in Denver, Colorado; \$100 to \$42 in Los Angeles, California; and \$200 to \$100 in Seattle, Washington.⁶

TABLE 6-2. CAPITAL INVESTMENT COMPONENTS FOR
EMISSION CONTROL DEVICE COST EVALUATION ¹

Capital Investment Cost Elements
<u>Direct costs (DC)</u> <ul style="list-style-type: none"> Purchased equipment costs (PEC): <ul style="list-style-type: none"> Control device and auxiliary equipment Instrumentation Direct installation costs (DIC) - 45 percent of PEC: <ul style="list-style-type: none"> Foundations and supports Handling and erection Electrical Piping Insulation for ductwork Painting
<u>Indirect installation costs (IIC) - 33 percent of PEC:</u> <ul style="list-style-type: none"> Engineering Construction and field expenses Contractor fees Startup Performance test Model study
<u>Contingencies (C) - 20 percent of PEC:</u> <ul style="list-style-type: none"> Equipment redesign and modifications Cost escalations Delays in startup
<u>Sales taxes (3 percent of PEC)</u>
<u>Freight (5 percent of PEC)</u>
<u>Production downtime (two days loss of production times average market value per ton of clinker)*</u>

* Average market value per short ton of clinker is \$72.59.⁷

TABLE 6-3. ANNUALIZED COST ELEMENTS AND FACTORS ¹

Direct annual costs (DC)	
1. Utilities:	
Coal ⁸	\$32.41 per short ton
Electricity ⁹	\$0.05 per kwh
Natural gas ¹⁰	\$3.59 per 1000 ft ³
Tires ¹¹	-\$42.50 per ton
2. Operating labor	
Operator labor ¹²	\$22.12 per hour
Supervising labor ¹	15 percent of operator labor
3. Maintenance^a	
Maintenance labor	\$24.33 per hour times 0.5 hours per 8 hour shift ^b
Maintenance materials	100% of maintenance labor
Indirect annual costs (IC)^a	
Overhead	60% of operating labor, supervisory labor, maintenance labor and materials
Property tax	1% of total capital cost
Insurance	1% of total capital cost
Administrative charges	2% of total capital cost
Capital recovery	capital recovery factor times total capital investment
TOTAL ANNUAL COST	DC + IC

^aReferences for costs are included in Section 6.1.3.

^bMaintenance labor is 1.1 times the operator labor.¹

6.1.3.2 Operating and Supervising Labor. No postcombustion NO_x control technologies were identified as currently operating on a cement kiln in the United States. Therefore, information for typical operating labor requirements from the cement industry was unavailable. A requirement of 0.5 hour of operator attention was assigned for an 8-hour shift, for

all technologies considered, regardless of the plant size. Operator wage rates were estimated to be \$22.12/hr in 1997.¹² Supervisory labor costs were estimated to be 15 percent of the operating labor costs consistent with the OAQPS Control Cost Manual.¹

6.1.3.3 Maintenance. Specific maintenance costs were not available from the control system vendors and manufacturers. The guidelines for maintenance costs in the OAQPS Control Cost Manual suggest a maintenance labor cost of 0.5 hours per 8-hour shift and a maintenance material cost equal to this labor cost.¹

6.1.3.4 Overhead. An annual overhead charge of 60% of the total maintenance cost was used, consistent with guidelines in the OAQPS Control Cost Manual.¹ As described above, the maintenance cost is 0.5 hours per 8-hour shift and a maintenance material cost equal to this labor cost.

6.1.3.5 Property Taxes. The property taxes were calculated as 1 percent of the total capital cost of the control system, as suggested in the OAQPS Control Cost Manual.¹

6.1.3.6 Insurance. The cost of insurance was calculated as 1 percent of the total capital cost of the control system, as suggested in the OAQPS Control Cost Manual.¹

6.1.3.7 Administrative Charges. The administrative charges were calculated as 2 percent of the total capital cost of the control system, consistent with the OAQPS Control Cost Manual.¹

6.1.3.8 Capital Recovery. In this cost analysis the capital recovery factor (CRF) is defined as¹:

$$CRF = i (1 + i)^n / ((1 + i)^n - 1) = 0.1098$$

where

i is the annual interest rate = 7 percent, and
n is the equipment life = 15 years.

The CRF is used as a multiplier for the total capital cost to calculate equal annual payments over the equipment life.

6.2 COSTS OF NO_x CONTROL APPROACHES

As discussed in Chapter 5, feasible NO_x control approaches include process modifications, combustion modifications, and NO_x removal controls. Process modifications include combustion zone control of temperature and excess air, feed mix composition, kiln fuel, and increasing thermal efficiency of the kiln. Combustion modifications include staged

combustion of air and staged combustion of fuel. NO_x removal controls that are presented include selective catalytic and noncatalytic reduction of NO_x using either ammonia or urea. This chapter includes costs for approaches and technologies that will reduce NO_x emissions and focuses on four technologies; changing the feed mix composition (CemStar), installation of a low NO_x burner (staged combustion of air), installation of a mid-kiln firing system (staged combustion of fuel), and noncatalytic reduction of NO_x using biosolids (biosolids injection).

6.2.1 Process Modifications

As discussed in Section 5.1, process modifications can be highly site specific and data from one site cannot be directly translated to other sites. Data are not available to determine costs of individual process modifications. Quite often a number of process modifications and combustion control measures are implemented simultaneously. Similar to combustion process control approaches, process modifications have also shown to reduce energy requirement and increase productivity, thus providing an economic incentive to implement them in addition to NO_x reduction.

