Flue Gas Desulfurization by In-Duct Dry Scrubbing Using Calcium Hydroxide

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Although there is an on-going debate regarding the extent to which sulfur dioxide emissions from coal-fired electric power generation plants cause the environmental problems associated with acid rain, public concern has led to the development of numerous new SO_2 abatement processes (Makansi, 1985, 1986; Borgwardt, 1970; Babu et al., 1986; Blythe et al., 1986; Seeker et al., 1986; Pennline and Drummond, 1987). Several of them involve what is loosely termed "dry scrubbing," in which the SO_2 removed leaves as part of a dry solid.

Consequently, processes which involve spray drying of an alkaline solid dissolved in water are classified as "dry," as are processes in which a dry powdered sorbent is directly injected into a flowing flue gas. The latter method is used in this paper; because it is relatively inexpensive, it is attractive for retrofitting older pilot plants to meet emissions regulations. A common feature of direct in-duct injection processes is that micron-sized sorbent particles are injected downstream of the boiler and travel as an entrained dust reacting with SO_2 in the flue gas at relatively low temperature, e.g., 65 to 100°C, until being collected by an electrostatic precipitator and/or a fabric filter.

The process most closely corresponding to the one studied here is called Hydrate Addition at Low Temperature (HALT) (Babu et al., 1986); in it a dry sorbent such as $Ca(OH)_2$ and a fine spray of water are introduced separately. Adsorbed water appears to play a key role in promoting SO_2 capture and subsequent reaction on the sorbent; because the water content of the sorbent is governed by the relative humidity of the flue gas, the latter is a very important process variable. Adsorbed water is also believed to be important in minimizing the negative influence of a phenomenon termed "blinding," in which access of SO_2 to the interior of the sorbent via diffusion in pores becomes increasingly restricted as the reaction proceeds (Jorgensen et al., 1987). The increase in pore diffusional resistance is generally attributed to the molar volume of the reaction products, e.g., $Ca(SO_4)_2$, being appreciably greater than that for $Ca(OH)_2$.

Mathematical models such as the "grain model" (Wen and Ishida, 1973; Hartman and Coughlin, 1976; Bhatia and Perlmutter, 1981a,b) and the "pore tree model" (Simons et al., 1986, 1987), which attempt to describe heterogeneous reactions, predict that the formation of such a product layer can severely hinder pore diffusion. It is also obvious that, all other factors being equal, it is advantageous to have the minimum practical average particle size and a high specific surface area for the sorbent. Recognizing this, various methods for preparing sorbents with these characteristics have been studied (Babu et al., 1986; Makansi, 1983), as has the potentially beneficial effect of adding hygroscopic additives such as $CaCl_2$ and NaOH to the sorbent (Blythe et al., 1986) to enhance adsorption of water vapor (and thus SO_2).

Pilot- and demonstration-scale tests of dry injection (Babu et al., 1986; Blythe et al., 1986) have shown that SO_2 removal efficiencies as high as 50 to 70% can be achieved for flue gas with an inlet concentration of 2,000-3,000 vppm SO_2 using a 2:1 $Ca(OH)_2$ to SO_2 molar feed ratio and a close approach, e.g., 6 to 12°C, to adiabatic saturation temperature, corresponding to a relative humidity of 50 to 70%. Appreciable SO_2 removal was observed to take place not only during sorbent flight but also on the fabric filter dust cake. The work described in this current paper was undertaken as a preliminary study of the effect of a variety of parameters on flue gas desulfurization efficiency for a dry sorbent injection process. Two notable differences between this study and those mentioned above are that it involved a higher temperature range and an appreciably lower relative humidity range and that it focused exclusively on prefilter SO_2 removal.

