



Project Summary

Humidification of Flue Gas to Augment SO₂ Capture by Dry Sorbents

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In a coal-burning power plant, humidification of the flue gas in a low temperature duct is a possible way to increase SO₂ removal by dry calcium-based sorbents. In particular, humidification may be a desirable modification of EPA's LIMB process, which is based on the injection of limestone or hydrated lime in the furnace; it could augment SO₂ removal by adding post-furnace removal to that occurring in the injection zone. Southern Research has investigated certain aspects of low-temperature SO₂ removal in humidified flue gas as part of the research effort funded by the EPA.

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

EPA has been developing the dry-sorbent technology known as LIMB over the past several years as a means of lowering SO₂ emissions from coal-fired power boilers. The acronym stands for Limestone Injection, Multistage Burners. Originally, the process was envisioned as one based on limestone as the specific calcium-based sorbent; currently, however, the process emphasizes the use of hydrated lime — that is, Ca(OH)₂ — as a more reactive sorbent in place of limestone. LIMB based on either sorbent, however, depends on the injection of the sorbent in the furnace at a temperature above 1100°C, which leads to the

calcination of the sorbent and the reaction of the resulting CaO with SO₂ in the presence of O₂ to produce CaSO₄.

The utilization of the sorbent under these conditions does not exceed 25 to 30% on the mole basis and, thus, accounts for removal of 50 to 60% of the SO₂ present at a practical 2:1 Ca/S mole ratio. Such utilization levels are acceptable for retrofit operations in boilers predating new source performance regulations. Still, increased utilization is obviously desirable if it can be attained.

Humidification and cooling of the flue gas in a post-furnace duct, beginning at a temperature of about 150°C, is one conceivable way to enhance the utilization of furnace-injected sorbent. At relatively low temperatures, SO₂ can react with the calcine of limestone or hydrated lime to produce CaSO₃; whereas, at high temperatures in the furnace, it reacts only in combination with O₂ to produce CaSO₄. The critical issue, however, is not temperature and the thermodynamic possibility of sulfite formation but humidification and the kinetic enhancement of low-temperature reactions, which would be slow without humidification.

Humidification is a way to enhance SO₂ removal with furnace injection of dry sorbents and to remove SO₂ with direct injection of Ca(OH)₂ in either the dry or the wet state. Extensive research under the auspices of the Department of Energy has been recently performed and is now continuing on duct-injection processes, which take two basic forms: (1) separate injections of dry Ca(OH)₂ and a water spray, and 2) simultaneous injection of a Ca(OH)₂ and water in a slurry. In either process, the sorbent reaches the particulate collector (ESP or baghouse) in

a dry state, after the water has evaporated. Maintaining proximity to vapor saturation, however, is the key to effective SO₂ removal.

Scope of the Investigation

This research project addressed four topics within the general area of sorbent reaction with SO₂ under conditions of low-temperature flue-gas humidification.

- *Pilot-scale investigation of post-furnace humidification to achieve sorbent activation.* This investigation was carried out with Southern Research's 1 x 10⁶-Btu/h (300-W) coal combustor to support EPA's LIMB demonstration at Ohio Edison's Edgewater power plant at Lorain, Ohio. The central issue was to determine what humidification conditions are required for sulfated calcine from the furnace to undergo low-temperature reaction with SO₂. Is humidification by water vapor alone adequate, or is humidification with a water spray required because of the need for physical wetting of the sorbent particles?
- *Pilot-scale investigation of charge-augmented sorbent humidification (CASH).* Once again, the Southern Research pilot-scale combustor was used to address a question relevant to the Edgewater demonstration. Can opposite electrical charging of sorbent particles and water droplets increase collisions sufficiently to enhance SO₂ removal?
- *Laboratory studies of water-vapor adsorption by Ca(OH)₂ with and without additives.* A brief experimental program was conducted to quantify the effects of certain additives on water-vapor uptake by Ca(OH)₂. If Ca(OH)₂ is to be used in a duct-injection process, use of a deliquescent additive may be desirable. Alternatively, if partially sulfated calcine from furnace-injected sorbent is to be rehydrated outside the power plant and reinjected in a duct process, it may be advantageously treated with a water-attracting additive.
- *Mathematical modeling of humidification and SO₂ removal processes.* A mathematical model was developed to treat two processes: (1) the collision of sorbent particles and water droplets from a spray nozzle, and (2) the capture of SO₂ by the wetted sorbent particles. Interaction parameters considered included particle and droplet

sizes, relative velocities, proximity to saturation residence time, and Ca/S ratio.