6.2.1.1 Combustion Zone Control of Temperature and Excess Air. Approaches aimed at improving the energy efficiency of the process indirectly reduce NO_x emissions per ton of clinker product. These approaches rely on continuous monitoring of O₂ and CO and in some cases NO_x emissions for controlling the excess air, fuel rate, and the combustion zone temperature. These measures are usually undertaken to increase process energy efficiency by reducing over-burning of the clinker. Maintaining the combustion zone temperature to a necessary minimum value using process control systems minimizes both the process energy requirement and increases refractory life. Because continuous monitoring of emissions is necessary for efficient process control, the cost of monitors is not considered as a NO_x control cost. Further, the information obtained during this study indicated that some plants relied on process monitoring, including NO_x monitoring, as a means to maintain NO_x emissions within their respective permit limits.

Based on existing installations, the cost of a commercially available kiln process control system is in the neighborhood of \$750,000.¹³ The resulting savings due to reduced energy and fuel requirements and increased refractory life were estimated to be about \$1.37 per short ton of clinker. Thus, for a cement kiln facility producing 300,000 tons/year of clinker the reduced cost of producing cement is expected to recover process control installation costs in less than 2 years.

6.2.1.2 CemStar Process. As discussed in section 5.1.2.2, the CemStar process (which involves the substitution of steel slag for raw materials) reduces the kiln temperature in the region of the flame and results in lower NO_x emissions. In addition, because the chemical composition and structure of steel slag is similar to cement, the heat required to convert a ton of steel slag to clinker is substantially lower than the heat required to convert a ton of raw materials to clinker.¹⁴ The costs associated with installing this process are primarily material handling equipment for the steel slag. Cost information was obtained from TXI and are summarized in Table 6-4.¹⁵ The cost of the material handling equipment can range from \$200,000 to \$500,000.

TABLE 6-4. BASIS FOR COST ANALYSIS OF CEMSTAR (1997 \$)

Capital Cost of Material Handling Equipment	\$500,000
Type of Kiln	Wet
Primary Fuels	Coal and natural gas
Kiln Production Rate	
Before CemStar	42 tons/hour
After CemStar	45 tons/hour
Quantity of Steel Slag	3.2 tons/hour
Average kiln heat requirement	5.00 MMBtu/ton
Total Capital Investment	\$1,176,000
Annualized Cost ^a	\$220,000

^a Includes cost of steel slag, royalties, and credit for the reduction in raw materials.

CemStar model plants costs could not be developed because the addition of steel slag is completely plant dependant. There is no set ratio of steel slag injection to kiln production rate. The amount of steel slag needed depends on the plants raw materials. The ratio can vary anywhere from five to ten percent addition of steel slag, based on kiln production. For the example presented in this document, the addition of steel slag was 7.7 percent of the kiln production prior to production with the CemStar process. The addition of steel slag typically reduces the need for iron used in raw material feed. Monetary savings from the reduction in iron can range from \$0.5 to \$1.00 per ton of clinker produced. A reduction in shale and/or clay may also result from the addition of steel slag. The amount of shale and/or clay reduction varies based on each facilities raw materials. Depending on the raw material characteristics, the need for shale and/or clay may be eliminated. CemStar charges royalties that are paid by the facility installing the technology. The royalties are approximately \$16 per ton of steel slag used.¹⁶

Cost savings associated with the CemStar process are based on production increase with the addition of steel slag compared to the cost benefit. Due to steel slag addition you get approximately one ton of clinker per ton of steel slag added. Steel slag cost \$5-15 per ton,¹⁵ whereas clinker cost \$72.59 per ton. Average cost savings equals \$62.59 per ton times increase in production. Most plants increase production by five to ten percent with the addition of the CemStar process.

6.2.2 Combustion Modifications

As discussed in section 5.2 there are several combustion modifications that can be implemented to reduce NO_x emissions. This section presents costs for low NO_x burners (staged combustion of air) and mid-kiln firing (staged combustion of fuel).

6.2.2.1 Low NO_x Burners. Cement kiln burners, specifically marketed as low NO_x burners, require an indirect-fired kiln system. Therefore, to install a low NO_x burner in an existing direct-fired kiln, it is necessary to convert the kiln-firing system to an indirect firing system. Two sets of costs are therefore developed: (1) to install a low NO_x burner in an existing indirect-fired kiln, and (2) to install a low NO_x burner in an existing direct-fired kiln. In the first case, only the costs of the low NO_x burner equipment are considered, whereas in the second case the costs of conversion of a direct-fired system to an indirect-fired system are added to the low NO_x burner cost.

Information was obtained from a supplier of low-NO_x burners regarding costs and heat duty.¹⁷ The cost of a burner depends upon the size or heat duty as well as on the number of different types of fuels that can be burned, e.g., only coal, or coal and gas, or coal, waste-derived liquid fuel and gas. The cost also depends on whether the burner is being installed in a new plant or is a retrofit in an older plant. The PEC of a low NO_x burner retrofit using coal as a fuel is typically about \$100,000 for a 200 MM Btu/hr heat duty. For a multi-channel burner the cost is higher. The capital cost of a multi-channel retrofit low NO_x burner is about 100 percent greater than that for a single channel burner for the same heat duty.

From the limited available data a linear correlation ($R^2 = 0.98$) developed for an approximate purchase cost for a retrofit application as a function of heat duty is given as:

$$PEC = 172,000 + 152 \quad H$$

where

PEC = Multi-channel low NO_x burner purchase equipment cost in \$, and
H = Burner heat duty in MM Btu/hr.

The cost of a single channel low NO_x burner is obtained by dividing the PEC of a multi-channel burner by 2.