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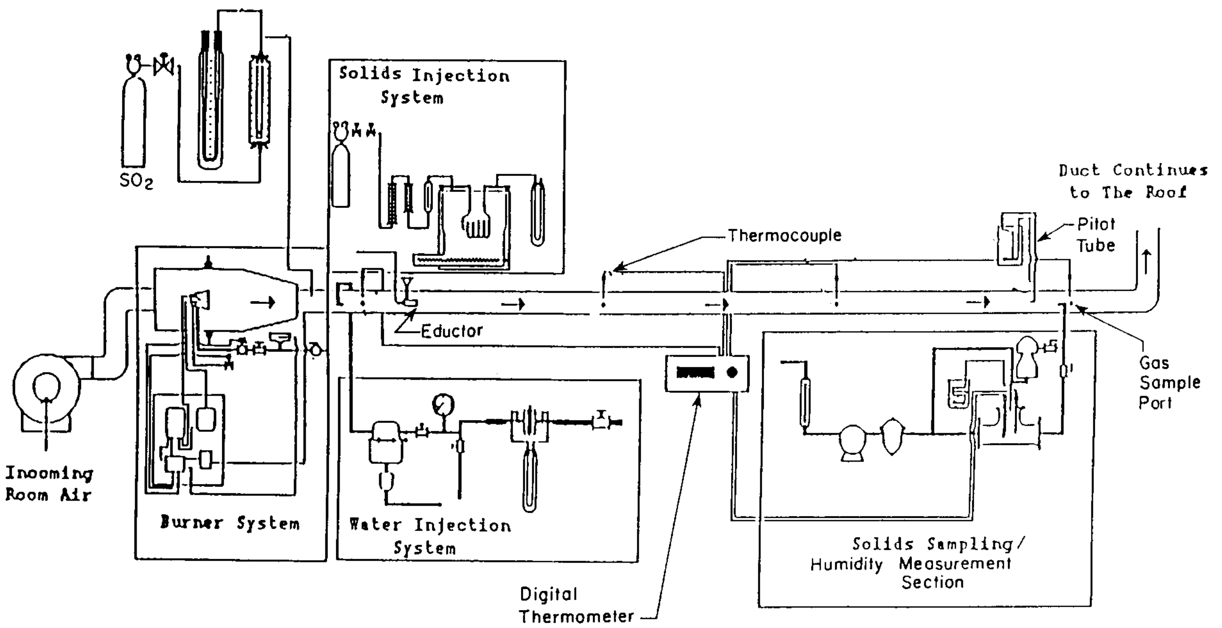

Figure 1. Flue gas desulfurization system.

Experimental Apparatus and Procedure

The main apparatus used was a pilot-scale in-duct flue gas desulfurization system specifically constructed for this study. As shown in Figure 1, it consists of five subsystems:

1. The burner system
2. The flue itself including provisions for SO_2 injection, gas sampling and temperature measurement
3. The water injection system
4. The solids injection system
5. The solids sampling/humidity measurement system

The burner system consists of an Eclipse Model AH-MA air heat burner which uses propane as a fuel, a specially constructed housing for the burner, various burner controls, and an air blower. The flue attached downstream of the burner has a horizontal straight run of roughly 14 meters of 12.8-cm galvanized stove pipe (which constituted the portion studied) before a bend, beyond which it is routed another 20 meters to exhaust on the roof of the laboratory. The straight run of ductwork is surrounded by 2.5-cm-thick calcium silicate insulation. Sulfur dioxide (99.98% SO_2) is metered into the flue through a calibrated rotameter. Four gas sampling ports spaced at 4-m intervals are installed using 0.64-cm bulkhead tubing unions fitted with rubber septa. At the same four locations, 0.32-cm-OD stainless steel sheathed iron-constantan thermocouples are projected into the center of the duct and are connected to a digital thermometer. The water injection system involves metering low-pressure steam through a calibrated orifice into an entrainment separator and finally into the flue where it is injected concurrent with the hot air flow.

The solids injection system consists of a calibrated variable speed vibrating screw-type solids feeder, transfer piping, and a small air-actuated venturi-eductor mounted horizontally in the center of the flue. The screw feeder, after being loaded with sorbent, is sealed with a Plexiglas cover and purged with dry nitrogen. The solids sampling/humidity measurement system uses a common port (roughly 11 m from the solids injection point) to achieve a dual purpose. When sampling spent sorbent, a 1.3-cm-OD copper tubing bend is positioned in direct opposition to gas flow at the desired radial position and the solid is sampled isokinetically through a filter canister by the action of a suction pump. When making a humidity measurement, flue gas travels from the probe through electrically heated piping to a glass pipe tee housing both wet and dry bulb thermocouples.