Procedures and Results

Mechanisms of post-furnace humidification. The first of the pilot-scale investigations listed above was concerned with how flue gas should be humidified to achieve effective capture of SO₂ in a post-furnace duct. Three humidification procedures were considered: (1) addition of water vapor alone, with separate cooling of the gas by conductive or convective processes; (2) addition of a water spray, resulting in simultaneous humidification and cooling of the gas by evaporation; (3) reinjection of sorbent in an aqueous slurry. The third procedure would provide chemical reactivation of the sorbent — conversion of CaO to the more reactive Ca(OH)₂ — and a humidified and cooled reaction environment. To evaluate these procedures, a large batch of partially sulfated calcine was generated by burning SO₂-doped natural gas in the combustor, injecting Ca(OH)₂ in the furnace, and collecting the resulting solid on a fabric filter at the point of gas discharge to the atmosphere. The solid was then reinjected either as a powder in a low-temperature duct that was humidified with water vapor of spray, or in a slurry. Reaction conditions were adjusted to provide reaction with SO₂ at the same temperature, humidity level, and approach to saturation.

The molar extent of conversion of CaO to CaSO₄ prior to reinjection of the solid, was 18%. The molar increments in conversion produced by further, low-temperature reaction with SO₂ were:

Humidification method	Increment in conversion, %
Cooling to enhance the effect of water vapor already present	1
Cooling and humidification with a water spray	6
Slurrying with liquid water and soray injection	33

Very little reaction of SO₂ with the calcine, producing an increment in conversion of only 1%, occurred when water vapor already present was cooled. A sixfold increase in reaction, giving an increment of 6% occurred when the dry

solid was subjected to the effects of water spray. An increment in excess 30% occurred with slurry injection. Comparison of the results obtained with the water spray and the slurry spray indicates that the extent of low-temperature reaction was controlled by the fraction of sorbent particles actually colliding with water droplets and becoming physically wet. The added increment due to the water spray (5%) divided by the increment due to the slurry spray (33%) indicates a collision efficiency of 15% ($5/33 \times 100 = 15$).

Further experiments were conducted with fresh Ca(OH)₂ injected in the low-temperature duct in place of the partially sulfated calcine. These experiments yielded:

Humidification method	Increment in conversion, %
Cooling to enhance the effect of water vapor already present	9.6
Cooling and humidification with a water spray	12
Slurrying with liquid water and soray injection	28

The results with the hydrated lime differ from those with the partially sulfated calcine primarily in terms of the effects produced by cooling alone and by the combination of spray humidification and cooling. Cooling alone gave utilization of nearly 10% with the hydrated lime but an increment of only 1% with the calcine. The presence of water spray, on the other hand, increased the utilization of hydrated lime only from 10 to 12% but increased that of the calcine from 1 to 6%. Slurrying gave about the same result with both sorbents: a utilization of about 30% totally with the hydrated lime or about 30% incrementally with the calcine.

The primary conclusion from this investigation, insofar as the Edgewater demonstration is concerned, is that water vapor alone is not effective for activating the removal of SO₂ by partially sulfated calcine at low temperature. Humidification of the sorbent with a water spray is more effective, but even its effectiveness is limited by the infrequency of collision between the sorbent particles and water droplets. The rapid and extensive rate of reaction of sorbent in a slurry, even after

very brief contact between sorbent and water, reveals that the key to successful humidification is increasing the frequency of sorbent-droplet collisions.

Water vapor alone is more effective for activating hydrated lime than for activating partially sulfated calcine. Clearly, however, an increased frequency of collisions between Ca(OH)_2 particles and water droplets would be even more effective.

Charge-augmented sorbent humidification. In studies of CASH, the usual procedure was to charge sorbent particles negatively and water droplets positively. The sorbent was injected in the furnace as Ca(OH)_2 with either gas- or coal-firing; it was subsequently charged on passing through a low-temperature duct. Two types of particle chargers were investigated: a disc-type ionizer or a wire-pipe ionizer. Water droplets were dispersed in the gas stream downstream from the particle charger; the spray nozzle was maintained at a high positive potential and thus the droplets were charged at the time of dispersion.

