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Project Summary

Bench-Scale Process Evaluation of Reburning and Sorbent Injection for In-Furnace NO_x/SO_x Reduction

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A study was initiated to investigate in-furnace NO_x/SO_x reduction techniques through the combined use of reburning and limestone injection. Reburning is a multistage combustion modification technique in which fuel is added downstream of the main firing zone to produce a fuel-rich zone where NO from the main firing zone is reduced. Burnout air is added farther downstream to provide for complete burnout of the reburning fuel. Sorbent injection involves injection, into the furnace, of calcium-based materials onto which SO_2 can be absorbed. The absorbed sulfur is removed from the flue gas with the particulate as calcium sulfate.

Tests have been carried out at bench scale (20.5 kW) to investigate the impact of process variables on the effectiveness of the combined technology. Under the best conditions, up to 80% NO_x reduction and 60% removal of SO_x at a calcium/sulfur ratio of 2 have been achieved. The impact of each variable in each zone was investigated independently. The dominant parameters were found to be the reburning condition and the primary NO level. The time, temperature, and stoichiometric requirements of the reburning zone influenced NO_x reduction efficiency in a manner consistent with a kinetically controlled process; i.e., higher temperatures and longer residence times at an optimum stoichiometry of 0.9 were favorable. SO_x reduction was most influenced by the location of injection of the sorbent; in particular, injection with the burnout air was optimum.

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 project addresses the combined technologies of reburning for NO_x reduction and sorbent injection for SO_x capture. The goal of the project was to provide an authoritative assessment of the application of these technologies to U.S.-designed pulverized-coal-fired boilers. Reburning involves the addition of downstream fuel to form a rich zone in which NO formed upstream is reduced. The concept of NO reduction by flames has been known for over a decade and is now being applied in Japan in large furnaces. The reburning process can be divided into three zones:

- *Primary Zone*: This main heat release zone accounts for about 80 to 90% of the total heat input to the system. The zone is operated under overall fuel-lean conditions, although the burners might be low-NO_x distributed mixing burners. The level of NO_x exiting from this zone is the level to be reduced in the reburning process.

- *Reburning Zone*: The reburning fuel (normally about 10 to 20% of the total fuel requirements) is injected downstream of the primary zone to create a fuel-rich reduction zone. The reactive nitrogen entering this zone comes from two sources: the primary NO level and the fuel nitrogen in the reburning fuel. These fuel nitrogen species apparently react with the hydrocarbon fragments from the reburning fuel to produce intermediate species such as NH_3 and HCN, while some is converted to N_2 and some is retained as NO. The products of this reduction zone are the reactive nitrogen species such as NO, char nitrogen, NH_3, and HCN, which will be referred to as total reactive nitrogen. To optimize the NO reduction by reburning, it is necessary to minimize the total reactive nitrogen exiting the reburning zone.
- *Burnout Zone*: In the burnout zone, air is added to produce overall lean conditions which oxidize all the remaining fuel and convert the total fixed nitrogen to either NO or N_2.

Reburning can be combined with furnace sorbent injection in an attempt to reduce both NO_x and SO_x. Calcium-containing sorbents, typically either calcitic or dolomitic limestones, lime, or hydrated lime, are injected directly into the furnace and absorb SO_2. The reaction is a gas/solid reaction of the form:

$$CaO(s) + SO_2(g) \rightarrow CaSO_3(s)$$

$$CaSO_3(s) + \tfrac{1}{2}\,O_2(g) \rightarrow CaSO_4(s).$$

The solid calcium sulfate, $CaSO_4$, formed is removed with the fly ash particulate. When combined with reburning, sorbents can be injected in a number of locations: with the primary fuel, with the reburning fuel, with the burnout air, or downstream of all the reburning zones.

The U.S. EPA has a major program to investigate the combined in-furnace NO_x/SO_x reduction technologies for pulverized-coal-fired furnaces. This program will attempt to define the process requirements and application techniques and will ultimately include estimates of capital and operating costs for application to new and existing boiler designs. The first phase of that program, reported here, is an experimental effort carried out at bench-scale to investigate the impact of process design variables on the effectiveness of the combined technologies. The bench-scale testing has provided fundamental insight into the chemical processes that control NO_x/SO_x reduction. The continuing effort will include pilot-scale tests at 10 x 10^6 Btu/hr (3 MW) on reburning/limestone injection performance in order to provide information on process scaling and hardware. The final task will be an engineering and economic assessment of the application of the technology as defined by the experimental program for the inventory of U.S. coal-fired furnaces.

