United States
Environmental Protection
Agency

Research and Development

Air and Energy Engineering
Research Laboratory
Research Triangle Park, NC 27711

EPA/600/S2-89/065 Apr. 1990

EPA

Project Summary

Furnace Sorbent Reactivity Testing for Control of SO_2 Emissions from Illinois Coals

Brian K. Gullett and Frank E. Briden

Research was undertaken to evaluate the potential of furnace sorbent injection (FSI) for sulfur dioxide (SO_2) emission control on coal-fired boilers utilizing coals indigenous to Illinois. Tests were run using four coals from the Illinois Basin and six calcium hydroxide [$Ca(OH)_2$] sorbents, including one provided by the Illinois State Geological Survey (ISGS). The evaluation included: pilot- and bench-scale sorbent reactivity testing, sorbent microstructure characterization, and injection ash characterization.

Pilot-scale FSI testing gave SO_2 removal greater than 60%, with some tests (including those with the ISGS sorbent) exceeding 70% removal for Ca/S ratios of 2:1. Bench-scale testing of injection at economizer tem-peratures (538°C) yielded com-parable removals of about 55%. X-Ray diffraction (XRD) tests of the sorbents showed a strong correlation between three measured crystallite micro-structural parameters and sorbent reactivity in the FSI tests. Extraction Procedure (EP) toxicity tests with the sorbent injection ash gave values well below Resource Conversation and Recovery Act (RCRA) limits for regulated metals.

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

Emissions of sulfur oxides, principally sulfur dioxide (SO_2), from combustion sources have increased awareness and concern in recent years. In particular, SO_2 emissions from coal-fired boilers used by utilities and industries have been implicated as major contributors to a growing acid precipitation problem. While long-term ecological effects of acid precipitation are being debated, it is clear that a reduction in SO_2 emissions is greatly desirable. Factors to weigh in determining an SO_2 control technology are cost, SO_2 removal efficiency, and ease of retrofitting to existing boilers. The optimum control technology would balance removal levels with the cost to the industry or utility (and ultimately the consumer). One technology that has received considerable attention is Furnace Sorbent Injection (FSI), which offers relatively low capital cost, ease of retrofitting, and reasonable removal efficiencies.

A large body of research on FSI is currently available. The effects of such fundamental parameters as injection temperature, sorbent type, particle size, and SO_2 concentration have been investigated on the pilot-scale. These investigations, along with on-going full-scale demonstrations, indicate that SO_2 removals of about 60% may be expected using commercially available calcium hy-droxide [$Ca(OH)_2$] sorbents. Noted potential impacts of FSI on the boiler include increased slagging and fouling, increased mass loading on particulate removal systems, and alteration of the chemical composition of boiler ash.

This current investigation is designed to provide data at the pilot-scale on SO_2 removal from a combustor fired with Illinois Basin coals and injected with a range of sorbent types. These comparative data, along with results from low temperature testing, physical analysis of the sorbents, and chemical analysis of the ash will be used to evaluate FSI as a control technology for facilities using Illinois Basin coals. Exceptionally high removal efficiencies could expand the range of applications for Illinois high sulfur coal at a lower cost than coal cleaning or wet flue gas desulfurization (FGD) alternatives.

The primary objective of the planned research has been to evaluate FSI as a potential SO_2 emission control technology for coal fired boilers burning Illinois Basin coals. FSI offers the benefits of being less capital intensive than wet FGD as well as the ability to be readily retrofitted to existing facilities with space limitations. To evaluate FSI potential, the following objectives have been outlined:

1. Develop a data base of sorbent SO_2 removal efficiencies using six sorbents with four coals at two Ca/S ratios in the Environmental Protection Agency's (EPA) Innovative Furnace Reactor (IFR) at a high injection temperature (1,200°C) regime.
2. Obtain comparative SO_2 reactivity data for the six sorbents at mid-range temperatures (538°C) in EPA's Graphite Furnace Reactor (GFR).
3. Characterize sorbent microstructure properties using x-ray diffraction (XRD) techniques in an effort to correlate these properties with sorbent SO_2 removal efficiencies.
4. Determine the potential for leaching of toxic metals from FSI ash using the EPA's Extraction Procedure (EP) toxicity test.

