



## Project Summary

# Development of Criteria for Extension of Applicability of Low-Emission, High-Efficiency Coal Burners: Fourth Annual Report

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This report summarizes technical progress during the fourth year of effort on EPA Contract 68-02-2667.  $\text{NO}_x$  and  $\text{SO}_x$  emission characteristics of two low- $\text{NO}_x$  distributed-mixing burners were tested with three coals in a large water-tube simulator furnace ( $50\text{-}70 \times 10^6 \text{ Btu/hr}$  firing rate). Increasing burner load, burner zone stoichiometry, or overall excess air increased  $\text{NO}_x$  emissions. Staging was limited by increases in CO emissions and problems with flame stability at burner zone stoichiometries below 0.6. The feasibility of using dry sorbents injected directly into the furnace for  $\text{SO}_2$  emission control was investigated. Sorbent type [ $\text{Ca}(\text{OH})_2$  vs.  $\text{CaCO}_3$ ] and injection location had a small effect on sulfur capture. Fuel sulfur content also affected sulfur capture. Sulfur captures on the order of 40-50 percent were obtained at Ca/S molar ratios of 2.0.

Parametric studies of the sulfur capture process were performed in a specially constructed Boiler Simulator Furnace fired at  $1.0 \times 10^6 \text{ Btu/hr}$ . Under fuel-lean conditions, thermal history exerted controlling influence on sulfur capture. Firing and heat extraction rates strongly influenced sulfur capture due to their effect on thermal history. Sorbent location, burner zone stoichiometry, overall excess air, and tertiary air velocity had secondary effects on cap-

ture. Capture under fuel-rich conditions was also investigated. Significant retention of sulfur in the solid phase and a gaseous sulfur species distribution considerably different than that expected from equilibrium calculations were observed. Sorbent injection location and method affected sulfur capture under fuel-rich conditions.

*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

This report describes the progress on EPA Contract 68-02-2667, "Development of Criteria for Extension of Applicability of Low-Emission, High Efficiency Coal Burners," from October 1, 1980, to October 1, 1981. The program, initiated in October 1977, was structured to provide data for a wider design base in applying the distributed mixing burner (DMB) as a means of controlling the emissions of  $\text{NO}_x$ . In this context, the program's main objectives were to:

- Expand the fuel capability of low  $\text{NO}_x$  burners to include the major types of

solid fossil fuels projected for use by the utility industry.

- Explore additional burner concepts and configurations that show potential for improving the emission and thermal performance of pulverized-coal burners.
- Determine the effects of multiple burner configurations that are encountered in utility boilers.
- Directly compare the experimental burners being developed here and the current state-of-the-art for commercially available coal burners.
- Provide testing in support of planned application of the burner technology.

To meet these objectives, the program was divided into seven tasks; see Figure 1. These tasks were designed to provide experimental data relative to the DMB. The work moves progressively from bench-scale studies of the basic processes, through single burner studies at a range of pilot scales, to multiple burner configurations and a comparison of DMB emission and operating characteristics with current commercial technology. The base program provides also for technology transfer and review of progress by the industry.

During the past reporting period, the main focus of the program has shifted

somewhat, and renewed attention has been directed toward dry sorbent  $\text{SO}_x$  control technology. The use of sorbents to control emissions of  $\text{SO}_x$  is not new and was extensively studied in the late 1960's and early 1970's in a series of development and demonstration projects. Although the pilot plant studies showed promise, the results could not be duplicated in full scale systems. This work, together with results from recent pilot scale studies, was reviewed; some of the more recent data suggest that burner conditions necessary to minimize  $\text{NO}_x$  are also favorable for sulfur capture by injected sorbents. This has led to the concept of a combined  $\text{NO}_x/\text{SO}_x$  control strategy and to the need for a definition of the conditions under which the emission of both pollutants can be minimized without significant impact on overall combustion system performance. A modified program plan approach for Contract 68-02-2667, which extends the original goals to include  $\text{SO}_x$  control, is shown in Figure 2. The experimental portion of this program includes both bench scale studies to define optimum conditions for sulfur capture, and pilot scale studies with real burner systems to optimize and evaluate the potential for combined  $\text{NO}_x/\text{SO}_x$  control.

The technology which has the potential to provide simultaneous control of  $\text{NO}_x$

and  $\text{SO}_x$  has been dubbed LIMB—lime-stone injection into multistage burners. Figure 3 shows the LIMB process, simplified. Coal, combustion air, and the sorbent (usually some form of calcium carbonate) are injected into the furnace. The sorbent may be mixed with the coal or injected with one of the combustion air streams (e.g., staging air). Subsequent events can be considered to take place in three regions:

1. Particle Heating—a short residence time region where the coal and sorbent are heated, typically at rates of  $10^4$  K/sec.
2. Fuel-Rich—a reducing region, deficient in oxygen.
3. Fuel-Lean—an oxidizing region where the coal is burned out and the combustion products are cooled before entering the convective sections.

The oxidation of fuel-bound nitrogen (producing fuel  $\text{NO}$ ) accounts for 80 percent of the total  $\text{NO}_x$  formed during the combustion of pulverized coal. The minimization of fuel  $\text{NO}$  formation requires that volatile fuel nitrogen species are prevented from reacting with oxygen and forming  $\text{NO}$ . During combustion the volatile fuel nitrogen species ( $\text{XN}$ ) can follow two general paths:

- Fuel-lean—  
 $\text{XN} + \text{O}_2 \rightarrow \text{NO}$  (1)
- Fuel-rich—  
 $\text{XN} \rightarrow \text{HCN} \rightarrow \text{N} \rightarrow \text{NH} \rightarrow \text{NH}_2 \rightarrow \text{NH}_3$  (2)  
 $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$  (3)

Reaction 2 summarizes the nitrogen shift reactions that produce  $\text{HCN}$  or  $\text{NH}_3$  under fuel-rich conditions. Reaction 3 is the most probable path forming  $\text{N}_2$  in pulverized coal flames. All fuel-bound nitrogen is not volatile, and the coal char contains nitrogen which can be oxidized. Since char burnout must be under oxidizing conditions,  $\text{NO}$  production from char nitrogen is unavoidable. Consequently, it is important that the conditions in the heating and fuel-rich zones promote the evolution of fuel nitrogen species.

