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EMISSIONS CONTROL FOR A BOILER FIRING HIGH-SULFUR COAL AND COAL/RDF MIXTURES

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Argonne National Laboratory (ANL) operates a stoker-fired boiler rated at 170,000 lb/h of steam as part of the site heating/cooling system. The flue-gas cleanup (FGC) equipment consists of a spray-dryer/fabric-filter combination, which was the first FGC system of its type to be installed and continuously operated on high-sulfur coal in the United States. The boiler and FGC system have been used by ANL for several large-scale research programs.

High-sulfur (4.2%) coal tests established the capability of the FGC system to achieve well over 90% SO_2 removal for an extended period with an economically acceptable sorbent stoichiometry. In addition, the importance of the fabric filter as a site for additional SO_2 removal was established and quantified.

Under a combined NO_x/SO_2 research program, changes in operating conditions and the addition of a chemical additive (NaOH) were studied. The results show that, under certain operating conditions, it is possible to achieve significant levels of combined control. Key variables include the spray-dryer exit temperature, the additive concentration, the SO_2 concentration in the flue gas, and the baghouse filter-cake thickness.

A third set of tests involved firing several mixtures of coal and binder-enhanced refuse derived fuel (RDF). Up to 30% RDF (based on Btu content) was used with several different levels of lime binder. No significant operating problems were encountered, all ash samples passed the EP toxicity test, no detectable levels of dioxins or furans were found in the ash or flue gas, and both SO_2 and NO_x emissions at the boiler exit were decreased.

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INTRODUCTION

Industrial consumption of energy is a significant fraction of the total energy use in the United States. In 1984, about 23% of the U.S. primary energy use was by industry, with another 34% consumed by electric utilities. The fuels used by industry were primarily liquids (23%) and gases (35%), with the balance coming from coal (16%), electricity (16%), and renewable sources (10%). However, the industrial use of coal is projected to approximately double by the year 2010[1].

Industrial emissions of sulfur dioxide (SO_2) are relatively low at about 15% of the national total in 1980, due to the high use of "clean" fuels. Nitrogen oxides (NO_x) emissions were also a smaller fraction than might be expected, although this was due largely to the very large contribution from the transportation sector. These factors, coupled with the great diversity of source characteristics in the industrial sector, have tended to divert regulatory attention to larger and more homogeneous sources such as electric utility plants. However, the technical difficulties and costs of making further emission reductions in the transportation and utility sectors, as well as projections of increased coal use by industry, have brought greater attention to bear on industrial sources, with federal new source performance standards (NSPS) for industrial boilers with heat inputs greater than 100×10^6 Btu/h being promulgated since 1984. The standards apply to particulate matter, NO_x, and SO_2, with the latter requiring a 90% reduction for coal-fired units.

Argonne National Laboratory (ANL) has been conducting research on environmental control technologies, including options for industrial boilers[2], since 1976. Beginning in 1981, the primary emphasis was placed on integrated systems that combined control of both NO_x and SO_2. This work has been focused on high-sulfur systems and has involved both laboratory-scale research and field tests using Argonne's stoker-fired boiler. This boiler is equipped with a spray-dryer/fabric-filter flue-gas cleanup (FGC) system, which was the first such system to be operated in this country on high-sulfur coal. In addition to acquiring over seven years of operating experience with this new FGC technology, ANL has conducted performance tests to explore SO_2 removal capability with very high-sulfur (4.2%) coal, to test a chemical additive and process modifications designed to enhance combined NO_x/SO_2 removal, and to study boiler/FGC system performance with a combination of coal and binder-enhanced, refuse derived fuel (RDF). The remainder of this paper describes these three research programs and discusses the results obtained.

ANL BOILER AND FGC SYSTEM

The boiler used for the research programs is a spreader-stoker unit with a capacity of 170,000 lb/h of 200 psig steam, the equivalent of about 20 MWe (all steam is used for site heating/cooling). It was installed in 1965 by the Wickes Boiler Company (now Combustion Engineering Company) and was converted to gas/oil firing in 1973. In 1979, the boiler was reconverted to coal firing with the expectation of burning high-sulfur (nominally 3.5%), Illinois-basin coal. Because the original emissions control equipment consisted only of a multiclone particulate-matter collector, additional SO_2 control was required. A number of possible FGC systems were evaluated and spray-dryer technology was selected on the basis of several factors that included system simplicity and dry-waste production.

The spray-dryer/fabric-filter system was installed by Niro Atomizer in 1981. Significant design features include a rotary atomizer, a pulse-jet fabric filter, and sorbent (lime-based) recycle. A diagram of the system is shown in Figure 1. The sorbent slurry used in the spray dryer is a blend of recycled solids and fresh milk of lime, which are combined with dilution water in the slurry mix tank to form a 35% (by weight) slurry that is then pumped to the slurry feed tank.