Experimental Procedures

The four coals used in testing were Illinois Basin Coal Sample Program (IBCSP) #1, #2, #6, and #9. Sorbents chosen for testing included three commercially available calcium hydroxides (Marblehead, Linwood, and Snowflake), a dolomitic hydroxide (Kemidol), a surfactant modified calcium hydroxide (lignosulfonate modified Marblehead), and an alcohol calcium hydroxide provided by the Illinois State Geological Survey (ISGS). The ISGS sorbent was tested by combining equal parts of each of the 10 batches provided. This insured that adequate sorbent was on hand for FSI testing in the IFR. Individual batches were tested on a limited basis in the other reactor systems.

Testing in the IFR consisted of determining baseline SO_2 concentrations in the flue gas while burning each of the coals at feed rates sufficient to yield a firing rate of approximately 49,600 KJ/h (47,000 Btu/h). After determining a stable SO_2 concentration, sorbent was injected at various Ca/S ratios between 1:1 and 2:1 and the SO_2 level monitored until equilibrium was achieved. The final SO_2 removal percentage was determined as the average of duplicate tests. The test matrix consisted of testing each coal with all six sorbents using duplicate runs (4 coals x 6 sorbents x 2 duplicates x 2 Ca/S ratios = 96 tests).

Current supply to the electrically heated GFR was regulated to yield a temperature profile with a peak of near 538°C while declining rapidly with residence time (or distance) in the reactor. Flow rates sufficient to give a residence time of 0.75 s between 538 and 427°C with an SO_2 concentration of 3,000 ppm were used. Each sorbent was injected under differential conditions with respect to SO_2 concentration and conversion to calcium sulfite (or sulfate) determined on solid samples collected by a cyclone separator.

Each of the six sorbents was analyzed using XRD. The Warren-Averbach method of peak analysis for separation of the crystallite size and strain components was used to determine major microstructure properties.

The individual values of the sorbent microstructural properties were related to IFR-determined reactivities by regression functions to test the hypothesis that various combinations of these properties could predict sorbent reactivity.

Toxicity tests were performed on ash taken from the IFR baghouse during each of the baseline coal tests excluding coal #1 for which insufficient sample was collected. Analyses on eight Resource Conservation and Recovery Act (RCRA) regulated metals (antimony, barium, cadmium, chromium, lead, mercury, selenium, and silver) and pH were carried out using methods outlined in EPA method 1310. Ash from sorbent injection using one coal (IBCSP #6) and all six sorbents (Ca/S = 2:1) was also tested to determine the impact of FSI on disposal of ash.

Tests were run on the Short Time Differential Reactor (STDR) using 4 mg of sorbent exposed to process gas consisting of 3,000 ppm SO_2 in 5 percent O_2 and a N_2 balance, preheated to 538°C. The reactor is designed to allow fixed bed sample exposure times in the range of 0.3 to 5 s, while maintaining conditions differential with respect to SO_2 concentration.

Results and Discussion

Figure 1 shows several data trends. SO_2 capture levels for the IBCSP #2 coal are substantially lower for all sorbents tested (with the possible exception of the Marblehead hydroxide) than for the other coals. It is interesting to note that while the sulfur content of the IBCSP #2 coal (3.23%) is bracketed by the other coals, it differs from them in one important aspect: unlike the other coals tested, pyritic sulfur accounts for most of the sulfur present in IBCSP #2, giving a pyritic/organic sulfur ratio of 2.53:1 compared to values less than 1:1 for the other coals. No explanation for the apparent adverse effect of a high pyritic/organic sulfur ratio on FSI is currently available. Results for FSI testing on the IFR are compiled in Figure 1. The data presented are estimated SO_2 removal percentages at Ca/S of 2:1, calculated by extrapolating linearly from the mean removals at both Ca/S ratios run for each coal/sorbent combination.

Furthermore, when the data from the three other coals (IBCSP #1, #6, and #9) are viewed collectively, the SO_2 removal by individual sorbents does not differ radically from coal to coal. For each, the relative standard deviation of the mean SO_2 removal percentage (standard deviation of mean removal divided by the mean) is less than 10%. This could indicate that the pyritic/organic sulfur ratio of each coal is the largest coal-specific factor in FSI performance using the same sorbent.

The commercially available $Ca(OH)_2$ sorbents (Linwood, Marblehead, and Snowflake) yield about the same values for SO_2 removal percentages when excluding the data from IBCSP #2. The sorbents hydrated under special conditions (the lignosulfonate modified Marblehead and the ISGS alcohol hydroxide) clearly exhibit superior performance. Past tests attribute the enhanced performance of the modified Marblehead to its ability to resist sintering at the high temperatures seen in FSI.