The oxidation of both organic and inorganic coal sulfur produces the  $\text{SO}_2$  emissions from pulverized coal combustion. The ultimate gas-phase sulfur speciation depends on the temperature and gas-phase stoichiometry. In the fuel-rich region sulfur will exist as  $\text{H}_2\text{S}$ ,  $\text{COS}$ , or  $\text{CS}_2$ , and in the fuel-lean region almost all the sulfur will exist as  $\text{SO}_2$ . An injected

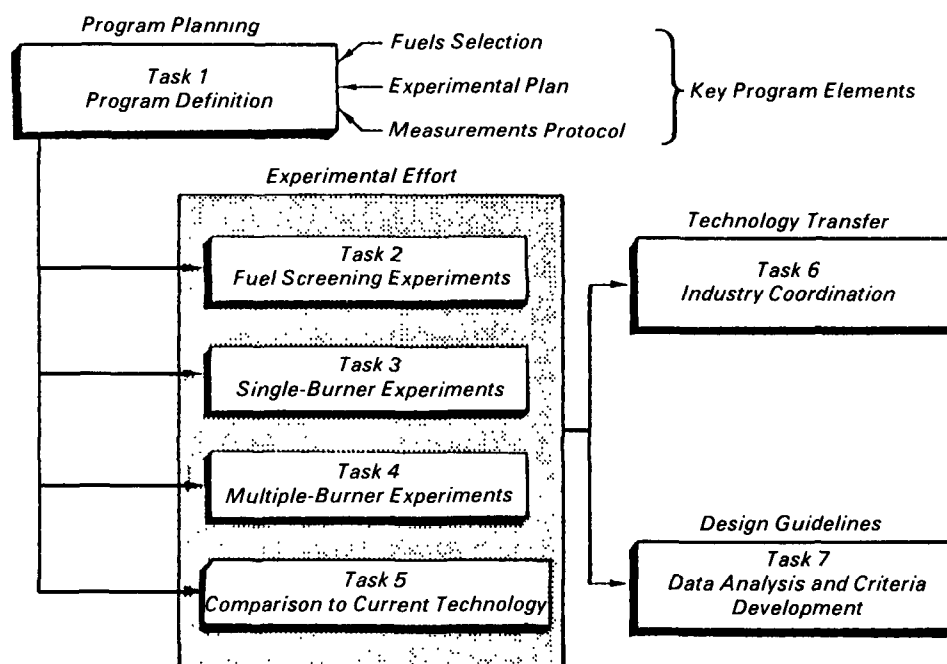


Figure 1. Program structure for developing criteria for extending applicability of low-emission/high-efficiency coal burners.

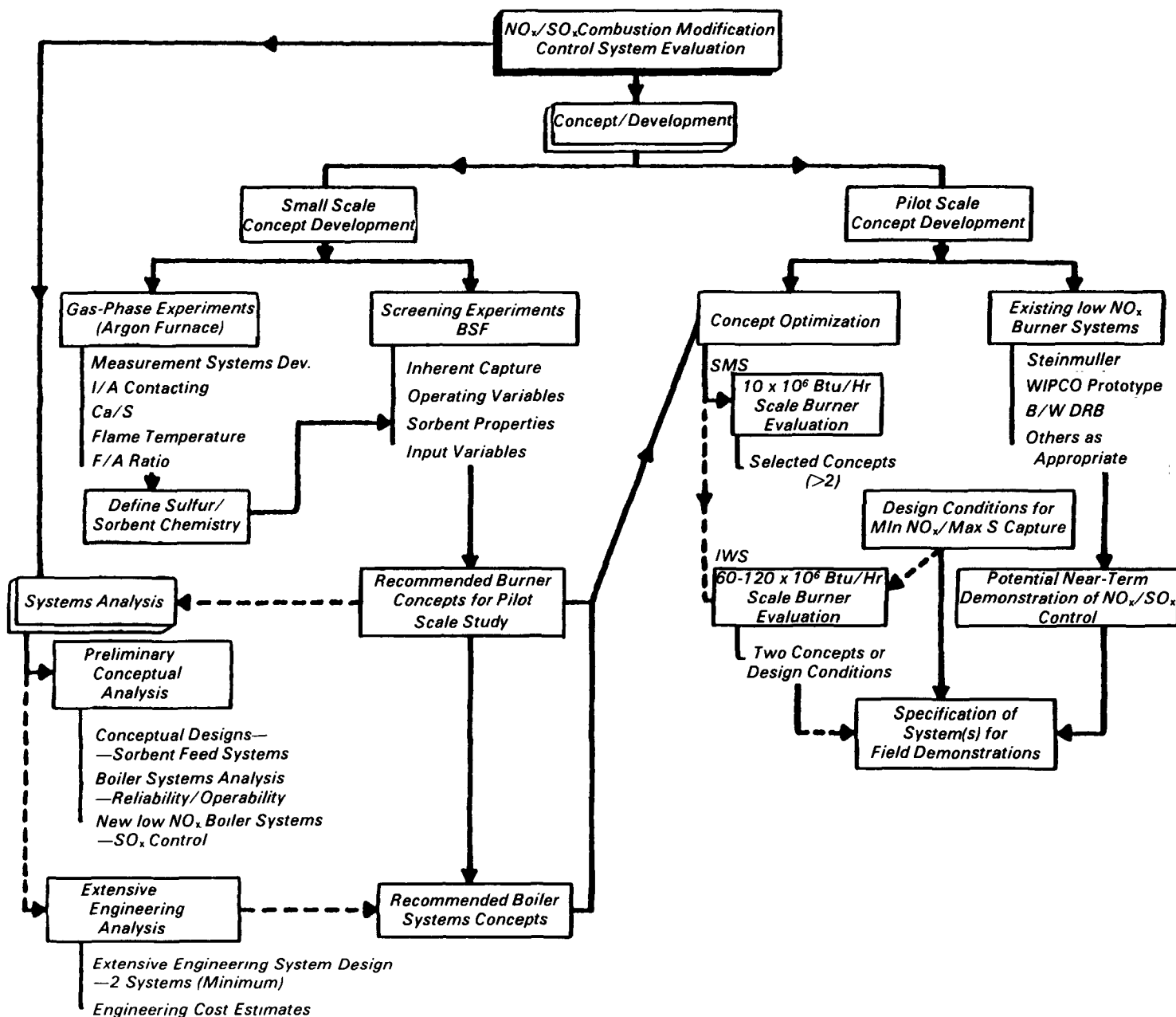
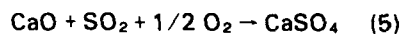


Figure 2. Program plan approach—combined NO<sub>x</sub>/SO<sub>x</sub> control.

sorbent can capture sulfur in both the fuel-rich and fuel-lean regions (see Figure 3). In the fuel-rich region the reduced sulfur species can react with sorbent directly, producing CaS:



under fuel-lean conditions SO<sub>2</sub> reacts with the calcined sorbent, producing CaSO<sub>4</sub>:



Rates of both reactions depend on the gas-phase sulfur concentration which benefits the fuel-rich capture because the reactants are more concentrated (if the sulfur content of the char is minimized). Fuel-rich capture could have the further advantage that calcium sulfide may not block the pore structure, allowing greater utilization of the limestone.

