



Project Summary

Influence of Coal Mineral Matter on the Effectiveness of Dry Sorbent Injection for SO₂ Control

D. M. Slaughter, W. J. Thomson, T. W. Peterson, S. L. Chen, W. R. Seeker, and D. W. Pershing

This report summarizes the results of a detailed examination of the interactions between calcium based sorbents and chemical species which could either enhance or detract from the sorbents' ability to capture SO₂ in pulverized coal flames. Previous, limited experimental studies had indicated that sorbent performance would be influenced by various inorganic compounds, particularly those occurring in coal mineral matter.

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).

Program Objectives

The overall program objectives were to: (1) determine the influence of mineral ash constituents on the sulfur capture performance of calcium based sorbents, (2) define the chemical compounds which can enhance the ability of the calcium based sorbents to capture SO₂ and identify the mechanism(s) of promotion, (3) establish the influence of mineral ash on the effectiveness of sorbent promoters, and (4) optimize the process for adding promoter materials to the sorbents.

Program Scope

A combined experimental and theoretical approach was used in this study. Programs examined the physical and chemical changes of a wide variety of sorbents with carefully selected chemical additives under different composition environments and over the range of time/temperature histories. Experimental testing was conducted in furnace facilities ranging from laboratory to small pilot scale with both natural gas and coal as the primary fuel. Thermal histories ranging from near isothermal to highly quenched conditions were considered. Fundamental mechanistic information on the interactions between the promoters and calcium based sorbents were obtained from a dynamic x-ray diffractometer (DXRD) and from extensive investigation of solid samples extracted from the combustion furnaces. Chemical and elemental analysis techniques included electron microscopy (scanning and transmission), energy dispersion spectroscopy, and x-ray diffractometry. DXRD was used to trace the formation of chemical species and the destruction of solid, promoted and unpromoted, calcium compounds as a function of time and temperature. Microscopy and spectroscopy techniques were used to characterize the physical morphology and elemental spatial distribution of the promoter, calcium sorbent, and chemical

constituents of the mineral ash. X-ray analysis was used to quantify chemical species present. Equilibrium calculations based on free energy minimization were used to characterize the probable gas and solid phase species. The MAEROS computer program was used to involve the multicomponent population balance equations governing the coagulation, fragmentation, condensation, and nucleation of the ash and promoter aerosols system.

Coal/Sorbent Interactions

Under certain limited conditions, coal mineral matter can influence the effectiveness of calcitic sorbents. If the mineral matter and sorbent are in direct intimate contact (particularly by simultaneous pulverization) prior to injection and if they are injected through the burner into the temperature regions of a boiler, sorbent performance may be reduced. The controlling mechanism appears to involve the formation of low melting eutectics: the calcium reacts chemically with various alumina and silica components of the ash and becomes unavailable for subsequent sulfation. Because of this interaction (and because of the deleterious effects of the flame zone on the sorbent itself) burner injection cannot be recommended. If, however, the sorbent is injected separately from the pulverized coal (either with the secondary air or downstream) then essentially no sorbent deactivation due to mineral matter occurs. Modelling calculations indicate that particle/particle collision frequencies are simply not adequate to deactivate a significant number of the sorbent particles. Figure 1 shows data obtained in the 293 kW boiler simulator furnace (BSF) with both limestone (i.e., Vicron) and hydrated (i.e., Longview) sorbents injected with the fuel and downstream. A wide range of normal and cleaned coals were tested in this sequence, and the results compare favorably with the data taken firing natural gas. No evidence of ash deactivation was observed with any coal. Therefore, the performance of the current limestone injection multistage burner (LIMB) concept (separate downstream sorbent injection) should not be significantly degraded by mineral ash effects.

Promoter/Sorbent Interactions

A major series of promoter screening tests indicated that chromium series transition elements and alkali metals can