Control Temperature Tower

The process studies were carried out in a refractory-lined Control Temperature Tower (CTT), shown schematically in Figure 1. The CTT has a total firing rate of between 18 and 24 kW (60,000 and 80,000 Btu/hr) in the main combustion chamber, which is 20.3 cm in diameter and includes a long quarl entry to promote flame stabilization and to provide for one-dimensional plug flow. The time/temperature profile along the furnace could be manipulated by using back-fired heating sections within the insulating refractory. The back-fired sections consisted of natural gas burners fired into refractory channels in the direction opposite to the main chamber. The high temperature gases pass through the channels surrounding the main chamber (see the radical cross-sectional view in Figure 1) and minimize the temperature decay along the furnace. A more rapid temperature decline can be achieved by leaving the back-fired channels off or by inserting cooling coils around the main chambers. The tower is equipped with numerous ports along the axis of the reactor which allow the installation of zone separation chokes, fuel and air injectors, cooling coils, and sampling probes.

The CTT was configured into three zones: (1) the primary zone, formed using a premixed burner fired on pulverized coal or propane doped with various levels of H_2S and NO, under lean conditions (typically 10% excess air); (2) the reburning zone, formed by injecting the reburning fuel (either coal or doped gas) at various flowrates to control the reburning zone stoichiometry; and (3) the burnout zone, in which air was injected to bring the overall stoichiometry to typically 25% excess air. The parameters in each zone were examined separately in terms of how they influenced the exhaust level of NO_x. The test series was performed by establishing the level of NO_x from the primary and then increasing the amount of reburning fuel addition and burnout air correspondingly to decrease the reburning zone stoichiometry and maintain the

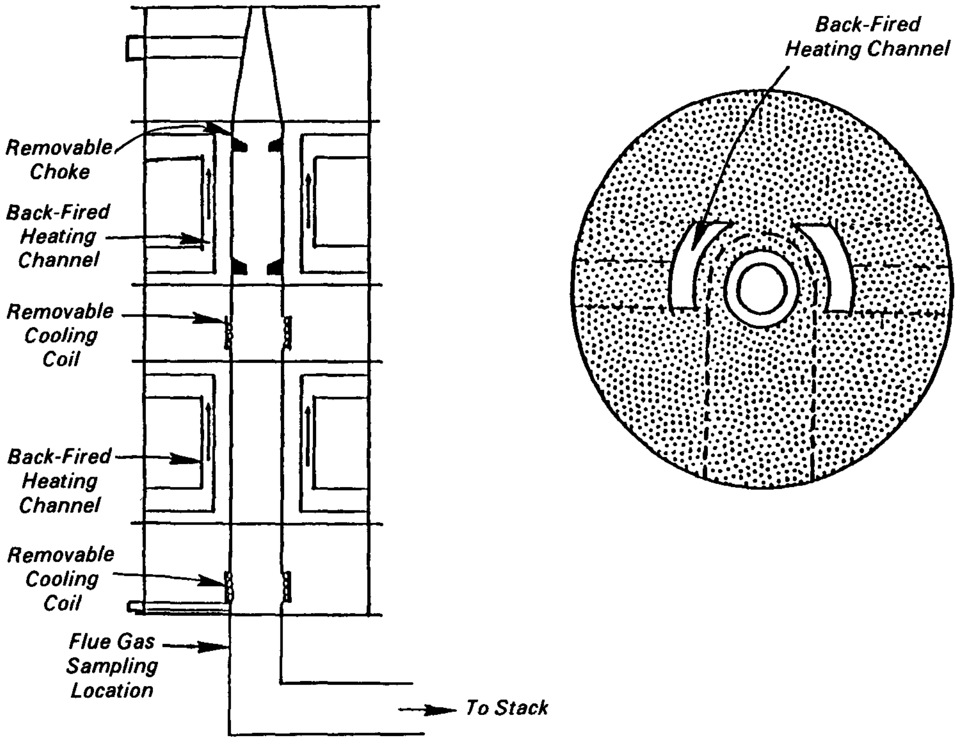

Figure 1. *Cross-sectional views of the control temperature tower.*

overall burnout zone stoichiometry. In this manner, the residence time and temperature in the reburning zone were maintained relatively constant while the reburning zone stoichiometry was varied.