Before the fuel-lean capture process can take place, the sorbent must be calcined. The reactivity of the calcine appears to depend most strongly on peak

temperatures. If temperatures are too high the material is dead-burned, resulting in a dramatic reduction in the surface area and a loss of reactivity. Consequently, the thermal history experienced by the sorbent particles is critical, and it may be advantageous if they are excluded from the heat release zone where peak temperatures are highest. Regeneration of SO<sub>2</sub> can occur: the sulfide is more stable at higher temperatures than the sulfate but, if capture occurs under fuel-rich conditions, the sulfide must be converted

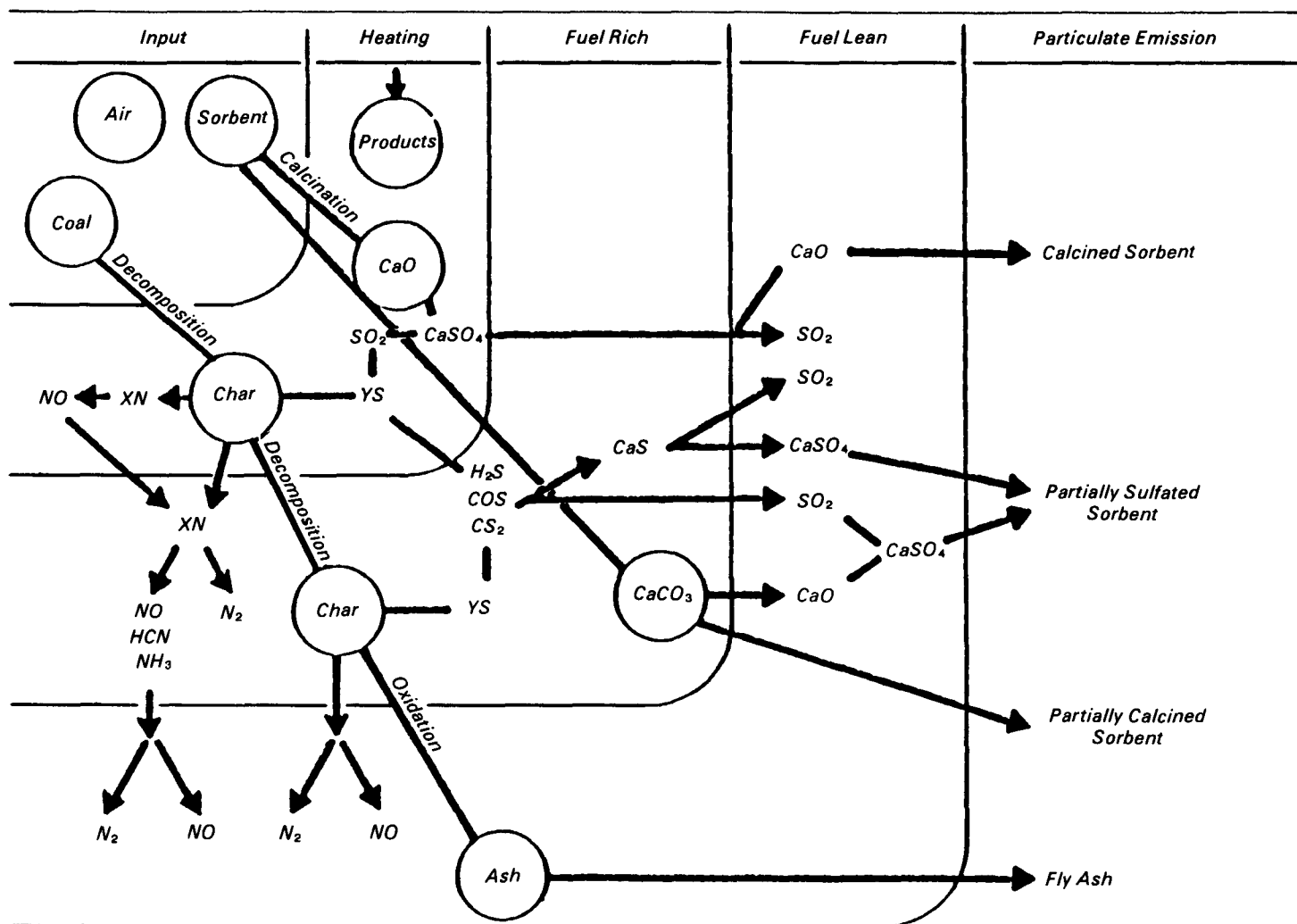


Figure 3. Simplified process description of LIMB.

to sulfate in the fuel-lean region without decomposing the CaO and SO<sub>2</sub>.

The sulfur capture process results in particulate emissions which potentially consist of: fly ash, partially calcined sorbent, calcined sorbent with varying degrees of reactivity, and partially sulfated sorbent. The composition and properties of the solid emissions will depend on coal and sorbent properties as well as the LIMB process.

In the present reporting period of the contract, pilot scale studies have been carried out with a reduced scale (50 x 10<sup>6</sup> Btu/hr) version of the Steinmüller Staged Mixing Burner to compare DMB performance and current commercial technology. A field prototype version of the DMB burner system has also been extensively tested under EPA Contract 68-02-3127. Both burner tests also provided an opportunity to investigate sorbent injection in unmodified (for SO<sub>x</sub> control) systems.

While the experimental data indicate some potential for significant SO<sub>x</sub> removal under low NO<sub>x</sub> conditions, the pilot scale results provide little further understanding of the basic mechanisms involved in sulfur capture, or of the ideal conditions required for process optimization.

Most experimental effort during this period was on characterizing the SO<sub>2</sub> capture process using bench-scale (up to 1.0 x 10<sup>6</sup> Btu/hr firing rate) facilities. During the bench scale studies, two experimental approaches were taken. The first attempted to remove some of the complexities associated with coal combustion and examined sorbent/sulfur interactions in a totally gas-phase system. In the second, studying coal combustion under furnace conditions which simulate the temperature/time history of a complete boiler system, it was necessary to construct a new Boiler Simulator Furnace (BSF) facility. Experimental results from

both phases of the bench-scale experimental program are presented and discussed.