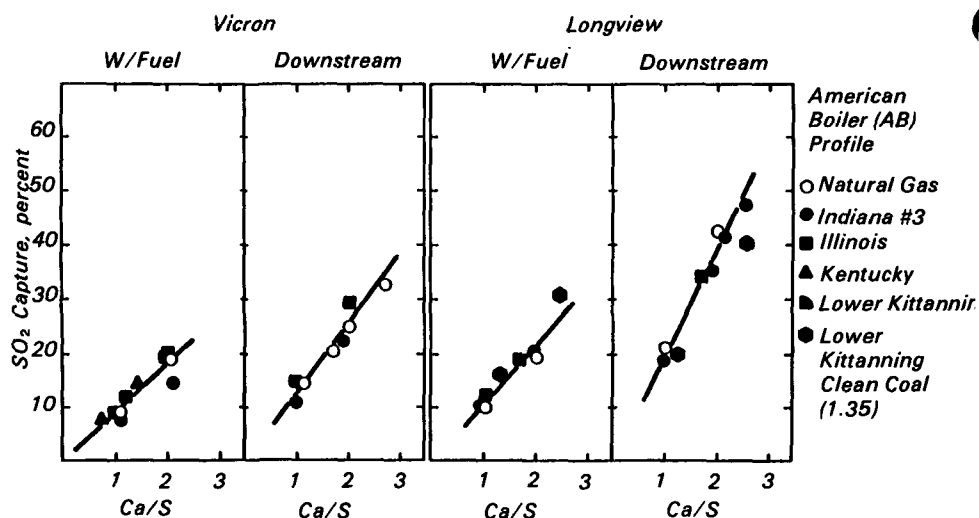


Figure 1. Effect of fuel type on SO₂ capture with Vicron and Longview.

effectively increase the ability of calcium based sorbents to capture SO₂. Figure 2 summarizes data obtained in the bench scale Control Temperature Tower (CTT) furnace with limestone and indicates that all of the alkali metals significantly enhance the measured SO₂ capture. The primary enhancement mechanism is not chemical catalysis of the SO₂ to SO₃ reaction step; rather, these materials react chemically with the CaO to produce local physical changes in the sorbent which enhance sorbent capture. In particular, both the chromium series elements and the alkali metals appear to induce particle fragmentation, creation of large cracks, and pore enlargement, all of which increase the accessibility of the interior calcium and decrease the rate of site loss by pore mouth plugging. In addition, the promoters often produce low melting eutectics with the CaO, and this liquid phase may enhance the local transport of the SO₂ to the unreacted CaO. In addition to affecting the sorbent morphology, the alkali metal promoters also directly react with SO₂ to produce sulfate products; they effectively function as sorbents themselves. The chromium compounds do not exhibit this behavior.

Coal/Promoter Interactions

Unfortunately, the effectiveness of promoted sorbents for SO₂ control may be significantly less in actual, coal fired systems than in SO₂ doped, natural gas tests due to the presence of coal mineral matter, in particular the submicron ash aerosol. Figure 3 summarizes a wide series of tests conducted to evaluate the

influence of coal mineral matter constituents on the promotion of limestone and hydrated sorbents by both NaHCO₃ and Cr₂O₃. These data indicate that under all conditions tested both the sodium and the chromium produced significant increases in sorbent utilization in the ash free experiments (natural gas firing). However, with all of the sodium promotion cases and with the chromium cases where the sorbent was added within the burner zone, the promotion effect was greatly reduced with coal firing. Only when the sorbent was added downstream and the promoter was Cr₂O₃, was the beneficial effect retained in the presence of coal firing. With sodium promotion external contact between the promoted sorbent and the coal is not required; separate injection still leads to deactivation. EDS analysis confirmed the presence of sodium on the mineral ash as well as the sorbent, suggesting that the controlling mechanism is vaporization and uniform sodium condensation. Condensation modeling calculations indicated that more than 90% of the added sodium could condense on the submicron ash aerosol if the sorbent particles are large and the internal surface area is not readily available. X-ray diffractograms indicated that the condensed sodium reacted with the refractory oxides in the coal ash to form sodium silicates, thereby effectively reducing the sodium available for direct reaction with SO₂. Thus, the effectiveness of sodium promotion is reduced in coal fired systems simply because the promoter itself condenses on the submicron ash aerosol and the amount available for enhancement of the calcium

