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ALTERNATIVE CONTROL TECHNIQUES DOCUMENT— NO_x EMISSIONS FROM CEMENT MANUFACTURING

Emission Standards Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
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ALTERNATIVE CONTROL TECHNOLOGY DOCUMENTS

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CHAPTER 1

INTRODUCTION

Congress, in the Clean Air Act Amendments of 1990 (CAAA), amended Title I of the Clean Air Act (CAA) to address ozone nonattainment areas. A new Subpart 2 was added to Part D of Section 103. Section 183(c) of the new Subpart 2 provides that:

> [w]ithin 3 years after the date of the enactment of the [CAAA], the Administrator shall issue technical documents which identify alternative controls for all categories of stationary sources of . . . oxides of nitrogen which emit, or have the potential to emit 25 tons per year or more of such air pollutant.

These documents are to be subsequently revised and updated as determined by the Administrator.

Cement kilns have been identified as a stationary source that emit more than 25 tons of nitrogen oxides (NO_x) per year. This alternative control technique (ACT) document provides technical information for use by State and local agencies to develop and implement regulatory programs to control NO_x emissions from cement kilns. Additional ACT documents are being or have been developed for other stationary source categories.

The information in this ACT document was generated from previous EPA documents and literature searches and contacts with cement manufacturers; engineering firms; control equipment vendors; and Federal, State, and local regulatory agencies. Chapter 2 presents a summary of the findings of this study. Chapter 3 provides a process description and industry characterization of cement manufacturing. A discussion of uncontrolled NO_x emission levels is presented in Chapter 4. Alternative control techniques and achievable controlled emission levels are discussed in Chapter 5. Chapter 6 presents control costs and cost effectiveness for each control technique. Environmental and energy impacts associated with the use of NO_x control techniques are discussed in Chapter 7.

CHAPTER 2
SUMMARY

This chapter presents a summary of the information contained in this document. Section 2.1 presents a summary of uncontrolled NO_x emission levels from different types of cement kilns. Section 2.2 presents a summary of NO_x emission control technologies and NO_x emission reductions for these technologies. Section 2.3 presents a summary of the capital and operating costs as well as the cost effectiveness of NO_x control technologies and Section 2.4 provides a summary of the impacts of these technologies.

2.1 UNCONTROLLED NO_x EMISSIONS

In cement manufacturing, conditions favorable for formation of nitrogen oxides (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 may also contain 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: long wet kilns, long dry kilns, kilns with a preheater, and kilns with a precalciner. The long wet and dry kilns and most preheater kilns have only one fuel combustion zone, whereas the newer precalciner kilns and preheater kilns with a riser duct have two fuel combustion zones. Since the typical temperatures in the two types of combustion zones are different, the factors affecting NO_x formation are also somewhat different in different kiln types. In a primary combustion zone at the hot end of a kiln, the high temperatures lead to predominantly thermal NO_x formation; whereas in the secondary combustion zone 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 would produce less NO_x emissions.

Since the four types of cement kilns exhibit different combustion characteristics as well as energy efficiencies and heat requirements, the available NO_x emissions data are grouped by these cement kiln types. The data indicate substantial spread in the reported NO_x emissions with large 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. The uncontrolled emission factors based on the information obtained during this study are given in Table 2-1. 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.

2.2 NO_x EMISSION CONTROL TECHNOLOGIES

TABLE 2-1. UNCONTROLLED NO_x EMISSION FACTORS FOR DIFFERENT KILN TYPES

Cement kiln type	Heat input requirement (MM Btu/ton of clinker)	NO_x emission rate (lb/ton of clinker)	Range of NO_x Emissions (lb/ton of clinker)
Long 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	3.4	0.9 - 7.0

NO_x control approaches applicable to the cement industry may be grouped in two categories:

- Combustion control approaches where the emphasis is on reducing NO_x formation, and
- Postcombustion control approaches which control the NO_x formed in the combustion process.

Process control approaches are based upon providing optimum kiln operating conditions which increase the energy efficiency and productivity of the cement-making process while minimizing NO_x emissions. Such measures will provide a baseline of NO_x emissions in cement kilns without any specific NO_x control equipment. Although these simple process control approaches will reduce NO_x emissions in poorly operated kilns, for the purposes of this ACT document, such approaches are considered to be needed for proper kiln operation and not specifically considered as NO_x control techniques.

Limited information is available regarding use of low NO_x burners in a cement kiln. Staging of combustion air as achieved by such burners is a possible technique for NO_x reduction in cement kilns. In the first stage, fuel combustion is carried out in a high temperature fuel-rich environment and the combustion is completed in the fuel-lean low temperature second stage. By controlling the available oxygen and temperature, low NO_x burners attempt to reduce NO_x formation in the flame zone.

The concept of external flue gas recirculation for NO_x reduction has not been demonstrated in cement kilns. Similarly, the potential of secondary combustion of fuel in conventional kilns (by "mid-kiln" firing) as an NO_x control technique has been evaluated for whole tire burning only. This technique can be potentially applied with other waste-derived fuels as well and needs further demonstration. Secondary combustion of fuel is inherently present in all precalciner kilns and preheater kilns with riser duct firing and such kilns produce less NO_x emissions compared to long dry kilns.

Selective catalytic reduction (SCR) uses ammonia in the presence of a catalyst to selectively reduce NO_x emissions. There have been limited pilot test programs of SCR. Selective noncatalytic reduction (SNCR) technology appears to be applicable to preheater/precalciner type kilns with limited data indicating its effectiveness. SNCR reduces NO_x with ammonia or urea without a catalyst. SNCR is not considered applicable to long wet and dry kilns due to difficulties involved in continuous injection of reducing agents. There have been a few demonstrations of SNCR at preheater/precalciner kilns. Molar reagent ratio, temperature, and gas residence time in the appropriate temperature window are primary factors affecting NO_x reduction efficiency. Table 2-2 presents the potential NO_x reductions with these techniques.

TABLE 2-2. ACHIEVABLE NO_x REDUCTIONS WITH VARIOUS NO_x CONTROL TECHNOLOGIES

NO_x CONTROL TECHNOLOGY	ACHIEVABLE NO_x EMISSIONS REDUCTION (%)
Process Modifications	25
Stayed combustion in precalciner	30 - 45
Conversion to indirect firing with a low NO_x burner	20 - 30
Mid-Kiln firing of tires in long kilns	20 - 40
SNCR	30 - 70
SCR	80 - 90

2.3 COSTS AND COST EFFECTIVENESS OF NO_x CONTROL TECHNOLOGIES

Capital and annualized operating costs as well as cost effectiveness were determined for technologies for which detailed costs could be developed: Low NO_x burner, mid-kiln firing conversion, SNCR and SCR. Since there are limited installations of these technologies, the capital and annualized costs were based on the information provided by vendors and guidelines provided by the U.S. Environmental Protection Agency/Office of Air Quality Planning and Standards (EPA/OAQPS) Control Cost Manual.

Tables 2-3 and 2-4 present the total capital and annualized operating costs for each of the three control technologies as applied to model plants defined in Table 6-1. The low NO_x burner capital costs range from $1,270,000 to $2,180,000, whereas the annual costs range from $267,000 to $423,000. Capital costs for mid-kiln firing conversion range from $391,000 to $707,000. Annual costs range from $128,000 to $207,000. The urea-based SNCR capital costs range from $671,000 to $1,240,000 for preheater/precalciner kilns. The urea-based SNCR annual costs range from $438,000 to $820,000. The ammonia-based SNCR

TABLE 2-3. CAPITAL AND ANNUAL COSTS OF NO_x CONTROL TECHNOLOGIES

			LOW NO_x BURNER		MID-KILN FIRING	
MODEL NO.	KILN TYPE	KILN CAPACITY (TONS/ CLINKER/HR	CAPITAL COSTS (10^3 $)	ANNUAL COSTS (10^3 $/YR)	CAPITAL COSTS (10^3 $)	ANNUAL COSTS 10^3 $/YR)
1	Long Wet	30	1,640	329	718	549
2	Long Wet	50	2,180	423	748	777
3	Long Dry	25	1,270	267	708	461
4	Long Dry	40	1,640	329	728	593
5	Preheater	40	1,490	305	*NA	NA
6	Preheater	70	2,040	398	NA	NA
7	Precalciner	100	1,720	344	NA	NA
8	Precalciner	150	2,170	421	NA	NA

*NA - NOT APPLICABLE

TABLE 2-4. CAPITAL AND ANNUAL COSTS OF NO_x CONTROL TECHNOLOGIES

			SNCR UREA-BASED		SNCR AMMONIA-BASED		SCR	
MODEL NO.	KILN TYPE	KILN CAPACITY (TONS/ CLINKER/HR	CAPITAL COSTS (10^3 $)	ANNUAL COSTS (10^3 $	CAPITAL COSTS (10^3 $)	ANNUAL COSTS (10^3 $)	CAPITAL COSTS (10^6 $)	ANNUAL COSTS (10^6 $)
1	Long Wet	30	*NA	NA	NA	NA	12.8	3.35
2	Long Wet	50	NA	NA	NA	NA	17.4	4.86
3	Long Dry	25	NA	NA	NA	NA	9.87	2.51
4	Long Dry	40	NA	NA	NA	NA	13.1	3.49
5	Preheater	40	671	438	1,340	518	12.0	3.09
6	Preheater	70	927	655	1,850	753	16.8	4.61
7	Precalciner	100	969	598	1,650	665	19.3	5.30
8	Precalciner	150	1,240	820	2,110	894	24.6	7.18

*NA - NOT APPLICABLE

capital costs for preheater/precalciner kilns range from $1,340,000 to $2,100,000. The ammonia-based SNCR annual costs for preheater/precalciner kilns range from $1,340,000 to $2,100,000. The capital costs for the SCR technology range from 9.9 to 24.6 million dollars. The annual costs for SCR are also the highest and range from 2.5 to 7.2 million dollars.

Cost effectiveness of a technology was calculated by dividing the total annual 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. To determine the cost effectiveness of control technologies, low NO_x burner technology and mid-kiln firing of tires were assumed to provide 25 percent NO_x reduction efficiency, whereas SCR technology was assumed to provide 80 percent NO_x reduction. SNCR technology was assumed to provide 50 percent NO_x reduction in preheater and precalciner kilns. Cost-effectiveness values were determined for each of the eight model plant scenarios.

Tables 2-5 and 2-6 present the expected NO_x reductions and the cost effectiveness for each model plant for the four technologies considered. The cost effectiveness for the low NO_x burner technology were within a close range for the model plants and ranged from $830/ton to $1,330/ton of NO_x removed. The cost effectiveness for mid-kiln firing of tires range from $430/ton to $610/ton for long wet and long dry kilns. Cost effectiveness for the ammonia-based SNCR range from $470/ton to $1,100/ton of NO_x removed. Cost effectiveness for SNCR are almost four times those for low NO_x burners. However, SNCR can provide much greater reduction in NO_x emissions compared to a low NO_x burner. Cost effectiveness for SCR range from $3,140/ton to $4,870/ton of NO_x removed. Cost effectiveness for SCR were almost two to three times those for the SNCR.

2.4 IMPACTS OF NO_x CONTROLS

Tables 2-5 and 2-6 present the possible NO_x emission reductions in the eight model plants using low NO_x burners, mid-kiln firing, SNCR and SCR techniques. With the postcombustion technologies of SCR and SNCR, expected annual NO_x emission

TABLE 2-5. COST EFFECTIVENESS OF NO_x CONTROL TECHNOLOGIES

			LOW NO_x BURNER		MID-KILN FIRING	
MODEL NO.	KILN TYPE	KILN CAPACITY (TONS/ CLINKER/HR	NO_x REMOVED (TONS/YR)	COST EFFECTIVE-NESS ($/TON NO_x REMOVED)	NO_x REMOVED (TONS/YR)	COST EFFECTIVE-NESS ($/TON NO_x REMOVED)
1	Long Wet	30	290	1,130	290	550
2	Long Wet	50	480	880	480	430
3	Long Dry	25	210	1,270	210	610
4	Long Dry	40	340	970	340	470
5	Preheater	40	230	1,330	*NA	NA
6	Preheater	70	410	970	NA	NA
7	Precalciner	100	340	1,010	NA	NA
8	Precalciner	150	510	830	NA	NA

*NA - NOT APPLICABLE

TABLE 2-6. CAPITAL AND ANNUAL COSTS OF NO_x CONTROL TECHNOLOGIES

			SNCR UREA-BASED		SNCR AMMONIA-BASED		SCR	
MODEL NO.	KILN TYPE	KILN CAPACITY (TONS/ CLINKER/HR	NO_x REMOVED (TONS/YR)	COST EFFECTIVENESS ($/TON NO_x REMOVED	NO_x REMOVED (TONS/YR)	COST EFFECTIVENESS ($/TON NO_x REMOVED)	NO_x REMOVED (TONS/YR)	COST EFFECTIVENESS ($/TON NO_x REMOVED)
1	Long Wet	30	[*]NA	NA	NA	NA	930	3,600
2	Long Wet	50	NA	NA	NA	NA	17.4	4.86
3	Long Dry	25	NA	NA	NA	NA	9.87	2.51
4	Long Dry	40	NA	NA	NA	NA	13.1	3.49
5	Preheater	40	671	438	1,340	518	12.0	3.09
6	Preheater	70	927	655	1,850	753	16.8	4.61
7	Precalciner	100	969	598	1,650	665	19.3	5.30
8	Precalciner	150	1,240	820	2,110	894	24.6	7.18

[*] NA - NOT APPLICABLE

reductions ranged from 470 tons/year to 1,550 tons/year, whereas annual NO_x emissions reductions of 210 tons/year to 510 tons/year are expected with the low NO_x burner technology for the eight model plants.

The low NO_x burner technology is not expected to have any measurable impact on CO emissions and its impact on hydrocarbon emissions is not known. For the postcombustion NO_x control approaches of SCR and SNCR, generally a little excess of reagent is used than that required stoichiometrically to ensure the desired percent reduction of NO_x. This results in ammonia emissions which is usually referred to as "ammonia slip" which are normally below 10 ppm. These techniques are not likely to affect the formation of other pollutants.

No data are available to determine the energy impacts of the low NO_x burner technology. Because of problems related to catalyst fouling, an SCR system may need to be installed downstream of a particulate control device. Since the SCR process requires gas temperature to be about 400 to 500 °C (750 to 930 °F), the gas stream may need to be reheated causing an additional energy cost. Additional energy is also needed due to the pressure drop across the catalyst bed. With no heat recovery in the flue gas reheater, additional energy required for flue gas reheating may be as high as 25 percent of the energy consumed in the cement-making process. With an energy recuperative type process heater with an energy recovery of 60 percent the energy requirement for the flue gas reheating would be approximately 10 percent of that consumed in the cement manufacturing. Additional electrical energy required to operate ammonia or urea solution pumps in the SCR or SNCR technologies is negligible.

CHAPTER 3
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. One need only mention reinforced-concrete walls and girders, tunnels, dams, and roads to realize the dependence of our society upon cement products. The hydraulic portland cement, produced by burning a mixture of limestone, clay, and other ingredients at a high temperature, is the primary product of the cement industry. 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 clinker consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate as an interground addition."[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] In addition, different varieties are prepared by using various blending formulations.[3]

Type I. <u>Regular</u> portland cements are the usual products for general concrete construction, 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 regular cements such as oil-well cement, quick-setting cement, and others for special uses.

TABLE 3-1. BASIC CLINKER COMPOUNDS[2]

Formula	**Name**
$2CaO\cdot SiO_2$	Dicalcium silicate
$3CaO\cdot SiO_2$	Tricalcium silicate
$3CaO\cdot Al_2O_3$	Tricalcium aluminate
$4CaO\cdot Al_2O_3\cdot Fe_2O_3$	Tetracalcium aluminoferrite
MgO	Magnesium oxide in free state or combined in di- or tri- calcium silicate lattice.

Type II. Moderate-heat-of-hardening and sulfate resisting portland cements are for use where moderate heat of hydration is required or for general concrete construction exposed to moderate sulfate action.

Type III. High-early-strength cements are made from raw materials with a lime to silica ratio higher than that of Type I cement and are ground finer than Type I cements. They contain a higher proportion of tricalcium silicate ($3CaO"SiO_2$) than regular portland cements.

Type IV. Low-heat portland cements contain a lower percentage of tricalcium silicate ($3CaO"SiO_2$) and tricalcium aluminate ($3CaO"Al_2O_3$) than type I, thus lowering the heat evolution. Consequently, the percentage of dicalcium silicate is increased substantially and the percentage of tetracalcium aluminoferrite ($4CaO"Al_2O_3"Fe_2O_3$) may be increased or may stay the same.

Type V. Sulfate-resisting portland cements are those which, by their composition or processing, resist sulfates better than the other four types.

The use of air-entraining agents increases the resistance of the hardened concrete to scaling from alternate freezing and thawing. By adding these materials to the first three types of cements, IA, IIA, and IIIA varieties of cements are produced. Additional varieties of cements are produced for special applications by blending different ingredients: masonry cement, expansive cement, oil-well cement, etc. Masonry cements are commonly finely ground mixtures of portland cement, limestone, and air-entraining agents. Granulated blast furnace slags and natural or artificial pozzolans are mixed and interground with portland cement to prepare still other varieties such as blended types IP, IS, S, I(PM), and I(SM).[3]

3.3 INDUSTRY CHARACTERIZATION

3.3.1 Description of the Cement Industry

About 80.8 million tons of gray portland cement were produced in a total of 213 cement kilns at 109 plants in the

United States in 1990.[3] In addition, about 290,000 tons of white cement were produced in three plants using four kilns. This was a 0.6 percent decline from the 1989 reported production of 81.5 million tons. Cement industry annual clinker capacity has steadily declined from the 1973 peak when 414 kilns had a total rated capacity of 91.1 million tons. Although 49 cement companies produced clinker in 1990, the top 10 companies provided about 58 percent of the total clinker production. Table 3-2 provides a list of all companies along with their share of the total clinker production. The locations of the operating kilns are shown in Figure 3-1. Table 3-3 lists the clinker producing capacity in the United States by States. California and Texas are the two largest states in terms of clinker capacity with Pennsylvania, Michigan, and Missouri rounding out the top five. Fourteen states had no cement clinker- producing plants in 1990.[3]

The large majority of the cement plants (about 75.9 percent) in the United States are coal fired with about 8 percent using natural gas, and 0.9 percent using oil as the primary fuel.[3] The remaining 15.2 percent of the plants used other combinations, e.g. coal/waste as primary fuel. In 1990, 55 of the 109 plants (50.5 percent) used waste as a primary and/or alternate fuel. The number of plants accepting waste as a fuel has increased significantly within the last 2 years.