Two methods were used for determining SO_2 concentration in the flue gas, both of which involved as the initial step gas sampling via a syringe inserted through a sample port septum. In the first method, the gas sample was rapidly transferred to an aqueous solution containing hydrogen peroxide, sodium hydroxide, bromcresol green, methyl red, and methyl alcohol; and then titration of the H_2SO_4 formed was conducted using a 0.00025 molar NaOH solution and a pH meter. Because the gas sample generally also contained an appreciable concentration of unreacted, highly basic $Ca(OH)_2$, a significant correction had to be made in the titration calculations to factor out this effect.

Consequently, although the values obtained using this technique were often in good agreement with those obtained using the second method, namely, gas chromatography, the results for the latter were more consistent. For this reason, the results reported here will be those obtained using gas chromatography. This method allowed the sample to be immediately injected into a Carle Model 8700 chromatograph equipped with a 1.8 m × 0.32 cm column packed with 80/100 mesh Porapak Q and operated at 60°C. For a given run data point samples were generally taken and analyzed until three successive sample analyses agreed within 10%, and the mean value was used. In several runs samples of partially reacted sorbent were taken as described earlier and analyzed via X-ray fluorescence.

The primary sorbent used in the study is calcium hydroxide purchased commercially in 10- and/or 50-lb (4.5- and/or 22.7-kg) bags as Kemikal Rotary Kiln High Calcium Hydrated Lime manufactured by U.S. Gypsum Co. Specific surface area measurements via BET nitrogen adsorption showed a modest variation for the various bags used, with a value of 11 m^2/g being representative of the sorbent used in the majority of the runs. *In situ* tests of the average particle size of this sorbent made using an Andersen eight-stage Stack Sampler/Impactor consistently indicated a size range of 0.3 to 12 μm with an aerodynamic average diameter of 3.5 μm, which corresponded to an actual mass mean diameter of roughly 2.5 μm. Other sorbents which were briefly studied include calcium carbonate (2 m^2/g) and sodium sesquicarbonate ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, SA $\approx$ 0.2 m^2/g) obtained from FMC Corp.

Preliminary experiments confirmed that before the gas reached the third and fourth sample ports downstream of the injection point there was negligible radial variation in SO_2 concentration. Unless otherwise stated, results reported for % SO_2 removal and humidity are based on samples taken from the fourth (final) sample port and the temperature is a weighted average of the four values measured along the flue. In a typical run the gas temperature varied by less than 10°C over the length of the flue.

The standard procedure for conducting a run began with loading roughly 4 kg of sorbent into the hopper of the screw feeder, starting the air blower, setting the desired propane flow, igniting the burner, and introducing the desired flow of steam. Once the flue had reached a steady-state temperature, the motive air flow for the sorbent eductor was turned on and the average gas velocity (typically 13 m/s) was determined using a pitot tube. Within several minutes, a stable humidity measurement was obtained and this value was consistently within 10% of that calculated by material balance considering the combined contributions of steam, air, and water formed by propane combustion. Next, the desired flow of SO_2 was introduced into the flue, and gas samples in the absence of sorbent were taken and analyzed to obtain the initial SO_2 concentration. The desired flow of sorbent from the screw feeder to the flue via the eductor was then started and, finally, gas samples were taken and analyzed. Further details are given by Bond (1988).

Results and Discussion

In designing a grid of experiments it was recognized that, due to time constraints, not all of the many potentially important variables could be examined in detail; thus it was decided to focus on the effect of temperature, humidity, and sorbent/SO_2 feed ratio. The initial strategy was to establish a "base case" set of operating variables generally characteristic of flue conditions in a typical power plant and to observe the sensitivity of desulfurization to changes in variables relative to this reference case. Base case target conditions were: 0.06 kg $Ca(OH)_2$/min fed, 15 actual m^3/min total gas flow at 175°C and 1 atm, with an initial SO_2 concentration of 1,600 to 1,800 vppm and an absolute humidity of 0.07 kg H_2O/kg dry gas. These conditions correspond to a sorbent to SO_2 feed molar ratio in the range 1.0 to 1.2, a linear velocity of 13.7 m/s, and a relative humidity of roughly 1%.

