



## Project Summary

# Bench Scale Studies of Limestone Injection for SO<sub>2</sub> Control

P. L. Case, L. Ho, M. P. Heap, R. Payne, and D. W. Pershing

**This report describes research carried out in one task of an EPA program entitled, The Development of Criteria for Extension of Applicability of Low Emission, High Efficiency Coal Burners. The task involved using a series of bench-scale facilities to determine the process parameters controlling the capture of sulfur species by calcium-based sorbents when pulverized coal is burned under low NO<sub>x</sub> conditions.**

***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).***

### Objectives

Although coal is the most abundant source of fossil fuel energy in the U.S., its use poses several serious problems for society, not the least of which is the emission of atmospheric pollutants. The combustion of coal results in the formation of sulfur and nitrogen oxides (SO<sub>x</sub> and NO<sub>x</sub>), which have been identified as precursors of acid precipitation. Although evidence is not conclusive, it is generally recognized that the environmental damage caused by acid precipitation can be mitigated by reducing emissions of these precursors from coal-fired power plants. Consequently, there is a need to develop efficient and cost effective control techniques for these pollutants for retrofit applications. This report addresses the use of calcium based sorbents for *in situ* sulfur capture under combustion condi-

tions that minimize NO<sub>x</sub> formation from pulverized coal combustion.

The use of calcium based sorbents to remove SO<sub>2</sub> from the combustion products of coal and oil flames is not a new concept. Considerable effort was expended during the late 1960s and early 1970s to develop the dry limestone injection process. These activities were curtailed because sulfur capture was not particularly efficient and injecting limestone caused considerable operating problems (e.g., fouling in the convective sections and plugging of the air heater). Recent studies in Germany indicate that this process could be a viable means of reducing SO<sub>2</sub> emissions if the sorbent were injected under low NO<sub>x</sub> conditions. In the earlier studies, poor sulfur capture was attributed to thermal deactivation of the sorbent (deadburning) and poor sorbent dispersion throughout the boiler. These problems may be overcome if the sorbent is injected with one of the air or fuel streams in a low NO<sub>x</sub> burner. This would solve the problem of dispersion since all the fuel and air must mix if combustion is to be completed. Thermal deactivation could be reduced because low NO<sub>x</sub> conditions minimize peak flame temperature. Objectives of the bench scale studies described in this report were:

1. To determine if the reduced peak flame temperatures and extensive fuel-rich zones typical of low NO<sub>x</sub> combustion conditions are conducive to sulfur capture by dry sorbent.
2. To determine the optimum time/temperature stoichiometry history of the sorbent for sulfur capture during coal combustion.