3.3.2 Overview of Cement Manufacturing Process

The process of portland cement manufacture consists of[4]:

- Quarrying and crushing the raw materials,
- Grinding the carefully proportioned materials to a high degree of fineness,
- Pyroprocessing the raw mix in a rotary kiln to produce clinker, and
- Grinding the clinker to a fine powder along with the appropriate proportion of gypsum to produce cement.

A layout of a typical plant is shown in Figure 3-2 which also illustrates differences between the two primary types of

TABLE 3-2. UNITED STATES CEMENT COMPANY CAPACITIES-1990[3] [a]

Rank	Clinker (10^3 tons)	Percent industry	Company name
1	10,140	12.5	Holnam Inc.
2	7,790	9.6	Lafarge Corporation
3	4,960	6.1	Southdown Inc.
4	4,090	5.0	Lone Star Industries
5	3,990	4.9	Ash Grove Cement Company
6	3,900	4.8	Lehigh Portland Cement
7	3,340	4.1	Blue Circle Inc.
8	3,220	4.0	Essroc Materials
9	2,850	3.5	California Portland Cement
10	2,830	3.5	Medusa Cement Company
11	2,020	2.5	Texas Industries
12	1,880	2.3	Gifford-Hill & Company, Inc. (bought out by Blue Circle and Riverside Cement Companies)
13	1,670	2.1	Mitsubishi Cement Corp.
14	1,600	2.0	Kaiser Cement Corporation
15	1,290	1.6	Centex
16	1,180	1.5	River Cement Company (RC Cement)
17	1,120	1.4	Kosmos Cement Co.
18	1,120	1.4	Roanoke Cement Company
19	1,080	1.3	Calaveras Cement Company
20	1,030	1.3	Tarmac Florida, Inc.
21	1,010	1.2	Independent Cement Corporation
22	1,000	1.2	Boxcrow Cement
23	990	1.2	Texas-Lehigh Cement Company
24	970	1.2	Monarch Cement Company
25	930	1.1	Allentown Cement Company Inc.
26	900	1.1	North Texas Cement
27	870	1.1	Giant Cement Company

[a] Includes gray and white plants.

TABLE 3-2. (con.)

Rank	**Clinker (10^3 tons)**	**Percent industry**	**Company name**
28	860	1.1	Capitol Aggregates, Inc.
29	850	1.0	National Cement Company of Alabama
30	820	1.0	Capitol Cement Corporation
31	800	1.0	RMC Lonestar
32	770	0.9	Dakotah Cement
33	750	0.9	Alamo Cement Company
34	720	0.9	Hercules Cement Company
35	710	0.9	Phoenix Cement Company
36	650	0.8	National Cement Company of California
37	610	0.8	St. Mary's Peerless Cement Corporation
38	600	0.7	Carlow Group (Midwest Portland Cement)
39	600	0.7	Keystone Cement Company (Giant Cement Company)
40	600	0.7	Continental Cement Company, Inc.
41	570	0.7	Florida Crushed Stone
42	560	0.7	Rinker Portland Cement Corporation
43	520	0.6	Dixon-Marquette
44	500	0.6	Glens Falls Cement Company Inc.
45	460	0.6	Dragon Products Company
46	450	0.6	Signal Mountain Cement Company
47	340	0.4	Heartland Cement Company
48	310	0.4	Armstrong Cement & Supply Corporation
49	260	0.3	Hawaiian Cement Company
Total	***81,100***		

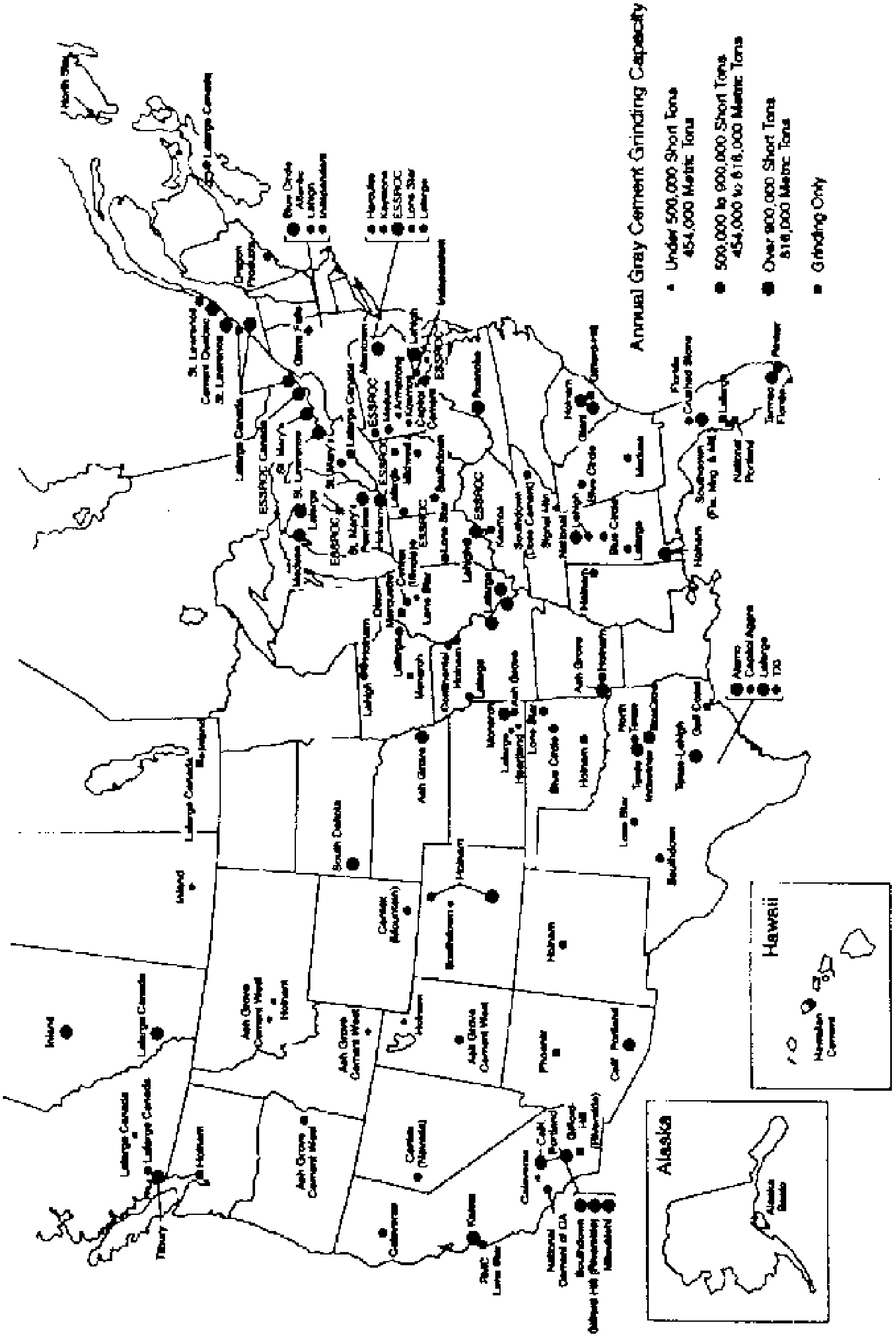


Figure 3-1. U.S. Portland cement plant locations, December 31, 1990.[3]

TABLE 3-3. UNITED STATES CLINKER CAPACITIES BY STATE-1990[3] [a]

Rank	Clinker (10^3 tons)	States
1	10,390	California
2	8,590	Texas
3	6,640	Pennsylvania
4	4,900	Michigan
5	4,680	Missouri
6	4,260	Alabama
7	3,360	Florida
8	3,100	New York
9	2,830	Indiana
10	2,810	Iowa
11	2,590	Illinois
12	2,580	South Carolina
13	1,890	Kansas
14	1,890	Oklahoma
15	1,860	Maryland
16	1,800	Colorado
17	1,770	Arizona
18	1,700	Ohio
19	1,380	Georgia
20	1,310	Arkansas
21	1,120	Virginia
22	1,050	Tennessee
23	960	Nebraska
24	930	Utah
25	820	West Virginia
26	770	South Dakota
27	720	Kentucky
28	590	Montana
29	500	Mississippi
30	500	Oregon

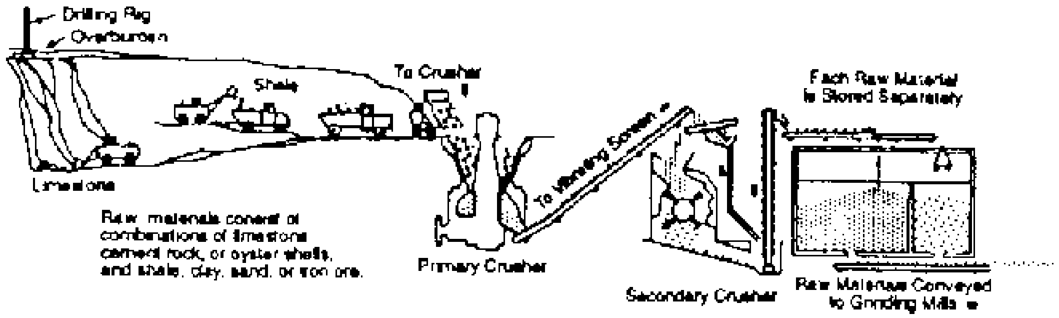
*Includes gray and white plants.

Table 3-3. (con.)

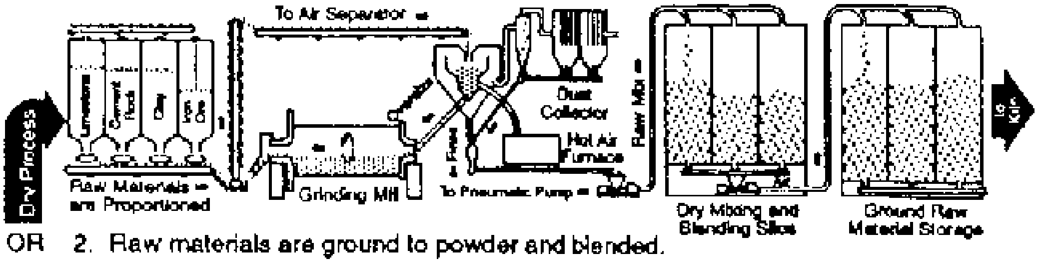
Rank	**Clinker (10^3 tons)**	**States**
31	490	New Mexico
32	470	Washington
33	460	Wyoming
34	460	Maine
35	420	Nevada
36	260	Hawaii
37	210	Idaho
Total	***81,100***	

There are no clinker-producing plants in the following states:

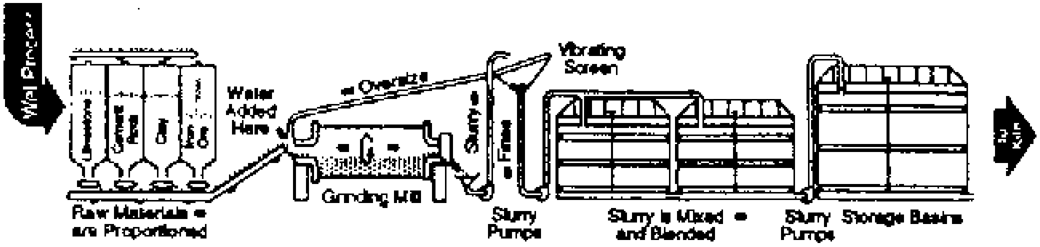
Alaska
Connecticut
Delaware
Louisiana
Massachusetts
Minnesota
New Hampshire
New Jersey
North Carolina
North Dakota
Rhode Island
Vermont
Wisconsin



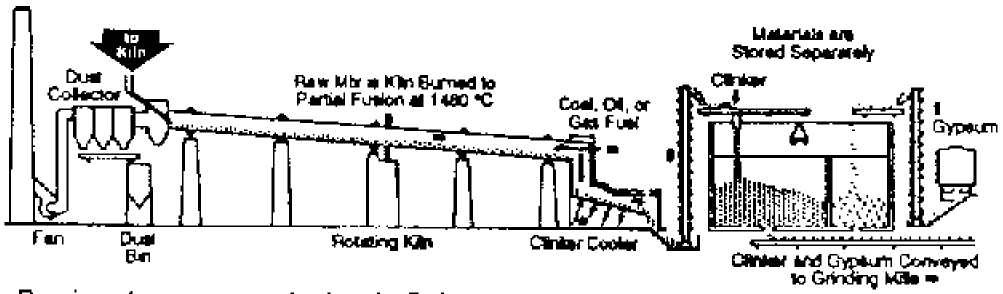
1. Stone is first reduced to 13-cm size, then to 2 cm and stored.



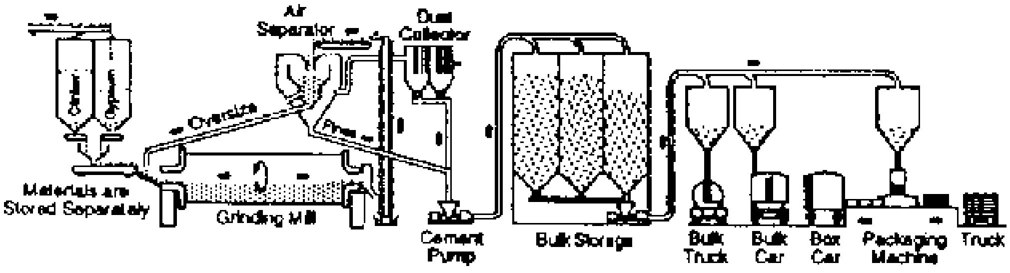
OR 2. Raw materials are ground to powder and blended.



2. Raw materials are ground, mixed with water to form slurry, and blended.



3. Burning changes raw mix chemically into cement clinker.



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

Figure 3-2. Steps in the manufacture of portland cement.[5]

cement processes: wet process and dry process.[5] Newer designs of dry process plants are equipped with innovations such assuspension preheaters or precalciners to increase the overall energy efficiency of the cement plant. A cyclone preheater system typically achieves 40 to 50 percent calcination of the feed before it enters the rotary cement kiln, whereas a precalciner system uses an additional firing system to achieve almost 95 percent calcination of feed before it enters the kiln.[4]

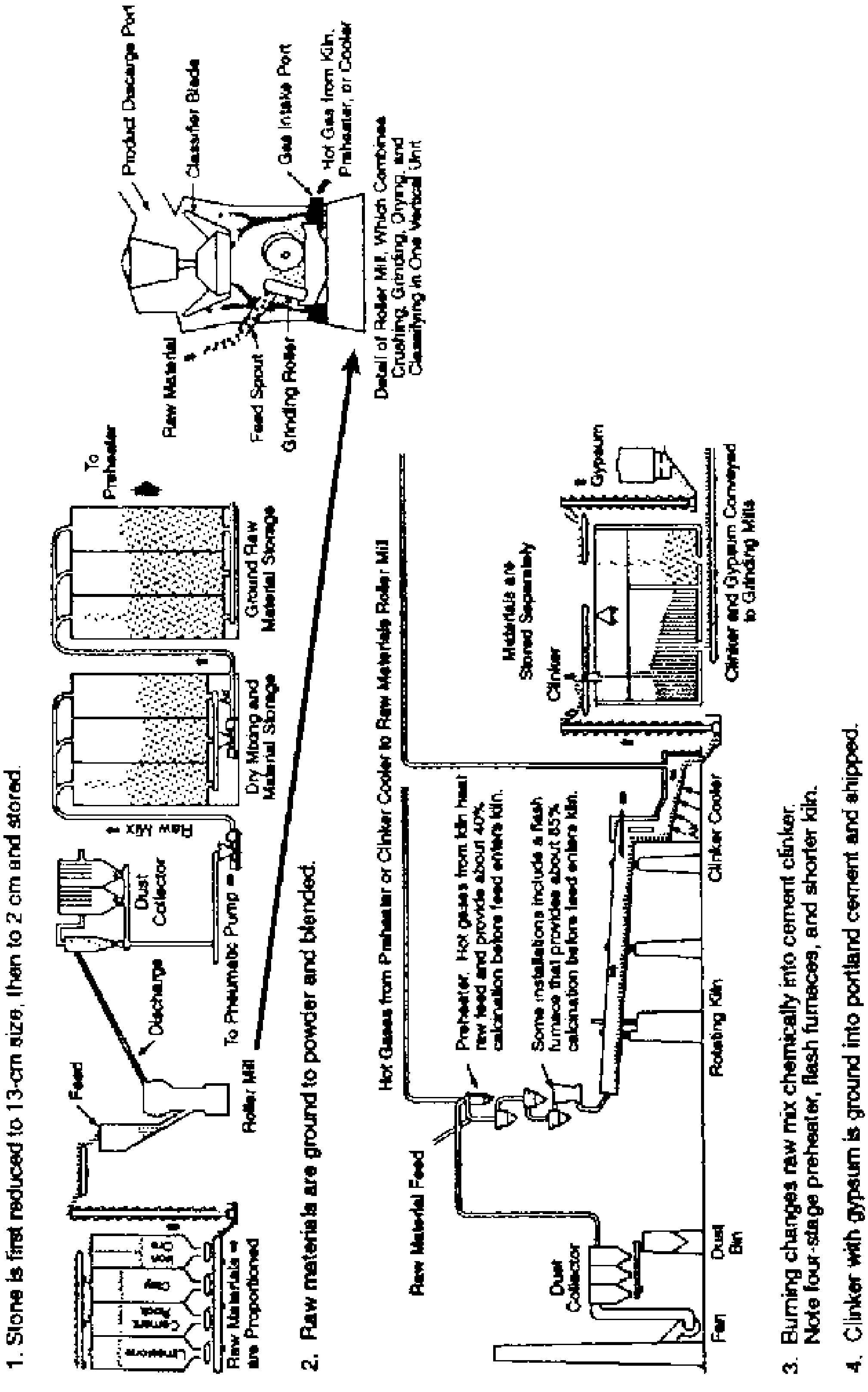


Figure 3-3. New technology in dry-process cement manufacture.[5]

Figure 3-3 is an illustration of a preheater/precalciner type of dry process system.[5]

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 1990, about 25 million tons of clinker were produced by the wet process with 55.8 million tons produced by a dry process. Within the dry process category, 15.7 million tons were produced by facilities equipped with a preheater system and 21.4 million tons were produced by facilities equipped with a precalciner system.[3]

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

3.3.3 Raw Materials and Kiln Feed Preparation

Oxides of calcium, silicon, aluminum, and iron comprise the basic ingredients of cement. Because of the large requirement of CaO, 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 raw mix, whereas alumina can be furnished by bauxites and alumina-rich flint clays.[4] Industrial by-products 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 dispersed 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 utilize exit gases from the kiln or clinker cooler to dry wet material during crushing. Each of the raw materials is stored separately and fed into the grinding mills separately using weigh feeders or volumetric measurements. Ball mills are used for both wet and dry processes to grind the material to a fineness such that only 15 to 30 wt% is retained on a 74-µm (200 mesh) sieve.

