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Project Summary

Evaluation of Combustion Variable Effects on NO_x Emissions from Mineral Kilns

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Results of tests performed on a lime kiln, precalciner cement kiln, and conventional wet process cement kiln are presented and discussed. Where applicable, the effectiveness of excess air variations on pollutant emissions is quantified and compared to previous results. Mass balances were also calculated for the two cement kilns.

A subscale cement kiln simulator was designed, fabricated and operated to determine the effect of burner operating variables on near-flame NO_x production. The effects of combustion air preheat, carrier air dilution and fuel injection velocity were the primary variables assessed for both natural gas and coal.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction and Summary

The activities reported here include tests on a rotary lime kiln (Location 6), precalciner cement kiln (Location 8), and conventional wet process cement kiln (Location 9). Fuel oil was used in the lime kiln, and coal in both cement kilns.

Variation in excess air was the NO_x control implemented on the lime kiln and wet kiln. Only as-found tests were performed on the precalciner kiln because it had just recently been started up and its operation may not have been fully optimized.

For the lime kiln (Location 6), a reduction in excess air reduced NO_x emissions by 23 percent. Further reductions in excess air produced poor quality clinker. A new oil tip (with fewer orifices) caused oil to impinge on the kiln wall, an unacceptable operating condition.

As-found testing on the precalciner cement kiln (Location 8) resulted in emissions higher than the conventional wet process kiln tested at Location 9. This result may be due to kiln operation not being fully optimized at the time of the test program. Mass balances were performed for sulfur, sodium, and potassium by a contractor retained by the plant operator. Closure on these balances was good.

Testing at the conventional wet process cement kiln (Location 9) encompassed as-found, baseline, and variations in oxygen level. Linear regression analysis of the NO_x data predicted a 38 percent reduction in NO_x when the oxygen level was lowered from baseline conditions. However, a simultaneous increase in gaseous SO_2 of 47 percent was also predicted. Mass balances were made on seven kiln constituents: the largest single difference was 29.5 percent. The difference for all seven constituents was 3.8 percent.

A subscale cement kiln simulator was constructed and tested to determine the effect of burner parameters on near-flame NO_x levels for both natural gas and coal fuels. It was determined that combustion air preheat, fuel injection velocity, and oxygen content of the primary combustion air stream have first-order effects on NO_x levels. This subscale program will be used to select advanced combustion modifications for implementation at the pilot scale.

Comparison of Previous and Present Cement Kiln Programs

KVB, during a previous EPA contract and a contract from the California Air Resources Board, performed emission measurements on two conventional kilns. Table 1 summarizes the results obtained on all four kilns tested.

Of note for Location 3 are the higher emissions with natural gas fuel as opposed to either oil or a combination of coke and natural gas. A similar situation has been measured in glass furnaces where NO emissions on natural gas are higher than oil fuel despite the fuel-bound nitrogen content of oil fuel. This difference exists, but it might be due to higher radiant flame cooling for an oil or coal flame because of higher emissivity.

Of equal note is the very low NO value measured during the present EPA contract for the coal-fired wet process kiln. A review of the testing procedures indicated that all measurements were made properly. There is no explanation why this particular kiln is a low NO emission source.

Emissions Test Instrumentation

All emission measurement instrumentation for the full-scale testing was carried in an 8 x 42 ft (2.4 x 12.8 m) mobile laboratory trailer. The gaseous species measurements were made with analyzers located in the trailer. The emission measurement instrumentation used is listed in Table 2.

The instrumentation used during the subscale cement kiln testing is listed in Table 3.

Table 3. *Laboratory Instrumentation Employed*

Emission Species	Manufacturer	Measurement Method	Model No.
Oxygen	Teledyne	Fuel Cell	720P4
Carbon Dioxide	Horiba	NDIR	PIR2000
Carbon Monoxide	Horiba	NDIR	PIR2000
Nitrogen Oxides	Thermo Electron	Chemiluminescent	10A
Sulfur Dioxide	Du Pont	UV Spectrometer	411

Results

Location 6 Lime Kiln

The significant results on the lime kiln are shown in Figure 1 and Table 4. As noted, a reduction in oxygen from 4.4 to 2.8 percent (test 6/1-1 vs. test 6/1-2) produced a 23 percent decrease in NO emissions, while a 85.6 percent decrease in NO was measured when the oxygen was reduced to 1.5 percent (test 6/1-3). However, at 1.5 percent oxygen, lime clinker quality was poor.

Test 6/2-2 and 6/2-3 are of uncertain accuracy; they were performed during a ±50 percent change in fuel flow rate. The possibility exists that insufficient time was allowed after the fuel flow rate change to permit the kiln to stabilize thermally. The lower kiln front-end temperature for test 6/2-2 with respect to 6/2-1 is most likely a consequence of the reduced fuel flow rate. However, the still lower temperature for test 6/2-3 probably reflects an unstabilized kiln operating condition.