The spray dryer is 7.5 m in diameter with dual flue-gas inlets. About 60% of the flue gas enters downward through the roof gas disperser and the remainder of the gas enters upward through a central disperser. The two streams meet and mix in the vicinity of the centrally located atomizer, which consists of a 21 cm (diameter) disc with eight 1 cm holes in the periphery. The disc is spun by an electric motor at 14,000 rpm to produce a fine mist of slurry droplets that react with and are dried by the flue gas. Depending on the gas flow rate, about one-fourth to one-third of the powder produced falls to the bottom of the spray dryer and is removed by a conveyor. The remainder is entrained in the gas stream and is carried from the spray dryer to the fabric filter.

The fabric filter provides particulate-matter collection and also contributes significantly to removal of SO_2 as the flue gas passes through the dust cake on the bags[3]. It is a four-compartment pulse-jet system made by the Joy Manufacturing Company. Each compartment contains 28 rows of 10 bags, giving a total filtration area of 1950 m^2 and an air-to-cloth ratio of 1.5 cm/s. The bags are of a snap-ring design and are made of 468 g woven fiberglass. Cleaning is performed off-line for one compartment at a time and is initiated on the basis of pressure drop across the baghouse.

The FGC system is extensively instrumented in order to support research activities as well as normal operations. The flue gas is sampled at both the system inlet and the stack using an extractive system with sample dilution at the probes. Measurements are made of SO_2, CO_2, NO, and NO_x using one set of analyzers switched between the two streams. Another set of analyzers can be temporarily installed for field tests to measure the gas composition between the spray dryer and the fabric filter. Gas temperatures at several points, pressure drops across each component, all system flow rates, boiler conditions, and coal feed are monitored and recorded continuously by a computer-based data acquisition system.

It should be noted that all of the research activities were designed to operate within two principal sets of constraints. First, the boiler operates under permit conditions set by the State of Illinois, which limit SO_2 emissions to 1.8 lb/10^6 Btu and stack opacity to less than 20% . Also, the boiler is normally base loaded as the main steam supply source for the ANL site, thereby requiring that boiler capacity and availability not be adversely affected.

RESEARCH PROGRAMS

High-Sulfur Performance Tests

The ability of spray-dryer-based FGC systems to reliably control SO_2 emissions to NSPS levels (90% removal) has often been questioned. To explore the operating potential of such a system, ANL conducted a brief research program in cooperation with the Consolidation Coal Company and the Conoco Coal Research Division[4].

Test Program. The specific test objectives were to achieve 90% or greater SO_2 removal for at least 100 continuous hours, to achieve 90% or greater SO_2 removal at an external stoichiometry (based on fresh lime feed) of 1.35 or less, and to determine whether 70% or greater SO_2 removal could be achieved in the spray dryer alone (an important consideration for retrofit applications involving an electrostatic precipitator). The coal used was West Virginia bituminous with an average sulfur content of 4.2%.

Results. All of the initial objectives were attained. In addition, a number of insights into spray-dryer/fabric-filter system operation were gained. For example, the data plotted in Figure 2 show that over 90% removal is attainable at reasonable stoichiometries and that the required stoichiometry depends upon the coal sulfur content (inlet SO_2). In Figure 3, the importance of removal reactions in the baghouse filter cake is confirmed, with essentially equal percentage removals occurring in the spray dryer and the fabric filter. Other observations included the following.

- Under the conditions employed for these tests, available alkali in the recycled waste contributes 15-20% of the total (internal) stoichiometry, decreasing at high removals as fresh lime feed is maximized.

- Resistivities of waste particles are about 5×10^7 Ohm-cm, which should pose no problem for collection by an electrostatic precipitator.

- The approach to dew point of the spray-dryer exit gases is a strong determinant of removal. Decreasing the approach from 17°C (30°F) to 11°C (20°F) at a Ca/S ratio of 1.3 improved SO_2 removal from 74% to 87%.

Data from the test were used by Conoco to develop economic comparisons of spray drying with wet flue-gas desulfurization (FGD) for both new (NSPS-90% removal) and retrofit (70% removal) installations. In the first case, a spray dryer system was found to have essentially the same cost as the wet FGD system. In the retrofit case, the spray dryer system was projected to give a significant cost savings[4].

Combined NO_x/SO_2 Control Tests

Future regulations may well require flue-gas denitrification as well as desulfurization for both utility and large industrial boilers. Research for the U.S. Department of Energy at ANL has emphasized the development of integrated systems capable of removing both NO_x and SO_2. The benefits of such integration are expected to be better system operability, higher reliability, lower capital and operating costs, and reduced environmental impacts.