Process Parameters

The process zones and parameters investigated were:

- Primary Zone
  - —Stoichiometry
  - —Fuel type
  - —NO level
  - —SO_x level
- Reburning Zone
  - —Stoichiometry
  - —Mixing rate of reburning fuel
  - —Reburning fuel type (propane, hydrogen, CO, and coals)
  - —Nitrogen content of reburning fuel
  - —Temperature (peak temperature and temperature profile)
  - —Residence time
  - —Limestone sorbent type and Ca/S ratio
  - —Transport media for reburning fuel (air or inert)
- Burnout Zone
  - —Temperature
  - —Excess air
  - —Air mixing rate
  - —Limestone sorbent type and Ca/S ratio

The impact of each variable was investigated independently in terms of the reduction efficiency of NO_x and SO_2 capture by calcium.

NO_x Reduction by Reburning

Table 1 summarizes the influence of the process variables on effectiveness of the reburning process to reduce NO_x. The dominant parameters were found to be the reburning zone condition and the primary NO_x level. An optimum stoichiometry of 0.9 was found to exist independent of the primary zone stoichiometry for a wide variety of fuels and conditions. The time and temperatures within the reburning zone influenced the NO reduction efficiency in a manner consistent with a kinetically controlled process. Higher temperatures and longer residence times were favorable. The most dramatic impact was with the primary NO_x level, as shown in Figure 2. At high levels of primary NO_x, the reduction efficiency was relatively independent of NO_x level or reburning fuel type, and NO_x reductions of 70% were achieved. At lower levels of primary NO_x (<200 ppm),

Table 1. *Influence of Process Variables on Reburning Effectiveness for NO_x Reduction*

Parameter	*Impact*
Primary Zone	
Stoichiometry	• *No effect except will require more reburning fuel for burner operation.*
Fuel type	• *No direct effect. Can influence through temperature and NO_x level entering reburning zone.*
NO level	• *Strong effect. More difficult to reduce lower levels of primary NO_x.*
Reburning Zone	
Stoichiometry	• *Optimum at overall stoichiometry of 0.9.*
Mixing rate of reburning fuel	• *Faster mixing preferred.*
Fuel type	• *Hydrocarbon fuels more effective; fuel nitrogen content detrimental at lower primary NO_x level.*
Temperature	• *Reduction increases with increasing temperature (1316 - 1593°C).*
Residence time	• *Strong impact, increasing with time (100-750 msec).*
Transport media	• *Inert transport (oxygen free) is desirable since less reburning fuel is required to attain optimum stoichiometry.*
Burnout Zone	
Excess air	• *Not important except for burnout.*
Air mixing rate	• *Not important.*
Temperature	• *Not important unless temperature is dropped to 927°C where selective NH_i-NO_x reactions can take place to enhance reduction.*