The spread in baseline results (tests 6/1-1, 6/2-1, 6/3-1, and 6/3-4) is not considered unusual for an industrial combustion device with direct contact between the combustion products and process material. Variations in the process material composition and process rate will require adjustment of the firing rate and combustion air flow in order to produce an acceptable product. This lime kiln's firing rate was manually controlled by the operators to compensate for variations in process material composition and process rate. Therefore, it was not always possible to reproduce the exact firing conditions obtained during the baseline tests.

The total kiln ambient air flow is in two parts (neither of which could be measured): a primary supply coaxial with the oil gun and a secondary circuit distributed around the kiln interior. Each circuit is supplied by its own fan. Test 6/3-2 was conducted by increasing the secondary flow, decreasing the primary flow, and maintaining the overall O_2 at 3.9 percent. With respect to the nearest baseline in time (test 6/3-1), this reduced the NO emissions by 18.6 percent. Reducing the total air flow by closing down on both the primary and secondary air dampers (test 6/3-3) reduced the NO emissions by 31.9 percent; however, clinker quality was slightly degraded, but still usable.

The original oil tip had seven holes, each 5.79 mm (0.228 in.) in diameter, located on a 34.9 mm (1.375 in.) diameter circle and inclined at 35° from the oil gun axis. A new tip was designed, fabricated, and installed with the same oil flow area but with only four holes. The new tip was designed to delay mixing between the oil spray and combustion air and thereby reduce the NO emissions.

However, the initial testing of the four-hole tip resulted in the oil spray's impinging on the kiln insulation in four locations. In addition, the NO emissions increased by 22.8 percent. Testing with the new oil tip had to be suspended because of the concern for potential insulation degradation. The tests that were conducted had to be made with a lower fuel oil input.

In summary, the tests performed on the rotary lime kiln showed that lower excess air had a practical limit in reducing NO; i.e., to the point where lime quality was affected. This limitation corresponded to an NO reduction on the order of 23 percent.

Table 1. *Comparison of Cement Kiln NO Emissions*

Location	Process	Fuel	Condition	NO ppm, dry @ 3% O_2	NO kg/Mg Clinker	NO (lb/ton)
3	Dry	Coke + Nat. Gas	Baseline	1014	4.0	(8.0)
3	Dry	Nat. Gas	Baseline	1460	7.5	(14.9)
3	Dry	Oil	Baseline	640	3.3	(6.6)
9 (2144)[a]	Wet	Nat. Gas	Baseline	2474	9.1	(18.2)
8	Precalciner	Coal	As-found	1264	3.7	(7.5)
9 (2645)[b]	Wet	Coal	Baseline	183	0.88	(1.8)

[a]Location 9, EPA Contract 68-02-2144.
[b]Location 9, EPA Contract 68-02-2645.

Table 2. *Emission Measurement Instrumentation*

Species	Manufacturer	Measurement Method	Model No
Hydrocarbon	Beckman Instruments	Flame Ionization	402
Carbon Monoxide	Beckman Instruments	IR Spectrometer	865
Oxygen	Teledyne	Polarographic	326A
Carbon Dioxide	Beckman Instruments	IR Spectrometer	864
Nitrogen Oxides	Thermo Electron	Chemiluminescent	10A
Particulates	Joy Manufacturing	EPA Method 5 Train	EPA
Sulfur Dioxide	Du Pont Instruments	UV Spectrometer	400