Sorbent to sulfur dioxide mole ratio

The % conversion (removal) of SO_2 in the base case run was observed by both methods of analysis to be 20%, and this result was reproduced in a second run at the same conditions. Other runs in which the only appreciable deviation from base case conditions was in the sorbent/SO_2 feed ratio were conducted and the results are shown in Figure 2. Over the ratio range studied, i.e., 0.5 to 2.5, the conversion rose monotonically from a negligible value to roughly 30%. The error bars shown in this plot convey the moderately large uncertainty associated with a given measurement, but the trend is clear and agrees with that found in previous studies (Babu et al., 1986; Blythe et al., 1986). Similar error bars, although not shown explicitly, may be assumed on subsequent figures.

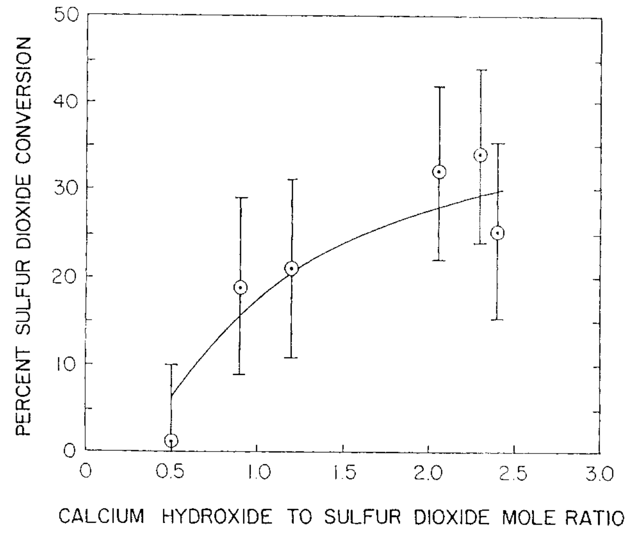

Figure 2. Sulfur dioxide removal as a function of $Ca(OH)_2/SO_2$ molar ratio at otherwise base conditions.

Error bars indicate approximate uncertainty.

Humidity

Tests were made of the effect of varying the absolute humidity of the flue gas (at otherwise base case conditions) by roughly an order of magnitude. Sulfur dioxide conversion, as shown in Figure 3, increased from essentially zero when no steam was added to between 30 and 40% near the upper end of the humidity range studied. The apparent occurrence of a local maximum around 0.09 kg H_2O/kg dry gas is felt to be merely a reflection of experimental variation, and thus the curve is drawn showing a constant, but gradually dampened, increase in SO_2

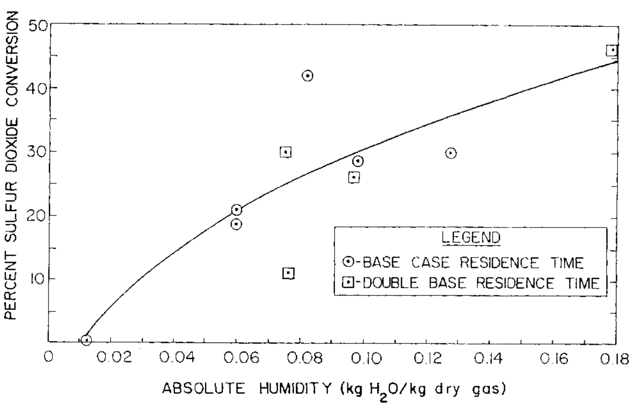

Figure 3. Sulfur dioxide conversion as a function of absolute humidity at otherwise base case conditions.

conversion with increased humidity. This interpretation of the data is reinforced by results described later.