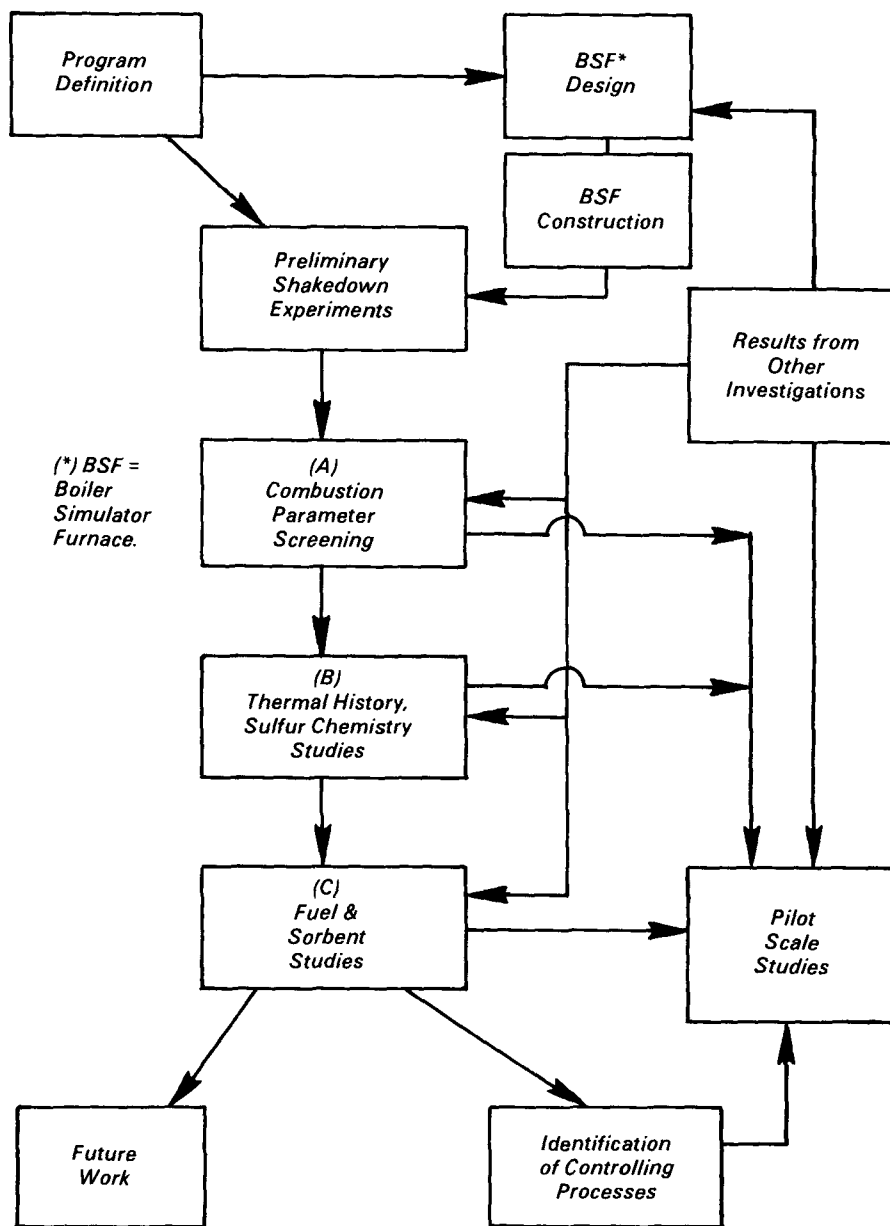
3. To determine if captures reported in several pilot scale tests are possible in the current boiler population.
4. To provide preliminary information on the impact of calcium based sorbents on boiler operability.

### Approach

When the task was initiated, insufficient information was available to allow a complete definition of the bench scale studies. The questions raised in previous experiments and the large number of process variables suggested that a phased approach was necessary. This method of planning and experimentation allowed the investigation of processes and parameters which proved most important and enabled a selection of test conditions which would develop an understanding of the sulfur capture process in the most cost effective manner. The program organization is shown schematically in Figure 1. The task was initiated by conducting a series of program definition tasks in an existing refractory tunnel furnace, concurrent with the design and construction of a boiler simulator furnace (BSF). Most of the experimental investigations were carried out in the BSF. Figure 1 shows that the BSF experiments were divided into three categories: (A) combustion parameter screening, (B) thermal history/sulfur chemistry studies, and (C) fuel and sorbent studies. The data from these experiments were used to plant the pilot scale studies carried out in other tasks of the same program and to define the needs for future experiments.

The BSF, simulating the thermal history of the products of combustion in a wide variety of pulverized coal fired boilers, was designed to satisfy the following criteria:

- Independent control of wall temperature throughout the furnace and convective sections.
- Fuel consumption rate nominally 80 lb/hr (36 kg/hr).
- Accommodate various firing systems.
- Variable preheat on all combustion air streams.
- Simulation of particulate dropout throughout the radiant and convective sections.
- Ability to rapidly and easily clean interior sections.
- Potential for near adiabatic operation by minimizing heat loss.



(\*) BSF = Boiler Simulator Furnace.

Figure 1. Organization of bench scale sulfur studies.

- Potential to extract heat at various locations.
- Ease of access for sampling probes.

However, foremost in the design was recognition that the times and temperatures experienced by the sorbent should cover as wide a range as possible to encompass those encountered in actual boilers. Figure 2 is a schematic of the BSF system, showing the sorbent and coal feed and air supply systems and the general arrangement of the furnace sections.