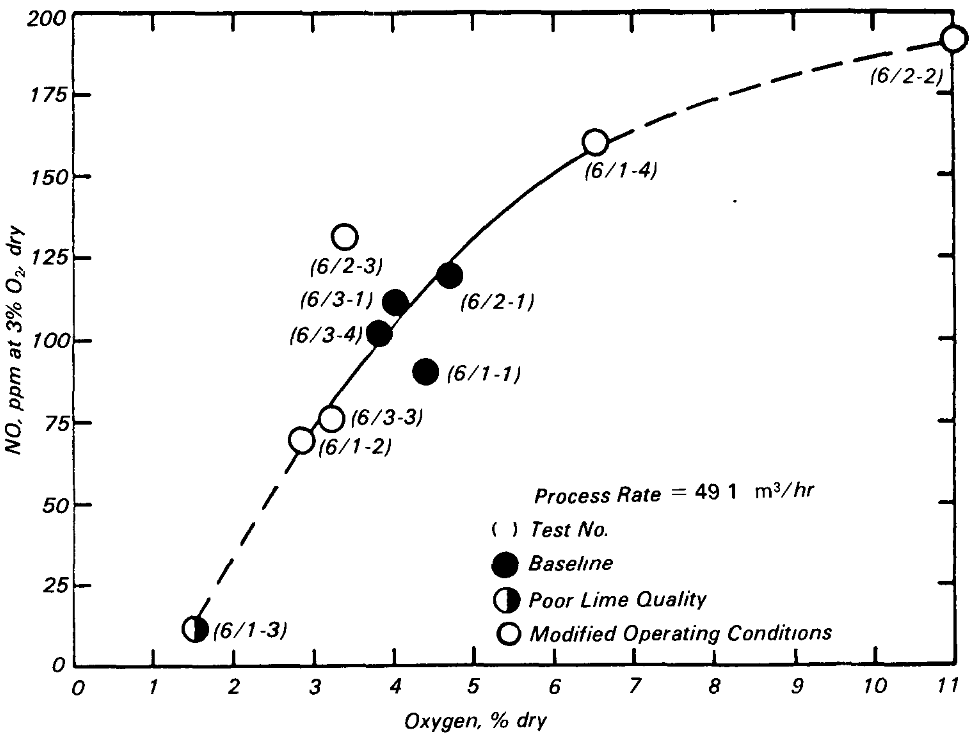

Figure 1. *Location 6 lime kiln-effect of O_2 on NO.*

Location 8 Precalciner Kiln

Only as-found tests were performed since it had recently come on-line and its operation may not have been fully optimized. Major system components are shown in Figure 2. It is claimed that the cyclone stages and flash furnace can complete up to 95 percent of the calcination prior to the feed's entering the rotary kiln.

The test results are given in Table 5. The average value of NO_x measured in the stack* was 972 ng/J (2.26 lb $NO_2/10^6$ Btu) which was higher than anticipated. (The high value of stack oxygen is due to the ambient temperature quench air introduced upstream of the alkali bypass baghouse.)

Samples were obtained of the coal, raw feed, clinker, alkali bypass baghouse catch, and crusher/dryer baghouse catch, for the purpose of performing mass balances for sulfur, sodium, and potassium. The sample analyses, together with the process weights, were analyzed by a contractor retained by the plant owner. The results of the mass balances are shown in Table 6. Of note is the high

*A single stack is used for the discharge streams from the alkali bypass baghouse and crusher/dryer baghouse. Stack measurements were made downstream of both streams

Table 4. *Summary of Gaseous Emissions from a Lime Kiln - Location 6*

Test No.	Date 1979	Process Rate m^3/h[a]	Fuel Flow m^3/h[a]	O_2 %	CO_2 %	NO ppm dry at 3% O_2	NO ppm wet	CO ppm dry at 3% O_2	SO_2 ppm wet	Kiln Front End Temp. K	Comments
6/1-1	10-25	49.1	1.63	4.4	19.9	90	-	33	-	1,402	Baseline
6/1-2	10-25	49.1	1.44	2.8	20.5	69	-	25	-	1,478	Minimum primary air
6/1-3	10-25	48.6	1.48	1.5	20.5	13	-	17	-	1,478	Low O_2
6/1-4	10-25	49 1	1.21	6.5	18.3	160	-	20	-	1,478	High O_2
6/2-1	10-25	49.1	1.21	4.7	18.8	119	-	20	-	1,478	Baseline
6/2-2	10-25	49.1	0.57	11.0	9.8	192	-	18	-	1,267	Low fire
6/2-3	10-25	49.1	1.82	3.4	20.0	132	-	15	-	1,200	High fire
6/3-1	10-25	49.1	1.21	4.0	19.2	113	-	13	-	1,436	Baseline
6/3-2	10-25	49.1	1.17	3.9	18.6	92	-	28	-	1,339	Increased secondary air flow
6/3-3	10-25	49.1	1.21	3.2	20.5	77	-	33	-	1,353	Low O_2
6/3-4	10-25	49.1	1.19	3 8	18.9	104	-	33	-	1,367	Baseline repeat
6/4-1	10-26	48 6	1.21	4.5	20.5	158	-	49	-	1,422	Baseline without secondary air
6/4-2	10-26	48.6	1.17	6.0	18.0	246	-	54	-	1,300	High O_2 without secondary air
6/4-3	10-26	48.6	1.21	3.0	21.0	90	-	45	-	1,381	Medium O_2 without secondary air
6/4-4	10-26	48.6	1.21	1.3	22.0	60	-	2,165	-	1,464	Low O_2 without secondary air
6/4-5	10-26	48.6	1.21	5.0	20.5	105	-	81	-	1,436	Baseline with minimum secondary air
6/4-6	10-26	49.1	1.17	5.8	18.8	115	-	62	-	1,378	High secondary air
6/4-1A	10-26	49.1	1.21	4.2	19.6	154	-	54	-	1,356	Baseline without secondary air
6/4-7	10-26	49.1	1.21	1.6	20.5	108	-	71	-	1,467	No secondary air - no odor gas
6/5-1	11-12	34.1	1.32	5.8	20.5	127	-	41	50	1,378	Baseline old oil tip
6/6-1	11-12	34.1	1.32	5.4	20.5	156	33	43	40	1,467	Baseline new oil tip
6/6-2	11-12	34.1	1.14	3.5	20.5	110	22	43	57	>1,478	No secondary air - new oil tip
6/6-3	11-12	34.1	1.14	4.2	20.5	119	18	37	38	1,450	No secondary air - no odor gas
6/6-4	11-12	34.1	1.14	4.8	20.5	138	15	34	110	1,461	No secondary air, high O_2 - no odor gas
6/6-5	11-12	34.1	0.40	6.7	16.0	162	16	43	105	1,456	Minimum secondary air - with odor gas
6/6-6	11-12	34.1	1.14	6.1	19.2	147	20	40	95	1,417	Min. sec. air, low prim. air - with odor gas
6/6-7	11-12	34.1	1.14	4.2	20.2	124	12	36	44	1,444	Minimum secondary air - no odor gas