Temperature

For otherwise base case conditions, lowering the gas temperature from the reference value of 175°C to 125°C raised the SO_2 conversion from 20% to 30%, while increasing the temperature to 240°C caused a marked drop in SO_2 conversion to about 5%. Given that the reaction rate constant for the surface reaction between SO_2 and $Ca(OH)_2$ would be expected to increase with increasing temperature, it is clear that the decline in observed reaction rate at higher temperature must be due to an unfavorable equilibrium overriding the effect of increase in the intrinsic rate constant. Data taken in previous work as well as those for runs discussed later strongly indicate that it is a decrease in H_2O and SO_2 adsorption as temperature increases which accounts for this trend. This highlights the fact that the reaction is, in a sense, mass-transfer-limited rather than surface-reaction-rate-limited. And when this fact is taken in conjunction with the strong dependence of SO_2 conversion on absolute humidity, it indicates that the variable with the greatest influence is relative humidity. This agrees qualitatively with the data of Babu et al. (1986) and Blythe et al. (1986).

It is clear that relative humidity which governs the adsorption of water and adsorbed water plays a key role in the overall SO_2 conversion sequence. This sequence involves mass transfer of SO_2 through the external gas film coating the sorbent particle, diffusion of SO_2 in the pores of the sorbent, adsorption of SO_2 on the surface, possibly some surface diffusion, and finally chemical reaction of the sorbent with SO_2, or, more probably, H_2SO_3 and/or H_2SO_4 formed by earlier reaction with adsorbed water. At the temperature studied, essentially no reaction was observed to occur between relatively dry $Ca(OH)_2$ and SO_2, implying either a negligible tendency for SO_2 to adsorb on $Ca(OH)_2$ *per se* or a negligible reaction rate for SO_2 relative to sulfurous or sulfuric acid. The fraction of the surface covered by adsorbed water would be very sensitive to changes in relative humidity in this low range for the latter, i.e., in the steep portion of the adsorption isotherm; and since the interaction of SO_2 with surface H_2O must precede reaction with $Ca(OH)_2$, the effects of humidity and temperature are understandably linked.

Recognizing this, a series of temperature-variation runs similar to those just described were conducted at an absolute humidity roughly twice that of the base case. As shown in Figure 4, this caused a nearly uniform upward shift of the % SO_2 conversion curve. Merging these two curves by plotting conversion vs. relative humidity yielded Figure 5. Although this plot shows a low slope near the upper end of the range studied it can be assumed that, if extrapolated to the much higher relative humidity (e.g., 50–70%) values used in the studies by Babu et al. (1986) and Blythe et al. (1986), it might predict conversions higher than the 50–70% values found in those studies. It is possible that above conversions of, say, 50%, the "blinding effect" described earlier begins to significantly offset the beneficial effect of boosting the relative humidity; even so, the SO_2 conversions achieved here at only modest relative humidities (but at absolute humidities equal to or greater than those in previous studies) were surprisingly high. This raised the question of whether the analytical methods used for SO_2 were giving artificially low values for exit SO_2 concentration. However, X-ray fluorescence analysis of spent sorbent taken from runs showing SO_2 conversions in the 20 to 40% range showed sulfur contents commensurate with the measured SO_2 conversions.

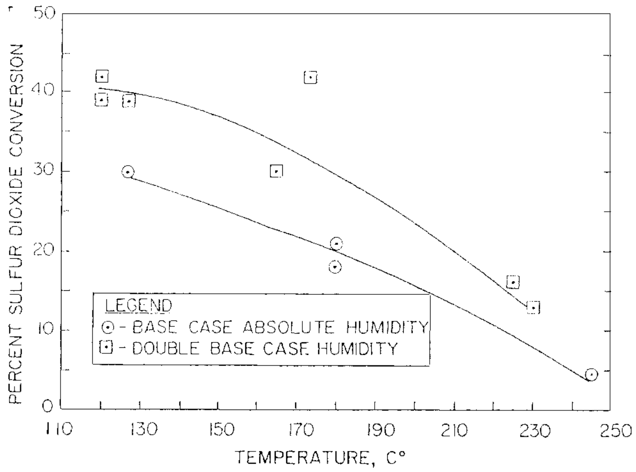

Figure 4. Sulfur dioxide conversion vs. temperature at two different values of absolute humidity, $Ca(OH)_2/SO_2 \approx 1.1$.