Analytical requirements for this program were extensive, and previous experience has shown the need for carefully controlled conditions when sampling for sulfur species in the presence of active sorbents. These requirements necessitated the development of several new sampling and analytical capabilities at EER, and these are described. Some conclusions (although still of an interim nature) drawn from the results of the work are presented.

### Pilot-Scale Results—NO<sub>x</sub> and SO<sub>x</sub> Control

Two low-NO<sub>x</sub> distributed-mixing burners were tested in the large watertube simulator (LWS) to determine the effect of various operational and fuel related parameters on NO<sub>x</sub> emissions. The results

obtained with these burners in the LWS are compared with results obtained in other facilities in Figures 4, 5, and 6. In general, even though absolute levels of  $\text{NO}_x$  emissions were different in the different facilities, effects of burner zone stoichiometry (Figure 4), overall excess air (Figure 5), and load (Figure 6) are similar. Effects of these operating parameters were also independent of coal type, although again the absolute levels of  $\text{NO}_x$  emissions were different for the different coals in the same facility (the LWS). In general, increased load, excess air, and burner zone stoichiometry (decreased staging) all increased  $\text{NO}_x$  emissions for all the coals in the facilities compared.  $\text{NO}_x$  emission characterization of the EPA prototype distributed mixing

burner was performed under EPA Contract 68-02-3921 and is described in detail in that contract report. In general, the effects of burner zone stoichiometry, excess air level, and load on  $\text{NO}_x$  emissions were similar to those observed with the Steinmüller burner; again, baseline  $\text{NO}_x$  emissions for the different coals were different and  $\text{NO}_x$  emission levels for the same coals were slightly different for the two burners.

In addition to the characterization of  $\text{NO}_x$  emissions, a series of experiments were carried out with both burners to determine the potential for  $\text{SO}_2$  removal by direct injection of calcium-based sorbents. These studies were carried out without modifying either burner and only at conditions which were optimized for

$\text{NO}_x$  emissions. No attempt was made to optimize the firing system for sulfur capture. Results of the sorbent injection tests in the two burners indicate that sorbent type [ $\text{Ca}(\text{OH})_2$  or  $\text{CaCO}_3$ ] and injection location (with fuel or staging air) had small effects on the sulfur capture in either burner. The effect of sorbent location was more pronounced with the prototype burner and appears to be a result of changes in sorbent thermal history. The data also indicate that sulfur capture increases with coal sulfur content. Figure 7 summarizes results from studies with the EPA prototype and Steinmüller burners in several furnaces. Results from Steinmüller tests in the LWS and in the IFRF furnace are included, along with data from the prototype burner. Comparing the LWS results using the prototype and Steinmüller burners with Indiana coal, shows that the prototype burner resulted in higher sulfur capture even though the burners were operated at comparable conditions. This perhaps indicates the influence of burner design conditions. The LWS results using a prototype burner with Utah coal and the low sulfur coal IFRF test results show good general agreement. This indicates that burner effects may be unimportant for low sulfur coals; since these results are from burners which were not optimized for  $\text{SO}_2$  capture, they should be treated with caution.

The good agreement between the LWS data for Indiana coal and the IFRF data with the high sulfur coal is somewhat surprising in light of the higher furnace temperature ( $1000^\circ\text{C}$  vs.  $600^\circ\text{C}$  in the LWS) employed at IFRF.

In general, the pilot-scale tests indicate a lack of more definitive assessments of the parameters controlling  $\text{SO}_2$  capture via dry sorbents. Of help would be studies focused on the potential for application of this technology in field boilers, and the optimum burner design and operating parameters required to maximize sulfur capture without affecting  $\text{NO}_x$  emissions or boiler efficiency. Further studies of sorbent injection for  $\text{SO}_2$  control are planned as a continuation of the 68-02-2667 contract effort. Several pilot-scale furnaces using two burners will be tested in the next year.

### Bench-Scale Studies of $\text{SO}_2$ Capture by Dry Solvent Injection

The major experimental effort during this reporting period was characterization of the  $\text{SO}_2$  capture process at bench-

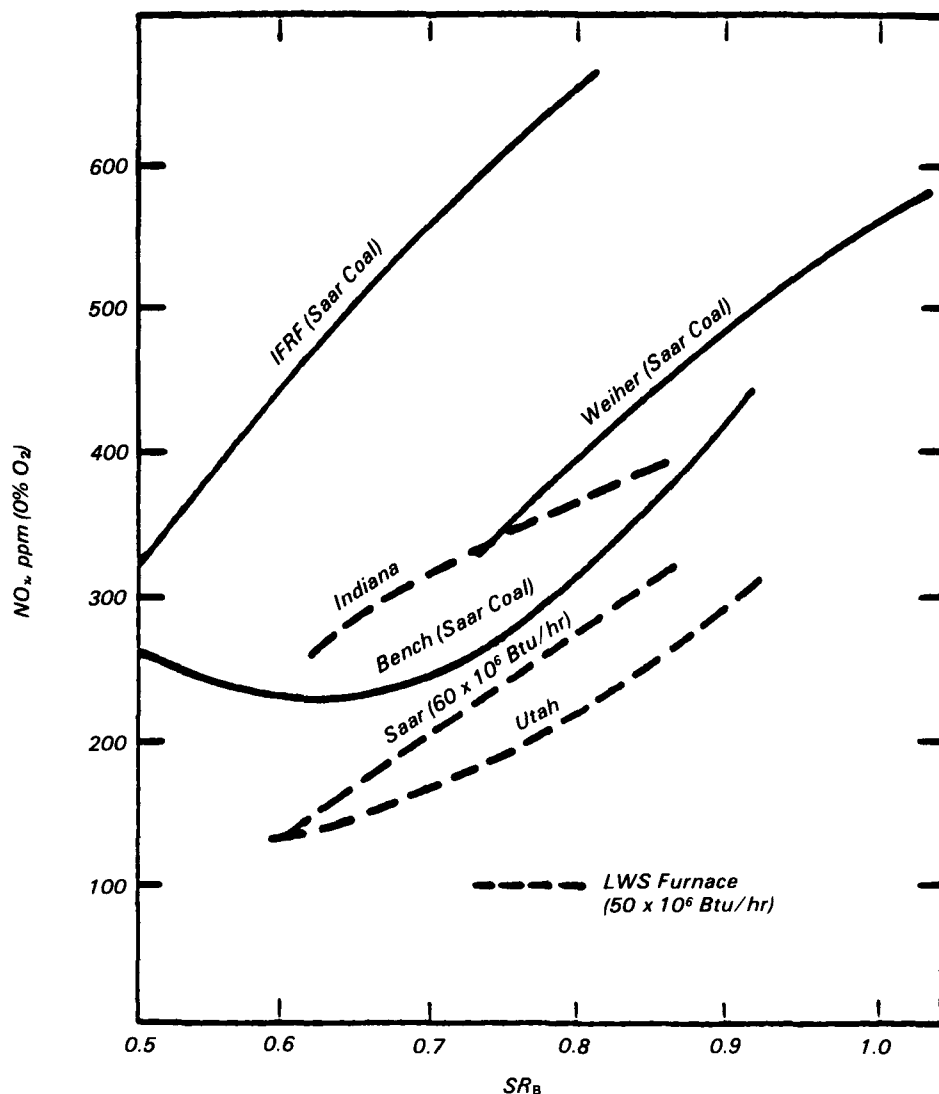


Figure 4. Effect of burner zone stoichiometry on  $\text{NO}_x$  emissions—comparison of data, Steinmüller burner.