[a]gal./min = $m^3/h \cdot 4.40$

degree of closure on all three mass balances.

Location 9 Wet Cement Kiln

NO_x results obtained on this kiln are shown in Figure 3 as a function of oxygen. Also shown is a linear regression between NO_x and O_2 which can explain 39.9 percent of the NO_x scatter. Figure 4 presents similar information on the variation in SO_2 with oxygen for which the linear regression can explain 43.6 percent of the data scatter. (Coal sulfur content was in excess of 3 percent.)

Based on these analyses it is predicted that a reduction in oxygen from 2.85 (baseline average) to 1.5 percent would reduce NO_x emissions by 37.6 percent.

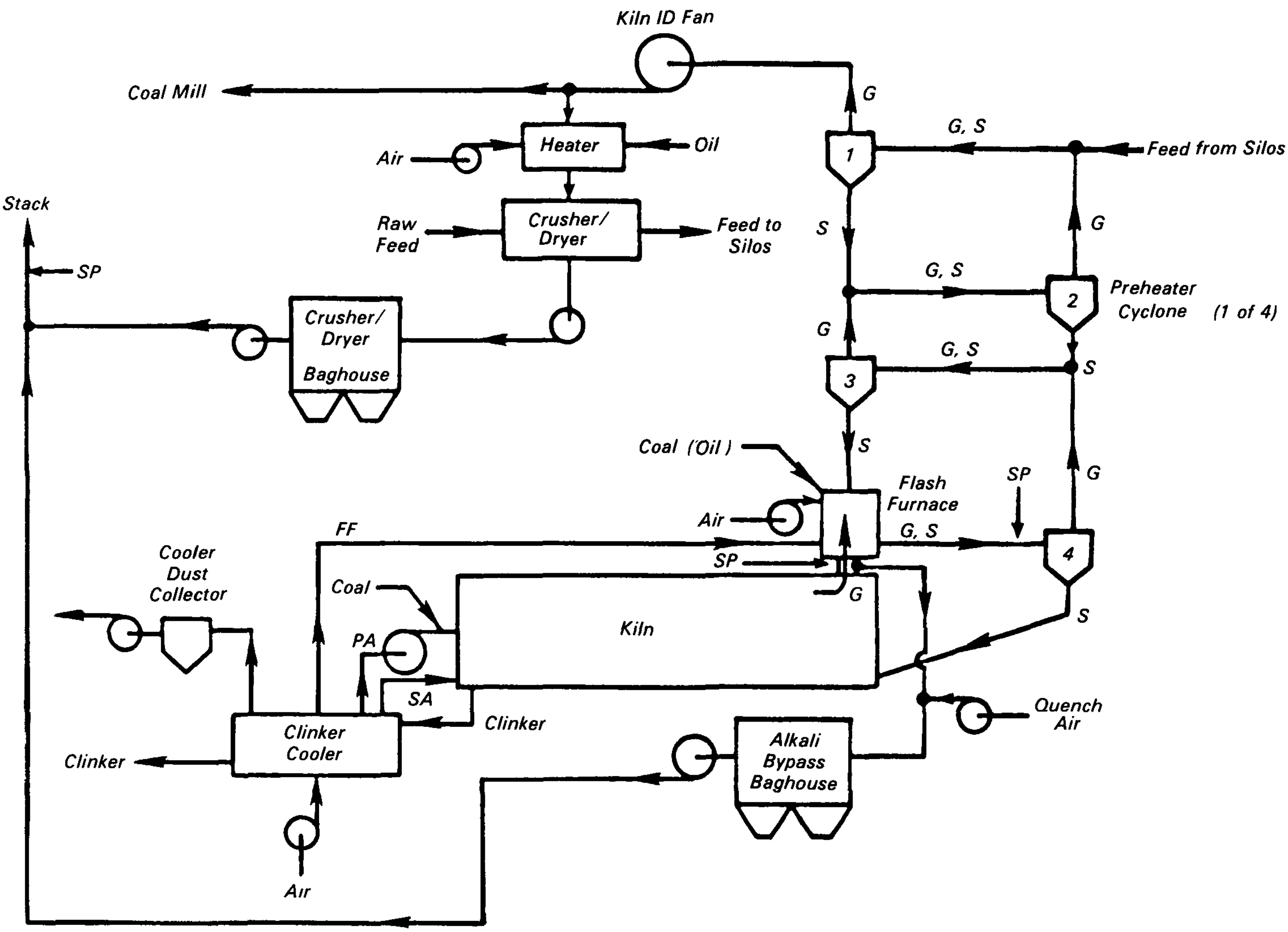

Figure 2. *Precalciner kiln arrangement (G = gas, S = solid, SP = sample point, PA = primary air, SA = secondary air, FF = flash furnace air).*

Table 5. *Emissions Data Summary - Precalciner Cement Kiln Location 8*

Test No	Date 1980	Kiln Feed Rate kg/s	(t/h)	O_2 %	CO_2 %	NO ppm[a]	NO_x[b] ng/J[c]	CO ppm[a]	SO_2 ppm[a]	Solid Particulate lb/10^6 Btu[c]	Solid Particulate ng/J[c]	Total Particulate lb/10_6 Btu[c]	Total Particulate ng/J[c]	Probe Location	Comments
8/1-1	8-6	24.1	(95.4)	13 5	12.8	1371	1054	241	51	--	--	--	--	Stack	As found, gaseous emissions
8/1-1P	8-7	26.5	(105)	13.4	13.7	1249	960	355	0	0.0886	38.1	0 1434	61.7	Stack	As found, particulates
