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Project Summary

Evaluation of Primary Air Vitiation for Nitric Oxide Reduction in a Rotary Cement Kiln

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Results of pilot-scale tests to evaluate combustion modifications for nitric oxide (NO) reduction and cement product quality in a long-dry-process cement kiln are reported, firing pulverized coal. The kiln is rated at 11.35 kg/s (1080 tons/day) of cement with a thermal input rate of 70.3 MW (240 x 10^6 Btu/hr). Of the combustion modifications evaluated in previous studies, vitiation of the primary air with inert gas (nitrogen) was considered to be the best alternative for NO reduction on a pilot-scale kiln.

As-found emissions (17 days of data, 89.75 hours) were about 3.6 kg (8 lb) NO as NO_2 per 907 kg (1 ton) of clinker. The uncertainty of the as-found mean mass emissions is estimated to be 10 percent. Lowered excess air (LEA) decreased NO volumetric and mass emissions by about 15-20 percent. The percent reduction was established from a reference baseline of 1050 ppm (corrected to 3 percent O_2) and a kiln exit oxygen of 1.82 percent. The NO volumetric emissions were lowered to 880 ppm (corrected to 3 percent O_2) with a kiln exit oxygen of 0.7 percent. NO_x reductions during the short term N_2 injection tests were about 25-30 percent with no adverse effects on product quality. Because of the interacting feed chemistry/kiln operations, it was not possible to clearly isolate the effect of N_2 injection. Longer term tests with improved process stability would help to evaluate the primary air vitiation.

This Project Summary was developed by EPA's Air and Energy Engineering 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

This program is a follow-on study to build on the results of the programs reported in EPA-600/7-83-045 and EPA-600/7-84-075. The objective of the earlier effort was to determine the effect of burner parameters on near-flame nitrogen oxide (NO_x) levels for natural gas and coal fuels. This laboratory effort determined that combustion air preheat, fuel injection velocity, and oxygen (O_2) content of the primary combustion air stream have first-order effects on NO_x levels. These parameters were then selected for implementation on a subscale kiln. Of these three combustion modifications, the effect of carrier (primary) air O_2 concentration on NO_x emissions was most significant.

The effect of carrier air O_2 content on NO_x emissions showed a strong influence of carrier gas O_2 concentration on NO_x emissions. NO_x emissions were reduced 37 percent by lowering the carrier gas O_2 to 12.5 percent. While NO_x reduction was significant, the subscale clinker quality was not comparable to production clinker, but primary air vitiation did not seem to affect clinker quality substantially from the baseline condition. Acceptable production clinker is about 0.5-1.5 percent free lime. The results of the combustion laboratory tests were corroborated by the subscale test results.

These test results indicated that dilution of the primary air stream with an inert gas offered the highest probability of NO_x reduction by combustion modification on a full-scale kiln.

Present Approach

The objective of this program was to implement the results of previous work on a full-scale cement kiln to investigate the effect of combustion modification on product quality.

This test program was conducted at a cement plant in California. The cement company was interested in such a test program because emission limit goals of 1.4 kg (3.1 lb) NO_x/907 kg (1 ton) clinker are being considered by the local air quality management district. Data with inert gas injection would be useful input in determining the feasibility of the emission limit.

Three alternatives were considered for partial inerting of the primary air stream:

- A 9.8 kW (600 hp) boiler supplying flue gas.
- Flue gas recirculation from the kiln stack.
- Nitrogen (N_2) injection.

Alternatives were analyzed for initial and operating costs, operability, and flexibility. N_2 injection into the primary air stream was the lowest cost alternative for a very short term test. If successful, flue gas recirculation would be more cost effective for long term operation.

Kiln System Description

The kiln is a long dry rotary cement kiln 149 m (490 ft) long and 4.1 m (13.5 ft) inside diameter. Kiln rated production is 11.35 kg/s (1080 tons per day). The thermal input rate is about 70.3 MW (240 x 10^6 Btu/hr). The kiln is direct fired with a Southern Utah bituminous coal at about 0.105 kg/s (10 tons/hr maximum).

N_2 Injection

Gaseous N_2 was injected at the coal mill inlet, downstream of the tempering air dampers. The N_2 injected into the primary air duct was maintained at about the same temperature as the primary air stream.