Test Program. Laboratory research at ANL and the Pittsburgh Energy Technology Center[5] identified several sodium-based chemical additives that enhance the NO_x-removal potential of the lime sorbent used in most spray-dryer systems. Process conditions that include increased spray-dryer exit temperature and high levels of SO_2 in the flue gas were also identified as beneficial for combined removal. In addition, this line of research was spurred by reports of brown plumes (NO_2) from a western utility operating a spray dryer system that uses soda ash as the sorbent, and initial data from Niro Atomizer on the effect of sodium hydroxide (NaOH) in a lime-based spray dryer for combined NO_x/SO_2 removal[6]. On the basis of these results, it was decided to conduct a field test of NaOH addition to a spray-dryer feed slurry at elevated spray-dryer exit temperatures using the ANL boiler/FGC system. An initial series of tests was conducted in August 1986 aimed at confirming the data reported by Niro Atomizer, attempting to identify the key variables associated with combined removal, and ascertaining the most favorable conditions for a combined removal process[7]. Further tests were conducted during the spring and summer of 1988 to confirm and refine the previous results, particularly with regard to the minimum required level of NaOH addition, the effects of baghouse pressure drop (cake thickness), and the attainment of steady state conditions. The test conditions are summarized in Table I.

Sulfur dioxide removals were maintained between 60% and 70% throughout the tests in order to maintain compliance with the operating permit. Inlet SO_2 levels to the spray dryer were typically 1200-1300 ppm for the 1986 tests and 1600 ppm for the 1988 tests. During the final phase of the 1986 tests, inlet SO_2 levels were decreased gradually to a low value of about 400 ppm by blending in low-sulfur coal. Inlet NO_x levels varied between about 225 to 260 ppm during the tests, with nitrogen dioxide (NO_2) levels of less than 10 ppm.

Results. The spray-dryer outlet temperature is one of the most important variables for system performance. While lower temperatures are beneficial for SO_2 removal, there is no appreciable removal of NO_x at these temperatures, as shown for 68°C (155°F) in Figure 4 from the 1986 tests. At 82°C (180°F), a dramatic transition was encountered which gave a very rapid increase in nitric oxide (NO) removal with temperature and a concurrent increase in net NO_2 production. Both effects appeared to take place in the fabric filter. The result for total NO_x was a decrease (removal), but at a somewhat lower level than that observed for NO. As the temperature was increased further, NO_x removals continued to increase, although the rate of increase slowed considerably. Further evidence of the removals was seen in the nitrates levels found in the recycle powder, which increased from about 200 ppm at low temperatures to approximately 4000 ppm at 99°C (210°F). However, attempts to use these data to achieve a material balance for nitrogen in the system have not been successful, indicating that there may exist other "sinks" such as the formation of N-S compounds.

The properties of the powder collected in the baghouse also changed with increasing temperature, giving a drier, more porous powder with increased surface area. The changes produced a reduced pressure drop through the filter cake for any given amount of powder on the bags. For example, Argonne's baghouse normally undergoes a cleaning cycle about every one and one-half hours. At a spray-dryer outlet temperature of 99°C (210°F), the interval between cleaning cycles expanded to about three hours for the same pressure-drop setpoint. Note that the particulate loading actually increased due to the increased sorbent stoichiometry required to maintain SO_2 removal.

The most noticeable effect from the addition of NaOH to the system was a further increase in filter cake porosity (lower pressure drop). Upon addition of NaOH at the 5% level, the time between baghouse cleanings increased from three to six hours, and then to 8 hours when the NaOH addition was increased to 10%.

Nitrogen oxides removal also increased with the addition of NaOH. At 88°C (190°F), 5% NaOH addition increased total NO_x removal by about 23%, while at 93°C (200°F) the increase was about 53%. Preliminary evaluation of the 1988 data indicates that there is little if any statistically significant improvement in NO_x removal as a result of increasing the NaOH addition rate from 2.5% to 5.0%. Thus, significant NO_x-removal enhancement may be possible with still lower additive levels and, hence, reduced operating costs.

The data indicate that a key factor in both NO_x and SO_2 removal is the thickness of filter cake that can be maintained on the bags. During the extended (6 hr) period between bag cleanings noted previously, steadily increasing removals of SO_2, NO, and NO_x were observed. However, cleaning of the bags removes most of the dust cake and thereby reduces the removal rates to minimum values from which they gradually increase as more powder is collected. This gives a cyclic removal profile that closely parallels the baghouse pressure drop, as shown in Figure 5 from the 1988 tests. An average NO_x removal of about 35% was attained in those tests over an extended period.

During the final phase of the 1986 tests, the SO_2 content of the flue gas was gradually decreased by blending in low-sulfur coal. As indicated in Figure 6, the SO_2 level in the flue gas and/or the ratio of SO_2 to NO_x has a strong influence on both NO and total NO_x removal, with the higher SO_2 levels clearly improving removals. During the 1988 tests, data taken at a still higher SO_2/NO_x ratio of about 6.5 gave average NO_x removals significantly higher than those in the earlier tests. This is a further indication that nitrogen-sulfur compounds may be a significant sink for nitrogen.

The addition of NO_x removal to a spray-dryer FGC system using the method described here will incur incremental costs for additional lime (less efficient SO_2 removal at higher temperatures) and NaOH. A preliminary estimate based on $70 per ton of lime, $250 per ton of 50% caustic soda, a 5% (by weight) NaOH addition rate, and 35% NO_x removal gave a cost of $2550 per ton of NO_x removal.