In a recently published article (Stouffer et al., 1989), data for SO_2 removal using $Ca(OH)_2$ with added steam appear to indicate that substantially lower SO_2 conversion values, e.g., 5–15%, might be expected in the relative humidity range examined here. In addition to involving sorbent injection upstream of the steam injection (the opposite of that used here), their tests involved a reaction zone temperature range substantially lower than that studied here. It is plausible that, for a given relative humidity value and thus a given equilibrium sorbent moisture content, operation at a higher temperature will result in a higher surface reaction rate and thus a higher SO_2 conversion, as observed here.

Residence time and gas velocity

In several of the runs already described, samples taken from a sample port only two thirds of the distance of the generally

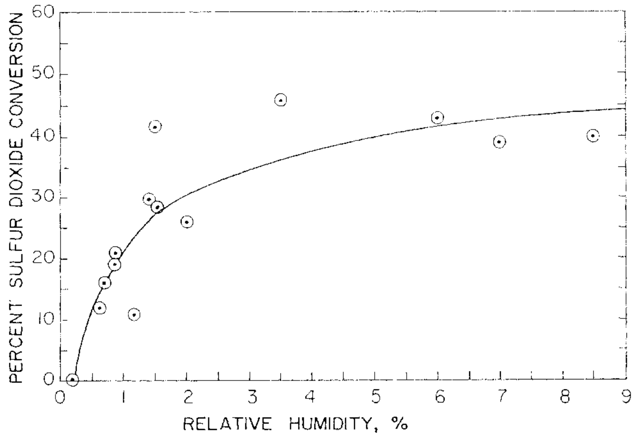

Figure 5. Sulfur dioxide removal as a function of relative humidity for $Ca(OH)_2/SO_2 \approx 1.1$.

used (final) sample port from the injection point had shown SO_2 concentrations statistically indistinguishable from those of the exit samples. This clearly implied that nearly all of the SO_2 capture was occurring in a relatively short region (and time) following sorbent injection; thus, above some value of residence time on the order of tenths of a second, no appreciable conversion benefit would accrue. Nevertheless, a run was made at double the normal residence time by using a gas velocity roughly one half of the standard value. The average conversion observed was 22% which was easily within experimental error the same as for the base case, indicating a low sensitivity of conversion to moderate changes in residence time. The data of Figure 3 also indicate no appreciable effect for doubling the residence time.

Miscellaneous runs

Having observed the separate effects of various parameters on SO_2 removal, a run was made in which only the temperature was at base case conditions (175°C) while the $Ca(OH)_2/SO_2$ ratio was 2.2, the absolute humidity was 0.19 kg H_2O/kg dry gas, the sorbent residence time was 1.3 seconds, almost twice the base case value, and the inlet SO_2 concentration was 3,000 vppm. A conversion of roughly 50% was observed. Another run was made to study whether improved desulfurization might be achieved by rotating the sorbent eductor 180° such that the initial spray of sorbent was countercurrent to the flue gas flow. The impetus for this was the observation that practically all of the reaction occurred very shortly after sorbent injection. It was felt that the brief period during which the sorbent was being accelerated before reaching the velocity of the entraining gas might be important, given that the external film mass transfer coefficient would be higher than once the relative velocity between the solid and gas was zero. With counterflow injection, the sorbent would exit from the eductor, decelerate as it moved in opposition to the gas, reverse direction, and finally accelerate to its terminal value. In addition, it was expected that the radial dispersion of the sorbent would be different from that of the cocurrent mode during the brief period just after injection and that this might have a measurable effect. However, when the run was made at base case conditions, the conversion observed was the same as in the conventional case.

Other sorbents

Based on the work of Jorgensen et al. (1987) and Keener and Davis (1984), sodium-based sorbents such as sodium bicarbonate and sodium sesquicarbonate may be more effective for SO_2 removal than $Ca(OH)_2$, but are not favored because of economics. Sodium sesquicarbonate was tested at base case conditions. The SO_2 conversion measured for this sorbent ranged from 27 to 39%, which is higher than that found for $Ca(OH)_2$ at the same conditions in spite of the fact that its specific surface area was much smaller than that of $Ca(OH)_2$ and agrees reasonably well with that reported by Seeker et al. (1986) in which 20 to 40% SO_2 conversion was achieved at conditions approximating those used here. On the other hand, when a similar run was made using calcium carbonate, $CaCO_3$, negligible desulfurization was observed.

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