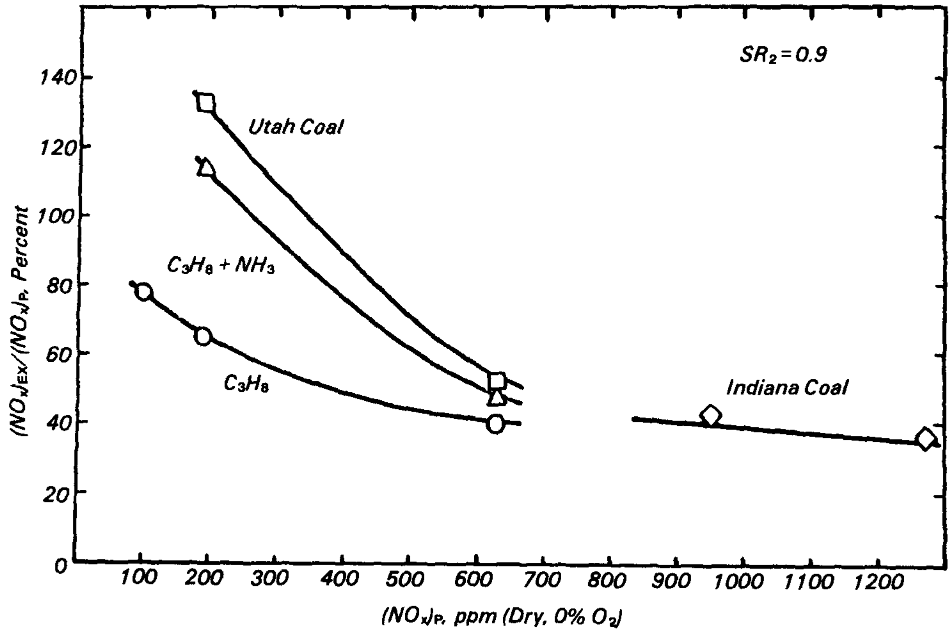

Figure 2. *Impact of primary NO_x on effectiveness of reburning.*

the reduction efficiency decreased with decreasing NO_x. The reduction was less for nitrogen-containing reburning fuels. Reburning with coals gave similar reductions to gaseous fuels except at primary NO_x levels below about 700 ppm. A wide variety of coals were tested including all ranks from lignite, subbituminous, and bituminous, to anthracite. All coals were found to behave similarly except at low primary NO_x levels where the coal nitrogen content became important. Some operational problems were encountered with lower volatile coals due to burnout limitations.

Combined NO_x/SO_x Reduction

Sulfur capture by calcium-containing sorbents was investigated when the sorbents were injected in the primary, along with the burnout fuel and with the burnout air. These studies were conducted under conditions that were found to favor NO_x reduction by reburning. The dominant parameters found to influence sulfur capture by sorbent injection were:

- Sorbent type (limestone, dolomite, or hydrate lime).
- Sorbent injection location (injection temperature).
- Temperature profile in sulfation temperature region (1250-950°C)
- Calcium/sulfur ratio.

The first two parameters were found to change the surface area of the sorbent after calcination which determines its ability to subsequently uptake sulfur. Figure 3 shows the sulfur capture data for one particular reburning condition as a function of specific surface area of the sorbents after calcination. The surface area was measured by extracting solid samples when sorbents were injected into the furnace in the absence of sulfur, since sulfation closes the surface area. There was found to be an almost linear relationship of sulfur capture with specific surface area and calcium/sulfur ratio. Injection of the sorbent with the burnout air was preferred due to the relatively low injection temperature which produced higher specific surface areas. Dolomite was found to achieve the highest captures of the sorbents tested, which could be attributed to its high specific surface area. In general, better capture was obtained with coal as the reburning fuel than with gas. The causes of this enhancement with coal are uncertain.

Process Models

A complete process model has been developed for both NO_x reduction by reburning and sulfur capture by limestone injection. These models allow the data to be interpreted and used to estimate reburning efficiency and sulfur capture in practical applications of the technologies. In both cases, the models are semi-empirical approaches, developed in modular fashion on the individual subprocesses.

The reburning process model treats separately the fuel-rich secondary flame, the post-flame reduction, and the lean combustion of the nitrogen species entering the burnout zone. The fuel-rich secondary flame module is a simple correlation of the speciation of nitrogen compounds which occurs when reburning fuel is mixed with the primary products. The post-flame reduction module is based on the combined effects of rich-gas-phase homogeneous reduction and heterogeneous reduction of NO on carbonaceous particulate, and describes the changes in total reactive nitrogen. The lean burnout module predicts final NO concentrations from the conversion of reactive nitrogen species. An empirical correlation is used which was originally developed to predict NO concentrations emitted from the lean stage of rich/lean-staged combustion. Submodels are required for coal-fired reburning which describe nitrogen speciation in pyrolysis and char nitrogen processing.