Cofiring Refuse-Derived Fuel

Refuse-Derived Fuel represents a technically and environmentally attractive approach to the use of municipal waste for energy. The fuel exhibits greatly improved storage and handling properties compared to raw waste and is potentially compatible with existing combustors. As part of Argonne's Energy from Municipal Waste Program, ANL and North Texas State University conducted a multi-phase study of low-cost binders for improving densified RDF pellets.[8] The top-ranked binder from this program was lime, which was subjected to a comprehensive full-scale test in Argonne's coal-fired boiler/FGC system during 1987.

Test Program. Binder-enhanced RDF pellets were blended with Argonne's normal high-sulfur (about 2.7% S) coal at 10, 20, or 30%, based on Btu content. When steady state operation was attained for each blend, data/samples were taken for mass and energy balances, emissions characterizations, and ash analyses. The pellets were produced in three lots with binder contents of 0, 4, and 8% by weight. Delivery was by covered trucks from the fabrication facilities in Minnesota and the pellets were stored outdoors under a polyethylene cover until needed. Overall, about 575 tons of pellets were used in the tests. Typical fuel characteristics are given in Table II.

For these tests, the FGC system was operated in its normal mode with regard to spray dryer exit temperature (approach to dew point), baghouse cleaning cycles, etc.

Results. The data and samples from the tests have been extensively analyzed and some of the information is still under evaluation. Results thus far include the following.

- Uncontrolled SO_2 and NO_x emissions decreased as the percentage of RDF in the fuel increased, as shown in Figure 7. For SO_2, the data also show a decrease as the binder percentage increased. For example, a 21% reduction was noted for pellets without binder at the 30% blend, while 4% and 8% binder gave SO_2 decreases of 24% and 27%, respectively.

- Uncontrolled HCl emissions increased above the coal baseline of 11.39 ppm as the percentage of RDF was increased. However, the emissions were reduced as the amount of lime binder increased. At a 30% blend and 8% binder, HCl emissions were 27.45 ppm, somewhat below the 30 ppm limit used in some areas. The FGC system removed about 90% of the HCl produced in the boiler.

- No detectable levels of fluorides or bromides were found in the flue gas either before or after the FGC system.

- No detectable levels of tetra through octa chlorinated dioxins or furans were found in either the flue gas or fly ash samples.

- All bottom ash and fly ash samples passed the EP Toxicity tests for all elements, including lead and cadmium.

CONCLUSIONS

The three research programs summarized in this paper have developed a considerable body of information on the performance of a coal-fired (or RDF/coal-fired) boiler combined with a spray-dryer/fabric-filter system. Some of the key results include the following.

- Sulfur dioxide removals meeting NSPS requirements are attainable under reasonable operating conditions and economics.

- Removal reactions in the baghouse filter cake contribute significantly to SO_2 removal and, under modified operating conditions, to NO_x removal.

- Significant removal of NO_x occurs when the spray dryer outlet temperature exceeds 82°C (180°F).

- The removal of NO_x decreases when flue gas with a low concentration of SO_2 is being treated by the system.

- The removal of NO_x increases in proportion to the buildup of cake on the filter bags, with a subsequent loss of removal efficiency after the filters are cleaned. Higher temperatures and NaOH addition increase the thickness of filter cake for a given pressure drop. No significant NO_x removal has been observed in the spray dryer itself.

- Cofiring of RDF and coal at blends up to 30% RDF is feasible without upsetting combustion stability or the ability of the boiler to maintain load. Higher percentages of RDF could be fired with modifications to the stokers to increase their capacities. Fuel handling, slagging, and clinkering problems were not noticeably worse than when firing only coal.

- Uncontrolled emissions of SO_2 and NO_x were reduced by cofiring RDF. Emissions of HCl were increased but were within acceptable limits. No dioxins or furans were detected.

- Ash residues from RDF/coal blends successfully passed the EP Toxicity test.

- Addition of a lime binder to RDF produces a better pellet, capable of extended storage, and contributes to the control of acid gases.

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REFERENCES

1. M. Placet, D. G. Streets, and E. R. Williams, "Environmental Trends Associated with the Fifth National Energy Policy Plan," Argonne National Laboratory Report ANL/EES-TM-323 (August 1986).

2. "Environmental-Control Strategies for Coal-Based Industrial Boilers: Analysis of Performance and Costs," Argonne National Laboratory Report ANL/ECT-10 (June 1981).

3. P. S. Farber, "Emissions Control Through Dry Scrubbing," Environmental Progress, 5(3):178-183 (Aug. 1986).

4. P. S. Farber, C. D. Livengood, H. S. Huang, M. I. Bin Thani, B. J. Koch, D. C. McCoy, and R. M. Statnick, "Evaluation of a Spray Dryer Flue Gas Cleaning System on High Sulfur Coal," paper presented at Coal Technology '83, Houston, Texas (November 15-17, 1983).