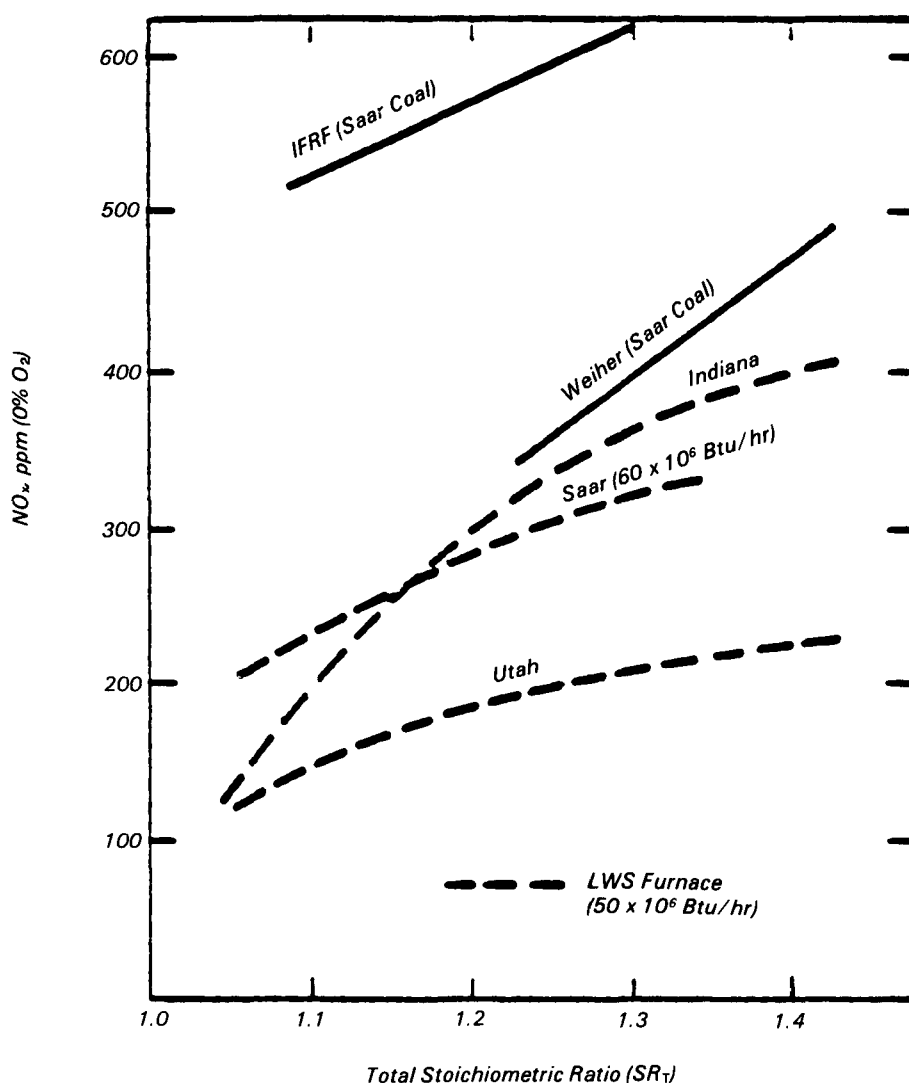


Figure 5. Effect of excess air on  $\text{NO}_x$  emissions—comparison of data, Steinmuller burner.

scale. The effort included: development of sampling and analytical systems for measuring  $\text{SO}_2$  and determining sulfur capture; design, construction, and testing of an experimental facility, the Boiler Simulator Furnace (BSF); and investigating the effect of various combustion and operational parameters on sulfur capture in the BSF. The measurement of sulfur species in combustion products containing active sorbents introduces several problems related to sample acquisition. A "phase discrimination" probe, which minimizes gas/solid contacting after sample extraction, was designed, constructed and tested. Methods for measuring sulfur species concentrations in fuel-rich combustion gases were developed as were methods for solids analysis (including

sorbent, ash, and coal composition and surface areas).

The bench-scale facility constructed for these studies can duplicate the thermal history of the solid particles (coal and sorbent) and the products of combustion in a pulverized coal-fired boiler. The facility consists of three major components:

- A convective section, cooled by banks of air-cooled stainless steel tubes, which simulates the superheater, air heater, and economizer.
- A radiant furnace, a horizontal refractory-lined cylinder which simulates the firing zone. Removable cooling tubes provide heat extraction.
- A post-flame cavity which simulates the space between the firing zone and the superheater of a conventional boiler.

a Schematic of the Boiler Simulator Furnace is shown in Figure 8.

A parametric screening study of the effect of combustion and operation variables on sulfur capture by sorbents directly injected into the furnace was planned; the first portion was completed. The results of program definition experiments were used to specify design criteria for the BSF and parameters for the first set of screening studies. Parameters investigated included: firing rate, heat extraction rate, sorbent injection location, overall excess air, burner zone stoichiometry, and tertiary air velocity. One sorbent (Vicron 45-3, a large-grain calcite limestone) and one coal (a medium sulfur [1-2 percent], bituminous Indiana coal) were used for all studies.

The studies established that under fuel-lean conditions, thermal history exerts a controlling influence on sulfur capture. Results shown in Figure 9 show total sulfur capture as a function of calcium-to-sulfur ratio for three thermal conditions. Furnace temperatures are also shown for the uncooled and most heavily cooled conditions.