The sulfation model involves dividing the process into two steps: sorbent activation and sorbent sulfation. Sorbent calcination is assumed to occur instantaneously, leaving an active stone. The specific surface area of the stone is determined by the peak injection temperature. A correlation has previously been developed which allows specific area to be estimated for a broad range of temperatures and sorbent types. The sulfation model treats the active sorbent particles as spheres enveloping a random distribution of cylindrical pores which provide the overall particle surface area. The reaction is initiated at the pore surface, and a layer of reaction product (calcium sulfate) forms around the pore. This reaction product layer separates the pore surface and the solid reactant surface. The gas (SO_2) must diffuse through the product layer to the surface of the solid reactant (CaO) where

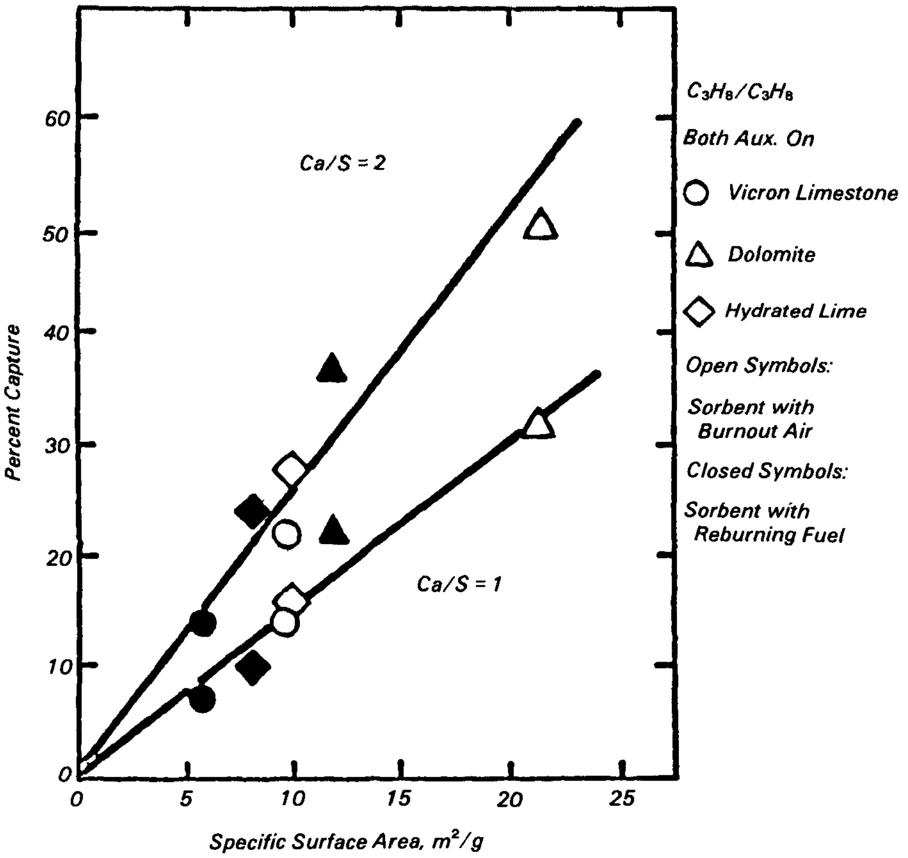

Figure 3. *Capture vs. sorbent surface area.*

the sulfation reaction takes place. The model also considers boundary layer diffusion and pore diffusion of the gas reactant. This model can successfully predict the capture data for the full range of conditions investigated in the bench-scale evaluation.

Conclusions

The process chemistry of the reburning technology has been examined in some detail and found to be similar to staged combustion processes. These data taken at bench-scale indicate that reburning for NO_x control is a viable technique that can achieve up to 70% NO_x reduction under optimum conditions. The parameters which most influence the efficiency of the process are those conditions in the reburning zone and the initial NO level. Levels below 100 ppm appear to be difficult to obtain with reburning. The optimum injection for limestones is with the burnout air. The reactivity of the limestone is determined by its surface area after calcination. To obtain high SO_2 capture levels will require stones with surface areas greater than 20 m^2/g which was found only for dolomitic stones in the present study.

These studies have concentrated on the chemistry of the reburning process under ideal conditions; i.e., rapid mixing and distinct zones. Activity in the next phase will be designed to investigate the impact of scale and finite rate mixing. These tests will be carried out at a firing rate of 3 MW (10 million Btu/hr) in a specially designed dispersion furnace.

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The complete report, entitled "Bench-Scale Process Evaluation of Reburning and Sorbent Injection for In-Furnace NO_x/SO_x Reduction," (Order No. PB 85-185 890/AS; Cost: $22.00, subject to change) will be available only from:
National Technical Information Service
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