For each model plant described in Table 6-1 purchase equipment costs for multi-channel burners were determined based on the heat duty needed by the kiln. For wet, long dry, and preheater kilns all the required heat is assumed to be provided by the low NO_x burner, whereas for precalciner kilns only 60 percent of the heat duty is assumed to be provided by the low NO_x burner at the hot end of the kiln. The capital costs for retrofitting the eight model plants described in Table 6-1 in an existing indirect-fired kiln are given in Table 6-5. Direct installation, indirect installation, and contingency costs were assumed to be 45, 33, and 20 percent, respectively, as discussed in Section 6.1.2. The capital costs of retrofit low NO_x burners for the eight model plants ranged from \$473,000 for the small long dry kiln to \$966,000 for the large preheater/precalciner kiln. The capital costs for retrofitting on a wet kiln compare well with the \$500,000 total installed cost estimated by a cement company.¹⁸

The annualized costs for low NO_x burners in an existing indirect-fired kiln are presented in Table 6-6. No additional costs for utilities were deemed necessary for NO_x control purposes. As described in section 6.1.3, 0.5 hours of operating labor were added per 8-hour shift and maintenance costs were estimated as 0.5 hours of labor per 8-hour shift with maintenance material costs equal to this labor cost. Indirect annual costs were determined as described in Section 6.1.3. The total annualized costs for the eight low NO_x burner retrofits ranged from a low of \$130,000/year for the small long dry kiln to a high of \$204,000/year for the large preheater/precalciner kiln.

Conversion of a direct-fired kiln to an indirect-fired kiln reduces the amount of primary air and increases the proportion of secondary air input to the kiln. The total cost to convert an existing dry process facility with two kilns, with a combined 100 tons/hr clinker capacity and a 225 MM Btu/hr heat duty, was \$5.6 million in 1998.^{19,20} The equipment list included a Pfister coal metering system, coal mill dust collector, Pillard burner and trolley, coal fire detection system, carbon dioxide inerting system, coal conveying blowers, pulverized coal bins, pulverized coal bin dust collector, instrumentation, primary air fan, and ductwork. Using the data provided by the facility and the cost calculation methodology presented in section 6.1 (which adds 8 percent PEC cost for sales tax and freight, 45 percent PEC cost for direct installation, 33 percent PEC cost for indirect installation, and 20 percent PEC cost for contingencies) the total installed capital cost is estimated at \$3.8 million (in 1997 dollars). The actual cost of \$5.6 million (in 1998 dollars) for the same facility includes \$2.3 million for contractor engineering and project management. When the costs are adjusted to include engineering and project management as part of the indirect installation costs¹ (approximately \$550,000), there is agreement between the two estimates.

Since the \$3.8 million equipment cost estimate was for two parallel systems, the cost of one conversion system to process coal for a 50 ton/hr dry facility²¹ was considered to be \$1.88 million in 1997 dollars. The amount of coal processed is proportional to heat requirement. For a dry process, the energy requirement is approximately 4.5 MM Btu/ton. Therefore, the cost of

TABLE 6-5. CAPITAL COSTS FOR RETROFIT LOW-NO_x BURNERS IN AN EXISTING INDIRECT-FIRED KILN (1997 \$)

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	PEC (\$)	Freight and sales tax (\$)	Installation costs \$		Contingency costs (\$)	Production Downtime (\$)	Total capital costs (\$)
						Direct	Indirect			
1	Wet	30	180	198,000	16,000	89,000	65,000	40,000	105,000	511,000
2	Wet	50	300	216,000	17,000	97,000	71,000	43,000	174,000	618,000
3	Long dry	25	113	187,000	15,000	84,000	61,000	37,000	87,000	473,000
4	Long dry	40	180	198,000	16,000	89,000	65,000	38,000	139,000	546,000
5	Preheater	40	152	193,000	15,000	87,000	64,000	39,000	139,000	538,000
6	Preheater	70	266	210,000	17,000	95,000	69,000	42,000	244,000	678,000
7	Precalciner	100	330	200,000	16,000	90,000	66,000	40,000	348,000	761,000
8	Precalciner	150	495	215,000	17,000	97,000	71,000	43,000	523,000	966,000

TABLE 6-6. ANNUALIZED COSTS FOR RETROFIT LOW-NO_x BURNERS IN AN EXISTING INDIRECT-FIRED KILN
(1997 \$)

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	Maintenance costs (\$/yr)	Other labor (\$)	Overhead costs (\$/yr)	Taxes insurance admin. (\$/yr)	Capital recovery (\$/yr)	Total annualized costs (\$/yr)
1	Wet	30	180	24,400	12,700	22,200	20,500	56,200	136,000
2	Wet	50	300	24,400	12,700	22,200	24,700	67,900	152,000
3	Long dry	25	113	24,400	12,700	22,200	18,900	51,900	130,000
4	Long dry	40	180	24,400	12,700	22,200	21,900	60,000	141,000
5	Preheater	40	152	24,400	12,700	22,200	21,500	59,000	140,000
6	Preheater	70	266	24,400	12,700	22,200	27,100	74,400	161,000
7	Precalciner	100	330	24,400	12,700	22,200	30,400	85,600	173,000
8	Precalciner	150	495	24,400	12,700	22,200	48,600	106,000	204,000

firing system conversion to process coal to provide 225 MM Btu/hr equivalent energy is considered to be \$835,000. Cost of firing system conversion for other heat capacities was estimated using 0.6 power rule:

$$\frac{\text{PEC for model plant}}{835,000} = \left(\frac{\text{Heat requirement for model plant}}{225} \right)^{0.6}$$

This cost includes the PEC for installing a low NO_x burner. For each model plant described in Table 6-1 the PEC for the firing system conversion as well as for the multi-channel burner was determined based on the heat duty needed by the kiln. For wet, long dry, and preheater kilns all the required heat is assumed to be provided by the low NO_x burner, whereas for precalciner kilns only 60 percent of the heat duty is assumed to be provided by the low NO_x burner at the hot end of the kiln. The capital costs for retrofitting the eight model plants in an existing direct-fired kiln are given in Table 6-7. The capital costs ranged from \$1.21 million for the small long dry kiln to \$2.54 million for the large precalciner kiln.