Data Acquisition Methods

The kiln system is instrumented for emissions data along with temperatures, pressures, and controls for the coal mill system, clinker cooler box, the kiln, and downstream components (e.g., multiclone and baghouse). Feed input and clinker product output are also monitored.

Gaseous emissions were measured using analytical instruments and equipment contained in a government-furnished mobile instrumentation laboratory. The laboratory is equipped with analytical instruments to continuously measure concentrations of NO, NO_2, CO, CO_2, and O_2. For the as-found, low excess air and N_2 injection test series, only NO was measured with CO, CO_2, and O_2. Measurement of total NO_x (NO + NO_2) requires a heated sample line and involves a differential measurement of NO and total NO_x (the difference is NO_2). Conditions in the kiln were not sufficiently steady to allow accurate differential determination of NO_2. The sampling system extracted gas from the exit of the kiln, where raw feed is injected.

An On-line Emissions Monitor Program was written for the Apple II Plus 48K computer to provide automatic digital data acquisition for real time monitoring of emissions data. The computer was programmed to scan every 5 seconds and print the gaseous emissions data averaged over 1, 3, or 5 minutes. The program provides a continuous visual display of time plots for any two of the gaseous species (e.g., NO, O_2) and records the data printed out on magnetic disk. Strip chart recorders are used to verify the data recorded on magnetic disk and fill in any gaps from the computer, if they occur.

O_2 levels in the primary air were sampled during the N_2 injection tests using a portable Teledyne Model 320A O_2 analyzer. The sample port for O_2 measurement was in the 41.6-cm (16 in.) diameter burner line about 15 m (50 ft) from the burner tip. During the N_2 tests, carrier gas O_2 was monitored every 1-2 minutes.

Data Analysis Methods

Daily kiln exit gaseous emissions normally analyzed were NO, CO, CO_2, and O_2. The O_2, CO_2, and CO data are reported on a dry volume basis, and the NO data were reported on a dry volume basis corrected to 3 percent O_2. The dry stack gas data were statistically analyzed for the arithmetic mean, standard deviation, coefficient of variation, and 95 percent confidence level.

The volumetric NO concentration was converted to pounds per ton of clinker and reported as NO_2. The plant measurements used for clinker rate are:

- Clinker Weigh Belt Scale.
- Kiln Feeder Speed (strip chart).
- Kiln Feeder Revolutions Counter.
- Kiln Speed.

Instantaneous clinker rate can also be calculated from a formula for million Btu per ton clinker based on gaseous emissions data (CO_2, O_2), heating value, ultimate analysis, and ignition loss of the raw feed. Once the million Btu per ton of clinker is calculated, the fuel rate and heating value are used to calculate the clinker rate. This method was found to be less reliable than using the plant instruments.

As-Found Test Series

Seventeen days of as-found data were collected to assess process variability. Twelve coal samples, 67 clinker samples, 30 raw feed samples, 2 multiclone dust samples, and 2 combined feed samples (raw feed plus multiclone dust) were collected. A multiclone dust sample was analyzed for particle size and chemical composition.

The coefficient of variation for the volumetric NO emissions has been plotted on a daily basis. The coefficient of variation ranges from a low of 14.5 percent to a high of 57.8 percent. A large dispersion from the mean (time weighted average coefficient of variation of 31 percent) shows that daily cement kiln emissions (volume basis) are extremely variable. The distribution of emissions factors has been plotted on a pound NO (as NO_2) per ton of clinker basis. The mean emissions factor for the 90 hours of testing was 3.6 kg (8.0 lb) NO (as NO_2) per 907 kg (1 ton) of clinker. The uncertainty of the mass emissions factor is about 10 percent based on the input data and measurements needed to calculate pounds NO_x per ton of clinker.

Clinker in the kiln is normally burned at the plant by maintaining a constant fuel rate and varying the kiln speed to hold the burning zone temperature at the desired level. When the material temperature is higher than the desired level, the kiln speed is increased to decrease the front-end temperature. Maintaining stable kiln conditions is difficult. The strip chart recordings for NO and kiln speed have been redrawn onto one figure (Figure 1) to show how closely the NO tracks the kiln speed changes. Also, the strip chart recordings for NO and material temperature have been redrawn onto another figure (Figure 2) to show how NO and material temperature coincide for underburning and overburning conditions. A strong correlation of NO with material temperature is evident.