The BSF was designed to simulate the various parts of a boiler. Thus, the radiant furnace simulates the main heat release zone; the postflame cavity, the region above the main heat release zone before the furnace exit; and air-cooled tubes, the superheater, reheat, and air heater sections of the convective pass.

### Significant Results

Task results are in three groups: combustion parameter screening, sulfur chemistry and thermal environment, and fuel and sorbent effects.

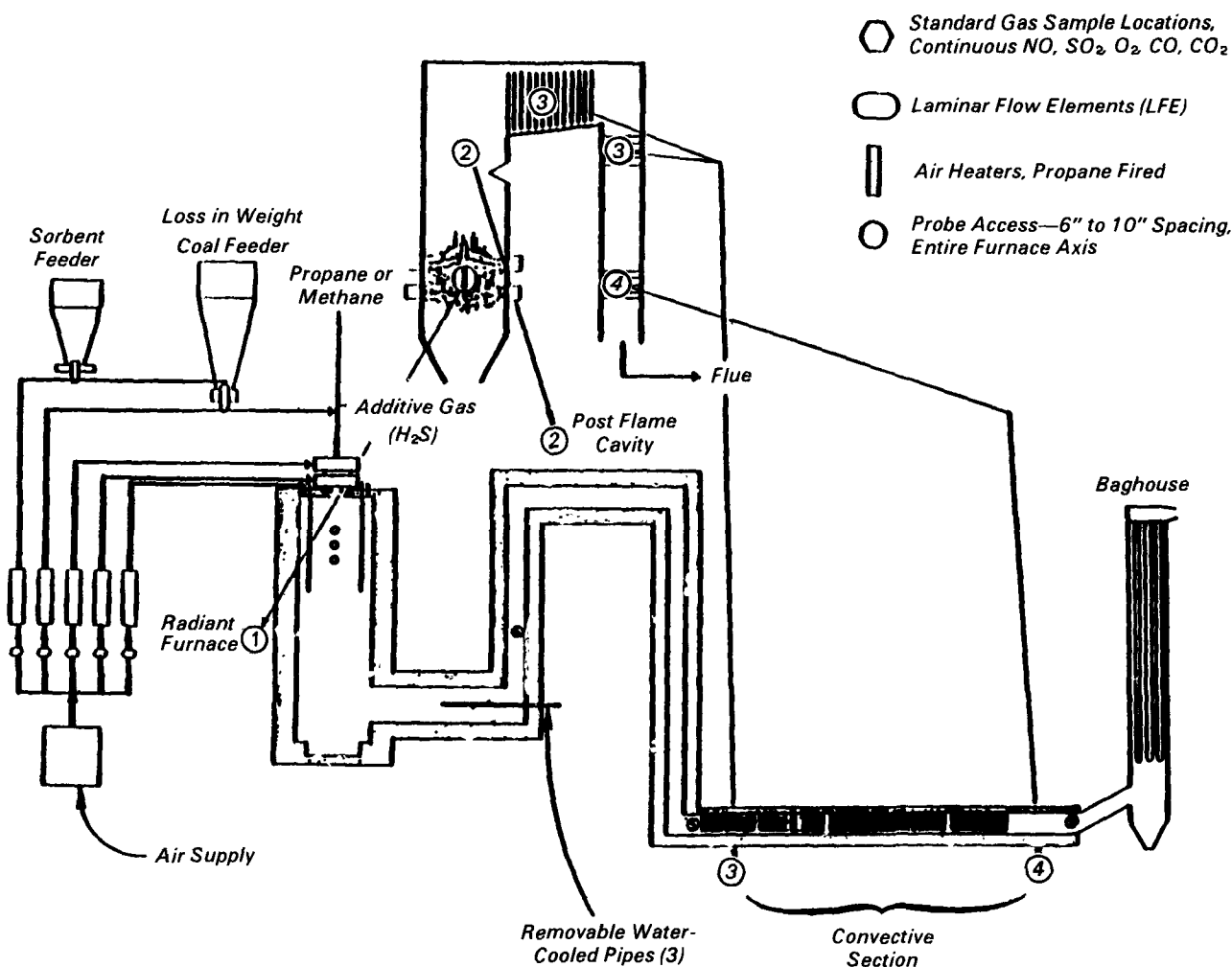


Figure 2. Functional schematic of boiler simulator furnace.