In the wet process the raw materials are ground with about 30 to 40 percent water, producing a well-homogenized mixture called slurry. Raw material for dry process plants is ground in closed-circuit ball mills with air separators, which may be set for any desired fineness. Drying is usually carried out in separate units, but waste heat can be utilized directly in the mill by coupling the raw mill to the kiln. 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 CaO 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.[4]

3.3.4 <u>Pyroprocessing</u>

Nearly all cement clinker is produced in large rotary kiln systems. The rotary kiln is a highly 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 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 onto 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. The cement formation process in the kiln may be divided into four stages, correlated with temperature of the materials in the rotary kiln[6]:

- Uncombined water evaporates from raw materials as material temperature increases to 100 °C (212 °F).
- As the material temperature increases from 100 °C (212 °F) to approximately 900 °C (1650 °F), dehydration and material heating occur.
- At 900 °C (1650 °F), calcination occurs in which CO_2 is liberated from carbonates.
- Following calcination, a chemical reaction of the dehydrated and decarbonated raw materials occurs in the burning zone of the rotary kiln at temperatures of about 1510 °C (2750 °F), producing clinker. About 20 to 25 percent of the material is molten.
- The cement clinker continues to change in character as it passes the zone of maximum temperature.

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. This is best achieved by using a short, intense flame as close to the discharge as possible. 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.

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. Because large quantities of water must be evaporated, most wet kilns are equipped with chains to maximize heat transfer from the gases to the slurry. The chains also serve to break up the slurry into nodules that can flow readily down the kiln without forming mud rings. 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 900 °C (1650 °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.[4]

Long process kilns typically represent an older cement technology with smaller capacity kilns. In the United States wet cement kiln capacities range from 90,000 to 1,312,000 tons/year with an average of 325,000 tons/year (41 tons/hour).[3]

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 long 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 good energy efficiency. Other than the need for evaporation of water, its operation is similar to that of a long wet kiln. To improve the energy efficiency of a dry process, variations such as suspension preheaters and precalciners have been introduced as discussed in the next sections.[4]

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 84,000 to 650,000 tons/year with an average capacity of 270,000 tons/year (34 tons/hour).[3]

3.3.4.3 Suspension Preheaters. In systems with suspension preheaters, the dry, pulverized feed passes through a series of cyclones 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 long wet or dry kilns. The intimate mixing of the hot gases and feed in the preheaters promotes condensation of alkalies 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 be bypassed and fewer cyclone stages used in the preheater with some sacrifice of efficiency.

Suspension preheater kilns represent a newer cement technology compared to the long kilns. They are also somewhat larger in production capacity than the long process kilns. In the United States the preheater type kiln capacities range from

126,000 to 963,000 tons/year with an average capacity of 400,000 tons/year (50 tons/hour).[3]

3.3.4.4 **Precalciner Systems**. The success of preheater kiln systems, particularly in Europe and Japan where low alkali specifications do not exist, led to precalciner kiln systems. These units utilize a second burner to carry out calcination in a separate vessel attached to the preheater. The flash furnace utilizes preheated combustion air drawn from the clinker cooler and kiln exit gases and 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.[4]

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 long kilns. The capacities of the precalciner type kilns in the United States range from 450,000 to 1,600,000 tons/year with an average of 890,000 tons/year (111 tons/hour).[3] Because of the new large precalciner plants replacing older and smaller long kiln plants, the overall average kiln capacity has been steadily increasing in the United States. It has increased from an average of 264,000 tons/year (33 tons/hr) in 1980 to an average capacity of 380,000 tons/year (48 tons/hr) in 1990.[3]

3.3.5 Finish Grinding

The cooled clinker is conveyed to clinker storage or 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 dia] containing a charge of steel balls, and rotating 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. These objectives 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.

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 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.

3.3.7 Emission Control Systems

Most cement plants are equipped with particulate collection devices to remove cement kiln dust (CKD) from the kiln exhaust gases as well as clinker cooler gases. Several small dust collectors are also installed at various dust emission points such as crushing 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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CHAPTER 4

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 high process temperatures involved. Essentially all of the NO_x emissions associated with cement manufacturing are generated in the cement kilns. Although, there are other heating operations in a cement plant, such as drying of raw feed or coal, often the heat from the kiln exhaust gases is used for these operations making their contribution to NO_x emissions negligible.

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

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

Sometimes the raw material feed to the kiln may also contain nitrogen compounds which may lead to feed NO_x formation similar to fuel NO_x formation. Because of the high temperatures involved in the burning or clinker formation step, the thermal NO_x formation provides the dominant mechanism for NO_x formation in cement manufacturing. The term NO_x includes both NO and NO_2 species, although NO_2 normally accounts for less than 10 percent of the NO_x emissions from a cement kiln exhaust stack.[1] The concentration and emission of NO_x are, however, typically expressed in equivalent NO_2 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:

$$N_2 + O \rightleftharpoons NO + N \quad k_f = 2 \times 10^{14}\ \mathrm{EXP}\ (-76500/RT) \tag{4-1}$$

$$N + O_2 \rightleftharpoons NO + O \quad k_f = 6\text{"}3 \times 10^{9}\ \mathrm{EXP}\ (-6300/RT) \tag{4-2}$$

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 O_2 further results in NO_2 formation.

The equilibrium concentrations of NO and NO_2 formed thus depend strongly upon the gas-phase temperature as well as the concentration of O_2 and N_2 in the gas phase. Table 4-1 shows the equilibrium concentrations of NO and NO_2 for two conditions.[3] First, the equilibrium concentrations of NO and NO_2 for N_2 and O_2 concentrations found in ambient air are shown. Secondly, Table 4-1 also shows the NO and NO_2 concentrations at flue gas conditions where the O_2 and N_2 concentrations are defined for this table as 3.3 percent O_2 and 76 percent N_2. The equilibrium NO concentrations for the flue gas conditions are lower than those for ambient conditions due to the lower O_2 concentration.

TABLE 4-1. CALCULATED EQUILIBRIUM CONCENTRATIONS (in ppm) OF NO AND NO_2 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

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).

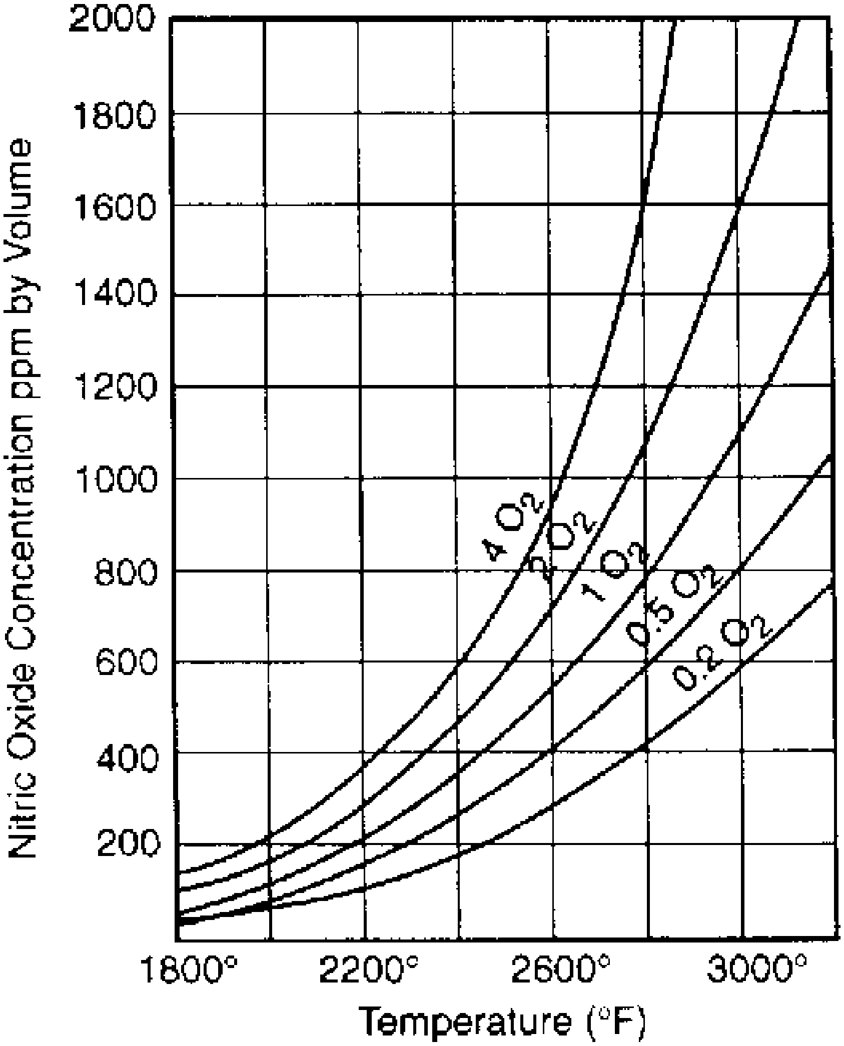


Figure 4-1. Theoretical equilibrium concentrations of NO in gas from combustion sustained in air.[1]

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.

4.1.2 <u>Fuel NO_x Formation</u>

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 76 percent of the energy requirement of the cement industry is

provided by coal.[5] Natural gas contributed about 8 percent of the energy demand, oil about 1 percent, and other fuels such as waste solvents provided about 15 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 organic solvents are finding an increasing application in the cement kilns. 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. 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 NO_2) would be produced per ton of clinker with 100 percent nitrogen conversion. Thus, even with only 10 percent conversion of coal nitrogen to NO_x, 1.5 lb of fuel NO_x (expressed as NO_2) may be formed per ton of clinker when coal is used as a primary fuel.

The amount of fuel NO_x formed is difficult to identify separately from thermal NO_x as measurements indicate the overall NO_x formed. In general, however, thermal NO_x is assumed to be the dominant mechanism in cement kilns.[6] 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 may typically produce almost three times more NO_x than the coal-fired, dry-process kilns.[6] This fact indicates the dominance of thermal NO_x in the overall NO_x formation.

4.1.3 Feed NO_x Formation

Similar to coal, the raw materials used in cement production may contain 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. A recent study indicated various kiln feeds to contain appreciable amounts of nitrogen, ranging from about 20 ppm up to as much as 1000 ppm (as N).[7] 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.[7] 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.[8]

4.2 FACTORS AFFECTING NO_x EMISSIONS IN CEMENT MANUFACTURING

Chapter 3 identified four different types of cement kilns used in the industry: long wet kilns, long dry kilns, kilns with a preheater, and kilns with a precalciner. The long wet and dry kilns have only one fuel combustion zone, whereas the newer preheater and precalciner kiln designs have two fuel combustion zones: kiln burning zone and secondary firing zone. Because the typical temperatures present in the two types of 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 less 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 which depends upon the combustion zone temperature, and 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 intensive 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 intensive 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 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, 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 in excess of 2,600 °C(4,710°F) and oxygen-rich environment. Often natural gas 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 excess oxygen needed to maintain the quality of the clinker produced. 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 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 need to be burned harder (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 from 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: 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 heat than a dry kiln. This means a greater amount of exhaust gas from a wet kiln. On the other hand, the greater amount of combustion air will also mean a somewhat lower secondary air temperature. Based on these contrasting 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 <u>NO_x Formation in Secondary Firing</u>

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

$$\text{"N"} + O \rightarrow NO \tag{4-3}$$

$$\text{"N"} + NO \rightarrow N_2 + O \tag{4-4}$$

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 in 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.[9] 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 <u>Suspension Preheater (SP) Kilns with Riser Duct Firing</u>. 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.[10] 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 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 the 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 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 production or a net reduction of NO in the calciner.

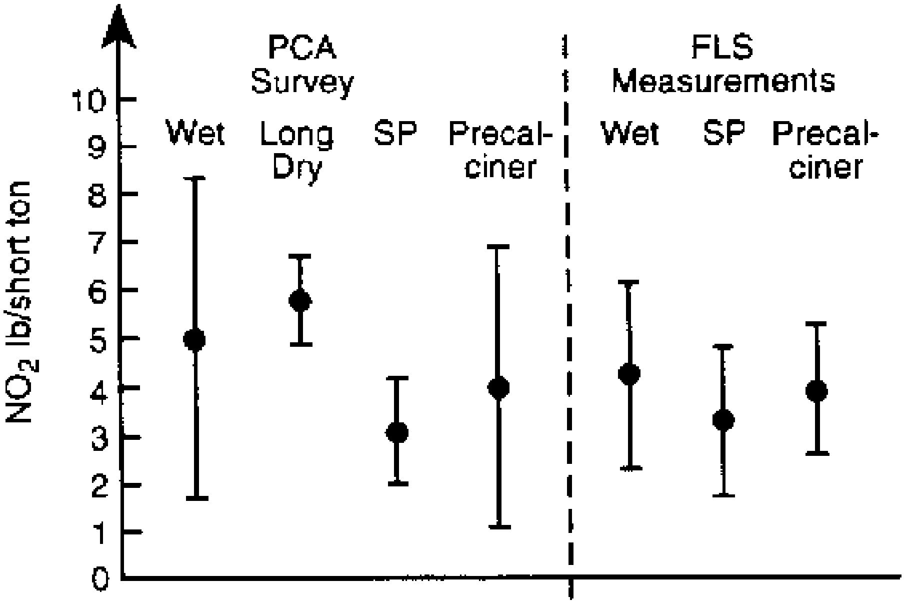
SLC systems: In these systems, the fuel combustion in the calciner takes place in pure hot air. In the case of oil firing, NO production in the calciner is negligible; but when using fuels containing fuel-bound nitrogen, up to 50 percent of the nitrogen compounds in the fuel may be converted into NO_x. 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 pet 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 the NO_x formation is directly related to the fuel combustion, any reduction in the amount of fuel burned per unit amount of cement produced should reduce NO_x emissions per unit amount of cement. Attempts to improve energy efficiency of the process by avoiding excessive clinker burning, 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 constructions 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 long wet or 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. The PCA conducted a survey of the NO_x and SO_x emissions from the cement industry in 1982.[11] Results of that survey are shown in Figure 4-2 which indicates an average and the range of the NO_x emissions



	PCA Wet	PCA Long Dry	PCA SP	PCA Precalciner	FLS Wet	FLS SP	FLS Precalciner
Number of Kilns	8	3	3	10	7	13	7
Average	4.97	5.70	2.98	3.86	4.07	3.13	3.77
Standard Deviation	3.28	0.85	1.05	2.89	1.89	1.57	1.31

Figure 4-2. Result of PCA NO_x emission survey.[1,10,11]

for different kiln types. This figure also includes NO_x emissions measurements at 9 cement kilns in Germany,[10] and measurements at 18 kilns performed by F.L. Smidth and Company in several other countries.[1] As seen from this figure, there are substantial variations in NO_x emissions even for cement kilns of the same type. The spread is greater with a greater number of kilns sampled. This survey provided average NO_x emission factors for four different kiln types: 4.97 lb/ton of clinker for wet process kilns, 5.7 lb/ton of clinker for dry process kilns, 2.98 lb/ton of clinker for kilns with SPs, and 3.86 lb/ton of clinker for kilns equipped with a precalciner.