A substantial part of the effort devoted to CASH involved equipment modifications. For example, the disc-type ionizer first used to charge sorbent particle was limited by sparking at low currents; the wire-pipe ionizer was developed to overcome these shortcomings. Furthermore, considerable effort was required to overcome current leakage in the spray unit and ensure adequate charging of the water droplets. Measured charge densities were in the range of 2 to 9 $\mu\text{C/g}$ for the sorbent particles and 0.2 to 2 $\mu\text{C/g}$ for the water droplets.

The usual procedure for determining the effect of CASH on SO_2 removal was to operate the sorbent and water injection apparatus for 20-30 minutes and then activate the two charging devices for a comparable period. The SO_2 concentration at the exit of the humidification zone was monitored continuously during both modes of operation. The effect of CASH was expected to appear as an increase in the slope of SO_2 versus time; generally speaking, however, the effects, if any, were miniscule. Additionally, solids were occasionally collected with and without the charging devices in operation, and the samples were then analyzed to determine the extent of reaction. Comparison of S/Ca ratios in the solids indicated that no difference was produced by charging.

In summary, no favorable effect of CASH on sorbent utilization was evident.

The reasons for this disappointing result are not clear. A possible explanation is

that the attractive force between oppositely charged sorbent particles and water droplets is small; it decreases with the square of the separating distance and is small in comparison with other electrical forces except when the separating distance is of the order of the particle-dimensions. The other electrical forces arise from the lack of precise electrical balance between positive and negative charges, thus creating a net "space charge" field. In the absence of zero as a net charge in the cloud of particles and droplets, an electrical force operates on each, bringing about a separation and deposition on the container walls.

Adsorption isotherms of water vapor. Adsorption isotherms of water vapor on Ca(OH)_2 prepared with and without additives were determined at 60°C using a commercial surface-area analyzer, which gives the absolute pressure of water vapor in equilibrium with a solid. The data were displayed in plots of a) the weight ratio of water absorbed to solid substrate ($\Delta\text{g/g}$) versus b) the relative partial pressure of water vapor (p/p^0 , the fraction of the saturation value). The additives investigated were LiCl , NaCl , Na_2CO_3 , and CaCl_2 , mole/mole for the 1:1 salts and 0.05 mole/mole for the 2:1 salts. Three of the salts (NaCl , Na_2CO_3 , and CaCl_2) have received significant attention as deliquescent additives in Ca(OH)_2 to achieve enhanced SO_2 capture; the fourth salt (LiCl) has not been investigated in this sense but it, like CaCl_2 , is more strongly deliquescent material in the pure state than either NaCl or Na_2CO_3 .

LiCl gave evidence of behaving as a deliquescent additive, as expected, throughout the range humidity values investigated ($p/p^0 = 0.2-0.9$). CaCl_2 , on the other hand, appeared to become deliquescent only at a much higher humidity threshold than expected ($p/p^0 = 0.6-0.7$). Evidently, the deliquescence of CaCl_2 in the pure state is inhibited by the presence of Ca(OH)_2 , which converts the normal chloride to a basic chloride. NaCl , as expected, exhibited deliquescence only in a range of high humidities ($p/p^0 \geq 0.75$). Na_2CO_3 also exhibited weak deliquescence, which suggests incomplete transformation to highly deliquescent NaOH through the double-decomposition reaction: $\text{Ca(OH)}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaOH}$

Deliquescence is clearly not the only mechanism by which so-called deliquescent additives enhance SO_2 capture by Ca(OH)_2 . None of the three compounds found beneficial — NaCl , Na_2CO_3 , and CaCl_2 — provides significantly enhanced water-vapor pickup by Ca(OH)_2 at

humidity levels where they do provide significantly enhanced SO_2 pickup. Deliquescence by some additives may be a contributing factor in SO_2 capture, but some other unidentified mechanism must be important also and must be dominant for these three salts.