The annualized costs for low NO_x burners in an existing direct-fired kiln are presented in Table 6-8. Operating labor was assumed to be 0.5 hour per 8-hour shift. Maintenance labor costs were assumed to be 0.5 hour per 8-hour shift and maintenance materials were assumed to be equal to 100% of the maintenance labor cost. The total annualized costs for the eight low NO_x burner retrofits in existing direct-fired kilns ranged from \$241,000 for the small dry kiln to \$439,000 for the large precalciner kiln. These values agree well with the costs, of converting a direct fired kiln to an indirect fired kiln and installing a low-NO_x burner, presented in the 1994 ACT.^{18,22,23}

6.2.2.2 Mid-Kiln Firing As discussed in Section 5.2.2.2, secondary combustion of fuel reduces thermal NO_x formation in cement kilns. Modification of a long kiln for secondary combustion of fuel is termed mid-kiln firing. The amount of fuel NO_x generated during the secondary combustion determines the net effectiveness of this technique for NO_x control. The costs associated with this process are those for kiln modifications necessary to facilitate secondary combustion of fuels as well as those for a conveying system required for the secondary fuel. Mid-kiln firing is now a proven technology with twenty one cement kilns in the U.S. that utilize mid-kiln firing. Costs were obtained from a vendor for four scenarios representing two wet kilns and two dry kilns.⁴ Typically, the secondary combustion approach allows burning waste-derived fuels and, as such, reduces the overall cost for the fuel. The purchased equipment cost for each of the four kilns is approximately \$1.5 million. This cost includes approximately \$1.0 million for a completely automated system for injecting tires or containerized solid or liquid fuels and \$500,000 for the modifications to the kiln. The cost of a fuel conveying system can be considerably lower for a semiautomatic, labor intensive system and may be expected to depend to a small extent upon the fuel conveying capacity needed. Costs for mid-kiln firing are not applicable to preheater or precalciner type kilns.

TABLE 6-7. CAPITAL COSTS FOR RETROFIT LOW-NO_x BURNERS IN AN EXISTING DIRECT-FIRED KILN (1997 \$)

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	PEC (\$)	Freight and sales tax (\$)	Installation costs \$		Contingency costs (\$)	Production Downtime (\$)	Total capital costs (\$)
						Direct	Indirect			
1	Wet	30	180	724,000	58,000	326,000	239,000	145,000	105,000	1,600,000
2	Wet	50	300	984,000	78,700	443,000	325,000	197,000	174,000	2,200,000
3	Long dry	25	113	546,000	43,700	246,000	180,000	109,000	87,100	1,210,000
4	Long dry	40	180	724,000	60,000	326,000	239,000	145,000	139,000	1,630,000
5	Preheater	40	152	655,000	52,400	295,000	216,000	131,000	139,000	1,490,000
6	Preheater	70	266	916,000	73,200	412,000	302,000	183,000	244,000	2,130,000
7	Precalciner	100	330	767,000	61,400	345,000	253,000	153,000	348,000	1,930,000
8	Precalciner	150	495	978,000	78,300	440,000	323,000	196,000	523,000	2,540,000

TABLE 6-8. ANNUALIZED COSTS FOR RETROFIT LOW-NO_x BURNERS IN AN EXISTING DIRECT-FIRED KILN (1997 \$)

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	Maintenance costs (\$/yr)	Operating labor (\$)	Overhead costs (\$/yr)	Taxes insurance admin. (\$/yr)	Capital recovery (\$/yr)	Total annualized costs (\$/yr)
1	Wet	30	180	24,300	12,700	22,200	63,900	175,000	298,000
2	Wet	50	300	24,300	12,700	22,200	88,100	242,000	389,000
3	Long dry	25	113	24,300	12,700	22,200	48,500	133,000	241,000
4	Long dry	40	180	24,300	12,700	22,200	65,300	179,000	304,000
5	Preheater	40	152	24,300	12,700	22,200	59,500	163,000	282,000
6	Preheater	70	266	24,300	12,700	22,200	85,200	234,000	378,000
7	Precalciner	100	330	24,300	12,700	22,200	77,100	212,000	348,000
8	Precalciner	150	495	24,300	12,700	22,200	102,000	279,000	439,000

Approximate capital investment costs were developed by assuming a total of \$1.5 million purchased equipment cost for kiln modifications and the fuel conveying and metering system for the four model plants. In this example approximately 15% of the heat duty is from tire derived fuel. This assumption results in a fuel credit (for the coal) as well as a tipping fee for the tires (also a credit). Because the purchased equipment cost does not vary with the heat duty of the kiln, the 0.6 power rule does not apply. Total capital investment was calculated using the methodology presented in section 6.1. It should be noted that the costs estimated are higher than the actual installation costs reported by the vendor.