Table 4-2 includes data collected by PCA during a recent revision of the AP-42 emission factors for the cement industry.[12] This table also includes data from other available emission test reports. The revised emission factors adopted for the AP-42 document for the same four kiln types mentioned above are somewhat different than the earlier PCA survey: 8.2 lb/ton of clinker for wet process kilns, 5.7 lb/ton of clinker for dry process kilns, 5.5 lb/ton of clinker for kilns with preheaters, and 4.8 lb/ton of clinker for kilns with precalciners. The NO_x emission rates given in Table 4-2 also exhibit substantial spread similar to that in Figure 4-2: long wet-kiln emissions ranged from 3 to 20 lb/ton of clinker, long dry-kiln emissions ranged from 3 to 17 lb/ton of clinker, preheater-kiln emissions ranged

TABLE 4-2. CEMENT KILN NO_x EMISSIONS

Plant company, location	Date	Process type	Uncontrolled NO_x emissions		Reference
			ppm @ 3% O_2	lb/ton clinker	
Ash Grove Cement Co.					
Leamington, UT	7/88	Dry - C	226 ppm @ 12.7% O_2	4.36	13
Durkee, OR	9/85	Dry - X	480	5.06	14
Calaveras Cement Co.					
San Andreas, CA	11/1/79	Wet	332	2.8	15
Redding, CA	5/81	Dry - X	-	2.4	16
California Portland					
Colton, CA					
Kiln - 1	3/91	Dry	-	5.3	17
Kiln - 2	3/91	Dry	-	7.4	17
Kiln - 1	8/13/91	Dry	670	5.4	18
Kiln - 1	1/29/90	Dry	188	3.25	19
Kiln - 1 Oil fired	9/74	Dry	600-1085	-	20
Kiln - 1 Gas fired	9/74	Dry	1680-2890	-	20
Kiln - 2 Gas fired	9/74	Dry	2790-3565	-	20
Kiln - 1	2/87	Dry	-	6.7	21
Kiln - 2	2/87	Dry	-	6.8	21
Kiln - 1	3/87	Dry	-	6.1	21
Kiln - 2	3/87	Dry	-	6.5	21
Kiln - 1	4/87	Dry	-	7.1	21
Kiln - 2	4/87	Dry	-	6.9	21
California Portland					
Cement Co., Mojave, CA	9/14/82	Dry - C	517	-	22
Coal fired	5/23/83	Dry - C	462	2.8	23
Coal fired	5/84	Dry - C	624	3.43	24
Coal and gas fired	5/85	Dry - C	639	3.88	25
Coal, gas, oil fired	5/86	Dry - C	276	1.72	26
Coal and gas fired	5/87	Dry - C	925	5.35	27
Coal fired	5/88	Dry - C	639	4.49	28
Coal and gas fired	5/89	Dry - C	842	5.49	29
Florida Mining &					
Materials, Inc.					
Brooksville, FL	8/82	Dry - X	-	1.1	30
	4/84	Dry - X	-	2.2	30
	4/85	Dry - X	-	1.96	30
	4/86	Dry - X	-	6.0	30
	5/86	Dry - X	-	3.44	30
	9/86	Dry - X	-	1.53	30
	4/87	Dry - X	-	2.23	30
	6/88	Dry - X	-	1.59	30
	5/89	Dry - X	-	1.7	30
General Portland,	4/82	Dry	420	3.3 -	31
Lebec, CA	9/82		945	14.0	31
Gifford Hill Cement Co.,					
Crestmore, CA	7/81	Dry	451	4.5	32
Midlothian, TX					
Kiln - 1	10/87	Wet	-	8.15	33
Kiln - 2	3/85	Wet	-	9.86	33
Kiln - 3	8/85	Wet	-	20.13	33
Kiln - 3	3/85	Wet	-	6.25	33

Plant company, location	Date	Process type	Uncontrolled NO_x emissions		Reference
			ppm @ 3% O_2	lb/ton clinker	
Kaiser Cement Co. Permanente, CA	11/27/79	Wet	1936	17.5	34
	12/12/79	Wet	1656	13.4	34
Kosmos Cement Co. Louisville, KY	6/89	Dry - X	396	5.78	35
Lafarge Corporation, Alpena, MI	3/89	Dry	232	4.25	36
Lehigh Portland Cement Co., Waco, TX	8/83	Wet	363 ppm @ 15% O_2	10.2	37
Lone Star Florida/Pennsuco Inc., Miami, FL	7/81	Wet	-	6.35	38
Kiln - 3	7/81	Wet	-	5.55	39
	12/86	Wet	582 @ --	6.83	40
Lone Star Industries Davenport, CA	9/24/80	Semi-Wet	406	3.3	41
	5/82	Dry - C	189 @ 14%	2.36	42
	8/82	Dry - C	-	4.02	43
Mill on	8/83	Dry - C	225 @ 10%	2.37	44
Mill off	8/83	Dry - C	198 @ 10%	2.08	44
Mill on	12/83	Dry - C	221 @ 11%	2.65	45
Mill off	12/83	Dry - C	184 @ 12%	1.84	45
Mill on	3/84	Dry - C	181 @ 11%	2.16	46
Mill off	3/84	Dry - C	206 @ 9%	2.16	46
Sweetwater, TX					
Kiln - 2	6/80	Dry - X	783 @ --	9.14	47
New Orleans, LA					
Kiln - 1	5/82	Wet	350 @ --	4.37	48
Kiln - 2	5/82	Wet	390 @ --	4.0	48
Monolith, Mojave, CA	12/6/79	Wet	642	6.9	22
Riverside Cement Co. Riverside, CA					
Gas fired	9/74	Dry	2400-5200	21.0	20
Coal fired	4/76	Dry	381	2.25	49
Gray kiln - 2					
Baghouse inlet	7/81	Dry	999	8.78	50
Baghouse outlet	7/81	Dry	1427	14.32	50
Gray kiln - 1					
Baghouse outlet	7/81	Dry	451	4.52	50
Gray kiln - 2					
Baghouse inlet	10/81	Dry	1310	14.0	51

TABLE 4-2. (con.)

Plant company, location	Date	Process type	Uncontrolled NO_x emissions		Reference
			ppm @ 3% O_2	lb/ton clinker	
Southwestern Portland Cement Co., Black Mountain, CA	5/78	Dry - oil	2289	21.8	52
	6/10/80	Dry - coal	548	4.0	53
	10/80	Dry - coal	770 @ 10%	7.35	54
	6/84	Dry - coal	453 @ 11%	5.17	55
	7/84	Dry - coal	419 @ 12%	5.16	56
Southwestern Portland Cement Co.					
Nephi, UT	5/84	Dry - C	882	7.5	57
Odessa, TX					
Coal fired	2/83	Dry - X	384	5.68	58
Gas fired	6/89	Dry - X	883	11.26	59
Victorville, CA					
Kiln - 6	8/80	Dry	687 @ 10%	9.1	54
Kiln - 7	8/80	Dry	235 @ 14%	4.05	54
Kiln - 9	8/80	Dry	971 @ 6%	14.7	54
Kiln - 5	10/80	Dry	1077 @ 9%	17.3	60
Kiln - 8	10/80	Dry	690 @ 10%	11.0	60
Kiln - 1	7/84	Dry	575 @ 8%	5.5	61
Kiln - 2	2/85	Dry - C	492 @ --	5.03	62
Kiln - 2	3/85	Dry - C	1074	7.12	63
Kiln - 2	2/87	Dry - C	891	6.41	64
Kiln - 2	3/87	Dry - C	954	6.64	65
Texas Cement Co. Buda, TX	6/86	Dry - C	-	3.8	66

from 2 to 9 lb/ton of clinker, and precalciner-kiln emissions ranged from 2 to 7 lb/ton of clinker.

During preparation of this ACT document, NO_x emissions data were collected from major cement companies in the United States. Out of 48 cement kilns providing NO_x emissions data, 22 were from long wet kilns, 8 were from long dry kilns, 8 were from preheater kilns, and 10 were from precalciner type cement kilns. Table 4-3 presents these most recent data on NO_x emissions along with the kiln types and fuels burned.

As seen from Table 4-3, 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 WDFs 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. 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 were found to consume significantly less energy than wet kilns (about 4.5 MM Btu/ton on average) and also were found to 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 long wet and dry kilns are similar in terms of structure and firing of fuels. The difference in the NO_x

TABLE 4-3. SUMMARY OF RECENTLY COLLECTED NO$_x$ EMISSIONS DATA

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	63
	2	Wet	36	As above	7.1	18.34	CEM Jul-92	63
	3	Wet	54	As above	7.05	15.65	CEM Jul-92	63
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	63
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	63
Nephi, UT	1	Precalciner	80	100% - Coal	3.6	3.43	Nov-82	63
						4.51	Jul-88	63
						1.31	Apr-92	63
2. Blue Circle Inc.								
Calera, AL	1	Dry	38	100% - Coal	3.8	9.58	CEM	68
Atlanta, GA	1	Dry	38.5	50% - Coal 50% - Coke	3.95	10.47	CEM	68
Ravena, NY	1	Wet	106.3	40% - Coal 60% - Coke	4.9	9.38	CEM	68
Tulsa, OK	1	Dry	38.5	100% - Coal	4	7.5	CEM	68
Harleyville, SC	1	Preheater	85	100% - Coal	3.5	5.87	CEM	68

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

CEM = Continuous emissions monitor

WDF = Waste-derived fuel

LWDF = Liquid waste-derived fuel

SWDF = Solid waste-derived fuel

TABLE 4-3. (con.)

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
3. California Portland Cement Inc.								
Rillito, AZ	1	Long Dry	17	71% - Coal 28% - Gas 1% - Coke	5	7.2 - 11 (9.1)	EPA Method 7E - CEM Jun-91	69
	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	69
	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	69
	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 1991	69
Mojave, CA	1	Precalciner	130	90.8% - Coal 4.7% - Oil 4.5% - Gas	3.1	3.9	CARB 100 Compliance Test May-92	69
4. CBR Cement Corporation								
Redding, CA	1	Preheater	85	80% - Coal 20% - Tires	3.1	2.5	CEM Jul-92	70
5. Holnam, Inc.								
Theodore, AL	1	Precalciner	193.8			4	EPA Method 7E 9/24/91	71
Florence, CO	3	Wet	60			5.8	EPA Method 7E 10/24/91	71

TABLE 4-3. (con.)

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 1992	71
Artesia, MS	1	Wet	62.5			12.5	CEM 7/16/92	71
Clarksville, MO	1	Wet	170			6.8	CEM	71
Three Forks, MT	1	Wet	37.7			11.6	EPA Method 7 2/10/86	71
Ada, OK	1	Wet	40			15.9	KVB System Jun-92	71
	2	Wet	40			19.5	KVB System Jun-92	71
Holly Hill, SC	1	Wet	60			5.7	CEM 6/28/92	71
	2	Wet	102			5.3	CEM 7/9/92	71
Morgan, UT	1	Wet	22			6.61	EPA Method 7E 11/21/91	71
	2	Wet	22			5.46	EPA Method 7E 11/27/91	71
Seattle, WA	1	Wet	56.2			8.12	EPA Method 7E 10/15/90	71
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	72

TABLE 4-3. (con.)

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
Davenport, IA	1	Preheater-precalciner	108.3	100% - Coal	3.2	217 lb/hr 2.61	EPA Method 7 9/21/82	73
						204.4 lb/hr 2.07	6/6/84	73

TABLE 4-3. (con.)

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	74
					6.17	~550 ppm 9/17/91		74
	2	Wet	28.5	100% - Coal	5.85	~500 ppm 9/18/91		74
Alpena, MI	1	Dry	70	78% - Coal 22% - WDF	5	957 ppm avg	CEM 8/7/92	75
	2	Dry	45	100% - Coal	4.6	393 ppm avg	CEM 8/7/92	75
Sugar Creek, MO	1	Dry	66.7	71.4% - Coal 23.8% - Coke 4.8% - Gas	4.52	6.1	EPA Method 7E 9/19/91	76
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	77
Whitehall, PA	3	Four-stage preheater	36	70% - Coal 30% - Coke	3.3	4.24	EPA Method 7E	78
						3.2 90:10::coal:tire	Dec-91	78
						3.3 80:20::coal:tire		78
						4.1 70:30::coal:tire		78
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	79
7. Lehigh Portland Cement Co.								

TABLE 4-3. (con.)

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
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	80
Cementon, Ny	1	Wet	77	100% - Coal	5.25	5.9	5/22/90	80
Buda, TX	1	Precalciner	138	95% - Coal 5% - Gas	3.63	3.8	6/30/86	80
Waco, TX	1	Wet	10	68% - Gas 32% - Coke	8.8	17.1	12/5/85	80
8. Lone Star Industries								
Oglesby, IL	1	Dry	64.6			8	CEM 5/92-6/92	81
						7.2	EPA Method 7 12/13/83	81
Greencastle, IN	1	Wet	91.7			5	CEM	81
Cape Girardeau, MO	1	Precalciner	139.4			1.4 (178 ppm)	CEM 4/13/92	81
	1	Precalciner	139.4			0.9 (115 ppm)	CEM 4/15/92	81
	1	Precalciner	139.4			1.5 (182 ppm)	CEM 6/25/92	81
Sweetwater, TX	3	Preheater	20.8			11.68	EPA Method 7 Apr-May 1991	81
9. Southdown, Inc.								
Brookesville, FL	1	Preheater	80	100% - Coal	3.2	3	CEM Feb-92	82
Fairborn, OH	1	Preheater	85	80% - Coal 20% - LWDF	3.9	11	CEM Dec-91	82

TABLE 4-3. (con.)

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
Knoxville, TN	1	Preheater-Precalciner	80	75% - Coal 12% - LWDF 13% - SWDF	3.6	7	CEM Jan-91	82

emission rates may thus be attributed to the difference in the energy consumption rates in these two types of kilns.

The preheater type of kilns was reported to produce 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 highest values of 8.1 and 11.7 were incidently 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 long wet or dry kilns.

The precalciner kilns produced the least NO_x emissions ranging from 0.9 to 7.0 with an average of 3.4 lb NO_x/ton of clinker. These kilns were also the most energy efficient with an average energy consumption of 3.3 MM Btu/ton of clinker. In precalciner kilns, the proportion of the fuel burned at the calcining temperature is much greater as compared to the preheater type kilns leading to lower NO_x emissions.

The literature data indicate 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. The emission factors based on the information obtained during this study will be used in estimating uncontrolled and controlled emissions from typical cement kilns and are given in Table 4-4.

This table also includes the heat input requirement for the

TABLE 4-4. 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)
Long 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

different cement kiln types which indicates a good correlation with the NO_x emission rates.

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CHAPTER 5

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 and the amount of nitrogen and oxygen available for the thermal reaction; and to reduce the amount of thermal NO_x formed, these variables need 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 amount of fuel and feed nitrogen, the greater the fuel NO_x emissions. Therefore, reducing the amount of fuel and feed-bound nitrogen will 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 4-4. 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 product. With the rising costs of energy and the very competitive cement market, greater attention is being paid to reduce over-burning of clinker, improving gas-solids heat transfer and increasing overall energy efficiency. Continuous emissions monitoring of CO, NO_x, and O_2 provide an indication of clinker burning conditions and also provide an input for process control. Newer cement kiln designs are generally based on preheater/precalciner systems which provide very efficient gas-solids contact and a greater energy efficiency.

NO_x control approaches applicable to the cement industry may be grouped in two categories:

- Combustion control approaches where the emphasis is on reducing NO_x formation, and
- Postcombustion control approaches which destroy the NO_x formed in the combustion process.

5.1 COMBUSTION CONTROL APPROACHES FOR REDUCTION IN NO_x FORMATION

5.1.1 Combustion Zone Control of Temperature and Excess Air

Continuous monitoring of O_2 and CO emissions in the cement kiln exhaust gases indicates the excess air being used in the process. At a given excess air level, NO_x emissions indicate the temperature of the combustion zone. 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.[1] The corresponding gas-phase temperature is usually greater than 1700 °C (3100 °F).[2] Maintaining the combustion zone temperature to 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 1 percent kiln exhaust oxygen level, typically the kiln operators strive for an oxygen level of 1 to 3 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 can be reduced by approximately 15 percent.[3]

With state-of-the-art continuous CO and NO_x monitoring 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 Process Modifications

By using the simple monitoring and feedback control approach, NO_x emissions would be minimized to a certain level. Process modifications that may be used for additional reductions in the NO_x formation are discussed below.

5.1.2.1 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 decreasing burnability of the raw feed, the heat requirement of clinker can be reduced by 15 percent.[4] 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 is produced. This approach of changing the feed composition may, however, be highly site specific and may not be applicable at all locations.

The alkali content of finished cement 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 molten clinker. Raw materials with greater alkali content need to be burned harder (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 from 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: 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. Reducing the alkali content of the raw feed mix will thus reduce the NO_x emissions.

5.1.2.2 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.[5] 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.[5] 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 gas to coal. A number of cement kilns have already made the switch from gas to coal fuel and currently almost 80 percent of the primary fuel burned in cement kilns is coal.[6]

Switching to a fuel with a higher heating valve 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. The petroleum coke is also more uniform in terms of heat value, lower in volatile matter content and burns with a lower flame temperature.

5.1.2.3 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 likely to be reduced per ton of clinker produced.

5.1.3 Staging Combustion Air, Low NO_x Burner, and Flue Gas Recirculation

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 primary, fuel-rich zone. This zone provides the high temperatures necessary for completion of the clinkering reactions. However, in this zone, due to fuel-rich conditions and lack of available oxygen, formation of thermal and fuel NO_x is minimized. 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. The temperature in this second zone is, however, much lower than the first zone because of mixing with the cooler secondary air. The formation of NO_x is thus minimized in spite of the excess available oxygen in the second zone. This approach can be used for combustion of all fossil fuels. The 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 a subsequent cooler zone.

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 termed as 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 compressor for additional power. Such conversion is, however, necessary for effective staging of combustion air to reduce NO_x emissions. Cement kiln burners, specifically marketed as low-NO_x burners typically use 5 to 7 percent primary air[7,8] and thus can be used only on indirect-fired kiln systems. An indirect-firing system increases overall energy efficiency by allowing a greater proportion of hot clinker cooler air as secondary combustion air.

The reduction in NO_x emissions with reduced primary air was demonstrated in an experimental study on a subscale coal-fired kiln.[9] The lowest proportion of primary air used in this study, however, was only 15 percent and the experimental results cannot be directly translated to a full-size kiln.

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. The oxygen content of the primary air may be reduced by recycling a portion of the flue gas into the primary combustion zone.[10] 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 effect of the primary air oxygen content was tested experimentally in a sub-scale kiln, which indicated about 37 percent reduction in NO_x emissions by reducing primary air oxygen content to 12.5 percent.[9] In this study the oxygen content of the primary air was diluted by adding inert nitrogen instead of FGR; however, similar results may also be expected with FGR which is also predominantly nitrogen.