8/1-1P	8-7	26 5	(105)	5.8	20.0	912	545[d]	12	0	--	--	--	--	Kiln Outlet	As found
8/1-1G	8-8	28.8	(114)	13.1	15.0	1173	902	365	24	--	--	--	--	Stack	As found
8/1-1A	8-8	28.8	(114)	8.5	--	--	--	--	--	--	--	--	--	Flash Furn. Outlet	As found, excess O_2 at flash furnace outlet

[a]dry, corrected to 3% O_2.
[b]NO_x as NO_2.
[c]dry, corrected to 3% O_2, corrected for CO_2 generation in the kiln and precalciner.
[d]dry, corrected to 3% O_2, corrected for CO_2 generation in the kiln only.

Table 6. *Mass Balances for Precalciner Cement Kiln*

Element		Input lb/hr	(kg/hr)		Output lb/hr	(kg/hr)	Output/Input
Sulfur	Coal	324	(147)	Clinker[a]	484	(220)	
	Raw Feed	319	(145)	Alkali Bypass Baghouse[b]	27	(12.3)	
		643	(292)	Crusher/Dryer Baghouse[c]	87	(39.5)	
				SO_2 in stack	0	(0)	
					598	(272)	0.93
Sodium	Coal	0	(0)	Clinker[a]	141	(64.0)	
	Raw Feed	139	(63.1)	Alkali Bypass Baghouse[b]	2	(0.9)	
		139	(63.1)	Crusher/Dryer Baghouse[c]	18	(8.2)	
					161	(73)	1.16
Potassium	Coal	0	(0)	Clinker[a]	859	(390)	
	Raw Feed	1081	(490)	Alkali Bypass Baghouse[b]	38	(17)	
		1081	(490)	Crusher/Dryer Baghouse[c]	183	(83.0)	
					1080	(490)	1.00

[a]Assumed clinker production = 0.65 of raw feed to preheater.
[b]Based on 0.5 ton/hr (454 kg/hr) of waste dust from alkali bypass baghouse.
[c]Based on 12 ton/hr (10,886 kg/hr) of return dust from crusher/dryer baghouse.