5. H. S. Huang, P. S. Farber, C. D. Livengood, J. T. Yeh, J. M. Markussen, and C. J. Drummond, "Simultaneous NO_x/SO_2 Removal in a Spray Dryer System," paper presented at 1987 AIChE Spring National Meeting, Houston, Texas (March 1987).

6. K. Felsvang, P. Morsing, and P. Veltman, "Acid Rain Prevention Through New SO_x/NO_x Dry Scrubbing Processes," paper presented at U.S. Environmental Protection Agency/Electric Power Research Institute Flue Gas Desulfurization Symposium, New Orleans (Nov. 1983).

7. P. S. Farber, H. S. Huang, and J. W. Allen, "NO_x and SO_x Removal in a High Sulfur Spray Dryer System," paper presented at Second International Conference on Processing and Utilization of High Sulfur Coals, Carbondale, Ill. (Oct. 1987).

8. O. O. Ohlsson, K. Daugherty, and B. Venables, "Emissions Resulting from the Full-Scale Cofiring of Pelletized Refuse-Derived Fuel and Coal," paper presented at Tenth Annual Industrial Energy Technology Conference, Houston, Texas (Sept. 13-15, 1988).

Table I

Combined NO_x/SO_2 Control Test Conditions

Duration (days)	Spray Dryer Exit Temp. (°C)	NaOH Feed Rate (% Lime Feed)	Comments
<u>1986 Tests</u>			
20	68	0	Baseline data
2	77	0	
2	99	0	
2	99	5	
2	99	10	
2	99	10	Inlet SO_2 decreased to 400 ppm
<u>1988 Tests</u>			
6	71	0	Baseline data
3	82	0	
3	82	2.5	
3	88	2.5	
3	88	5.0	
4	71	0	Recheck baseline after restart
3	82	5.0	
3	93	5.0	

Table II
Comparison of Coal and Binder-Enhanced RDF

	Coal	RDF (8% Binder)
Ultimate Analysis (As Received %)		
Moisture	6.28	3.99
Carbon	69.17	40.38
Hydrogen	4.79	5.17
Nitrogen	1.49	0.27
Chlorine	0.01	0.09
Sulfur	2.70	0.12
Ash	8.15	13.90
Oxygen	7.41	36.08
Btu/lb	12,200	6,800
Bulk Density (lb/ft^3)	42.0	45.6
Ash Fusion Temperature (°C) (Initial Deformation, oxidizing)	1304	1329

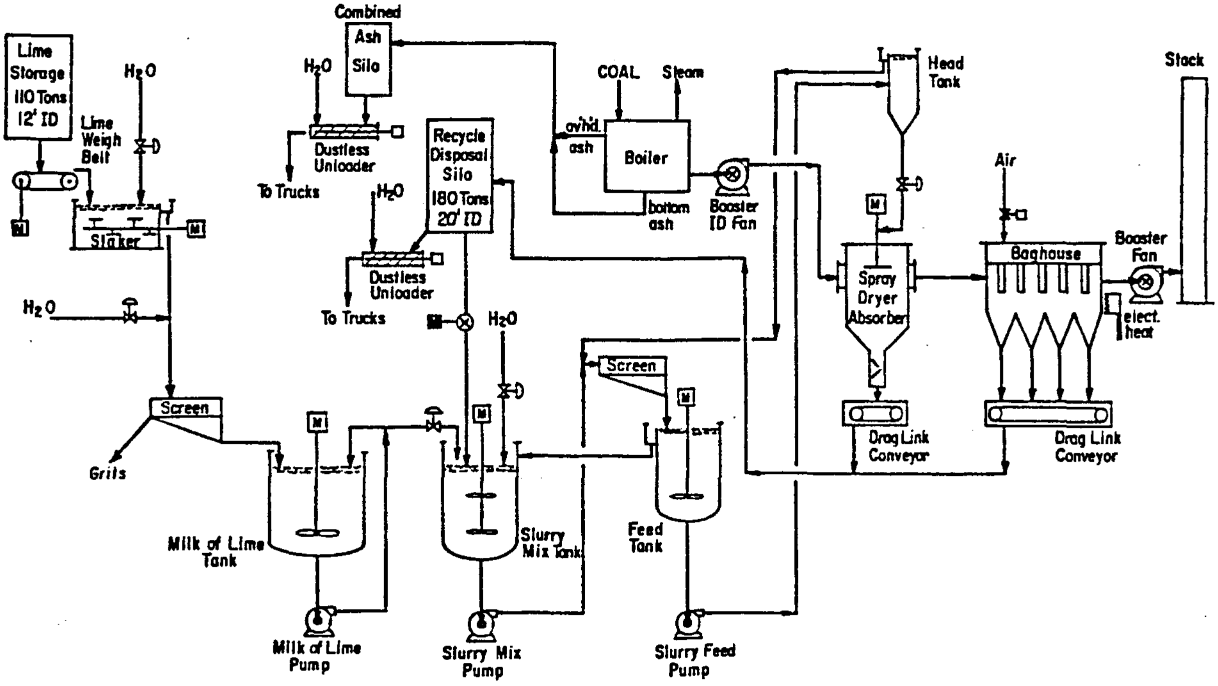

Figure 1. Argonne boiler and FGC system diagram.