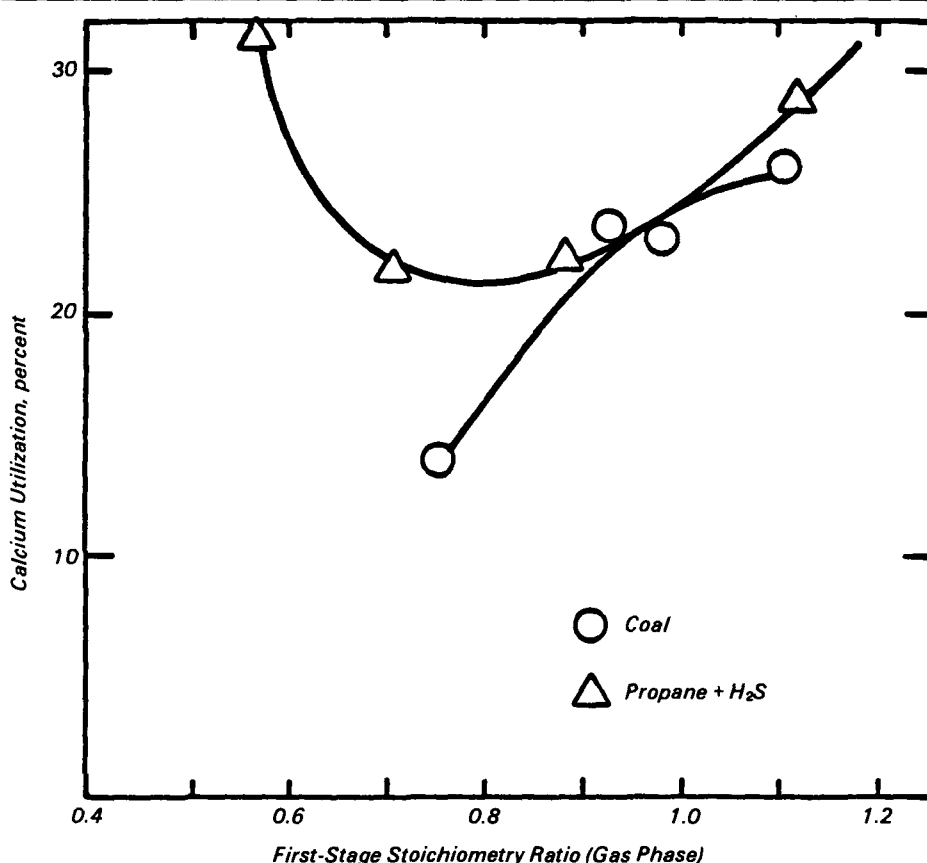
### Combustion Parameter Screening Studies (Series A)

The screening experiments defined the role of various combustion parameters in the sulfur capture process. The experiments were conducted in two sections, according to the method of combustion air staging used to simulate low  $\text{NO}_x$  combustion systems. In the first series of experiments (internally staged), a sub-scale distributed mixing burner was used and the parameters investigated included firing rate, heat extraction, burner zone stoichiometry, excess air level, sorbent injection location (with the fuel or staged air), and staged air velocity. The second series of experiments (externally staged) were designed to investigate sulfur capture under fuel-rich conditions using a system which provided for a relatively long (1-2 sec) residence time under fuel-

rich conditions. In this second series of tests, the parameters investigated included firing rate, sorbent injection, heat extraction rate, rich zone stoichiometry, excess air level, and tertiary air location.

The results of the screening studies indicated that thermal environment had the major impact on sulfur capture by dry sorbents injected directly into the furnace. The burner-staged experiments showed the influence of thermal environment most clearly: a reduction in peak furnace temperature due to cooling in the radiant furnace or to a reduction in load increased sulfur capture significantly. Changes in other parameters (e.g., sorbent location or injection velocity) had secondary effects on sulfur capture. The externally staged experiments indicated that sulfur capture was less dependent on overall heat extraction rate.