The effect of thermal history on capture in the various furnace zones was further analyzed. Capture was measured at the exit of the radiant and post-flame sections as well as at the furnace exit. Results summarized in Figure 10 show sulfur capture in the radiant and post-flame sections of the BSF as a function of  $\text{Ca}/\text{S}\sqrt{\text{SO}_2}$  in each zone. Three conditions are shown: high firing rate (with and without radiant zone cooling) and low load without cooling. Reducing the firing rate reduced the temperatures and increased the residence times. Cooling the radiant zone decreased peak temperatures with little effect on the residence times. Radiant zone cooling dramatically increased capture; the low-load conditions gave relatively poor capture in the radiant zone, but both reduced-temperature cases (cooled and low-load) gave approximately the same capture in the post-flame section.

Other parameters (including sorbent location, burner zone stoichiometry, overall excess air, and tertiary air velocity) had secondary effects, which

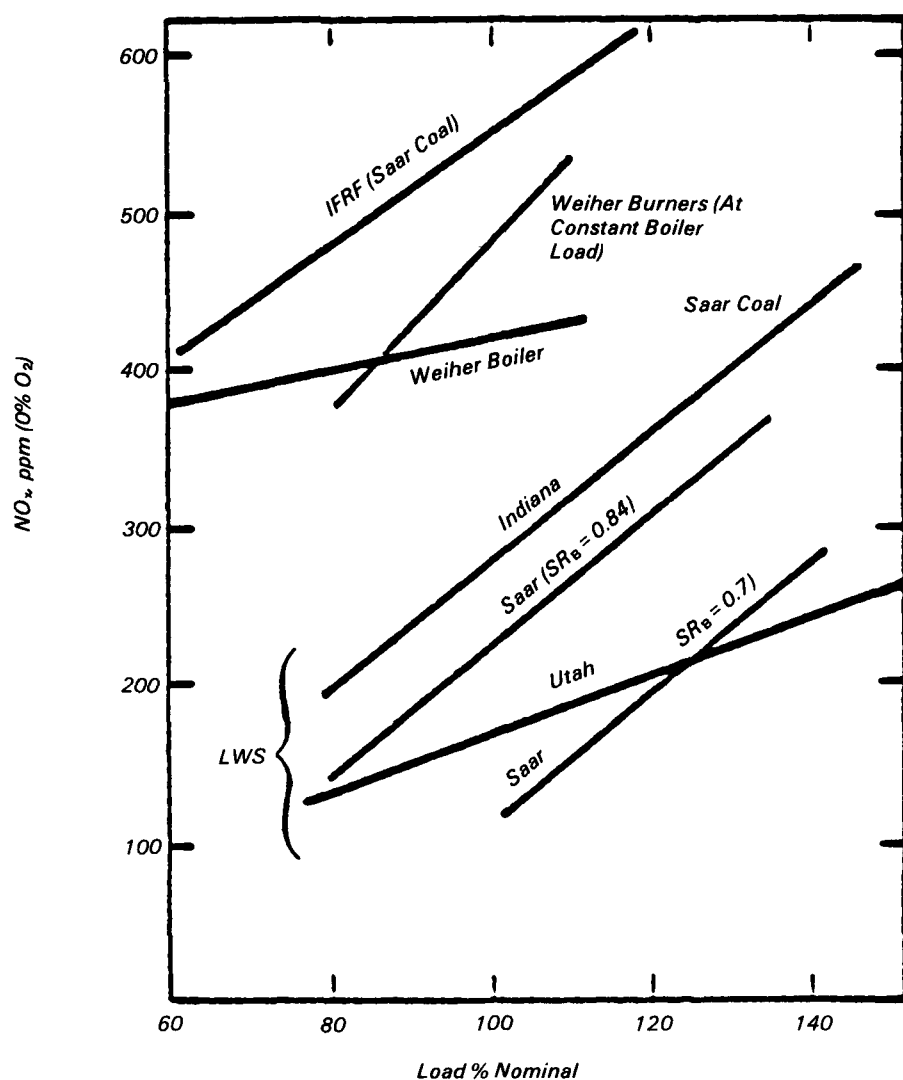


Figure 6. Effect of load on  $\text{NO}_x$  emissions—comparison of data, Steinmuller burner.

depended to some extent on other variables, on sulfur capture.

Sulfur capture under fuel-rich conditions was evaluated using both Indiana coal and propane/ $\text{H}_2\text{S}$  as fuels. Fuel-rich conditions were obtained by firing the burner with a sub-stoichiometric amount of air, running the entire radiant furnace fuel-rich, and adding the remainder of the combustion air at the base of the radiant furnace. Sulfur capture appears to be proportional to sulfur species driving force to the  $1/2$ -power. The increase in sulfur species concentration under fuel-rich conditions (due to reduced dilution) should benefit sulfur capture. Figure 11 summarizes data on sulfur species distribution as a function of stoichiometric

ratio based on equilibrium calculations (free energy minimization) and on actual experimental measurements of the gas phase in the BSF near the end of the fuel-rich zone. The equilibrium calculations indicate that (for stoichiometries below 0.95)  $\text{H}_2\text{S}$  is the only species of importance. However, data from propane/ $\text{H}_2\text{S}$  and Indiana coal measurements demonstrate that a wide spectrum of reduced sulfur species are present under these conditions. With the propane/air flames,  $\text{SO}_2$  was significantly more important at rich conditions than would have been anticipated from equilibrium calculations, and both  $\text{COS}$  and  $\text{CS}_2$  were nonnegligible. The data in Figure 11 indicate that with the Indiana coal