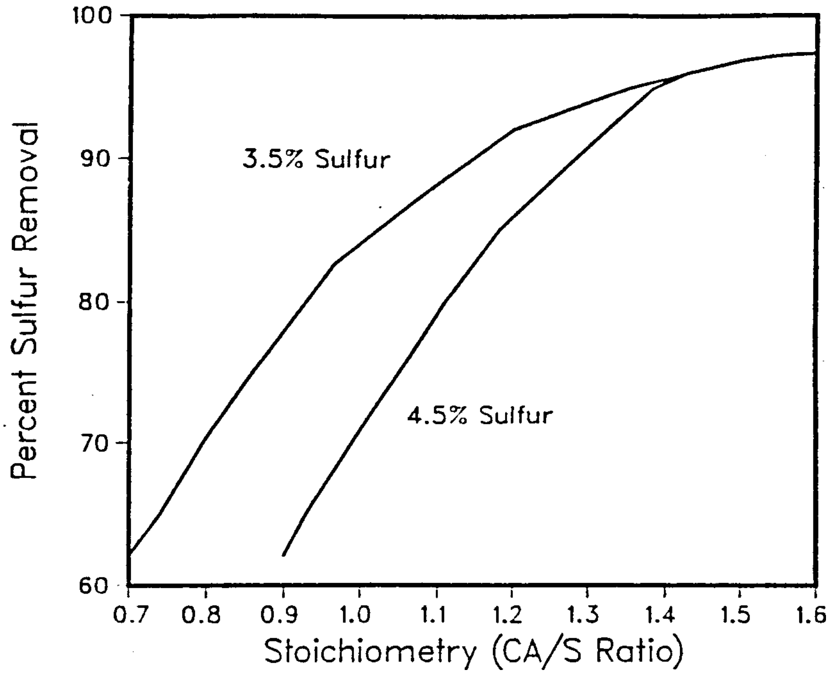

Figure 2. SO_2 removal vs. sorbent stoichiometry.

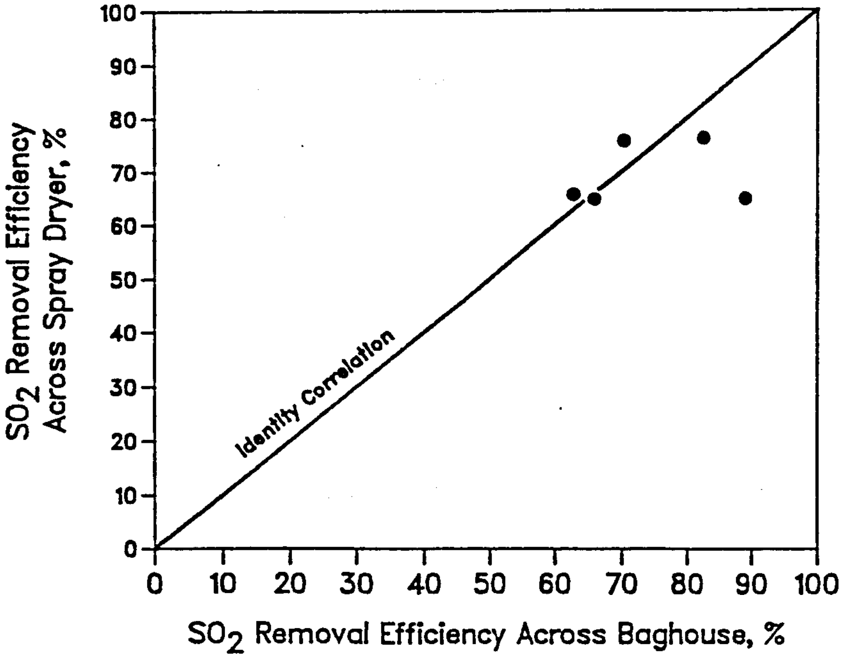

Figure 3. Spray dryer SO_2 removal vs. baghouse SO_2 removal.