Clinker analysis results for the as-found clinker samples showed the standard deviation of tricalcium silicate to be about 6.6 percent. The variability was traceable to homogenizing silo problems and rock mix difficulties.

During another test segment, 49 consecutive hours of as-found data were analyzed for 3- and 24-hour rolling averages. The 3-hour rolling averages ranged

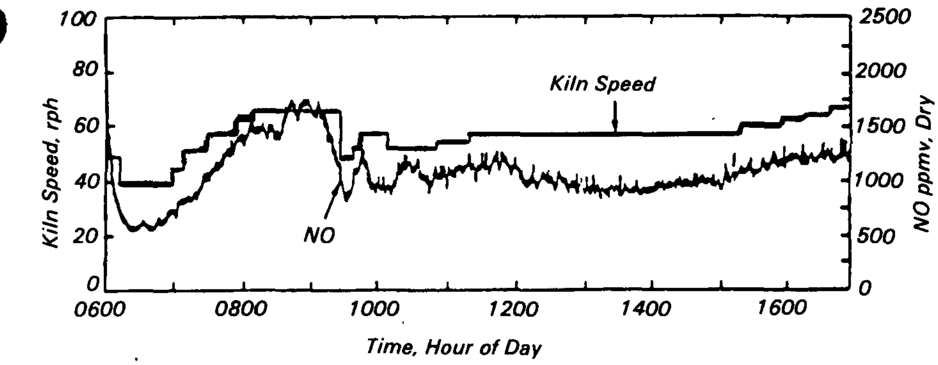

Figure 1. *Time trace of NO and kiln speed.*

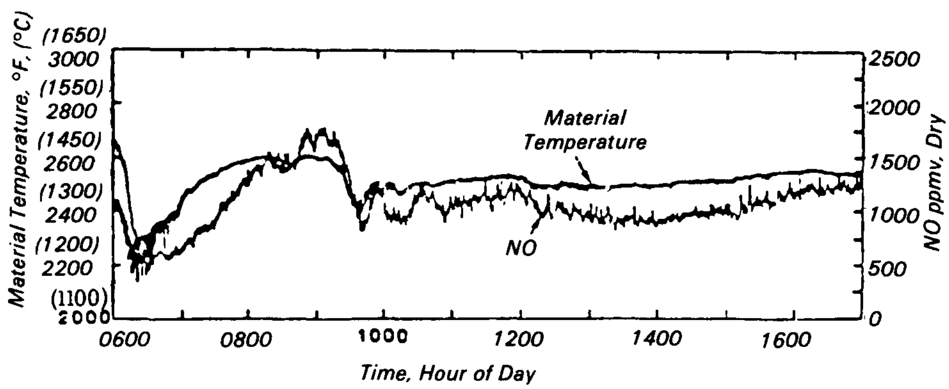

Figure 2. *Time trace of NO and material temperature.*

from 2.1 to 4.55 kg (4.62 to 10.04 lb) NO (as NO_2) per 907 kg (1 ton) of clinker and the 24-hour rolling averages ranged from 2.99 to 3.82 kg (6.60 to 8.42 lb) NO (as NO_2) per 907 kg (1 ton) of clinker.

The main conclusion from the as-found tests was that the wide variation in NO, the strong correlation of NO with material temperature, and the difficulty in maintaining stable operation of the kiln make controlling NO very difficult. On the other hand, if means can be found to stabilize the process using NO as a key control variable, product quality would be more uniform and controlling NO would be enhanced.

Initial N_2 Injection Results

Evaluation of the primary air vitiation system was based on tests conducted on three days (November 15 and 17, 1983, and April 17-18, 1984). Between the two November tests and the April test, low excess air tests were conducted.

The objective of the November 15 N_2 injection tests was to shake down the system to ensure that nominal flow rates of up to 0.80 m³/s (100,000 scfh) would not adversely affect mill operation or burner stability. The mill outlet average O_2 concentration was about 17 percent. NO emissions decreased during the N_2 injection tests. The extent of NO reduction with N_2 injection was more difficult to quantify because kiln speed changes affect NO emissions. Clinker analysis shows that the tricalcium silicate and dicalcium silicate for baseline and N_2 injections showed very little variation. The difference of the averages between baseline and N2 injection was 0.40 for tricalcium silicate and 0.09 for dicalcium silicate. The objective for the November 15 tests was achieved; N_2 could be injected with no detrimental effect on coal mill operation and no obvious effect on flame stability. The results with regard to the effect of N_2 injection on NO_2 emissions were inconclusive at 17 percent carrier air O_2.