A main point of interest in the parameter studies was to establish the importance of rich zone capture, since it was speculated that reactions involving reduced sulfur species (e.g.,  $\text{H}_2\text{S}$  or  $\text{COS}$ ) could be captured more easily than  $\text{SO}_2$ . Figure 3 shows overall sorbent utilization as a function of the stoichiometry of the fuel-rich zone for coal and propane doped with  $\text{H}_2\text{S}$  to give the same exhaust  $\text{SO}_2$  level. In this instance, the sorbent (Vicron) was added with air in the fuel-rich zone at the base of the postflame section. Rich zone stoichiometry is expressed in terms of the gas phase for both the gaseous and solid fuel. It can be argued that the difference in effectiveness with the two fuels is associated with coal: under fuel-rich conditions, much of the sulfur remains with the char and is not available for capture. When all sulfur is in the gaseous



**Figure 3.** Capture and retention of sulfur under external staged conditions for coal and propane doped with H<sub>2</sub>S, sorbent added with air at base of postflame section, uncooled.

stage, calcium utilization under fuel-rich conditions approaches 30 percent.

### Sulfur Chemistry and Thermal Environment Studies (Series B)

These experiments clarified the effect of thermal environment on sulfur capture, utilizing two series of experiments to:

1. Investigate sulfur evolution and speciation in the fuel-rich zone of a staged combustion system.
2. Define the influence of a wide range of thermal environments on sulfur capture under both internal and external staged conditions.

Results from these tests include:

- Under fuel-rich conditions, sulfur species appear to be far from equilibrium.
- Even with gaseous fuels, sulfur capture in the fuel-rich zone does not appear to significantly impact overall sulfur capture.

- With coal, capture in the fuel-rich zone is limited because of the reduced sulfur driving force when a large fraction of the sulfur remains in the solid phase.

### Fuel and Sorbent Effects (Series C)

The influence of fuel and sorbent properties on sulfur capture was investigated in the third series of bench-scale experiments. The sorbent parameters, which were varied, included particle size and composition. Sulfur capture was measured with a coal/water slurry and a lignite, as well as the baseline bituminous Indiana coal.

Figure 4 compares sulfur capture for the four fuels investigated with one sorbent. The capture is worst with the Indiana coal and very similar for the lignite, doped propane, and the coal/water slurry. The dotted line shown in Figure 4 corresponds to 50 percent capture at a calcium/sulfur ratio of 2 with 2,500 ppm SO<sub>2</sub>.

The influence of sorbent type on sulfur capture was fuel dependent. With the Indiana coal, dolomite was by far the most effective sorbent; whereas, with doped propane, captures with dolomite and Vicron were similar. The reasons for the interaction of fuel and sorbent effects are not now known.

### Conclusions

Results of the experiments in the boiler simulator furnace indicated that the parameters of major importance are thermal environment, calcium/sulfur ratio, and sorbent composition. Thermal environment (local temperature) was shown to have a strong effect on the utilization of dry sorbents injected directly into the furnace. The burner-staged experiments showed the influence of temperature most clearly: a reduction in peak flame temperature, due to cooling in the radiant zone or to a reduction in load, increased sulfur capture significantly. Changes in other combustion parameters (e.g., sorbent location and injection velocity) had secondary effects on sulfur capture.

The effect of thermal history under physically-staged conditions was less definitive. Changes in both load and thermal cooling in the radiant furnace were complicated by changes in furnace temperature due to the physical staging itself, since physically staging the coal flame significantly altered the furnace temperature profile. With external staging near stoichiometric conditions, the first (fuel rich) stage, which included the entire radiant furnace, and the second stage region (the first part of the post-flame cavity) were hotter than under burner-staged conditions. First stage stoichiometry and sorbent location both influence sulfur capture under externally-staged conditions; however, the results suggest that these influences may be more strongly related to thermal than to chemical changes. Further, the data do not support the concept that sorbent utilization is much higher under fuel-rich conditions.