The total capital costs for mid-kiln firing conversion of the four wet and long dry model kilns are given in Table 6-9. The total capital investment costs range from \$3.15 million for a small long dry kiln to \$3.24 million for a large wet kiln. The annualized costs for the mid-kiln firing conversions are presented in Table 6-10. Operating labor was assumed to be 0.5 hour per 8-hour shift. Maintenance labor costs were assumed to be 0.5 hour per 8-hour shift and maintenance materials were assumed to be equal to 100% of the maintenance labor cost. The annualized costs ranged from a credit of \$370,000 for the large wet kiln to a high cost of \$189,000 for the small long dry kiln.

These annualized costs were developed with a fuel credit (for the fuel that was replaced with waste tires) as well as a tire tipping fee. In 1998 270 million scrap tires were generated and the estimates of tires in stockpiles range from 500 million to 3 billion.²⁴ Although the tipping fees for tires may decline as markets for used tires increases, tire tipping fees are not likely to disappear in the near future. In 1997, average national tipping fees for tires ranged from \$20 to \$200 per ton (for whole tires).⁵ The annualized cost of mid-kiln firing without a tire tipping fee (but including the fuel credit: assuming the tires or other waste derived fuels are free) ranges from \$140,000 for the large wet kiln to a high cost of \$380,000 for the small long dry kiln.

6.2.3 NO_x Removal Controls

Two NO_x removal controls that are demonstrated in the United States for cement kilns are biosolids injection and NO_xOUT[®]. As discussed in Section 5.3.2, both of these technologies are only applicable to preheater/precalciner kilns. The capital costs of this control technique primarily include the cost of an injection system for either ammonia- or urea-based reagent, delivery system plus storage tanks, and control instrumentation. Operating costs include the cost of reagents and additives used, additional electricity cost for reagent pumping, and fuel penalty cost along with operating labor and maintenance requirements.

6.2.3.1 Biosolids Injection Process. As discussed in section 5.3.2.1, the biosolids injection process (which involves the injection of biosolids into a precalciner kiln) reduces the NO_x that was formed in the kiln. Biosolids injection has been installed on one kiln in Southern California and the costs of the installation were obtained for that facility.^{3,25} The costs associated with installing this technology include the sludge system and the sludge conveying system and

TABLE 6-9. CAPITAL COSTS FOR MID-KILN FIRING CONVERSION (1997 \$)

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	PEC (\$)	Freight and sales tax (\$)	Installation costs \$		Contingency costs (\$)	Production Downtime (\$)	Total capital costs (\$)
						Direct	Indirect			
1	Wet	30	180	1,490,000	119,000	670,000	491,000	298,000	105,000	3,170,000
2	Wet	50	300	1,490,000	119,000	670,000	491,000	298,000	174,000	3,240,000
3	Long dry	25	113	1,490,000	119,000	670,000	491,000	298,000	87,100	3,150,000
4	Long dry	40	180	1,490,000	119,000	670,000	491,000	298,000	139,000	3,210,000

TABLE 6-10. ANNUALIZED COSTS FOR MID-KILN FIRING CONVERSION (1997 \$)

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	Maintenance, other labor, and overhead costs (\$/yr)	Taxes, insurance, admin. (\$/yr)	Capital recovery (\$/yr)	Disposal revenue (\$/yr)	Fuel Credit (\$/yr)	Licence Fee (\$/yr)	Total annualized costs (\$/yr)
1	Wet	30	180	59,200	127,000	348,000	(306,000)	(300,000)	54,000	(14,600)
2	Wet	50	300	59,200	130,000	356,000	(510,000)	(500,000)	90,000	(370,000)
3	Long dry	25	113	59,200	126,000	346,000	(190,000)	(185,000)	34,000	189,000
4	Long dry	40	180	59,200	128,000	352,000	(306,000)	(300,000)	54,000	(9,340)

are summarized in Table 6-11 use of this technology results in a cost savings associated with the tipping fees for the biosolids. The annual costs include operating labor (assumed to be 0.5 hour per 8-hour shift), maintenance labor costs (assumed to be 0.5 hour per 8-hour shift), maintenance materials (assumed to be equal to 100% of the maintenance labor cost), credit for the biosolids tipping fee, and an electricity penalty of an additional 3% increase in fan capacity. Biosolid tipping fees range from \$0.00 to \$10.00 per wet ton. An average value of \$5.00/ton was used in this analysis.

TABLE 6-11. BASIS FOR COST ANALYSIS OF BIOSOLIDS INJECTION (1997 \$)

Purchased Equipment Cost	\$240,000
Type of Kiln	Preheater/precalciner
Primary Fuels	Coal and tire derived fuel
Kiln Production Rate	215 tons/hour
Quantity of Biosolids	20 tons/hour
Average kiln heat requirement	680 MMBtu/hour
Total Capital Investment	\$1,200,000
Annualized Cost	(\$322,000) ^a

^a Based on a biosolids tipping fee of \$5.00/ton.

6.2.3.2 NO_xOUT[®]. As discussed in section 5.3.2.2, the NO_xOUT[®] process using either ammonia or urea to reduce NO_x emissions from cement kilns has been used successfully in Europe. Two demonstrations of this technology^{26,27} for application to cement kilns has been made in the United States but there are no cement kilns currently operating in the United States using this technology. Costs for this technology were obtained from the equipment vendor for two preheater/precalciner kilns and are summarized in Table 6-12.^{28,29} The costs presented in Table 6-12 are consistent with values previously obtained and presented in the *Alternatives Control Techniques Document – NO_x Emissions from Cement Manufacturing*.^{30,31,32,33}

In addition to the vendor costs and the published literature, cost analyses were available from two facilities.^{27,34} The presented costs for both of these installations were much higher than the costs presented by the Vendor. It should be noted that the second facility has a long dry kiln and NO_xOUT[®] is generally not recommended for a mid-kiln installation due to the difficulties in providing for continuous injection of the reagent.