The so called low-NO_x burners are designed to reduce flame turbulence, delay fuel/air mixing, and establish fuel-rich zones for initial combustion. The longer, less intense flames resulting from the staged combustion lower flame temperatures and reduce thermal NO_x formation. Some of the burner designs produce a low pressure zone at the burner center by injecting fuel at high velocities along the burner edges. Such a low pressure zone, as shown in Figure 5-1,[7]

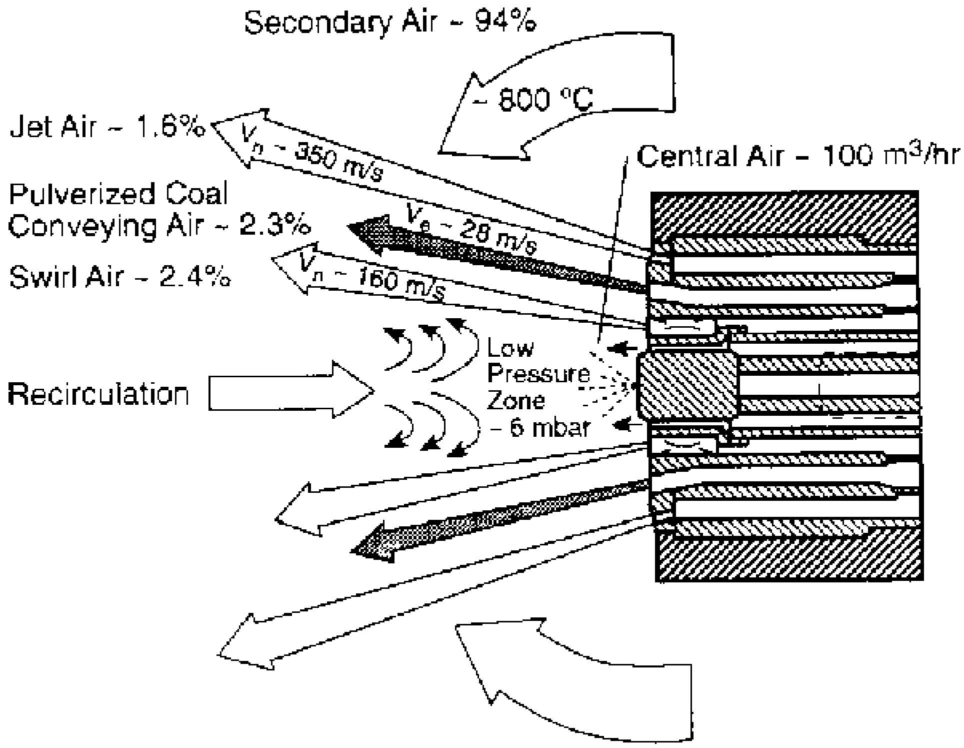

Figure 5-1. Schematic of a low-NO_x burner.[7]

tend 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 effect of FGR. Combustion of the fuel in the first stage thus takes place in oxygen-deficient zone before the fuel is diluted in the secondary air. Installing such a burner is claimed to reduce NOx emissions from the kiln-burning zone by up to 30 percent.7,11,12

Coupling a low-NOx step burner with flue gas recirculation has been shown to reduce NOx emissions further in a cement kiln.13 The additional NOx reduction attributable to FGR was estimated to

be about 15 to 38 percent depending upon the proportion of FGR used.13 Incorporation of FGR in a cement kiln also results in somewhat increased power consumption and reduced kiln output. Although low NOx burners have been reported being used in some European installations, very few of these burners have been installed in cement kilns in the United States.

The effectiveness of a low-NOx burner (Pillard) was tested in a cement kiln in the United States in 1984.14 In this test, NOx emissions from a straight pipe burner and a Pillard burner were compared. The NOx emissions with a straight pipe burner were 335 lb/hr for a kiln feed of 170 t/h. The tests with the Pillard burner indicated NOx emissions of 199 lb/h for a kiln feed of 163 t/h. However, during the 1-year interim period, a number of other changes were implemented prior to installing the Pillard burner, e.g., reduction in oxygen level. Thus, these results were not considered to be conclusive in evaluating the NOx reduction potential of a low-NOx burner.14

5.1.4 Secondary Combustion of Fuel

In conventional long 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 process, however, a large amount of heat is required to complete the preheating and calcination of the raw materials. Limestone calcination is typically conducted at a temperature of 870 to 980 °C (1600 to 1800 °F) which is much lower than the kiln clinker burning temperature.1 In the secondary combustion concept, part of the fuel is burned at a much lower temperature in a secondary firing zone to complete the preheating and the calcination of the raw materials.

The precalciner designs of the cement kilns are based on this concept of a secondary firing zone. Construction of almost all new cement kilns involve preheater/precalciner type designs. These systems typically employ a tower of four-stage cyclones for efficient gas-solids contact which improves the energy efficiency of the overall process. In a typical precalciner kiln almost 40 to 50 percent of the fuel is burned at a lower (calcination) temperature which is expected to reduce the thermal NOx formation considerably. The preheater kilns may also use the secondary firing to a lesser extent. Up to 15 to 20 percent of the fuel may be fired in the riser duct in preheater designs1 although the primary emphasis in these designs is on efficient heat recovery from kiln exhaust gases.

The concept of staged combustion may also be used in the precalciner designs by injecting part of the calciner fuel in the kiln exhaust gas entering the calciner (secondary combustor). The tertiary air is added at a later point to complete the combustion of the calciner fuel. The injection of fuel in the kiln exhaust gas creates a reducing zone which reduces the NOx formed in the kiln combustor by following simplified reactions:

$$NO + C \rightarrow N + CO \qquad (5\text{-}1)$$

and

$$NO + CO \rightarrow N + CO_2 \;. \qquad (5\text{-}2)$$

As discussed in Section 4.2.2, nitrogen present in the fuel may also participate in the reduction of NOx. The primary NOx formation mechanism in the secondary firing is the fuel NOx 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.15 Very promising results appear to have been obtained recently with the staged combustion system shown in Figure 5-2 in which the fuel was

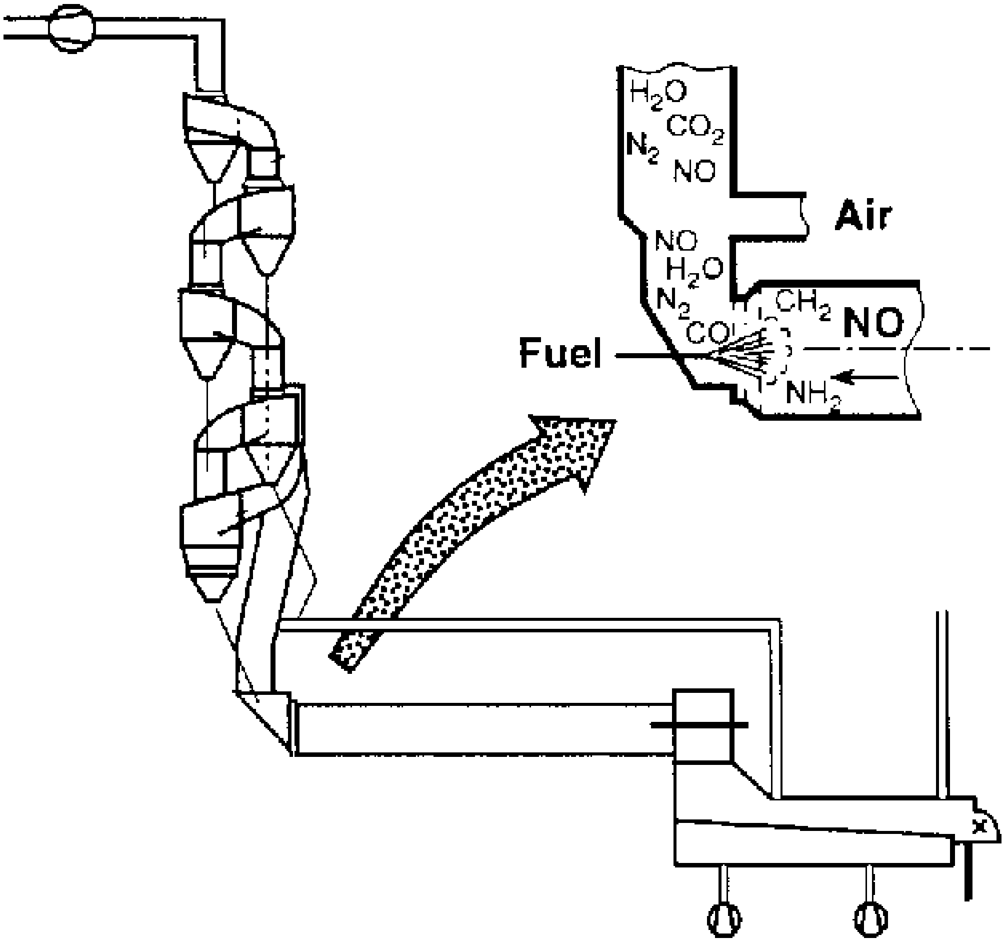

Figure 5-2. Reduction of NO_x emissions from precalcining kiln system by fuel injection in the rotary kiln gas outlet.[16]

simply injected countercurrent in the kiln exhaust gas.16 Up to 46 percent reduction of NOx emissions have been reported without causing excessive coating difficulties in the kiln.16 A similar effect was also observed by burning whole or shredded tires in the calciner zone. Substituting 47 percent of the coal fired in

the calciner by tire-derived-fuel, about 29 percent reduction was observed in NOx emissions.17

The concept of secondary firing may also be used in conventional long kilns by injecting solid fuel at an intermediate point in the rotating kiln using a specially designed feed injection mechanism.18 Such a scheme would allow burning part of the fuel at a material calcination temperature of 870 to 980 °C (1600 to 1800 °F) which is much lower than the clinker burning temperature. Due to the rotation of the kiln, fuel can be conveniently injected into the kiln only once, from the top, during its revolution as shown in Figure 5-3.19

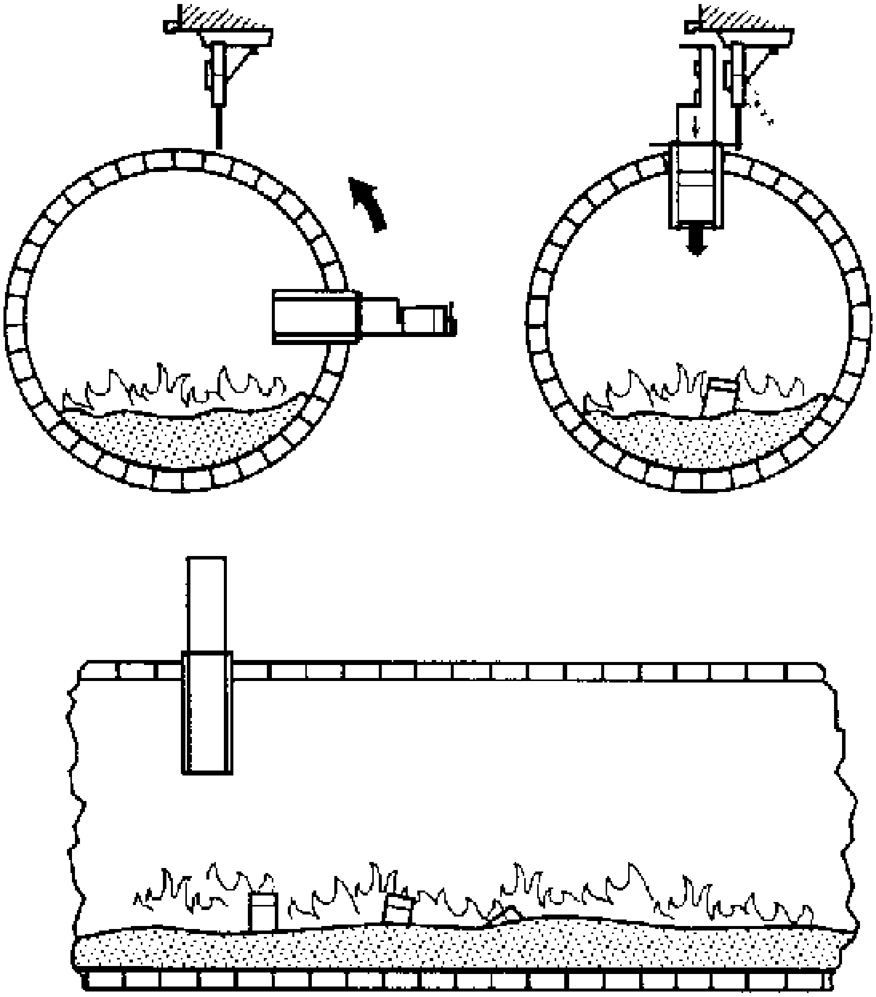

Figure 5-3. Schematic of hazardous waste container injection in kiln.[19]

Thus, to maintain a continuity in the heat input, solid and slow burning fuels (such as tires or containerized liquid or solid waste) are most amenable for this concept. The mid-kiln burning also allows burning tires or other waste-derived fuels without affecting the final product quality. 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.6 Secondary firing may reduce NOx by two mechanisms, (1) burning part of fuel at a lower temperature reduces thermal NOx formation, and (2) reducing conditions at the solid waste injection point may destroy some of the NOx formed upstream in the kiln burning zone. However, secondary firing may also produce additional fuel NOx depending upon the nitrogen content of the fuel. Recent tests have demonstrated feasibility of the mid-kiln firing and so far 10 long kilns have been modified to allow mid-kiln firing of solid and hazardous waste.19

The effect of mid-kiln firing of whole tires on NOx emission was recently investigated at two kilns. At one location NOx emissions were reduced from 20.1 lb/ton of clinker to 12.9 lb/ton of clinker, i.e., a reduction of 36 percent.20 At a second facility NOx emissions decreased from 16.6 lb/ton to 13.6 lb/ton clinker an 18 percent reduction in NOx emissions.21 The rates of substitution for fossil fuels by tires were 26 and 30 percent, respectively, at the two locations. Additional tests need to be

conducted to evaluate the effect of mid-kiln firing of other types of waste-derived fuels.

5.2 POSTCOMBUSTION CONTROL APPROACHES FOR NOx EMISSIONS CONTROL

5.2.1 Selective Catalytic Reduction (SCR)

SCR is a process of using ammonia in the presence of a catalyst to selectively reduce NOx emissions from exhaust gases. The SCR process has been used extensively in Japan to achieve a 90 percent reduction in NOx emissions from fossil fuel-fired boilers.22 In the United States SCR technology has successfully been used for gas turbines and internal combustion engines.22 In this process, 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 NOx reduction reactions. The two principal reactions are:

$$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O \qquad (5\text{-}3)$$

and

$$4\ NH_3 + 2\ NO_2 + O_2 \rightarrow 3\ N_2 + 6\ H_2O\ . \qquad (5\text{-}4)$$

Equation (5-3) represents the predominant reaction since 90 to 95 percent of NOx 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 SOx poisoning.23,24 Zeolite-based catalyst materials have also been developed capable of operating at higher temperatures than conventional metal based catalysts.24 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) which may be higher than typical cement kiln flue gas temperatures especially in plants using heat recovery systems or baghouses for particulate collection.

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. Recent developments have led to sulfur tolerant SCR catalysts which limit SO_2 oxidation to less than 1 percent.25 Soot blowers may be used to prevent dust accumulation on SCR catalysts. Since the typical SCR operating temperatures are greater than the typical kiln exhaust flue gas temperatures, installation of an SCR unit would also need flue gas reheating to increase the flue gas temperatures to an appropriate level.

Ammonia is typically injected to produce a NH_3 : NO_x mol ratio of 1.05-1.1 : 1 to achieve NO_x conversion of 80 to 90 percent with a "slip" of about 10 ppm of unreacted ammonia in the gases leaving the reactor.26 The NO_x destruction efficiency depends upon the temperature, NH_3 : NO_x mol 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.

There are currently no installations of SCR units in any United States cement plants or elsewhere. In 1976, Hitachi Zosen, an SCR manufacturer, conducted three pilot test programs to evaluate SCR on cement kilns.2 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 NOx removal efficiencies of 98 percent. However, after 5,400 hours of operation, NOx removal efficiencies dropped to about 75 percent due to catalyst coating.

SCR is a possible technology for the NOx reduction in cement kiln emissions. Based on the experience in other industries, NOx reductions in the range of 80 to 90 percent are considered possible, regardless of kiln type.22 However, further developmental studies are needed to demonstrate the specific NOx reduction in the cement kiln exhaust gas environment.

5.2.2 Selective Noncatalytic Reduction (SNCR)

This control technique relies on the reduction of NOx in exhaust gases by ammonia or urea in an appropriate temperature window of 870 to 1090 °C (1600 to 2000 °F) without using any catalyst. This process also involves 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 an appropriate temperature between 870 to 1090 °C (1600 to 2000 °F). At these temperatures urea decomposes to produce ammonia which is responsible for NOx 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 NOx becomes significant. At lower temperatures, the rates of NOx 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.27 Several other reagents can also shift the temperature window to the 700 °C(1290oF) level.28

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 solid or containerized liquid fuels allows injection of a certain amount of material once during the kiln revolution. Injection of solid ammonium or urea salts in this manner is not likely to work satisfactorily due to rapid decomposition of such salts. Therefore, SNCR technology is not considered to be applicable for long dry or wet kilns.

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.

Currently there are no installations of the SNCR process on cement kilns in the United States. SNCR has been experimentally tested on a preheater/precalciner kiln by F. L. Smidth and Company.2 In this experiment, ammonia was injected into the lower cyclone of the preheater tower where temperatures are favorable for the reduction reactions to occur. NOx emissions reductions during this experiment averaged 40 percent, but NOx reductions of over 90 percent were obtained when the ammonia injection rate was 10 to 20 percent in excess of stoichiometric.