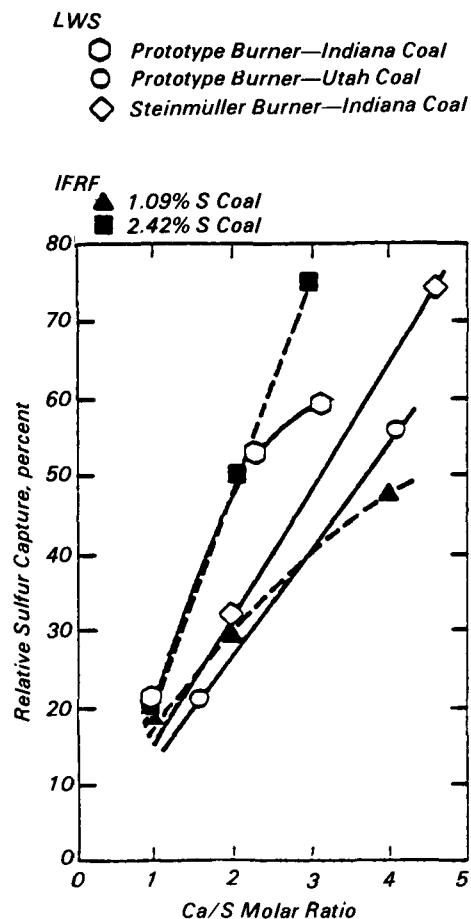
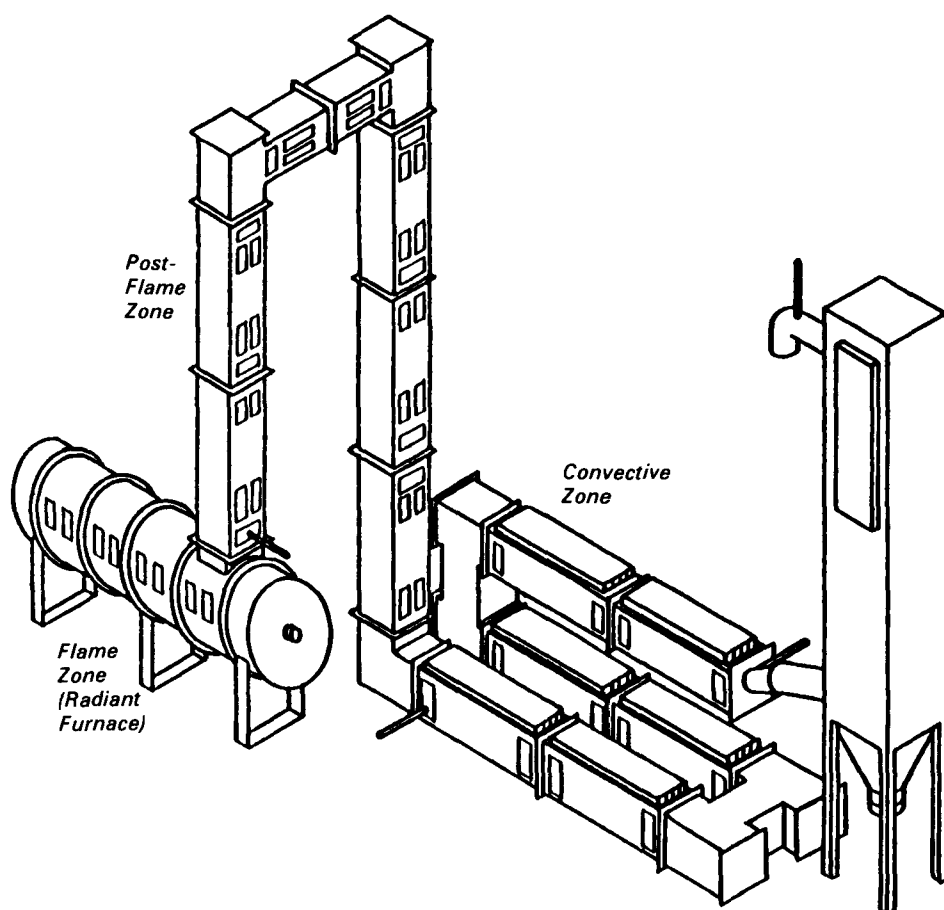


Figure 7. Comparison of Steinmuller and DMB data—limestone injected in tertiary ports

the gas-phase species distribution was non-equilibrium and that a significant amount of coal sulfur remained in the solid phase. These results emphasize two problems associated with sulfur capture under fuel-rich conditions:  $\text{SO}_2$  concentrations may be nonnegligible, and a large fraction of the sulfur may remain in the solid phase. Tests will be carried out in the next year with propane/ $\text{H}_2\text{S}$  in an attempt to separate the effect of sulfur evolution from the coal, and capture from the gas phase.

A further complication of the sulfur capture process under fuel-rich conditions is due to the impact of the physical staging method, used to obtain long residence times under fuel-rich conditions, on the thermal characteristics of the experimental system. The data presented in Figure 12 was obtained firing Indiana coal. The temperature profiles were derived from wall temperature measurements and



**Figure 8.** Boiler simulator furnace—original configuration.

calculated residence times (based on plug flow). It can be seen that first stage stoichiometry had a dramatic effect on the thermal history of the reactants. Under rich conditions, the radiant zone temperatures are significantly reduced, and the residence time is increased due to the decreased mass flow rate. The temperature at the entrance of the post-flame section, where the second-stage air is added, increases during burnout of the coal. The magnitude of this increase will depend on the primary-zone stoichiometry and on the inter-stage heat removal. As shown in Figure 12, the effect of first-stage stoichiometry on sorbent utilization for Indiana coal at rich-zone stoichiometries greater than 0.7 was slight. However, captures decreased dramatically for fuel-rich stoichiometries less than 0.7. This is probably due to a combination of regeneration during burnout, a reduction in sulfur species driving force because of sulfur retention in the char,

and a decrease in the reaction rate because of the lower temperatures in the fuel-rich region.

Further parametric screening studies at bench scale are planned. In the next year: sulfur capture will be investigated in the fuel-rich region of gas flames (eliminating the char sulfur retention complication) in the BSF; the effect of thermal environment on sulfur capture will be investigated in more detail; and the effect of fuel and sorbent type on sulfur capture will be investigated.



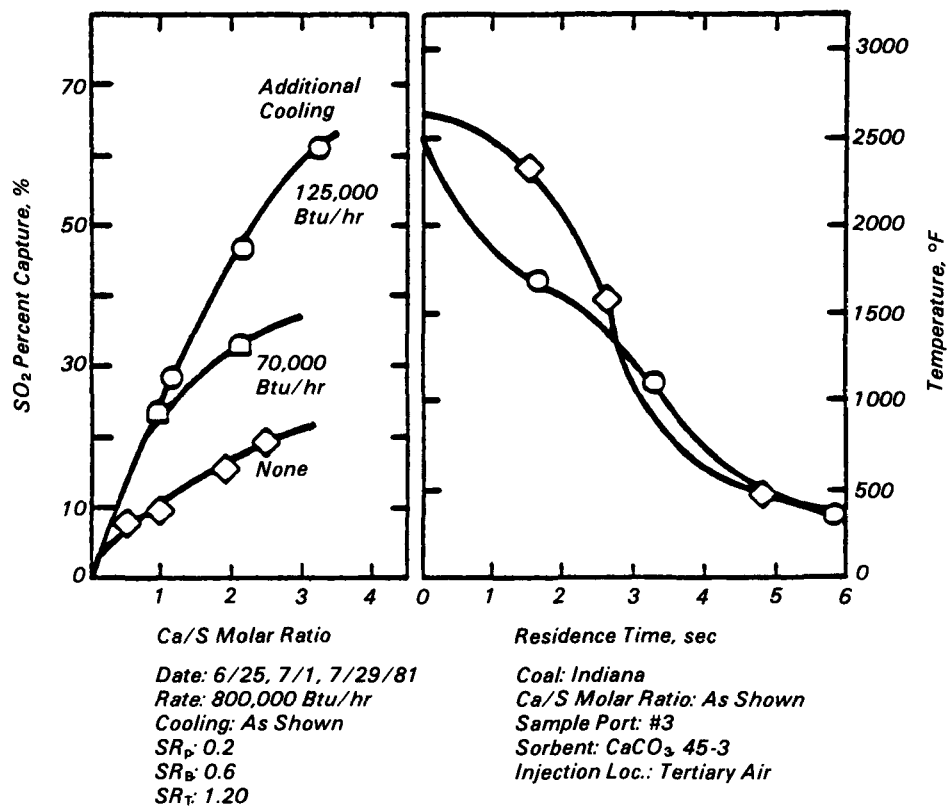


Figure 9. Influence of heat extraction rate—base case conditions.