TABLE 6-12. BASIS FOR COST ANALYSIS OF NO_xOUT[®] (1997 \$)

Capital Cost of Material Handling Equipment	Kiln A	Kiln B
Type of Kiln	Preheater/precalciner	Preheater/precalciner
Kiln Production Rate	92 tons clinker/hour	133 tons clinker/hour
Average kiln heat requirement	320 MMBtu/hour	440 MMBtu/hour
Total Capital Investment	\$1,060,000	\$1,200,000
Annualized Cost	\$560,000 ^a	\$2,000,000 ^a

^a Includes cost of reagent.

6.2.3.3 Selective Catalytic Reduction. Although no selective catalytic reduction (SCR) systems are currently being used on cement plants in the United States, this control technique has been applied successfully in other industries and pilot plant trials have been conducted in Europe. Capital costs for this control approach would include cost of the SCR unit, ammonia storage tank, and an ammonia heating/ vaporization injection system along with equipment needed for preheating flue gases to an appropriate temperature. Operating costs would include the cost of ammonia reagent, dilution steam, catalyst replacement and disposal costs, and energy cost associated with reheating the kiln exhaust gases as well as the operating labor and maintenance costs.

Since the SCR technology has not been proven in cement plants in the United States, approximate capital and operating costs as applicable to the model plants were not available from any of the SCR control system vendors in the United States. The following information was first presented in the 1994 ACT document and is repeated here. An equipment cost estimate of an SCR system was submitted by a Japanese supplier to a cement company in the United States in 1991.³⁵ For a dry long kiln with 1,120 tons/day (47 tons/hr) clinker capacity, the estimated equipment cost was 1 billion/Yen. With a 1992 exchange rate of 108 Yen/\$ and assuming 5 percent inflation, the estimated cost in 1992 U.S. dollars was about 9.72 million. This equipment cost estimate included SCR catalyst, SCR reactor, gas/gas heat exchanger, heater, ammonia injection grid, ammonia storage tank, ammonia vaporizer and supply unit, induced draft fan, instrumentation and all piping and ductwork. The reactor temperature was assumed to be 350 °C (660 °F) and design NO_x removal efficiency was 80 percent. Since the reactor, heat exchanger, and gas heater design strongly depend upon the flow rate of flue gas to be treated, the equipment costs for the model plants may be scaled based upon flue gas flow rate:

$$\frac{\text{PEC for model 1}}{\text{PEC for model 2}} = \left(\frac{\text{Gas flow for model 1}}{\text{Gas flow for model 2}} \right)^{0.6}$$

Table 6-13 presents estimated capital costs for the eight model plants. Direct and indirect installation costs were assumed to be 45 and 33 percent of PEC, respectively, and an additional 20 percent contingency cost was added to determine total capital cost for the SCR systems. The estimated capital costs range from \$9.9 million for the small dry long kiln to \$24.6 million for the large precalciner kiln.

The estimated annualized costs for SCR systems on the eight model plants are shown in Table 6-14. These include operating labor and maintenance costs, capital recovery, gas reheating, ammonia reagent, and catalyst replacement costs.^{35,36} The individual operating costs were obtained by appropriately scaling the vendor provided operating costs to the model plants. The total annualized costs ranged from \$2.5 million/yr for the small long dry kiln to \$7.2 million for the large precalciner kiln.

6.3 COST EFFECTIVENESS OF NO_x CONTROLS

Cost effectiveness for the model plants was determined for three technologies for which detailed costs could be developed as presented in the last section: low NO_x burners (on an existing indirect fired system and with conversion to an indirect firing system), and mid-kiln firing (with a credit for firing tires or just firing coal). Limited cost data are available for a CemStar, biosolids injection, or NO_xOUT[®] installation in the U.S. Cost effectiveness was calculated by dividing the total annualized cost of a given technology by the annual NO_x reduction likely to be achieved by that technology and is expressed in the units of \$/ton of NO_x removed. Cost effectiveness was determined for each of the model plant scenarios.

6.3.1 CemStar

As discussed in section 6.2.1.2, the costs of installing CemStar were obtained from the vendor for one kiln configuration (a wet kiln) at one facility. Data for other installations of CemStar were not available for this report. The kiln capacity was 42 tons clinker/hour prior to the installation of CemStar and 45 tons clinker/hour after the installation of CemStar. The annualized cost for the conversion was calculated as \$220,000. This annualized cost does not include a credit for the increased production of clinker (approximately 3 tons/hour). Uncontrolled emissions were calculated as approximately 1600 tons NO_x/year. An average emission reduction of 30% was determined for the installation of CemStar which results in 100 tons NO_x/year. The cost effectiveness for this example facility was \$550/ton of NO_x reduced.

6.3.2 Low NO_x Burner

The NO_x reduction that may be achieved with a low NO_x burner depends mainly on the operating parameters. In fact, no guarantee on the NO_x reduction level is usually provided by burner vendors. With proper operation of the low NO_x burner, 15 to 40 percent reduction in NO_x emissions should be possible.³⁷ An average NO_x reduction efficiency of 25 percent was used in determining controlled NO_x emissions and cost effectiveness of the low NO_x burner