A longer term N_2 injection test (about 3-1/2 hours) at higher N_2 flow rate was performed on November 17. Plotting the emissions data for NO and kiln exit O_2 as a function of time shows a distinct decrease in NO. But also apparent is a decrease in kiln O_2 that closely follows the NO decrease. At the lowest NO point, CO spikes of 1000 ppm or more were observed. It was not clear from these tests if the NO decreased as a result of N_2 injection or because the O_2 decreased. Free lime and x-ray diffraction analyses did not indicate any deterioration of product quality during the injection tests.

Low Excess Air Tests

Initial tests with short-term N_2 injection (1-3 hr) indicated that the N_2 injection caused a reduction in excess air as the result of flow balance changes in the kiln. Therefore, prior to proceeding with further N_2 injection, a 4-day test was conducted to evaluate more closely the effect of excess air on NO.

Test results indicated a significant effect of kiln exit O_2 on NO, but also showed a strong effect of material temperature. Lowered excess air (LEA) decreased NO volumetric and mass emissions by about 15-20 percent. The percent reduction was established from a reference baseline of 1050 ppm (corrected to 3 percent O_2) and a kiln exit oxygen of 1.82 percent. The NO volumetric emissions were lowered to 880 ppm (corrected to 3 percent O_2) with a kiln exit oxygen of 0.7 percent. The average calculated kilograms (pounds) NO as NO_2 per 907 kg (1 ton) of clinker was 3.66 (8.07) at reference baseline conditions and 3.18 (7.02) at low excess air conditions: the resultant reduction was 16.5 percent. The average burning zone temperature, as measured by an optical pyrometer, was 1358 °C (2477 °F) at reference baseline conditions and 1349 °C (2460 °F) at LEA conditions. The effect of kiln feed burnability factor on NO emissions was not included in this analysis.

Final N_2 Injection Tests

The final N_2 injection tests were performed for about 8 hours on April 17 and 18. The objective of the tests was to adjust kiln operating conditions during N_2 injection so that kiln exit O_2 would remain as constant as possible. A constant O_2 would factor out the effect of O_2 which has complicated the data analysis for previous tests.

A time plot of pounds NO_2/ton of clinker, kiln exit O_2, and mill exit O_2 showed that the objective of holding kiln O_2 constant was not completely met, but the O_2 was considerably steadier than in previous tests. The plot also showed the period of N_2 injection: pounds NO_2/ton of clinker was reduced from about 3.9 to 3.2 kg/907 kg (8.6 to 7.0 lb/ton) with a primary air O_2 at 13 percent. The percent NO reduction was 19 percent. This degree of reduction cannot be attributed entirely to the N_2 injection. Changes in kiln speed, coal flow, material temperature, feed composition, and other variables, in spite of the operator's desire to maintain constant conditions, complicate the data analysis. The data were subject to a statistical time series analysis to attempt to isolate the effects of the important variables. The data show that the NO concentration change per 1 percent change in mill outlet oxygen ranges from 16 to 76 ppm NO decrease per 1 percent mill outlet O_2 decrease. The actual effect depends on what is held constant by the model. NO check was made for the linearity of this effect.

High speed motion pictures were taken of the flame near the tip of the burner at 2,000 frames per second. These films and operator observations indicated a definite lengthening and cooling of the flame. This effect is normal for low NO operation on other combustion devices, but would require further investigation over a longer time to determine if this effect could be acceptable for clinker quality and kiln life.

Analysis of raw feed and clinker samples indicates that most of the clinker variability could be explained by feed composition variation. A time trace of the NO volumetric emissions, free lime, and material temperature for the nitrogen injection tests showed that the free lime content throughout the tests was less than 0.3 percent and alkali content remained less than 0.6 percent. It was concluded that the test did not result in deterioration of clinker quality, but it was apparent that the clinker was being overburned, probably due to the kiln operator's concern for avoiding an upset as the result of the test.

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The complete report consists of three volumes, entitled "Evaluation of Primary Air Vitiation for Nitric Oxide Reduction in a Rotary Cement Kiln:," (Set Order No. PB 87-113 239/AS; Cost: $64.00)
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