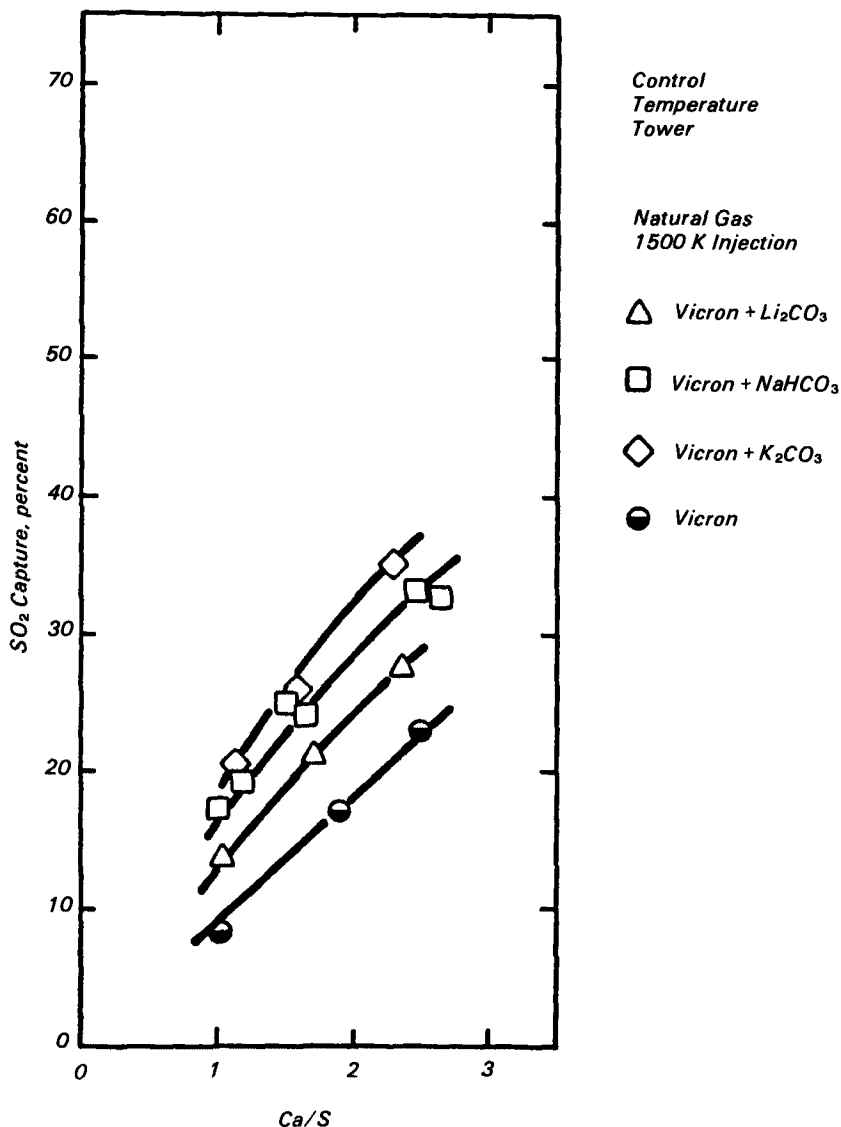


Figure 2. Summary of SO_2 capture with alkali metals.

sorbents is greatly reduced. The coal ash has less influence on chromium promotion because chromium is a far less volatile promoter. EDS analysis indicated that the chromium was primarily associated with the calcium; little chromium was found with the ash, particularly in the downstream injection cases.

Application Considerations

Parametric process studies indicated that the chemical form of the sodium promoter is not significant. Particle size can influence promotion; large particles may not be completely vaporized and dispersed in the residence time available. Because of the vapor phase transport of

the alkali metals, they need not be injected with the sorbent particles to provide effective promotion (in the absence of an ash aerosol).

Various, externally generated promoted sorbents were produced and evaluated in an attempt to avoid the deleterious effects of the ash aerosol. However, even hydration in the presence of sodium did not overcome this problem; at normal LIMB injection temperatures the sodium still tends to vaporize initially and a large fraction ultimately condenses on the submicron aerosol. Conversely, chromium promotion can be optimized to produce extremely high capture levels, although chromium promoted sorbents

are almost certainly environmentally unacceptable. Figure 4 illustrates data obtained with a chromium-promoted pressure-hydrated calcitic sorbent and indicates that capture levels in excess of 70% were achieved at a Ca/S ratio of 2.0. Unfortunately, to date it has not been possible to identify an environmentally acceptable promoter capable of inducing the morphological changes produced by chromium with a sufficiently low volatility to avoid vaporization and subsequent scavenging by the ash aerosol.