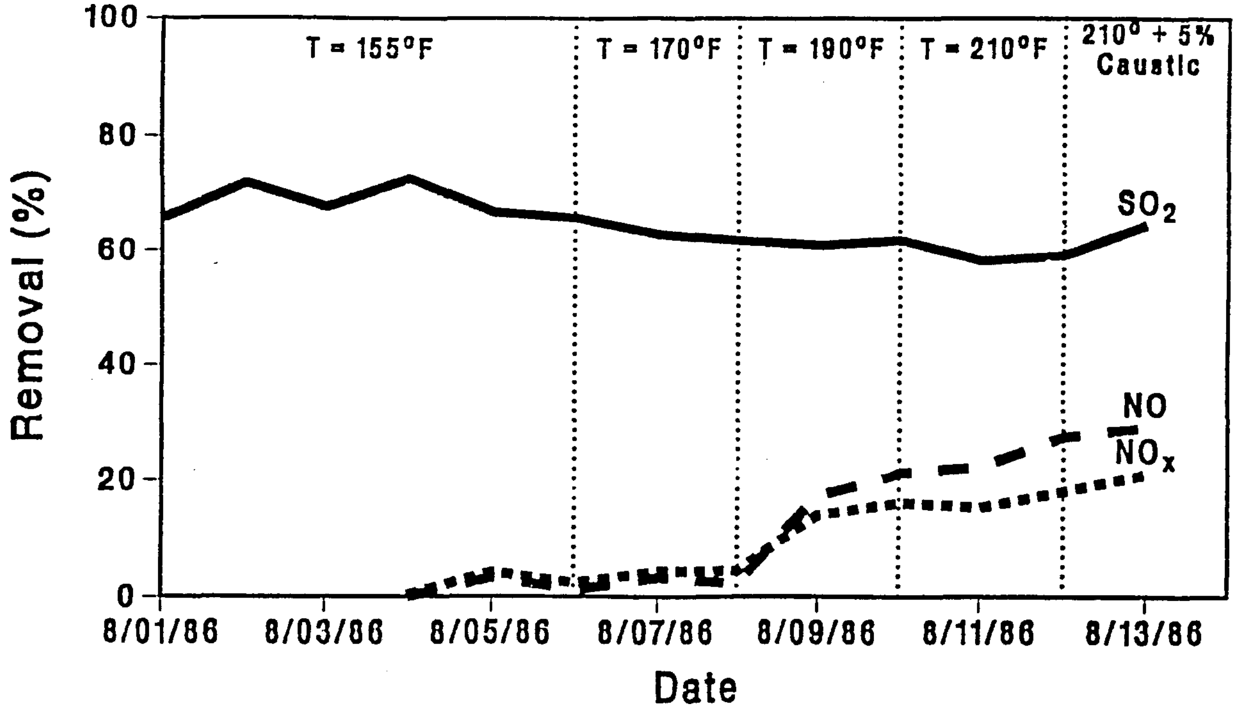

Figure 4. NO_x/SO_2 removals as a function of spray dryer exit temperature.

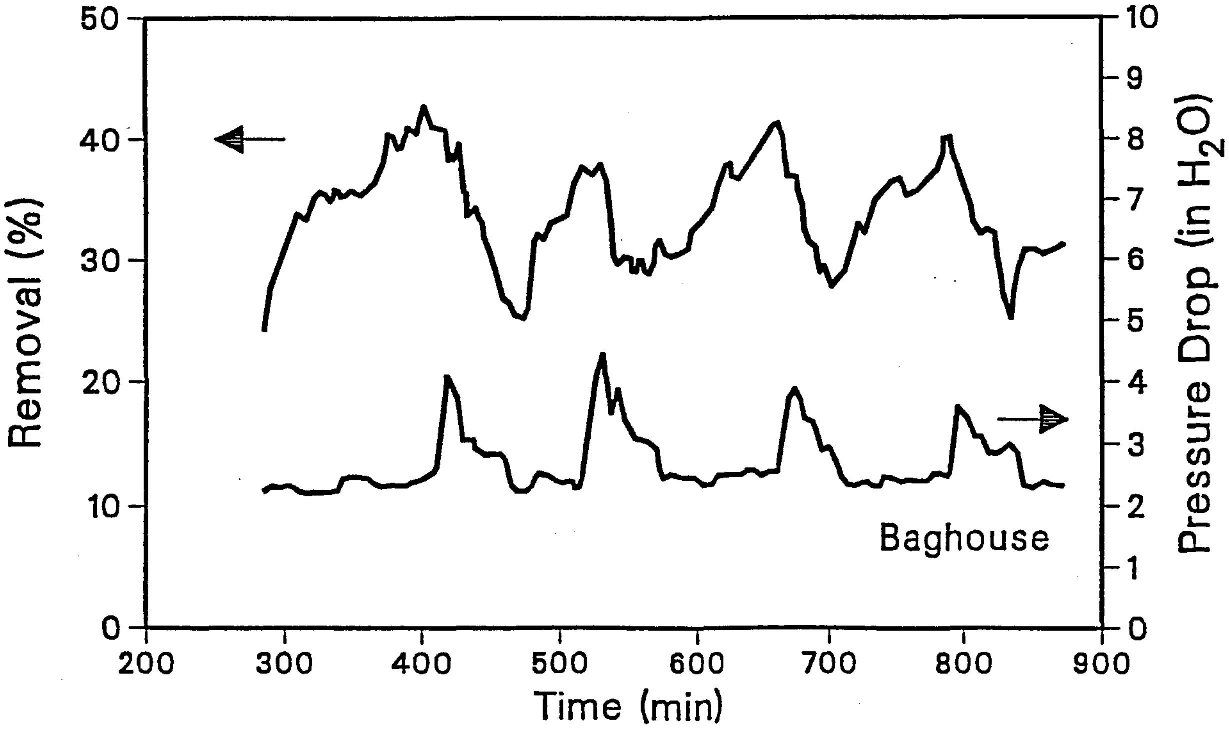

Figure 5. Comparison of NO_x removal and baghouse pressure drop.