A demonstration of the Nalco Fuel Tech NOxOUT System (urea-based SNCR) using NOxOUT-A (stabilized urea) was performed on a preheater/precalciner kiln system in October 1993. The kiln processes 160 TPH of solids and can fire coal or gas. NOxOUT-A was injected at the top, halfway and the bottom points of the calciner. While firing gas into the kiln and coal in the calciner, uncontrolled NOx emissions averaged 2.8 pounds per ton(lb/T) of material input. Uncontrolled NOx emissions increased to 2.9 lb/T, when gas is fired in both units. Limited short term data were obtained. At a normalized stoichiometric ratio(NSR) of 0.5, NOx was reduced ~27%. At an NSR of 1.0, NOx was reduced ~55%.29

The SNCR process was recently 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 5-4.30 With a molar ratio of regent to NO2 of 1:1, about 70 percent reduction in NOx emissions was observed with ammonia-based reagent and about 35 percent NOx reduction was obtained with urea.30 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 NOx reductions were observed with more than stoichiometric amount of reagent, although there was increasing ammonia 'slip' in the exhaust gases.

In the United States the SNCR process has been used for controlling NOx emissions from other combustion sources. Two commercial systems are available. In Exxon Thermal DeNOx process, anhydrous ammonia is mixed with a carrier gas of air or steam to provide good mixing of ammonia with the flue gas. Multipoint injection grids are used to compensate for varying temperatures in the injection locations. The Exxon DeNOx process has been installed in several combustion processes worldwide between 1975 and 1991. However, no installations of this process have yet been made on a cement kiln.28,31 Although originally designed to use anhydrous ammonia, concerns about safety and the need for high-pressure storage has led to the development of a process using aqueous ammonia.28

An SNCR process using aqueous urea rather than ammonia was developed by Electric Power Research Institute (EPRI) and is now marketed by Nalco Fueltech under the trade name of NOxOUT. The exact reaction mechanism with urea is not well understood, but it probably involves decomposition of urea with subsequent reaction of NHx groups with NO.24 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 developed by Nalco apparently widen the temperature window.24,32 One recent modification of the urea-based

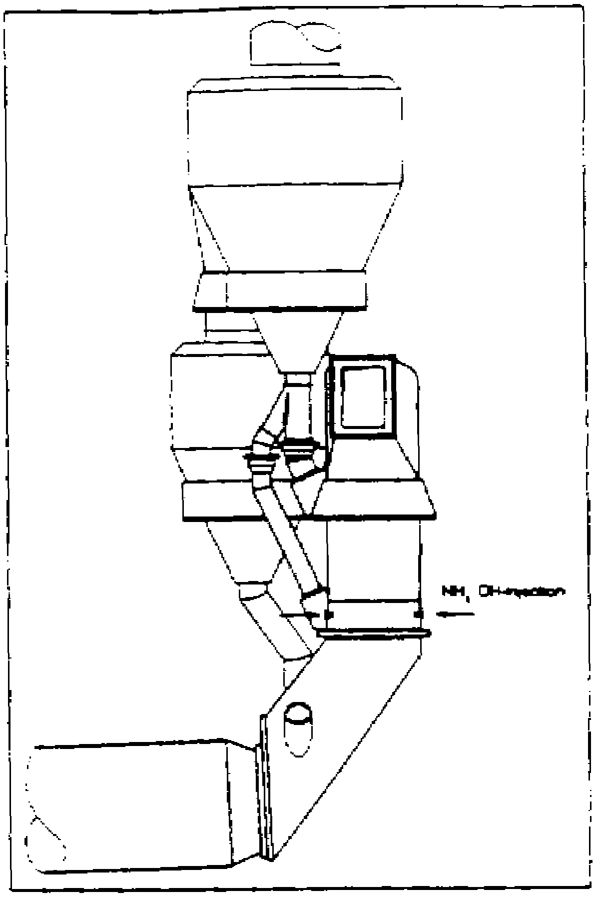

Figure 5-4. Application of the selective noncatalytic reduction technique (SNCR) in preheater kilns.[29]

SNCR system is the addition of methanol injection downstream of the urea injection point to improve overall NOx removal. Nalco also recently introduced an improved NOxOUT PLUS, which is said to broaden the operating temperature window and to reduce ammonia slip and CO and NO2 formation.

The NOx reduction efficiency of SNCR depends upon the temperature, residence time, as well as ammonia and NOx concentrations in the flue gas. Injection of ammonia at a NH3: 3NOx proportion of 1 to 1.5 will reduce NOx emissions between 60 to 80 percent. Using a mol ratio of 0.5 will give NOx reductions of approximately 40 percent.23 The reagent consumptions 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 N2O.33 The rate of N2O formation is a weak function of both the reactant and the NO concentration. However, N2O formation seems to be inherently more prevalent in systems using urea than those using ammonia.34

The NOx 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 NOx destruction. Maximum achievable NOx reduction in a cement kiln may thus depend upon the gas temperature profile.

5.3 SUMMARY OF APPLICABLE NOx CONTROL TECHNOLOGIES

Combustion zone control approaches discussed in Section 5.1.1 are based upon providing optimum kiln operating conditions which will increase the energy efficiency and productivity of the cement-making process while minimizing NOx emissions. Such measures will provide a baseline of NOx emissions in cement kilns without any specific NOx control equipment. Although these simple process control approaches will reduce NOx emissions in poorly operated kilns; for the purposes of this ACT document, such approaches are considered to be needed for proper kiln operation and not specifically considered as NOx control techniques.

Information obtained during this study indicated that some plants indeed relied on process monitoring and control and process modifications as a means to maintain NOx emissions within their respective permit limits.

The NOx reduction effect of process modifications discussed in Section 5.1.2 is usually difficult to isolate from other factors. Data are not available to explicitly determine the NOx reduction effectiveness of changing raw feed mix, fuel used, or other energy efficiency measures employed. 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 to obtain an overall effect of all measures. For example, a number of such measures collectively produced about 25 percent reduction in NOx emission at one site.17 Most of these approaches also result in increased energy efficiency and plant productivity providing another incentive to implement them. For example, at the same site mentioned above, over 15 percent reduction was also observed in the energy requirement per ton of clinker.

Limited information is available regarding the use of low NOx burners in a cement kiln. Staging of combustion air as achieved by such burners is a possible technique for NOx reduction in cement kilns. An integral requirement of a low NOx burner system is conversion of a direct-fired kiln to an indirect-fired one to allow using a much smaller proportion of combustion air as primary air. The low-NOx burner itself may become only a small part of the changes required to install a low-NOx burner. The conversion of a direct-fired kiln without a low-NOx burner may also have certain NOx reduction potential. The contribution of the low-NOx burner by itself and of the firing system conversion cannot be isolated from the limited data available.

Available data also are limited to assess the effectiveness of flue gas recirculation with only one reference to full size kiln use. The effect of secondary combustion as in mid-kiln firing has been evaluated for whole tire burning only. This technique can potentially be applied with other waste-derived fuels as well and needs further demonstration. Secondary combustion of fuel is inherently present in all precalciner kilns and preheater kilns with riser duct firing, and, as seen in Chapter 4, such kilns produce less NOx emissions compared to long dry kilns.

SNCR technology appears to be applicable to preheater/ precalciner type kilns with limited data indicating its effectiveness in full-size kilns. SNCR is not considered applicable to long wet and dry kilns due to difficulties involved in continuous injection of reducing agents. No data are available regarding effectiveness of SCR in full-scale cement kilns. SCR, however, has been successfully used in coal-fired boiler applications where exhaust gases contain a significant amount of particulate matter and SO_2, although the nature of fly ash is different than that in cement plants. Installation of an SCR system would require an efficient particulate collection as well as reheating of exhaust gases to appropriate temperatures. SCR's effectiveness needs to be extrapolated from results in other industries because of lack of performance data on cement kilns. Table 5-1 presents the potential NOx reductions with various techniques.

TABLE 5-1. POSSIBLE NOX REDUCTION WITH VARIOUS NOX CONTROL TECHNOLOGIES

NOx control technology	**Possible NOx emissions reduction (%)**
Process modifications	<25
Conversion to indirect firing with a low-NOx burner	20-30
Staged combustion in precalciner kilns	30-45
Mid-kiln firing of whole tires in long kilns	20-40
SNCR in preheater/precalciner kilns	30-70
SCR[a]	80-90

[a] Based on data from coal-fired boilers

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CHAPTER 6

COSTS OF NOx CONTROL TECHNIQUES

This chapter presents the cost estimates for the NOx 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 in-combustion 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 1992 dollars.

6.1 COST CALCULATION METHODOLOGY

6.1.1 Model Plants

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	Long wet	30	6.0	9.7	291	59,100
2	Long 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 ft^3.

As discussed in Chapter 3, existing cement kilns in the United States may be grouped in four types: long wet, long dry, suspension preheater, and precalciner types. Coal is the most common fuel used in all types of kilns.1 As seen from data presented in Chapter 4, the NOx emissions from individual kilns expressed as lb NOx/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 NOx 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 7,500 hours per year which would account for scheduled

downtime for maintenance operations. Although waste-derived fuels are finding increasing applications in cement kilns, not enough data are available to characterize fully the effect of waste-derived fuels on NOx emissions. In addition, coal provided more than 75 percent of the energy requirement of the cement industry.1 Therefore, the model plants were assumed to use only coal as a fuel.

6.1.2 Capital Cost Estimation

TABLE 6-2. CAPITAL COST COMPONENTS FOR EMISSION CONTROL DEVICE COST EVALUATION[2]

Capital cost elements
Direct costs (DC) Purchased equipment costs (PEC): • Control device and auxiliary equipment • Instrumentation • Sales taxes (3 percent of PEC) • Freight (5 percent of PEC) Direct installation costs (DIC): • Foundations and supports • Handling and erection • Electrical • Piping • Insulation for ductwork • Painting
Total direct cost (DC) = PEC + DIC
Indirect costs (IC) Indirect installation costs (IIC): • Engineering • Construction and field expenses • Contractor fees • Startup • Performance test • Model study Contingencies (C): • Equipment redesign and modifications • Cost escalations • Delays in startup
Total indirect cost (IC) = IIC + C
TOTAL CAPITAL COST (TCC) = DC + IC

The total capital cost is the sum of the purchased equipment costs, direct installation costs, indirect installation costs, and contingency costs. 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.2 A contingency factor of 20 percent was added to the vendor costs in all cases to cover contingencies as listed in Table 6-2. The capital costs of in-combustion approaches such as low NOx burner 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

TABLE 6-3. ANNUALIZED COST ELEMENTS AND FACTORS[2]

Direct annual costs (DC)	
1. Utilities:	
Natural gas[3]	\$5.17/1000 ft^3 ~\$5/MM Btu
Coal[3]	\$45.84/ton ~\$2.5/MM Btu
2. Operating labor[a]	
Operator labor	\$28.22 per hour
Supervising labor[b]	15% of operator labor
3. Maintenance[b]	10% of purchased equipment costs
Indirect annual costs (IC)[b]	
Overhead	60% of maintenance cost
Property tax	1% of total capital cost
Insurance	1% of total capital cost
Administrative charges	2% of total capital cost
Capital recovery	CRF x total capital investment
TOTAL ANNUAL COST	DC + IC

[a] From Reference 4, escalated at 5 percent per year.
[b] References for costs are included in Section 6.1.3.

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.

6.1.3.2 **Operating and Supervising Labor**. There are no postcombustion NOx control technologies currently being used in the United States. Therefore, information for typical operating labor requirements from the cement industry was unavailable. A requirement of 1 hour of operator attention was assigned for an 8-hour shift, for all postcombustion technologies considered, regardless of the plant size. For in-combustion techniques such as low NOx burner, additional operator assistance required solely for NOx control purposes was assumed to be negligible. Operator wage rates were estimated to be $28.22/hr in 1992, based on escalating the costs presented in Reference 4 by 5 percent per year to account for inflation. Supervisory labor costs were estimated to be 15 percent of the operating labor costs consistent with the OAQPS Control Cost Manual.

6.1.3.3. **Maintenance**. Specific maintenance costs were not available from the control system vendors and manufacturers. The guidelines for maintenance costs in Reference 2 suggest a maintenance labor cost of 0.5 hours per 8-hour shift and a maintenance material cost equal to this labor cost. Alternatively, a maintenance cost of 10 percent of the PEC is used to prevent excessive maintenance costs relative to the PEC.

6.1.3.4 **Overhead**. An annual overhead charge of 60 percent of the total maintenance cost was used, consistent with guidelines in Reference 2.

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 Reference 2.

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 Reference 2.

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 Reference 2.

6.1.3.8 Capital Recovery. In this cost analysis the capital recovery factor (CRF) is defined as2:

$$CRF = i(1+i)^n/((1+i)^n - 1) = 0.1315$$

where

i is the annual interest rate = 10 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 NOx CONTROL APPROACHES

As discussed in Chapter 5, feasible NOx control approaches include both in-combustion and postcombustion control techniques. In-combustion approaches considered include combustion zone process control, use of low NOx burners, and secondary combustion of part of the fuel. Postcombustion approaches considered include selective catalytic and noncatalytic reduction of NOx using either ammonia or urea.

6.2.1 Combustion Control Approaches for Reduction in NOx Formation

6.2.1.1 Combustion Zone Control of Temperature and Excess Air. Approaches aimed at improving the energy efficiency of the process indirectly reduce NOx emissions per ton of the clinker product. These approaches rely on continuous monitoring of NOx, O2, and CO 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 NOx emissions and increases refractory life. Because continuous monitoring of emissions is necessary for efficient process control, the cost of monitors is not considered as a NOx control cost. The optimum kiln operating conditions provide a baseline of NOx emissions in a cement kiln. The information obtained during this study indicated that some plants indeed relied on process monitoring and control as a means to maintain NOx emissions within their respective permit limits. These plants also indicated that no additional costs were involved in these process control measures.5

Based on existing installations, the cost of a commercially available kiln process control system is in the neighborhood of $750,000.6 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 <u>Process Modifications</u>. As discussed in Sections 5.1.2 and 5.3, process modifications measures 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 NOx reduction.

6.2.1.3 <u>Low NOx Burners</u>. Cement kiln burners, specifically marketed as low NOx burners, require an indirect-fired kiln system. Therefore, to install a low NOx burner in an existing direct-fired kiln, it is necessary to convert the kiln-firing system to an indirect-firing one. Two sets of costs are therefore developed: (1) to install a low NOx burner in an existing indirect-fired kiln, and (2) to install a low NOx burner in an existing direct-fired kiln. In the first case, only the costs of the low NOx 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 NOx burner cost.

At this time only three installations of low NOx burners in cement kilns exist in the United States.7 Information was obtained from the supplier of these burners regarding costs and heat duty for all three cases. 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 NOx burner retrofit using coal as a fuel is typically about $100,000 for a 200 MM Btu/hr heat duty, whereas for a new plant the purchase equipment cost is about $200,000 for the same heat duty.8 For a multichannel burner the cost is higher. For cofiring of coal and gas, the cost of additional equipment is about $50,000, whereas for co-firing of coal, gas, and liquid fuel the cost of additional equipment is about $150,000 for the same 200 MM Btu/hr heat duty.9 The capital cost of a multichannel retrofit low NOx burner may thus be considered to be about 100 percent greater than that for a single channel burner for the same heat duty.

From the limited available data7 (retrofit burner costs of $80,000 for 142 MM Btu/hr heat duty and $90,000 for 200 MM Btu/hr heat duty) a linear correlation developed for an approximate purchase cost for a retrofit application as a function of heat duty is given as:

$$\mathrm{PEC} = 55{,}500 + 175 \text{ " } H$$

where

PEC = Single channel low NOx burner purchase equipment cost in $, and

H = Burner heat duty in MM Btu/hr.

The cost of a multichannel low NOx burner is obtained by multiplying the PEC of a single channel burner by 2.

For each model plant described in Table 6-1 purchase equipment costs for multichannel burners were determined based on the heat duty needed by the kiln. For long wet, long dry, and preheater kilns all the required heat is assumed to be provided by the low NOx burner, whereas for precalciner kilns only 60 percent of the heat duty is assumed to be provided by the low NOx burner at the hot end of the kiln. The capital costs for retrofiting the eight model plants described in Table 6-1 in an existing indirect-fired kiln are given in Table 6-4. 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 NOx burners for the eight model plants ranged from $310,000 for the small long dry kiln to $444,000 for the large long wet kiln. The capital costs for retrofitting on a wet kiln compare well with the $500,000 total installed cost estimated by a cement company.10

TABLE 6-4. CAPITAL COSTS FOR RETROFIT LOW NO$_x$ BURNERS IN AN EXISTING INDIRECT-FIRED KILN

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	PEC ($)	Freight and sales tax ($)	Installation costs $		Contingency costs ($)	Total capital costs ($)
						Direct	Indirect		
1	Long wet	30	180	174,000	14,000	78,000	57,000	35,000	358,000
2	Long wet	50	300	216,000	17,000	97,000	71,000	43,000	444,000
3	Long dry	25	113	150,000	12,000	68,000	50,000	30,000	310,000
4	Long dry	40	180	174,000	14,000	78,000	57,000	35,000	358,000
5	Pre-heater	40	152	164,000	13,000	74,000	54,000	33,000	338,000
6	Pre-heater	70	266	204,000	16,000	92,000	67,000	41,000	420,000
7	Pre-calciner	100	330	180,000	14,000	81,000	59,000	36,000	370,000
8	Pre-calciner	150	495	215,000	17,000	97,000	71,000	43,000	443,000

The annualized costs for low NOx burners in an existing indirect-fired kiln are presented in Table 6-5.