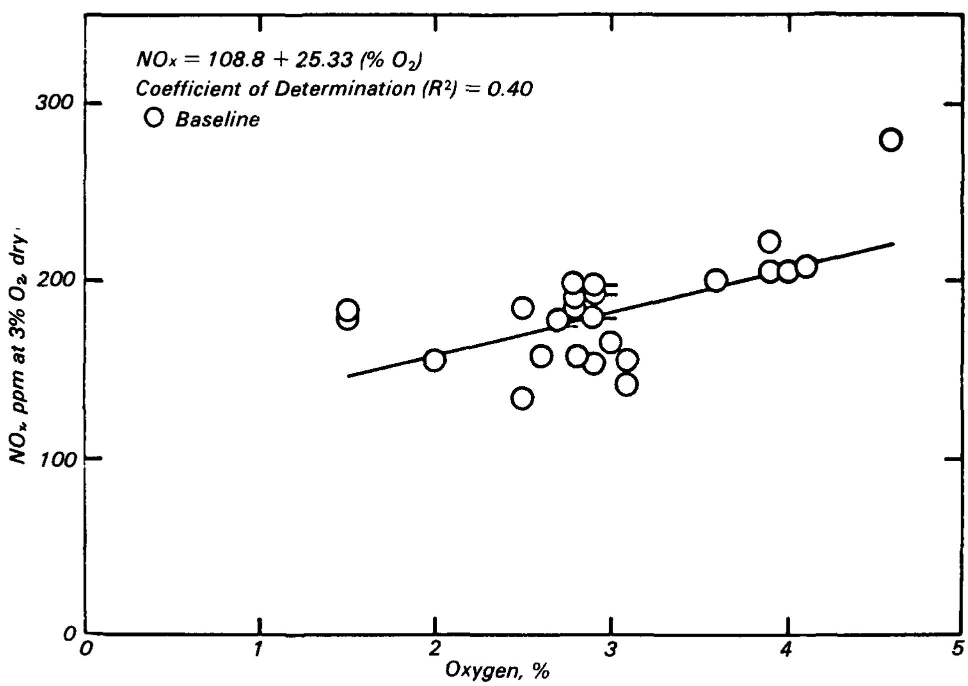

Figure 3. *Location 9—NO_x vs. oxygen.*

However, it is also predicted that the SO_2 emission would increase by 46.6 percent.

The SO_2 dependence suggests a reaction between SO_2 and feed alkali components in the presence of oxygen. Laboratory and full-scale tests have also shown that water vapor speeds up the reaction between SO_2 and alkali. In this respect the cement feed is performing as a flue gas desulfurization agent; i.e.,

$$SO_2(g) + 0.5\ O_2(g) + CaCO_3(s) + 2\ H_2O(g) \rightarrow CaSO_4 \cdot 2\ H_2O(s) + CO_2(g)$$

The above global reaction indicates that both oxygen and water vapor are required for the reaction between SO_2 and limestone (or lime).

Samples of coal, feed, clinker, and precipitator catch were obtained and analyzed in order to perform constituent mass balances. The measured SO_2 volumetric concentration was converted to the corresponding sulfur mass rate. The mass balance results are presented in Table 7, which shows an overall balance within 4 percent on a total basis.

Subscale Cement Kiln Simulator

The cement kiln simulator (Figure 5) was designed to investigate four effects (combustion air preheat, fuel injection velocity, primary air oxygen content, and excess air) on near-burner NO_x for both natural gas and coal fuels. Results obtained at the subscale level are to be used to select advanced combustion modifications for implementation at full scale.

Figure 6 shows the significant effect of preheat on NO_x production in the near-burner zone. Also of importance is the effect of fuel injection velocity, especially at the higher preheats investigated. The data at high preheat suggest that NO_x decreases at very high fuel injection velocities. This effect may be due to the decreased gas residence time within the combustor which would inhibit NO_x production. Another possible explanation would be that, at very high fuel injection velocities, the mixing is so rapid that the combustion would correspond to a premixed flame for which the maximum NO_x would occur at 0 percent excess air.

The curve shown at high preheat is a quadratic regression of NO_x as a function of fuel injection velocity, V_{jet}; i.e.,

$$NO_x = a + b\ V_j + c\ V_{jet}^2$$

This function is able to account for 56 percent of the data scatter. The effect of high fuel injection velocity on NO_x is less pronounced at the lower combustion air temperatures.

Figure 7 quantifies the impact of carrier oxygen content on NO_x with coal fuel. The implementation on full-scale kilns could be accomplished by replacing a portion of the carrier air with inert gas; e.g., flue gas.

Overall oxygen content effectiveness in reducing NO_x is shown in Figure 8 for coal fuel with and without air preheat.