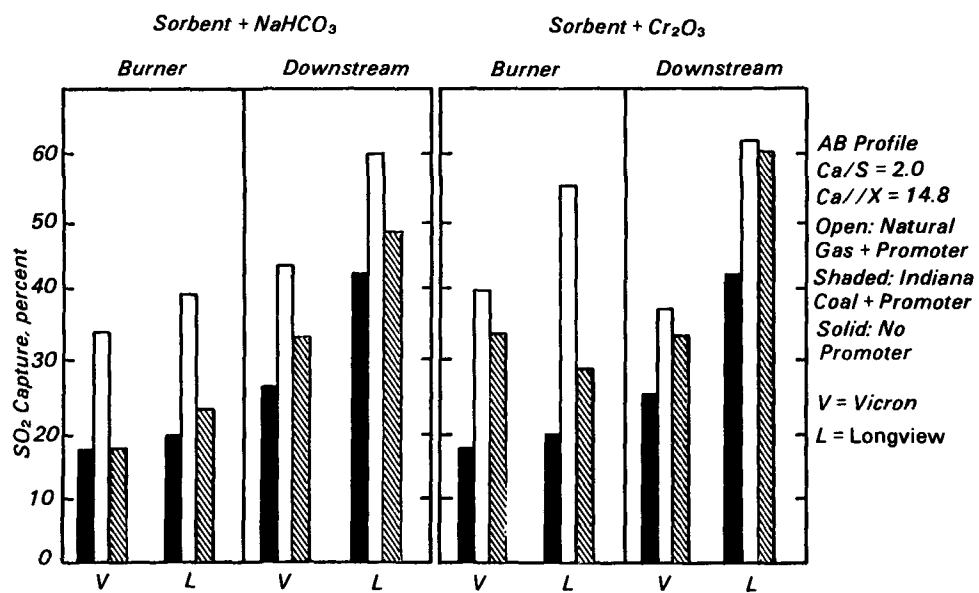


Figure 3. Enhancement comparison between coal and gas.

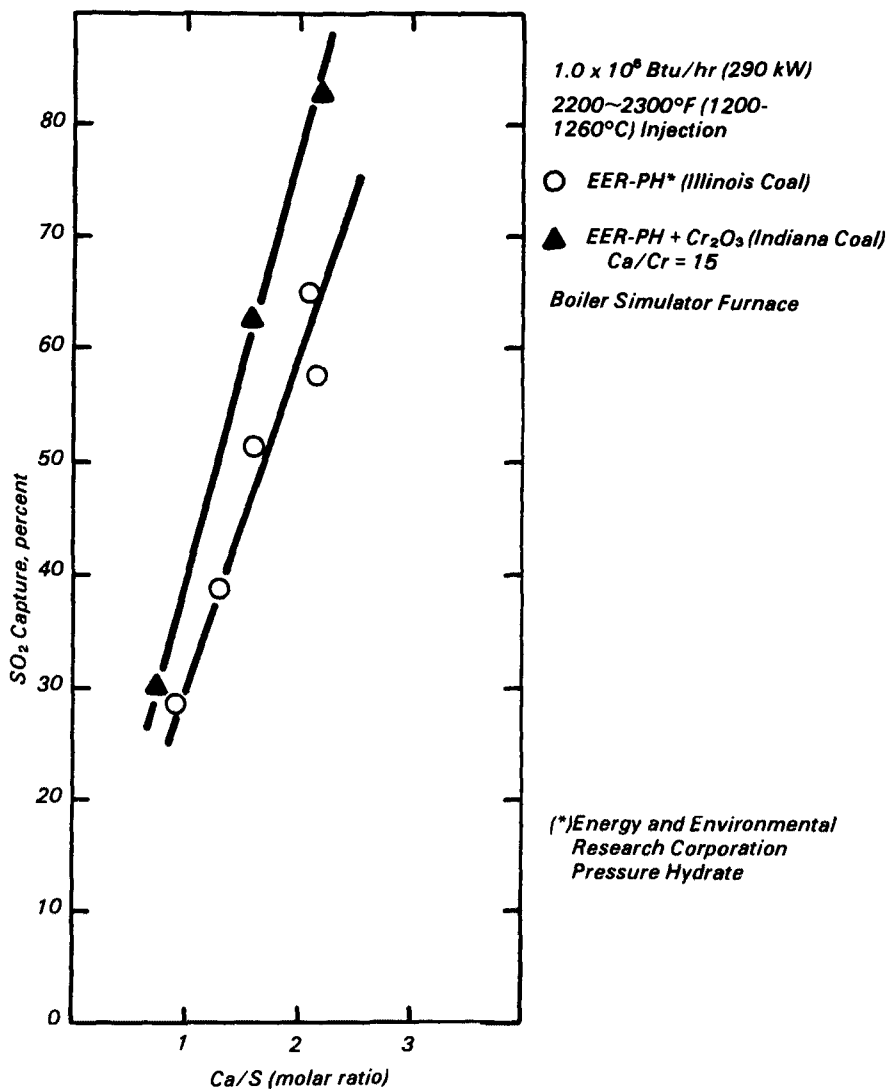


Figure 4. Chromium-promoted, calcitic pressure hydrate.

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David A. Kirchgessner is the EPA Project Officer (see below).

The complete report, entitled "Influence of Coal Mineral Matter on the Effectiveness of Dry Sorbent Injection for SO₂ Control," (Order No. PB 88-178 587/AS; Cost: \$25.95, subject to change) will be available only from:

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