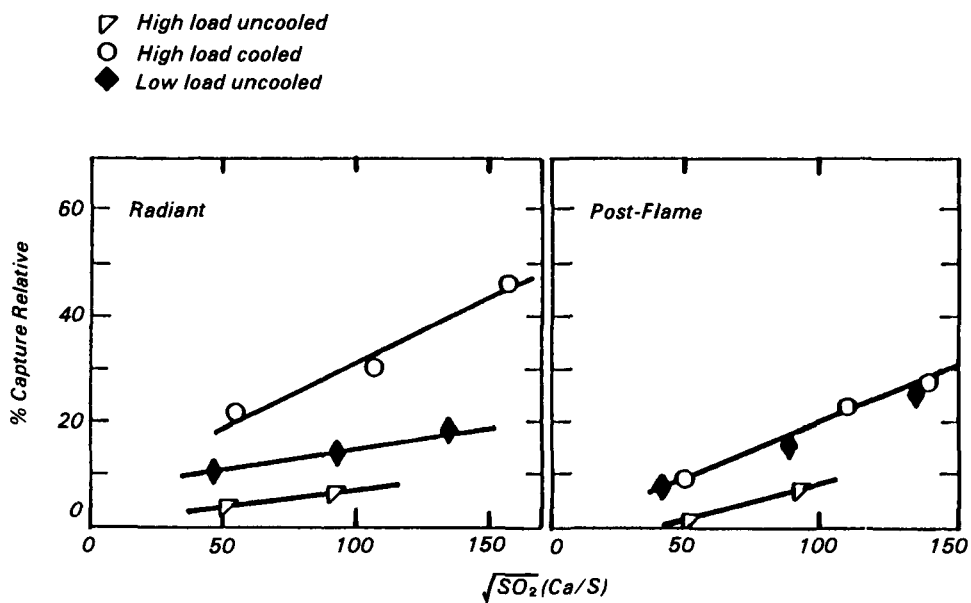
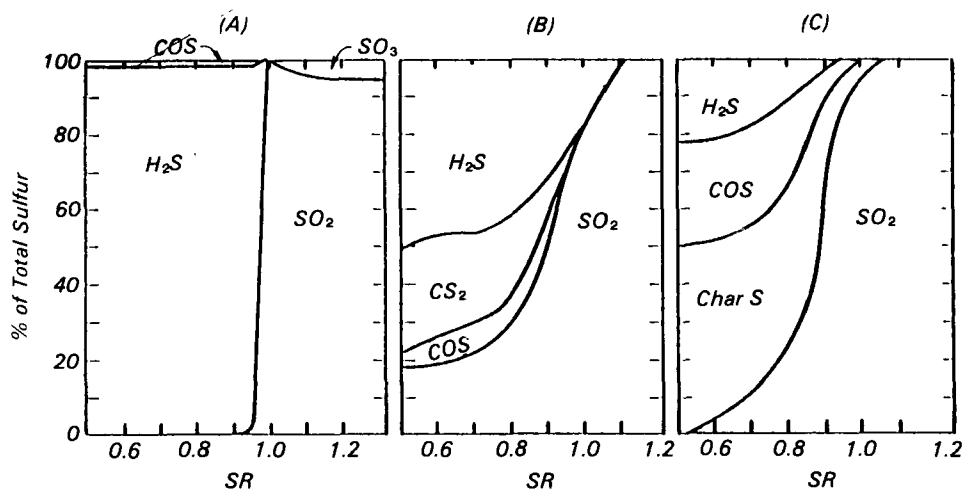
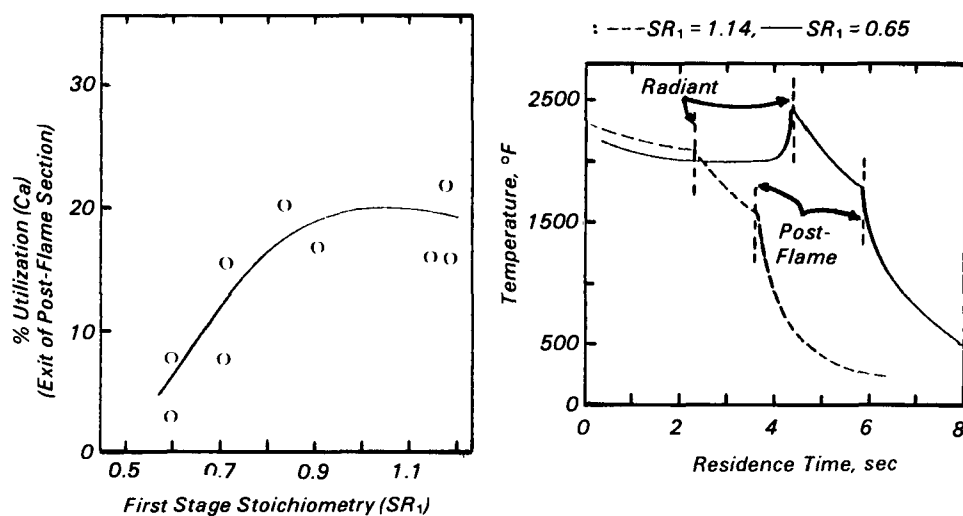


Figure 10. Effect of load and radiant zone cooling on sulfur capture.



**Figure 11.** Effect of stoichiometry on sulfur species distribution. A, equilibrium calculations; B, propane and  $H_2S$ ; C, Indiana coal.



**Figure 12.** The effect of rich-zone stoichiometry on sorbent utilization and thermal history, Indiana coal-fired.

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The complete report, entitled "Development of Criteria for Extension of Applicability of Low-Emission, High-Efficiency Coal Burners: Fourth Annual Report," (Order No. PB 84-240 654; Cost: \$28.00, subject to change) will be available only from:

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