The performance of the ISGS sorbent may be related to its very small particle size. Recent tests have demonstrated the importance of sorbent particle size to sulfur capture. Mixing studies have shown that, in many instances, sorbent injection takes place under conditions

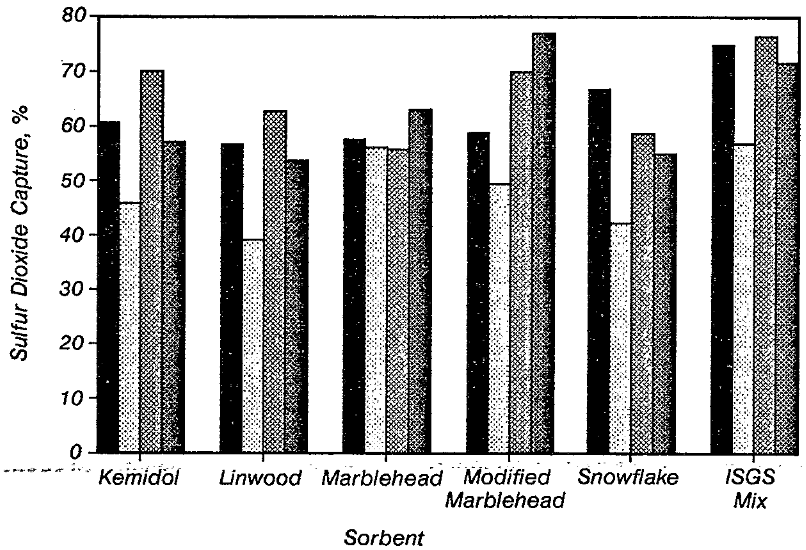

Figure 1. *IFR Sorbent Reactivity.*

likely to result in limitations on mass transfer rates of SO_2 to the reacting particle. In such a regime, ultimate sorbent reactivity will be inversely related to the size of the reacting particle.

The overall impression of the applicability of FSI as a SO_2 control technology for Illinois coals is positive. Except for IBCSP #2, which gave lower results for unknown reasons discussed earlier, SO_2 removals for each of the coal/sorbent tests approached or exceeded 60% at a Ca/S ratio of 2:1. Indeed, tests with the specially modified sorbents routinely exceeded 70%. These test results strongly recommend FSI as a cost effective means of controlling SO_2 emissions from coal-fired combustors.

Results from economizer temperature (538°C) sorbent injection testing on the GFR are shown in Table 1. The data show a clear inverse relationship to sorbent particle size as measured using the sedigraph; as particle size decreases, the conversion of the sorbent to the calcium sulfite product in the GFR increases. Again, this indicates mass transfer resistances acting to control the rate of reaction, rather than other potentially faster mechanisms such as inherent chemical kinetics. Removing these resistances may show a faster true rate of reaction.

Results from testing in the STDR with an SO_2 concentration of 3,000 ppm using ISGS BH-29 sorbent are shown in Figure 2. Similar conversions were obtained with Linwood hydroxide over the same time range. These results predict an SO_2 removal of roughly 55% for a 1 s residence time and Ca/S ratio of 2:1 when injecting sorbent at or near 538°C. More work is needed to accurately quantify the fundamental rate of the sorbent/SO_2 reaction under economizer injection conditions using reactors like the STDR prior to predicting potential SO_2 removal levels. The effects of parameters such as SO_2 concentration, sorbent surface area, and sorbent porosity on reaction have not been thoroughly investigated.

Table 1. *Results from Economizer Injection Tests on GFR*

Sorbent	*Mean Conversion (%)**
Marblehead	*9.8 ± 0.7*
Modified Marblehead	*11.0 ± 1.1*
Snowflake	*11.7 ± 1.0*
Linwood	*15.2 ± 2.9*
ISGS BH-20	*17.7 ± 1.0*
ISGS BH-24	*17.6 ± 1.1*
ISGS BH-29	*19.9 ± 2.2*
Kemidol	*15.3 ± 2.5*

(*)Data obtained from minimum of 10 runs at 538°C, resisdence time = 0.75 s, 3,000 ppm So_2, 5% O_2, N_2 balance.