TABLE 6-13. CAPITAL COSTS FOR SCR PROCESS (1992 \$)³⁸

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	PEC (\$)	Freight and sales tax (\$)	Installation costs direct and indirect (\$)	Contingency costs (\$)	Total capital costs (\$)
1	Wet	30	180	6,200	496,000	4,840,000	1,240	12,800
2	Wet	50	300	8,430	674,000	6,570,000	1,690	17,400
3	Long dry	25	113	4,790	383,000	3,740,000	958	9,870
4	Long dry	40	180	6,350	508,000	4,950,000	1,270	13,100
5	Preheater	40	152	5,820	466,000	4,540,000	1,160	12,000
6	Preheater	70	266	8,140	651,000	6,350,000	1,630	16,800
7	Precalciner	100	330	9,400	749,000	7,310,000	1,870	19,300
8	Precalciner	150	495	11,900	956,000	9,330,000	2,390	24,600

TABLE 6-14. ANNUALIZED COSTS FOR SCR(1992 \$)³⁸

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Operating labor (\$/year)	Ammonia reagent costs (\$/year)	Maintenance & overhead costs (\$/yr)	Energy and fuel costs (\$/year)	Catalyst costs (\$/year)	Taxes insurance admin. (\$/yr)	Capital recovery (\$/yr)	Total annualized costs (\$/yr)
1	Wet	30	30,400	287,000	24,300	468,000	326,000	511,000	1,680,000	3,350
2	Wet	50	30,400	485,000	24,300	779,000	544,000	694,000	2,280,000	4,860
3	Long dry	25	30,400	218,000	24,300	304,000	212,000	395,000	1,300,000	2,510
4	Long dry	40	30,400	337,000	24,300	487,000	339,000	523,000	1,720,000	3,490
5	Preheater	40	30,400	238,000	24,300	421,000	293,000	480,000	1,580,000	3,090
6	Preheater	70	30,400	406,000	24,300	736,000	513,000	571,000	2,210,000	4,610
7	Precalciner	100	30,400	337,000	24,300	930,000	649,000	772,000	2,540,000	5,300
8	Precalciner	150	30,400	505,000	24,300	1,400,000	974,000	985,000	3,240,000	7,180

technology. For precalciner kilns, although only 60 percent of the heat duty was assumed to be provided by the low NO_x burners, all of the NO_x emissions were assumed to result from these burners. For existing direct-fired kiln systems, the costs involved in conversion of the firing system increase the costs of NO_x removal considerably. Table 6-15 presents the uncontrolled and controlled NO_x emissions for the eight model plants along with the cost effectiveness of low NO_x burner in an existing indirect-fired kiln. The cost effectiveness were within a close range for the model plants and ranged from \$300/ton of NO_x for the large wet kiln to \$620/ton of NO_x for the small long dry kiln.

Table 6-16 presents the cost effectiveness of low NO_x burner installed in an existing direct-fired kiln scenario. The cost effectiveness ranges from \$760/ton to \$1,200/ton of NO_x removed. The cost of firing system conversion doubled the cost effectiveness as compared to those in Table 6-15. The conversion from direct fired to an indirect firing system is expected to reduce the energy requirement per ton of clinker. The energy savings associated with the increased efficiency and productivity are not considered in determining the cost effectiveness.

6.3.3 Mid-Kiln Firing of Tires

The cost effectiveness for the four model plants are given in Table 6-17 which range from a credit of \$460/ton to a cost of \$730/ton of NO_x removed. A NO_x reduction efficiency of 40 percent was calculated for wet kilns and 30 percent for long dry kilns. This cost effectiveness value includes a fuel credit for using waste-derived fuel and a tipping fee for the tires. If the tire tipping fee is removed (but the fuel credit is retained - assuming waste material is free), the cost effectiveness will range from \$150/ton of NO_x to \$680/ton of NO_x reduced.

6.3.4 Preheater/Precalciner Tire Derived Fuel

Costs for installing a tire derived fuel system at a precalciner kiln were obtained from one facility. The purchased equipment and total capital investment costs were similar to the mid-kiln firing costs (the majority of the cost is in the tire handling system). Cost effectiveness for this kiln is based on the annualized costs of (\$1,600,000/year), the emission reduction achieved at that facility (emissions decreased approximately 30% from 3.4 lb/ton of clinker to 2.4 lb/ton of clinker), a kiln capacity of 215 tons/hr, and an annual operation of 8,000 hr/yr. Cost effectiveness is a credit of (\$1,900/ton) for installing a tire derived fuel system on this kiln. This cost effectiveness value includes a fuel credit for using waste-derived fuel and a tipping fee for the tires. If the tire tipping fee is removed (but the fuel credit is retained - assuming waste material is free), the cost effectiveness is calculated as a credit of (\$480/ton) of NO_x reduced.

TABLE 6-15. COST EFFECTIVENESS OF RETROFIT LOW-NO_x BURNERS IN AN EXISTING INDIRECT-FIRED KILN (1997 \$)

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	Uncontrolled NO _x emissions (tons/yr)	Controlled NO _x emissions (tons/yr)	NO _x removed (tons/yr)	NO _x reduction (%)	Total annualized costs (\$/yr)	Cost effectiveness (\$/ton NO _x removed)
1	Wet	30	180	1,200	880	320	25	136,000	425
2	Wet	50	300	2,000	1,500	500	25	152,000	300
3	Long dry	25	113	860	650	210	25	130,000	620
4	Long dry	40	180	1,400	1,000	400	25	141,000	350
5	Preheater	40	152	940	700	240	25	140,000	580
6	Preheater	70	266	1,700	1,200	500	25	161,000	320
7	Precalciner	100	330	1,400	1,000	400	25	173,000	430
8	Precalciner	150	495	2,000	1,600	400	25	204,000	510

TABLE 6-16. COST EFFECTIVENESS OF RETROFIT LOW-NO_x BURNERS IN AN EXISTING DIRECT-FIRED KILN (1997 \$)