TABLE 6-5. ANNUALIZED COSTS FOR RETROFIT LOW-NO_x BURNERS IN AN EXISTING INDIRECT-FIRED KILN

Model no.	Kiln type	Kiln capac-ity (tons clinker/hr)	Heat duty (MM Btu/hr)	Maintenance costs ($/yr)	Overhead costs ($/yr)	Taxes insurance admin. ($/yr)	Capital recovery ($/yr)	Total annualized costs ($/yr)
1	Long wet	30	180	17,400	10,400	14,300	47,100	89,000
2	Long wet	50	300	21,600	13,000	17,800	58,400	111,000
3	Long dry	25	113	15,000	9,000	12,400	40,800	77,000
4	Long dry	40	180	17,400	10,400	14,300	47,100	89,000
5	Pre-heater	40	152	16,400	9,800	13,500	44,400	84,000
6	Pre-heater	70	266	20,400	12,200	16,800	55,200	105,000
7	Pre-calciner	100	330	18,000	10,800	14,800	48,700	92,000
8	Pre-calciner	150	495	21,500	12,900	17,700	58,300	110,000

No additional costs for utilities or operating labor were deemed necessary for NOx control purposes in addition to those required for normal burner operation. The low NOx burner maintenance costs were included at 10 percent of the PEC. Indirect annual costs were determined as described in Section 6.1.3. The total annualized costs for the eight low NOx burner retrofits ranged from a low of $77,000/yr for the small long dry kiln to a high of $111,000/yr for the large long wet 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 compressor for additional power. To reduce explosion potential due to concentrated coal flow, explosion vents are used. The total cost of equipment needed to convert an existing dry process facility with three kilns, with a combined 90 tons/hr clinker capacity, was estimated to be about $1.3 million in 1988.[11] The equipment list included three parallel trains, each with dust collector, grit separator, screw conveyer, blower, primary air fan, explosion vent, ductwork, and auxiliary equipment such as flowmeters. Adding 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 may be estimated to be about $2.7 million. This estimate agrees well with a contractor's estimate of $2.9 million for the same facility.12

Since the $1.3 million equipment cost estimate was for three parallel systems, the cost of one conversion system to process coal for a 30 ton/hr dry facility was considered to be $522,000 accounting for 5 percent annual inflation rate. The amount of coal processed is proportional to heat requirement. For a dry process approximately 4.5 MM Btu/ton of clinker energy is required. Therefore, the cost of firing system conversion to process coal to provide 135 MM Btu/hr equivalent energy is considered to be $522,000. Cost of firing system conversion for other heat capacities was estimated using 0.6 power rule:

$$\frac{\text{PEC for model plant}}{522{,}000} = \left(\frac{\text{Heat requirement for model plant}}{135}\right)^{0.6}.$$

The PEC for installing a low NOx burner in an existing direct-fired kiln is determined by adding the cost of firing system conversion to the low NOx burner cost. For each model plant described in Table 6-1 the PEC for firing system conversion as well as for multichannel burner was determined based on the heat duty needed by the kiln. For long wet, long dry, and preheater kilns all the required heat is assumed to be provided by the low NOx burner, whereas for precalciner kilns only 60 percent of the heat duty is assumed to be provided by the low NOx 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 6-6. The capital costs ranged from $1.27 million for the small long dry kiln to $2.18 million for the large long wet kiln.

TABLE 6-6. CAPITAL COSTS FOR RETROFIT LOW NO_x BURNERS IN AN EXISTING DIRECT-FIRED KILN

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	PEC ($)	Freight and sales tax ($)	Installation costs $ Direct	Installation costs $ Indirect	Contingency costs ($)	Total capital costs ($)
1	Long wet	30	180	794,000	64,000	357,000	262,000	159,000	1,640,000
2	Long wet	50	300	1,059,000	85,000	477,000	349,000	212,000	2,180,000
3	Long dry	25	113	618,000	49,000	278,000	204,000	124,000	1,270,000
4	Long dry	40	180	794,000	64,000	357,000	262,000	159,000	1,640,000
5	Preheater	40	152	725,000	58,000	326,000	239,000	145,000	1,490,000
6	Preheater	70	266	988,000	79,000	445,000	326,000	198,000	2,040,000
7	Precalciner	100	330	837,000	67,000	377,000	276,000	167,000	1,720,000
8	Precalciner	150	495	1,053,000	84,000	474,000	347,000	211,000	2,170,000

TABLE 6-7. ANNUALIZED COSTS FOR RETROFIT LOW NO_x BURNERS IN AN EXISTING DIRECT-FIRED KILN

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	Operating labor costs ($/yr)	Maintenance and overhead costs ($/yr)	Taxes insurance admin. ($/yr)	Capital recovery ($/yr)	Total annualized costs ($/yr)
1	Long wet	30	180	30,400	48,700	65,400	215,000	329,000
2	Long wet	50	300	30,400	48,700	87,300	287,000	423,000
3	Long dry	25	113	30,400	48,700	50,900	167,000	267,000
4	Long dry	40	180	30,400	48,700	65,400	215,000	329,000
5	Pre-heater	40	152	30,400	48,700	59,700	196,000	305,000
6	Pre-heater	70	266	30,400	48,700	81,400	268,000	398,000
7	Pre-calciner	100	330	30,400	48,700	69,000	227,000	344,000
8	Pre-calciner	150	495	30,400	48,700	86,800	285,000	421,000

The annualized costs for low NOx burners in an existing direct-fired kiln are presented in Table 6-7. Operating labor was assumed to be 1 hour per 8-hour shift. Maintenance labor and material costs were also assumed to be 1 hour per 8-hour shift. The total annualized costs for the eight low NOx burner retrofits

in existing direct-fired kilns ranged from $267,000 for the small dry kiln to $423,000 for the large long wet kiln.

6.2.1.4 <u>Secondary Combustion of Fuel</u>. As discussed in Section 5.1.4, secondary combustion of fuel is expected to reduce the thermal NOx formation in cement kilns. The amount of fuel NOx generated during the secondary combustion determines the net effectiveness of this technique for NOx 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. Typically, the secondary combustion approach would also allow burning waste-derived fuels and, as such, would reduce the overall cost for the fuel. Modification of a long kiln for secondary combustion is a recent technology and very limited information is available regarding costs involved. According to one source, the cost of kiln modifications is approximately $25,000 with additional $25,000 for seals.13,14 According to the same supplier, the cost of fuel metering and conveying system depends upon the degree of automation desired and also on the type of fuel burned. For a completely automated system for injecting tires or containerized solid or liquid fuels, the equipment cost could be as much as $250,000 for a typical wet kiln with a 40 ton/hr clinker capacity, whereas for a completely automated coal-feeding system the capital cost can be as much as $100,000.13,14 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. These costs are not applicable to preheater or precalciner type kilns.

Approximate capital costs were developed by assuming a total of $300,000 equipment cost for kiln modifications and fuel conveying and metering system to provide 40 percent of heat requirement of a 40 ton/hr long wet kiln. The heat duty provided by mid-kiln-fired fuel in this example would be about 100 MM Btu/hr. The equipment cost may be scaled to the four long kiln model plants using the 0.6 power rule:

$$\frac{\text{PEC for model plant}}{300{,}000} = \left(\frac{\text{Heat requirement for model plant}}{240} \right)^{0.6}$$

The total capital costs for mid-kiln firing conversion of the four long dry and wet model kilns are given in Table 6-8. The total capital costs range from $391,000 for a small dry kiln to $707,000 for a large wet kiln. The annualized costs for the mid-kiln firing conversions are presented in Table 6-9. Operating labor was assumed to be 1 hour per 8-hour shift, and maintenance labor was assumed to be 10 percent of PEC. The annualized costs ranged from a low of $128,000 for the small dry kiln to a high of $207,000 for the large wet kiln.

TABLE 6-8. CAPITAL COSTS FOR MID-KILN FIRING CONVERSION

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	Long wet	30	180	252,000	20,200	197,000	50,400	520,000
2	Long wet	50	300	343,000	27,400	268,000	68,600	707,000
3	Long dry	25	113	190,000	15,200	148,000	38,000	391,000
4	Long dry	40	180	252,000	20,200	197,000	50,400	520,000

TABLE 6-9. ANNUALIZED COSTS FOR MID-KILN-FIRING CONVERSION

Model no.	Kiln type	Kiln capacity (tons clinker/ hr)	NO_x emissions (lb/hr)	Operating labor costs ($/yr)	Maintenance and overhead costs ($/yr)	Taxes insurance admin. ($/yr)	Capital recovery ($/yr)	Total annualized costs ($/yr)
1	Long wet	30	290	30,400	40,320	20,800	68,400	160,000
2	Long wet	50	490	30,400	54,880	28,300	93,000	207,000
3	Long dry	25	220	30,400	30,400	15,600	51,400	128,000
4	Long dry	40	340	30,400	40,320	20,800	68,400	160,000

6.2.2 Postcombustion Control Approaches for NOx Emissions Control

6.2.2.1 Selective Noncatalytic Reduction. Although no selective noncatalytic reduction (SNCR) systems are currently being used on cement plants in the United States, this control technique has been applied successfully in other industries. Due to difficulties in continuous injection of reagent in a rotating kiln, SNCR technology is considered to be applicable only to preheater/precalciner kilns. Two types of SNCR systems are commercially available based on either ammonia- or urea-based reagents. The capital costs of this control technique primarily include 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. As discussed in Section 5.2.2, SNCR process is considered applicable only for preheater and precalciner types of cement kiln processes.

The equipment and operating costs of urea-based reagent systems as applicable to model plant #6 and #8 were obtained from two sources.15,16 Both of these cost estimates were comparable. Costs

$$\frac{\text{PEC for model 1}}{\text{PEC for model 2}} = \left(\frac{\text{NO}_x \text{ emissions for model 1}}{\text{NO}_x \text{ emissions for model 2}} \right)^{0.6}.$$

were developed for model plant #5 and #7 using the 0.6 power rule:

The estimated capital costs of urea-based SNCR systems for the four model plants are given in Table 6-10. For both the preheater and precalciner type kilns it was assumed that reducing reagent would be injected in an existing ductwork between the cooler end of the kiln and the preheating tower or the riser duct. The capital costs essentially include the cost of the complete urea delivery and injection system. Direct and indirect installation costs were assumed to be 45 and 33 percent of PEC and an additional 20 percent contingency cost factor was added to determine the total capital cost. The total capital costs for the urea-based SNCR systems as applied to the model plants ranged from a low of $671,000 for the small preheater kiln to a high of $1,236,000 for the large precalciner kiln.

TABLE 6-10. CAPITAL COSTS FOR A UREA-BASED SNCR PROCESS

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	NO_x emissions (lb/hr)	PEC ($)	Sales tax and freight ($)	Direct and indirect installation ($)	Contingency costs ($)	Total capital costs ($)
5	Preheater	40	152	240	326,000	26,100	254,000	65,200	671,000
6	Preheater	70	266	410	450,000	36,000	351,000	90,000	927,000
7	Precalciner	100	330	340	470,000	37,600	367,000	94,000	969,000
8	Precalciner	150	495	510	600,000	48,000	468,000	120,000	1,240,000

The annualized costs expected for urea-based SNCR systems are given in Table 6-11 and include operating labor costs, maintenance and overhead costs, and the indirect operating costs. The urea reagent costs were estimated assuming 50 percent NOx removal efficiency, 35 percent reagent utilization, and 80 cents per gallon of 50 percent reagent solution.16 Because in an SNCR process, an aqueous solution of the urea- or ammonia-based reducing agents is used along with cooler carrier air or steam, there will be a certain loss of heat from the kiln gases. The associated energy penalty is assumed to be 0.3 percent of the kiln fuel costs. Because coal is the most predominant fuel used in cement kilns, the fuel costs are assumed to be approximately $2.5/MM Btu. The total annualized costs for the four model plants varied significantly, due to different levels of annual NOx emissions. The estimated annualized costs range from a low of about $438,000/yr for the small preheater kiln to a high of $820,000/yr for the large precalciner kiln.

TABLE 6-11. ANNUAL OPERATING COSTS FOR A UREA-BASED SNCR PROCESS

Model no.	Kiln type	Kiln capac-ity (tons clinker/ hr)	NO_x emissions (lb/hr)	Operating labor costs ($/yr)	Operating material costs ($/yr)	Maintenance and overhead costs ($/yr)	Fuel penalty costs ($/yr)	Taxes insurance admin. ($/yr)	Capital recovery ($/yr)	Total annualized costs ($/yr)
5	Preheater	40	240	30,400	235,000	48,700	9,100	26,800	88,200	438,000
6	Preheater	70	410	30,400	401,000	48,700	16,000	37,100	121,900	655,000
7	Precalciner	100	340	30,400	333,000	48,700	19,800	38,800	127,400	598,000
8	Precalciner	150	510	30,400	499,000	48,700	29,700	49,400	162,500	820,000

Approximate equipment costs for an ammonia-based SNCR system for a 2,000 tons clinker/day (83 tons/hr) preheater kiln as

provided by another vendor were about $1.0 million.18 Capital costs estimated on this basis for ammonia-based SNCR systems for the four preheater/precalciner model plants are given in Table 6-12. The costs were scaled for different NOx emissions in the model plants using the 0.6 power rule. The estimated capital costs range from $1.34 million for the small preheater kiln to $2.11 million for the large precalciner kiln.

TABLE 6-12. CAPITAL COSTS FOR AN AMMONIA-BASED SNCR PROCESS

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	Heat duty (MM Btu/hr)	NO_x emissions (lb/hr)	PEC ($)	Sales tax and freight ($)	Direct and indirect installation ($)	Contingency costs ($)	Total capital costs ($)
5	Preheater	40	152	240	650,000	52,000	507,000	130,000	1,340,000
6	Preheater	70	266	410	897,000	71,800	700,000	179,400	1,850,000
7	Precalciner	100	330	340	801,000	64,100	625,000	160,200	1,650,000
8	Precalciner	150	495	510	1,022,000	81,800	797,000	204,400	2,110,000

The annualized costs expected for the ammonia-based SNCR systems are given in Table 6-13. The ammonia reagent costs were estimated assuming 70 percent NOx removal efficiency with 70 percent reagent utilization,[17] and 60 cents per gallon of 25 percent ammonia solution. The estimated annualized costs for the four model plants ranged from $518,000 for the small preheater kiln to $894,000 for the large precalciner kiln.

TABLE 6-13. ANNUAL OPERATING COSTS FOR AN AMMONIA-BASED SNCR PROCESS

Model no.	Kiln type	Kiln capacity (tons clinker/ hr)	NO_x emissions (lb/hr)	Operating labor costs ($/yr)	Operating material costs ($/yr)	Maintenance and overhead costs ($/yr)	Fuel penalty costs ($/yr)	Taxes insurance admin. ($/yr)	Capital recovery ($/yr)	Total annualized costs ($/yr)
5	Preheater	40	240	30,400	200,000	48,700	9,100	53,600	176,100	518,000
6	Preheater	70	410	30,400	341,000	48,700	16,000	73,900	243,000	753,000
7	Precalciner	100	340	30,400	283,000	48,700	19,800	66,000	217,000	665,000
8	Precalciner	150	510	30,400	424,000	48,700	29,700	84,200	277,000	894,000

6.2.2.2 **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. 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. An equipment cost estimate of an SCR system was submitted by a Japanese supplier to a cement company in the United States in 1991.19 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 current 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(660oF) and design NOx 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 6-14 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.

TABLE 6-14. CAPITAL COSTS FOR SCR PROCESS

Model no.	Kiln type	Kiln capacity (tons clinker/ hr)	Heat duty (MM Btu/hr)	NO_x emissions (lb/hr)	PEC (10^3 \$)	Sales tax and freight (\$)	Installation costs direct and indirect (\$)	Contingency costs 10^3 (\$)	Total capital costs (10^3 \$)
1	Long wet	30	180	290	6,200	496,000	4,840,000	1,240	12,800
2	Long wet	50	300	490	8,430	674,000	6,570,000	1,690	17,400
3	Long dry	25	113	220	4,790	383,000	3,740,000	958	9,870
4	Long dry	40	180	340	6,350	508,000	4,950,000	1,270	13,100
5	Pre-heater	40	152	240	5,820	466,000	4,540,000	1,160	12,000
6	Pre-heater	70	266	410	8,140	651,000	6,350,000	1,630	16,800
7	Pre-calciner	100	330	340	9,400	749,000	7,310,000	1,870	19,300
8	Pre-calciner	150	495	510	11,900	956,000	9,330,000	2,390	24,600

The estimated annualized costs for SCR systems on the eight model plants are shown in Table 6-15. These include operating labor and maintenance costs, capital recovery, gas reheating, ammonia reagent, and catalyst replacement costs. The individual operating costs were obtained by appropriately scaling the vendor provided operating costs[19,20] 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.

TABLE 6-15. ANNUALIZED COSTS FOR SCR

Model no.	Kiln type	Kiln capacity (tons clinker/hr)	NO_x emissions (lb/hr)	Operating labor costs ($/yr)	Ammonia reagent costs ($/yr)	Maintenance and overhead costs ($/yr)	Energy and fuel costs (10^3 $/yr)	Catalyst costs ($/yr)	Taxes insurance admin. ($/yr)	Capital recovery ($/yr)	Total annualized costs (10^3 $/yr)
1	Long wet	30	290	30,400	287,000	48,700	468	326,000	511,000	1,680,000	3,350
2	Long wet	50	490	30,400	485,000	48,700	779	544,000	694,000	2,280,000	4,860
3	Long dry	25	220	30,000	218,000	48,700	304	212,000	395,000	1,300,000	2,510
4	Long dry	40	340	30,400	337,000	48,700	487	339,000	523,000	1,720,000	3,490
5	Pre-heater	40	240	30,400	238,000	48,700	421	293,000	480,000	1,580,000	3,090
6	Pre-heater	70	410	30,400	406,000	48,700	736	513,000	571,000	2,210,000	4,610
7	Pre-calciner	100	340	30,400	337,000	48,700	930	649,000	772,000	2,540,000	5,300
8	Pre-calciner	150	510	30,400	505,000	48,700	1,400	974,000	985,000	3,240,000	7,180

6.3 COST EFFECTIVENESS OF NOx CONTROLS

Cost effectiveness was determined for four technologies for which detailed costs could be developed as presented in the last section: low NOx burner, mid-kiln firing of tires, SNCR, and SCR. The effectiveness of low NOx burner was evaluated for existing direct-fired as well as indirect-fired kilns. Cost effectiveness was calculated by dividing the total annualized cost of a given technology by the annual NOx reduction likely to be achieved by that technology and is expressed in the units of $/ton of NOx

removed. Cost effectiveness were determined for each of the model plant scenarios.