The influence of sorbent type (Vicron 45-3, Vicron 15-15, Michigan marl, hydrated lime [Ca(OH)<sub>2</sub>], and dolomite) on sulfur capture was studied at five different combustion conditions: Indiana No. 3 coal fired in the distributed mixing burner with and without external cooling, Indiana No. 3 coal under externally-staged conditions, and propane doped with H<sub>2</sub>S. In general, dolomite gave good capture under all conditions. Hydrated lime ap-

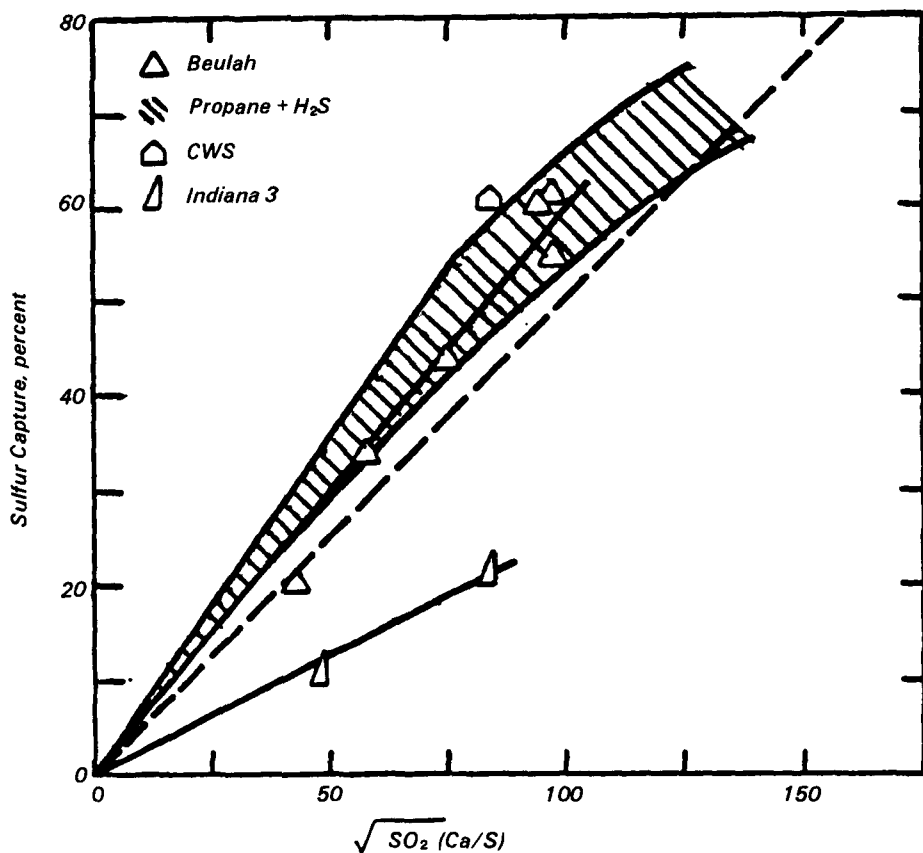


Figure 4. Effect of fuel on sulfur capture (Vicron 45-3)

peared to be most sensitive to thermal environment, and dolomite was least sensitive. High captures were observed for all sorbents when the primary fuel was propane/H<sub>2</sub>S. The effect of fuel sulfur on sorbent utilization was investigated by studying: Indiana No. 3 coal, Beulah lignite (from North Dakota), propane doped with H<sub>2</sub>S, and a coal/water slurry. All fuel screening tests were conducted with Vicron 45-3 as the sorbent, the boiler simulator furnace was fired with the distributed mixing burner, and no additional cooling was added. Sorbent utilization was significantly least with Indiana coal. Adiabatic flame temperatures were calculated for all fuels at stoichiometric ratios from 0.6 to 1.2: the calculated temperatures for the solid fuels rank the same as for sulfur capture (the highest sorbent utilization was with the fuel producing the lowest theoretical temperature). However, the differences in calculated temperature do not appear to be significant enough to explain the large differences in capture. The data strongly suggest that the difference between the relatively poor sorbent utilization

with the Indiana coal and the excellent sorbent utilization with the propane/H<sub>2</sub>S cannot be attributed solely to thermal effects.

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*The complete report, entitled "Bench Scale Studies of Limestone Injection for SO<sub>2</sub> Control," (Order No. PB 85-224 657/AS; Cost: \$23.50, subject to change) will be available only from:*

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