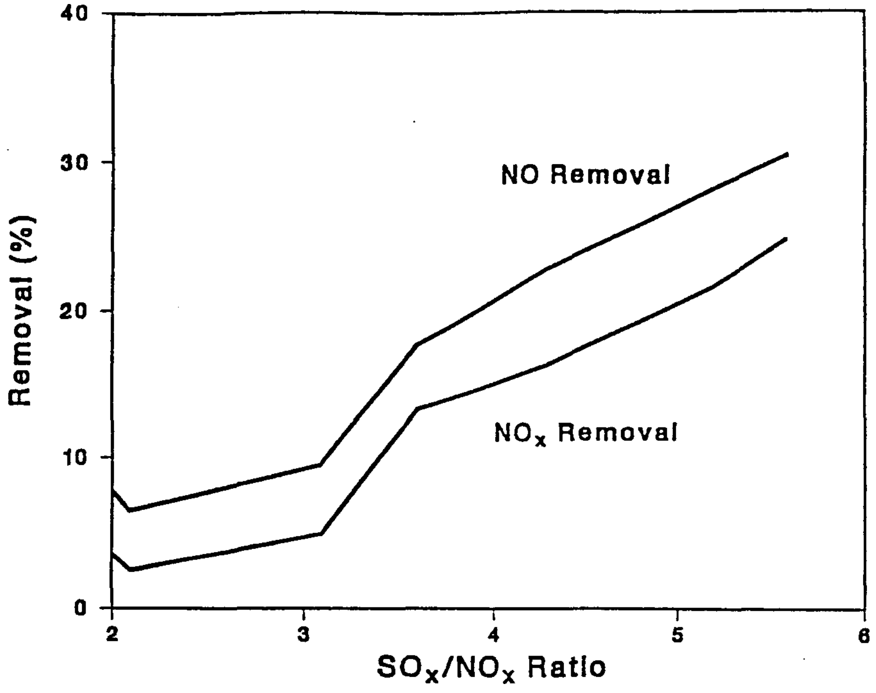

Figure 6. NO_x removal vs. SO_x/NO_x ratio in flue gas.

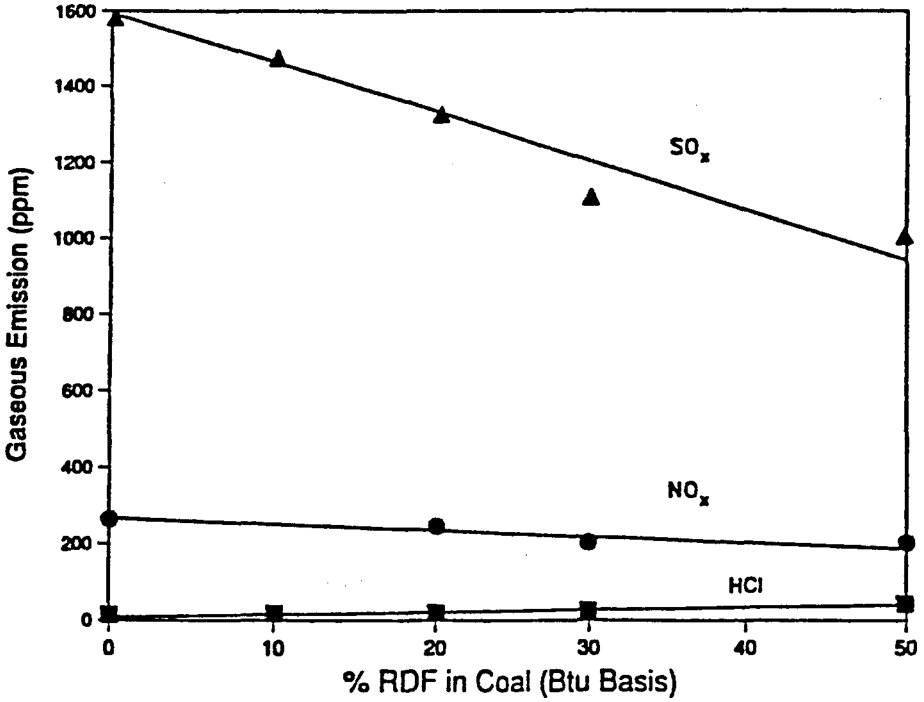

Figure 7. Boiler emissions as a function of RDF fraction in fuel.