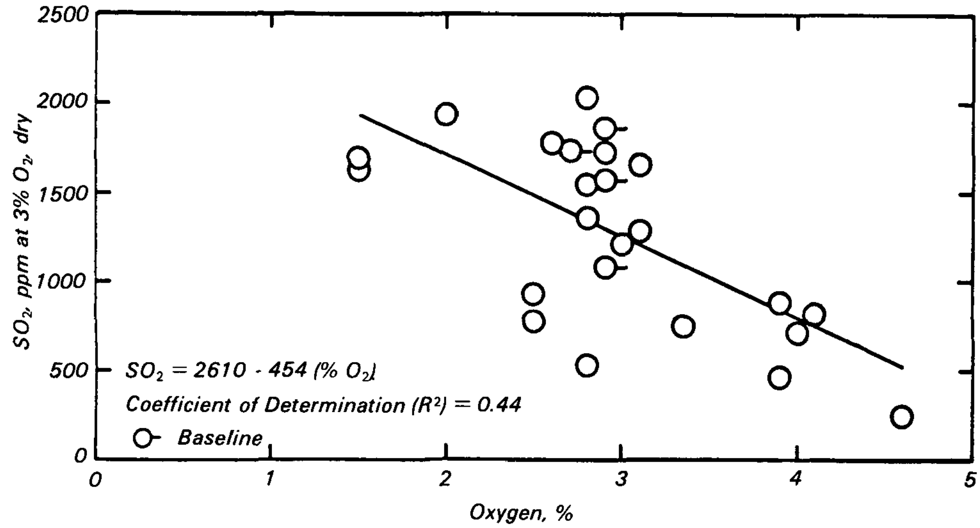

Figure 4. *Location 9 - SO_2 vs. oxygen.*

Table 7. *Mass Balance Results*

Constituent	In Mg/d	In (tons/day)	Out Mg/d	Out (tons/day)	% Difference[a]
Al_2O_3	40.1	(44.2)	41.4	(45.6)	3.2
SiO_2	152.1	(167.7)	143.0	(157.6)	-6.0
Fe_2O_3	21.7	(23.9)	28.1	(31.0)	29.5
CaO	468.2	(516.1)	443.9	(489.3)	-5.2
MgO	25.4	(28.0)	25.5	(28.1)	0.4
K_2O	5.96	(6.57)	5.03	(5.55)	-15.6
S	5.98	(6.59)	5.30	(5.84)	-11.4
Total	719.4	(793.1)	692.2	(763.0)	-3.8

[a] $\frac{(Out-In)}{In} \cdot 100.$

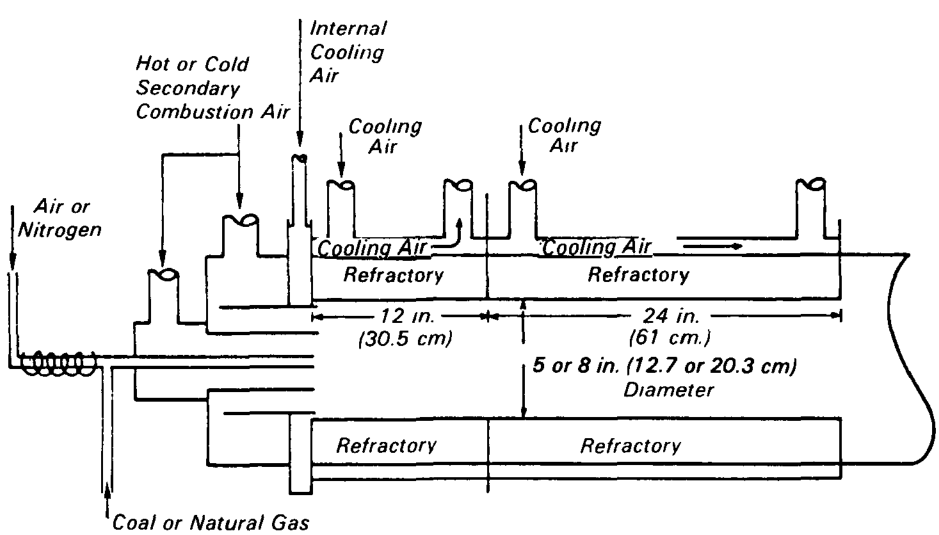

Figure 5. *Schematic of subscale test furnace.*

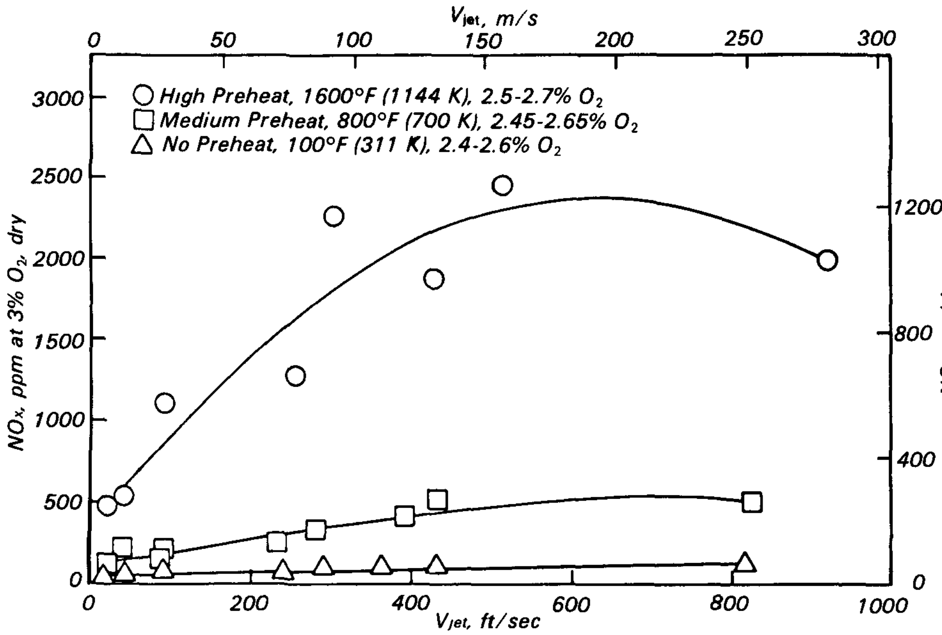

Figure 6. NO_x emissions vs. injection velocity - natural gas fuel.