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	Uncontrolled NO _x emissions (tons/yr)	Controlled NO _x emissions (tons/yr)	NO _x removed (tons/yr)	NO _x reduction (%)	Total annualized costs (\$/yr)	Cost effectiveness (\$/ton NO _x removed)
1	Wet	30	180	1,200	880	320	25	298,000	930
2	Wet	50	300	2,000	1,500	500	25	389,000	780
3	Long dry	25	113	860	650	210	25	241,000	1,100
4	Long dry	40	180	1,400	1,000	400	25	304,000	760
5	Preheater	40	152	940	700	240	25	282,000	1,200
6	Preheater	70	266	1,700	1,200	500	25	378,000	760
7	Precalciner	100	330	1,400	1,000	400	25	348,000	870
8	Precalciner	150	495	2,000	1,600	400	25	439,000	1,100

TABLE 6-17. COST EFFECTIVENESS OF MID-KILN FIRING

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	Uncontrolled NO _x emissions (tons/yr)	Controlled NO _x emissions (tons/yr)	NO _x removed (tons/yr)	NO _x reduction (%)	Total annualized costs (\$/yr)	Cost effectiveness (\$/ton NO _x removed)
1	Wet	30	180	1,200	700	500	40	(14,600)	(29)
2	Wet	50	300	2,000	1,200	800	40	(368,000)	(460)
3	Long dry	25	113	860	600	260	30	189,000	730
4	Long dry	40	180	1,400	960	440	30	(9,300)	(21)

6.3.5 Biosolids Injection

One facility in the United States is currently using biosolids injection technology on one preheater/precalciner kiln. Cost effectiveness for this kiln is based on the annualized costs of (\$320,000/year), the emission reduction achieved at that facility (emissions decreased from 2.4 lb/ton of clinker to 1.2 lb/ton of clinker), a kiln capacity of 215 tons/hr, and an annual operation of 8,000 hr/yr. Cost effectiveness is a credit of (\$310/ton) for installing biosolids injection on this kiln.

6.3.6 Selective Noncatalytic Reduction

NO_xOUT[®] is estimated to provide 40 percent NO_x reduction based on the available test data. Cost effectiveness for the two kilns described in section 6.2.3.2, using urea as the reagent, is based on an uncontrolled emission rate of 3.8 lb NO_x/ton of clinker, kiln capacities of 92 and 130 tons/hr respectively, annual operation of 8,000 hr/yr, and a NO_x control efficiency of 40%. Cost effectiveness is \$1,000/ton for the smaller kiln and \$2,500/ton for the larger kiln.

6.3.7 Selective Catalytic Reduction

The NO_x reduction that may be achieved with SCR technology depends upon the reagent stoichiometric ratio used, and the gas phase residence time in the SCR reactor. Although there are no installations of the SCR technology in cement plants, 80 to 90 percent reduction in NO_x emissions has been achieved in SCR installations in other applications such as utility boilers and gas turbines.³⁹ The SCR equipment costs developed in Section 6.2.2.2 were based upon SCR costs quoted for application on dry kiln exhaust gases with 80 percent design reduction in NO_x emissions. To determine the cost effectiveness of the SCR technology in cement kiln applications, an 80 percent NO_x reduction efficiency was therefore assumed and the results are shown in Table 6-18. The cost effectiveness ranged from \$3,140/ton to \$4,870/ton of NO_x removed and are almost five to six times greater than the corresponding values for the ammonia-based SNCR technology.

TABLE 6-18. COST EFFECTIVENESS OF SCR PROCESS³⁸

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	Uncontrolled NO _x emissions (tons/yr)	Controlled NO _x emissions (tons/yr)	NO _x removed (tons/yr)	NO _x reduction (%)	Total annualized costs (\$/yr)	Cost effectiveness (\$/ton NO _x removed)
1	Wet	30	180	1,160	230	930	80	3,351,000	3,600
2	Wet	50	300	1,940	390	1,550	80	4,864,000	3,140
3	Long dry	25	113	860	170	690	80	2,506,000	3,630
4	Long dry	40	180	1,380	280	1,100	80	3,486,000	3,170
5	Preheater	40	152	940	190	750	80	3,087,000	4,120
6	Preheater	70	266	1,650	330	1,320	80	4,610,000	3,490
7	Precalciner	100	330	1,360	270	1,090	80	5,304,000	4,870
8	Precalciner	150	495	2,040	410	1,630	80	7,179,000	4,400

6.3.8 Summary of Cost Effectiveness

Table 6-19 summarizes the cost effectiveness for the various technologies. Table 6-19 also presents the ozone season cost effectiveness. The ozone season cost effectiveness is based on the emission reduction that will be achieved in the 5 month ozone season (May-September).

TABLE 6-19. SUMMARY OF COST EFFECTIVENESS
(1997 \$/ton NO_x Reduced)

Technology		Range of Annual Cost Effectiveness	Average Annual Cost Effectiveness	Average Ozone Season Cost Effectiveness
CemStar		n/a	550	1,100
Low-NO _x Burners	Indirect-Fired Kilns	300 to 620	440	1,060
	Direct-Fired Kilns	760 to 1200	940	2,260
Mid-Kiln Firing		(460) to 730	55	130
Tire Derived Fuel at a Precalciner ^a		(1,900) ^b	(1,900) ^b	(4,500) ^b
Biosolids Injection		n/a	(310) ^b	(740) ^b
NO _x OUT [®]		1,000 to 2,500	1,740	2,160

N/A - not applicable

() - indicates a negative cost

^a The purchased equipment and total capital investment costs for a tire derived fuel installation on a precalciner are very similar to mid-kiln firing.

^b Represents a single installation.

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