6.3.1 Low NOx Burner

The NOx reduction that may be achieved with a low NOx burner depends mainly on the operating parameters. In fact, no guarantee on the NOx reduction level is usually provided by burner vendors. With proper operation of the low NOx burner, 20 to 30 percent reduction in NOx emissions should be possible.8 An NOx reduction efficiency of 25 percent was therefore used in determining controlled NOx emissions and cost effectiveness of the low NOx burner technology. For precalciner kilns, although only 60 percent of the heat duty was assumed to be provided by the low NOx burners, all of the NOx emissions were assumed to result from these burners. For existing direct-fired kiln systems, the costs involved in conversion of firing system increase the costs of NOx removal considerably. Table 6-16 presents the uncontrolled and controlled NOx emissions for the eight model plants along with the cost effectiveness of low NOx burner in an existing indirect-fired kiln. The cost effectiveness were within a close range for the model plants and ranged from $220/ton to $370/ton of NOx removed.

Table 6-17 presents the cost effectiveness of low NOx burner installed in an existing direct-fired kiln scenario. The cost effectiveness range form $830/ton to $1,330/ton of NOx removed. The cost of firing system conversion increased the cost effectiveness by almost four times as compared to those in Table 6-16. The conversion of firing system from direct fired to an indirect one 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 but are considered in energy impact analysis in the next chapter.

TABLE 6-16. COST EFFECTIVENESS OF RETROFIT LOW NO_x BURNERS IN AN EXISTING INDIRECT-FIRED KILN

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	Long wet	30	180	1,160	870	290	25	89,000	310
2	Long wet	50	300	1,940	1,460	480	25	111,000	230
3	Long dry	25	113	860	650	210	25	77,000	370
4	Long dry	40	180	1,380	1,040	340	25	89,000	260
5	Preheater	40	152	940	710	230	25	84,000	370
6	Preheater	70	266	1,650	1,240	410	25	105,000	260
7	Precalciner	100	330	1,360	1,020	340	25	92,000	270
8	Precalciner	150	495	2,040	1,530	510	25	110,000	220

TABLE 6-17. COST EFFECTIVENESS OF RETROFIT LOW NO_x BURNERS IN AN EXISTING DIRECT-FIRED KILN

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	Long wet	30	180	1,160	870	290	25	329,000	1,130
2	Long wet	50	300	1,940	1,460	480	25	423,000	880
3	Long dry	25	113	860	650	210	25	267,000	1,270
4	Long dry	40	180	1,380	1,040	340	25	329,000	970
5	Preheater	40	152	940	710	230	25	305,000	1,330
6	Preheater	70	266	1,650	1,240	410	25	398,000	970
7	Precalciner	100	330	1,360	1,020	340	25	344,000	1,010
8	Precalciner	150	495	2,040	1,530	510	25	421,000	830

6.3.2 Mid-Kiln Firing of Tires

The cost effectiveness for the four model plants are given in Table 6-18 which range from $430/ton to $610/ton of NOx removed. A NOx reduction efficiency of 25 percent was assumed

based on the limited available data. The expected reduction in the cost of fuel by substituting primary fuels by cheaper waste-derived fuels is not considered in determining cost effectiveness but is included in the energy impact analysis in the next chapter.

6.3.3 Selective Noncatalytic Reduction

The NOx reduction that may be achieved with SNCR technology depends upon the reagent stoichiometric ratio used, and the gas phase residence time in the appropriate temperature window. Due to difficulties involved in continuous injection of reagent in a rotating kiln, SNCR technology is considered to be applicable only to preheater/precalciner kilns. SNCR is estimated to provide 50 percent NOx reduction based on the limited available data and SNCR performance in other industries. The costs of the two types of systems were found to be different based on the available information.

TABLE 6-18. COST EFFECTIVENESS OF MID-KILN FIRING OF TIRES

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	Long wet	30	180	1,160	870	290	25	160,000	550
2	Long wet	50	300	1,940	1,460	480	25	207,000	430
3	Long dry	25	113	860	650	210	25	128,000	610
4	Long dry	40	180	1,380	1,040	340	25	160,000	470

Table 6-19 presents the uncontrolled and controlled NOx emissions for the four model plants along with the cost effectiveness for the urea-based SNCR NOx control technology. The corresponding values for ammonia-based process are given in Table 6-20. The total annualized costs for both systems were similar. Cost effectiveness for the urea -based process were slightly lower. The cost effectiveness for the urea-based SNCR process ranged from $ 790/ton to $ 930/ton of NOx removal, whereas the cost effectiveness for the ammonia-based SNCR process ranged from $ 880/ton to $ 1,100/ton of NOx removed.

TABLE 6-19. COST EFFECTIVENESS OF UREA-BASED SNCR PROCESS

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 (10^3 \$/yr)	Cost effectiveness (\$/ton NO_x removed)
5	Preheater	40	152	940	470	470	50	438,000	930
6	Preheater	70	266	1,650	825	825	50	655,000	790
7	Precalciner	100	330	1,360	680	680	50	598,000	880
8	Precalciner	150	495	2,040	1,020	1,020	50	820,000	800

TABLE 6-20. COST EFFECTIVENESS OF AMMONIA-BASED SNCR PROCESS

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)
5	Preheater	40	152	940	470	470	50	518,000	1,100
6	Preheater	70	266	1,650	825	825	50	753,000	910
7	Precalciner	100	330	1,360	680	680	50	665,000	980
8	Precalciner	150	495	2,040	1,020	1,020	50	894,000	880

6.3.4 Selective Catalytic Reduction

The NOx 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 NOx emissions has been achieved in SCR installations in other applications such as utility boilers and gas turbines.21 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 NOx

emissions. To determine the cost effectiveness of the SCR technology in cement kiln applications, an 80 percent NOx reduction efficiency was therefore assumed and the results are shown in Table 6-21. The cost effectiveness ranged from $3,140/ton to $4,870/ton of NOx removed and are almost five to six times greater than the corresponding values for the ammonia-based SNCR technology.

TABLE 6-21. COST EFFECTIVENESS OF SCR PROCESS

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	Long wet	30	180	1,160	230	930	80	3,351,000	3,600
2	Long 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

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CHAPTER 7

ENVIRONMENTAL AND ENERGY IMPACTS OF NOx CONTROLS

This chapter presents the environmental and energy impacts for the NOx emissions control techniques described in Chapter 5. The impacts of in-combustion control approach of low NOx burners as well as postcombustion control approaches of selective and nonselective catalytic reduction on environmental pollution, and energy consumption are discussed. None of the NOx reduction technologies considered produce any water pollution impacts. Section 7.1 presents the environmental impacts, and Section 7.2 presents the energy consumption impacts.

7.1 ENVIRONMENTAL IMPACTS OF NOx CONTROLS

7.1.1 NOx Emission Reductions

Tables 7-1

TABLE 7-1. REDUCTION IN NO_x EMISSIONS WITH LOW NO_x BURNER FOR EXISTING INDIRECT AND DIRECT FIRED KILNS

Model Plant No.	Kiln Type	Kiln capacity (tons clinker/hr)	Uncontrolled NO_x emissions (tons/yr)	Controlled NO_x emissions (tons/yr)	NO_x Removed (tons/yr)	NO_x reduction (%)
1	Long Wet	30	1,160	870	290	25
2	Long Wet	50	1,940	1,460	480	25
3	Long Dry	25	860	650	210	25
4	Long Dry	40	1,380	1,040	340	25
5	Preheater	40	940	710	230	25
6	Preheater	70	1,650	1,240	410	25
7	Precalciner	100	1,360	1,020	340	25
8	Precalciner	150	2,040	1,530	510	25

TABLE 7-2. REDUCTION IN NO_x EMISSIONS WITH MID-KILN FIRING

Model Plant No.	Kiln Type	Kiln capacity (tons clinker/hr)	Uncontrolled NO_x emissions (toxs/yr)	Controlled NO_x emissions (toxs/yr)	NO_x Removed (toxs/yr)	NO_x reduction (%)
1	Long Wet	30	1,160	870	290	25
2	Long Wet	50	1,940	1,460	480	25
3	Long Dry	25	860	650	210	25
4	Long Dry	40	1,380	1,040	340	25

thru 7-4 present the possible NOx emission reductions in the eight

TABLE 7-3. REDUCTION IN NO_x EMISSIONS WITH SCR

Model Plant No.	Kiln Type	Kiln capacity (tons clinker/hr)	Uncontrolled NO_x emissions (toxs/yr)	Controlled NO_x emissions (toxs/yr)	NO_x Removed (toxs/yr)	NO_x reduction (%)
5	Preheater	40	940	470	470	50
6	Preheater	70	1,650	825	825	50
7	Precalciner	100	1,360	680	680	50
8	Precalciner	150	2,040	1,020	1,020	50

model plants described in Section 6.1.1 using low NOx burners, mid-kiln firing, selective noncatalytic reduction (SNCR), and selective catalytic reduction (SCR) techniques, respectively. The NOx emission reduction efficiencies used are 25 percent for low NOx burners, and for mid-kiln firing of tires, 50 percent for SNCR, and 80 percent for SCR technology. As seen from these tables, substantial reductions in NOx emissions are possible with postcombustion technologies of SCR and SNCR. With these technologies, annual NOx emissions reduction ranged from 470 tons/year to 1,630 tons/year for the eight model plants. The annual NOx emissions reductions with the low NOx burner technology and mid-kiln firing of tires ranged from 210 tons/year to 510 tons/year.

As discussed in Section 6.2.1.1 combustion zone control of

TABLE 7-4. REDUCTION IN NO_x EMISSIONS WITH SCR PROCESS

Model Plant 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 (%)
1	Long Wet	30	180	1,160	230	930	80
2	Long Wet	50	300	1,940	390	1,550	80
3	Long Dry	125	113	860	170	690	80
4	Long Dry	40	180	1,380	280	1,100	80
5	Preheater	40	152	940	190	750	80
6	Preheater	70	266	1,650	330	1,320	80
7	Precalciner	100	330	1,360	270	1,090	80
8	Precalciner	150	495	2,040	410	1,630	80

temperature and excess air may be used to ensure optimum operating conditions and as such would not involve any additional environmental or energy impacts. Although the concept of secondary combustion of a part of the fuel in the calcining zone may reduce NOx emissions, as discussed in Section 6.2.1.3, confirming data regarding the extent of NOx reduction are not available.

7.1.2 Emission Tradeoffs

In-combustion control approaches attempt to change combustion conditions to reduce NOx formation. Since the combustion conditions also strongly affect formation of CO, SO2, hydrocarbons, and possibly hazardous air pollutants (HAPs), the in-situ control approaches are likely to affect these emissions. To reduce NOx emissions, these approaches generally attempt to reduce excess air and combustion temperature which may lead to incomplete combustion and may lead to increases in CO and hydrocarbon emissions. However, with optimum operating conditions, the oxygen content in the combustion air may be reduced to an optimum level without increasing CO and hydrocarbon emissions. In a study to determine the effect of excess air on CO and NOx emissions in a long dry kiln, an excess air level of 1 percent was found to reduce NOx emissions without increasing CO emissions.1 Such behavior of CO emissions was also observed in two other studies, where the CO concentration in the exhaust gases did not appear to increase until the excess air level was reduced below 1.5 percent.2,3 Thus, it appears to be possible to operate a cement kiln at a certain optimum level of excess air without impacting CO and hydrocarbon emissions.

The low NOx burner designs targeted for cement kilns induce internal flue gas recirculation and staging of combustion. According to one supplier of low NOx burners, these burners would not have any effect on CO emissions, and their impact on hydrocarbon emissions is not known.4

The sulfur present in the fuel and in the raw kiln feed is converted to SO2. The calcined lime present in the solids in the kiln is an excellent absorber for SO2, forming calcium sulfites and sulfates. An oxidizing atmosphere in the kiln burning zone, facilitates oxidation of SO_2 to SO_3 and retention of sulfur in the clinker or in the dust.[2] Thus, SO_2 emissions from cement kilns also depend upon the excess air level. Also some pyritic sulfur in kiln feed oxidizes to SO_2 before there is an opportunity to react with CaO.

Secondary combustion of fuel in the calcination zone is practiced for economic reasons. Solid and liquid wastes with a high heating value, such as tires and hazardous waste, represent an economical source of fuel and may be burned in the secondary firing zone. The NO_x reduction potential of secondary firing, however, has not been confirmed. Burning hazardous waste may obviously lead to emissions of certain HAPs and hydrocarbons if not completely destroyed in the kiln. The destruction and removal efficiency (DRE) of the calcining zone of the kiln 820 to 870 °C (1500 to 1600 °F) will thus be an important parameter in determining the HAP emissions in such cases.

Postcombustion NO_x control approaches include SCR and SNCR of NO_x with either ammonia or urea in the appropriate temperature zone. In order to ensure the desired percent reduction of NO_x, generally a little excess of reagent is used than that required stoichiometrically for the desired NO_x reduction. This results in NH_3 emissions which are usually referred to as "ammonia slip." Thus, these approaches will involve a certain level of emissions of ammonia reagent which is normally kept below 10 ppm. In some European SCR installations even lower ammonia slip has been observed.[5] At a demonstration of the Nalco system on a preheater/precalciner kiln, NH_3 emissions were 10 ppm at NSR of 1 and 6.5 ppm under uncontrolled conditions.[6] With the presence of sulfuric and hydrochloric acids in the kiln exhaust gases, any NH_3 slip will likely result on detached plumes of NH_4SO_4 and NH_4Cl.

Reheaters may be required for some SCR systems installed downstream of a particulate control device to reheat gas temperature to 400 to 500 o C (750 - 930 oF). Additional

NOxemissions will form. The heater exhaust gas could be combined with the kiln exhaust gas prior to the SCR unit.

The SNCR processes may also increase CO concentrations in the flue gas, although this increase for urea-based systems is apparently much less than that due to combustion modifications such as overfire air and sub-stoichiometric combustion used in utility boilers.7 On the other hand, one reference claims that ammonia injection has no effect on CO emissions.8 Interestingly, the intentional addition of CO in the reaction zone of the process broadens the operating temperature window for urea-based systems, even at CO concentrations as low as 500 ppm, although it increases N2O emissions.9 At a demonstration of the Nalco urea based SNCR system, CO and SO2 emissions were unaffected when the NSR was less than 0.7 or when the preheater exit oxygen was greater than 2.3%. At lower O2 and at NSR's greater than 0.7, both SO2 and CO increased.6

The SCR employs catalysts that are composed of various active materials, such as titanium dioxide, vanadium pentoxide, and tungsten trioxide, as well as inert ingredients to impart structural strength and ease of forming.5 Most concerns over hazards have centered on vanadium pentoxide, which is a toxic compound. After deactivation, these catalysts must be disposed of properly. Some catalyst manufacturers may take back any spent catalyst for reactivating and recycling. Where the spent catalyst cannot be recycled, it must be disposed in an approved landfill.7

7.2 ENERGY IMPACTS OF NOx CONTROLS

7.2.1 <u>In-combustion NOx Control Systems</u>

Combustion control techniques for NOx reduction rely on reducing excess air and excess burning (or high flame temperatures) for optimum conditions. Both of these factors will likely increase the energy efficiency of the cement-making process. Thus by intuition, NOx reduction measures based on combustion process controls are also likely to reduce the energy requirement per ton of clinker produced. Techniques such as secondary firing allow combustion of low grade fuels such as solid wastes with high heating value. These fuels are much cheaper than the primary fuels and are likely to result in significant cost savings. Secondary firing in the calcining zone results in efficient utilization of energy and is likely to reduce the energy requirement per unit amount of clinker produced. The NOx reduction potential of the secondary firing technique, has, however, not been confirmed experimentally. Quantitative information is not available regarding the impact of low NOx burners on the energy consumption in cement kilns.

7.2.2 Postcombustion NOx Control Systems

Both the SCR and SNCR involve high operating costs associated with the ammonia or urea reagent used and their delivery systems. Since there are no catalysts involved, SNCR process is not susceptible to particulate fouling and, thus, may be implemented within the kiln at an appropriate location. The catalysts used in the SCR process may, however, be susceptible to SO2 and particulate fouling. Thus, the SCR system may need to be installed downstream of a particulate control device. Since the SCR process requires gas temperature to be about 300 to 425 °C (575 to 800 °F), the gas stream may need to be reheated causing an additional energy cost.

The energy penalty associated with reheating of gases for SCR application may be determined approximately as shown below:

In cement kilns, heat consumption of 1 MM Btu/hr produces about 350 std ft3/min of flue gas. Assuming the flue gas temperature at the exit of a particulate control device of 300 °F, an SCR reactor temperature of 850 °F, molecular weight of flue gas of 30, and an average specific heat of the flue gas during reheating of 0.255 Btu/lb-°F the heat requirement for reheating the flue gas is about 246,000 Btu/hr. Thus, with no heat recovery in the flue gas reheater, approximately 24.6 percent of additional energy would be required for flue gas reheating. With an efficient, energy recuperative type process heater an energy recovery of 60 percent may be possible. With 60 percent energy recovery in a flue gas reheater, the energy requirement for the flue gas reheating would be approximately 9.8 percent of that consumed in the cement manufacturing.

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