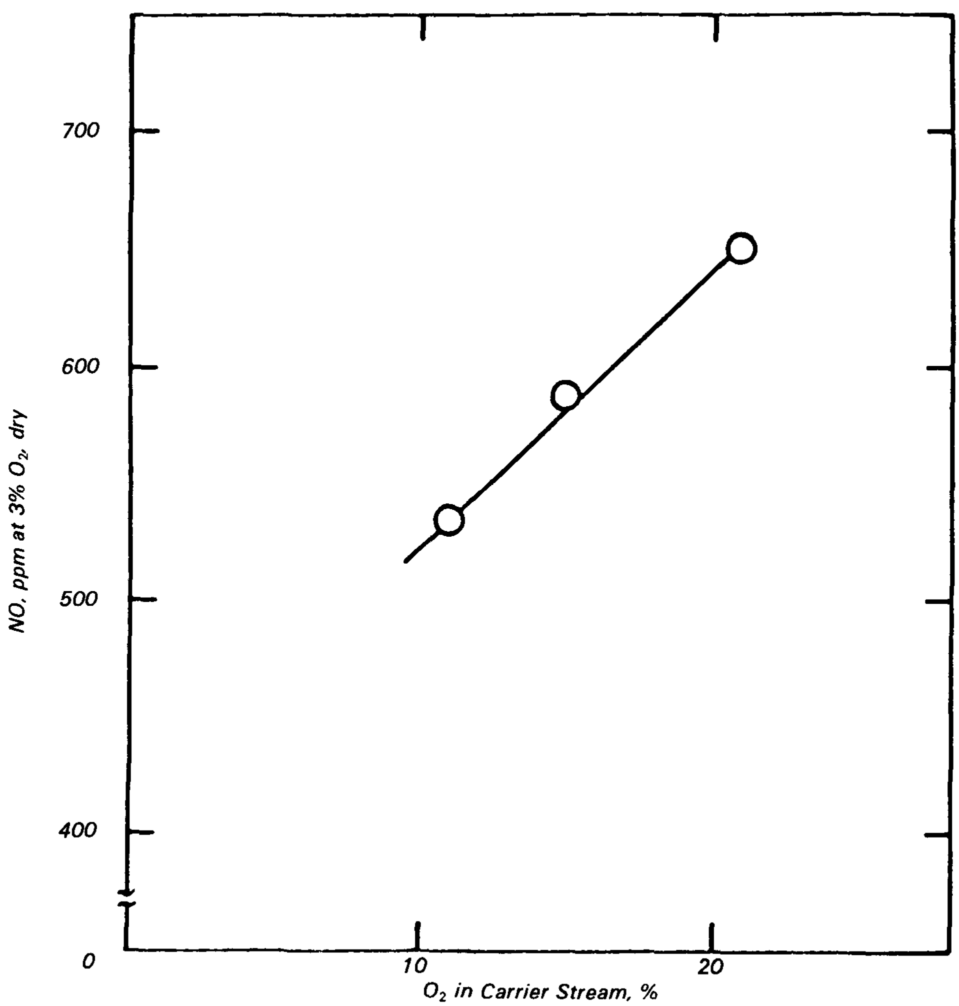

Figure 7. Effect of carrier O_2 on NO_x - coal fuel (V_{jet} = 31 ft/sec).

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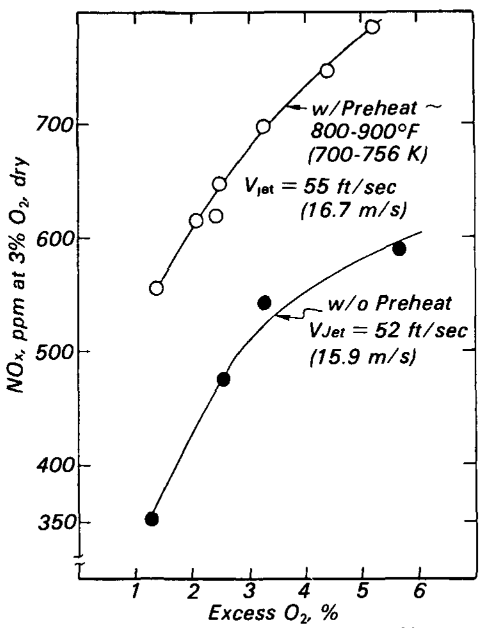

Figure 8. NO_x vs. O_2 - coal-constant V_{jet}.

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***Robert E. Hall** is the EPA Project Officer (see below).*

The complete report, entitled "Evaluation of Combustion Variable Effects on NO_x Emissions from Mineral Kilns," (Order No. PB 83-259 655; Cost: $11.50, subject to change) will be available only from:

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