It has been proposed that crystallite size can affect the gas-solid reactions by modifying the interface between the two phases. It is further proposed that crystal lattice strain could contribute to reactivity by decreasing the stability of the solid and producing a source of activation energy from the strain energy stored in the lattice.

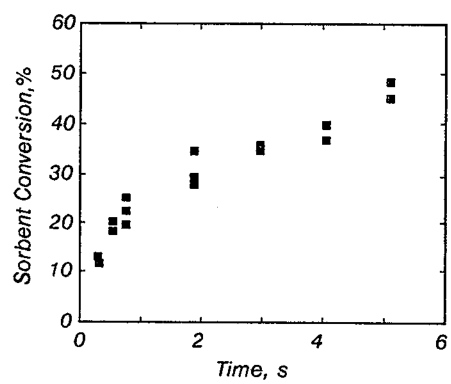

Figure 2. *STDR Alcohol Sorbent Reactivity.*

The IFR reactivities for IBCSP coals #1, #6 and #9 were quite similar. To test the hypothesis that the individual x-ray line broadening (XLB) factors were related to reactivities, regression functions were derived using the observed experimental reactivities for coals #1, #6 and #9. For the first stage of this study, it was found that the best single estimator of IFR reactivity was maximum column length, a value representing the maximum dimension within the distribution of dim-ensions measured in a crystallite.

In the next stage, regression equations were derived for relating the XLB factors two at a time to the observed IFR reactivities. For the 15 pairs of factors, the correlation coefficients varied from 0.13 to 0.79. The best pair of estimators was maximum column length and the strain at maximum column length with a correlation coefficient of 0.79. This value is considered quite significant, considering its derivation was subject to coal and furnace variability.

Since the increase in correlation was vastly improved by using two factors, the third stage was to use three factors for the analysis. For triplets, the correlation coefficient varied from 0.40 to 0.99. It would appear that it is possible to almost completely characterize the microstructural relation to reactivity with three XLB factors. The best correlation coefficient of 0.99 was derived from the average column length, modal column length, and strain at maximum column length.

Those three XLB factors appear to be the best estimators of reactivity from the number of samples analyzed to date. Future studies of other sorbents could further establish the reliability of this method and its application toward ranking sorbent reactivity without undergoing large-scale testing.

Values for all of the regulated metals are below the RCRA limits. Sorbent injection would appear to stabilize many of the metal species, particularly arsenic and cadmium. While the final pH values are below RCRA limits, they are high enough to elicit some concern. Methods for stabilizing the ash or neutralizing leachate from the ash may bear investigation.

Conclusions and Recommendations

Pilot-scale testing of the SO_2 removal potential of FSI with Illinois Basin coals showed that removal in excess of 60% can be readily achieved using commercially available sorbents and a Ca/S ratio of 2:1. The ISGS alcohol sorbent and the Marblehead lignosulfonate modified sorbent gave removals in excess of 70%. Lower removals were noted for the coal high in pyritic sulfur (as opposed to organic sulfur). Further investigation is necessary to verify and explain this phenomenon. The greatest removals were seen using the ISGS alcohol hydroxide. It is believed that its performance is enhanced by its small particle size and the resultant mixing benefits.

Testing of sorbent injection at economizer temperatures (538°C) showed that removals of roughly 55% at a Ca/S ratio of 2:1 can be expected. However, not much is currently known about fundamental reaction kinetics for this mid-temperature sorbent/SO_2 reaction. To more accurately predict the full-scale performance of injecting sorbent in this temperature region, the effects of more temperature, SO_2 concentration, and sorbent characteristics on reactivity need to be clarified.

XRD tests indicated that the sorbent microstructural characteristics of average column length, modal column length, and strain at maximum column length can provide a basis for prediction of sorbent performance in FSI applications.

Analyses of the FSI ash showed that it could be considered nonhazardous in terms of RCRA limits for leaching of heavy metals. The pH of the leachate is a concern, however, because of its alkaline nature.

*The EPA authors, **Brian K. Gullett** (also the EPA project officer) and **Frank E. Briden**, are with the U.S. EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC 27711.*
***Brian K. Gullett** is the EPA Project Officer (see below).*
The complete report, entitled "Furnace Sorbent Reactivity Testing for Control of SO_2 Emissions from Illinois Coals," (Order No. PB90-150 830/AS; Cost: $17.00, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

United States Environmental Protection Agency

Center for Environmental Research Information
Cincinnati OH 45268

EPA/600/S2-89/065