Mathematical modeling. A mathematical model was developed to help understand the complex set of mechanisms involved in low-temperature desulfurization processes. The "first-generation" model treats the process in two steps: (1) the "activation" of the sorbent is modeled in terms of the collisions between sorbent particles and water droplets; and (2) the capture of SO_2 by the activated sorbent is modeled in terms of gas-phase diffusion of SO_2 by the sorbent/droplet ensemble, chemically enhanced absorption into the liquid phase, and liquid-phase mass transfer of the reacting species.

The results of the modeling study show that, when lime and water are injected separately, the SO_2 removal efficiency is governed by the degree of sorbent wetting by collisions between sorbent particles and water droplets. The sorbent/droplet collision rate is maximized by making the droplet size and velocity as large as possible. In actual practice, however, the droplet size must be well below the optimum value in order to ensure complete evaporation and avoid wetting of the duct walls. If the humidification process could be modified to allow larger droplets, it would be possible to significantly improve on the sulfur capture achieved.

The sulfur capture is strongly influenced by approach to saturation, Ca/S ratio, residence time, and droplet size and velocity. To maximize SO_2 removal, the approach should be as close as possible. However, it may be difficult to consistently maintain dry duct walls at approaches of less than 11°C. Increasing the sorbent injection rate, or Ca/S ratio, is also beneficial, but reaches a point of diminishing returns due to increased operating cost and particulate loadings. The effect of the latter on ESP performance must also be considered.

Increasing the residence time is beneficial only up to the point of complete droplet evaporation. Conversely, the residence time must be at least sufficient to allow complete evaporation. For more retrofit situations, the residence time will be fixed. This means that the droplet size must be selected to make maximum use of the available time without allowing droplets to reach the ESP. The model can be used to predict the optimum

droplet sizing for a given duct residence time.

Conclusions and Plans for Further Work

The significance of the principal findings are discussed above in the concluding paragraphs on each of the four experimental tasks. Conclusions, stated more succinctly, are:

- Insofar as enhancement of SO₂ capture at the Edgewater demonstration of LIMB is concerned, humidification by water spray will be required. A spray of pure water would suffice if the frequency of collisions between sorbent particles and water droplets could be increased. Otherwise, isolation of partially sulfated sorbent followed by rehydration and reinjection in a spray will be necessary.
- Charge-augmented sorbent humidification (CASH) - entailing the charging of sorbent particles and water droplets negatively and positively, respectively - appears unlikely to enhance sorbent reaction with SO₂ under post-furnace conditions.

- So-called deliquescent additives that are known to enhance SO₂ capture by Ca(OH)₂ under low-temperature conditions clearly must operate to some extent by mechanism other than deliquescence.

- The mathematical model gives an improved appreciation of factors that are critical to SO₂ capture by Ca(OH)₂ when the sorbent particles are subject to wetting. The model gives an improved rational basis for upgrading the performance of duct processes for SO₂ removal.

During the forthcoming Edgewater demonstration of LIMB, with Ca(OH)₂ injected in the furnace, the flue gas will be humidified before it enters the electrostatic precipitator. This will be done to treat the electrical resistivity of the mixture of sorbent-ash solids and improve the efficiency of precipitation. Relatively small increases in SO₂ removal are expected, with the size of the increases depending primarily on the droplet/sorbent collision efficiency. In a pilot-scale adjunct to the full-scale Edgewater operation, humidification will

be tested in conjunction with the low-temperature duct injection of a modified calcium-based solid. This low-temperature process, developed by EPA, is known as ADVACATE; it employs the product of hydrating LIMB sorbent-ash mixtures under pressure and generating a more reactive calcium-based sorbent.

Subsequently, the Department of Energy will use the Edgewater facilities to demonstrate a commercial process based on separate duct injections of Ca(OH)₂ and water. Meanwhile, DOE will be sponsoring a broad research program on generic duct-injection processes, ranging from laboratory-through pilot-scale studies with ultimate full-scale applications in mind.

A specific need during the further research is elucidation of the role of additives in the category known as deliquescent materials, which may or may not be actually deliquescent under the conditions of use, as this report shows. Further studies are needed to elucidate the mechanisms of action so that both the compounds and the conditions of use may be selected more intelligently.

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The complete report, entitled "Humidification of Flue Gas to Augment SO₂ Capture by Dry Sorbents," (Order No. PB 89-169 841/AS; Cost: \$15.95, subject to change) will be available only from:

National Technical Information Service
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