ADSORPTION AS A MECHANISM IN INCREASED SPRAYDRYER FGD EFFICIENCIES USING PRODUCT RECYCLE

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Bench-scale tests were conducted on calcium-based products generated at a nominal 1000 ACFM Spray dryer/fabric filter FGD pilot plant to study their adsorptive behavior. When used the initial products were generated at different reagent stoichiometric ratios. As a result of the analyses of the bench-scale and pilot plant data, it was concluded that the increase in SO2 removal efficiencies observed at the pilot plant due to the product recycle could be due to adsorption of the calcium hydroxide on the surface of the reacted products. It was also hypothesized that the formation of CaCO3 due to the reaction of the Ca(OH)2 with CO2 in the flue gas may have a negative effect on the potential beneficial effects of product recycle.

Overview of Process:

Dry sorbent FGD processes involve injection of a sorbent in powder form or a water-based slurry into the flue gas stream. In powder form, the sorbent is injected into a flue gas duct upstream of a fabric filter. In a slurry type, hereafter referred to as dry FGD, a slurry of reactive sorbent in water is atomized to small droplets of 70 - 200μm diameter by a spinning disk or nozzle atomizer and sprayed into the flue gas bearing SO_2. The flue gas is adiabatically humidified and the slurry is evaporated to form an apparent dry product. For FGD applications the sorbent is often a calcium-based slurry or a sodium solution which is contacted with flue gas containing SO_2 during and following the drying (1). However, the chemical reactions in this process are similar to reactions in wet scrubbers. The presence of CO_2 in

the flue gas and the simultaneous drying that occurs make the dry FGD process more complex.

According to Getler(2), the reactions occur in several steps in the spray dryer and can be described as follows:
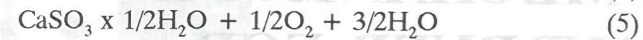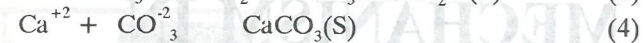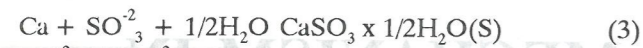
1. Diffusion of SO_2 and CO_2 through liquid film of the atomized $Ca(OH)_2$ droplet containing calcium hydroxide.

2. Dissolution of SO_2 and CO_2 into the aqueous phase:

$$SO_2 + H_2O \quad H_2SO_3 \tag{1}$$
$$CO_2 + H_2O \quad H_2CO_3 \tag{2}$$
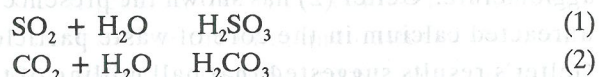
3. Dissociation in alkaline medium and dissolution of the solids.

4. Formation of salts

$$Ca + SO_3^{-2} + 1/2H_2O \quad CaSO_3 \times 1/2H_2O(S) \quad (3)$$
$$Ca^{+2} + CO_3^{-2} \quad CaCO_3(S) \quad (4)$$
$$CaSO_3 \times 1/2H_2O + 1/2O_2 + 3/2H_2O$$
$$CaSO_4 + 2H_2O \quad (5)$$

Since the above reactions require an aqueous medium, the amount of water present in the slurry and spray-dried solids is an important factor. From the above reactions it can be seen that both SO_2 and CO_2 react with the available lime. The partial pressure of CO_2 in the flue gas is at least 100 times that of SO_2 but, due to rapid hydration and oxidation of SO_2 in solution, SO_2 has higher mass transfer rates than CO_2. The mass transfer coefficients for the spray drying process are not known, but liquid phase mass transfer coefficients (air-water interface) for SO_2 and CO_2 are 34420 cm/hr and 20 cm/hr, respectively (3).

The rate of moisture loss by the products is controlled by the approach to the saturation temperature at the outlet to the spray dryer. The closer the approach to the adiabatic saturation temperature is, the longer the evaporation period of the resulting product in higher SO_2 removal efficiencies. It has been reported that a 10°F reduction in the temperature at the outlet of the spray dryer (from 30°F approach to a 20°F approach), could result in an increase of 10 percent in SO_2 removal efficiencies (11). However an approach-to-saturation of less than 20°F results in potential maintenance problems in both the spray dryer and the fabric filter due to the residual moisture content of the dried product. As a result of the short residence time of the droplet and its dried product in the spray dryer, the utilization of available lime has been less than 100%.

Waste product recycle has been shown to be beneficial with regard to increased SO_2 removal efficiencies. According to Gude (4) several features of the products contribute to the observed benefit: recycled material has some unreacted lime, fly ash in the product has available alkalinity, and product provides a surface on which fresh lime particles can agglomerate. Gelter (2) has shown the presence of unreacted calcium in the core of waste particles. Gelter's results suggested that ball milling of the solids would expose the unreacted lime, but limited tests conducted by Stern (5) have shown little benefit from this concept. Similar tests conducted at the
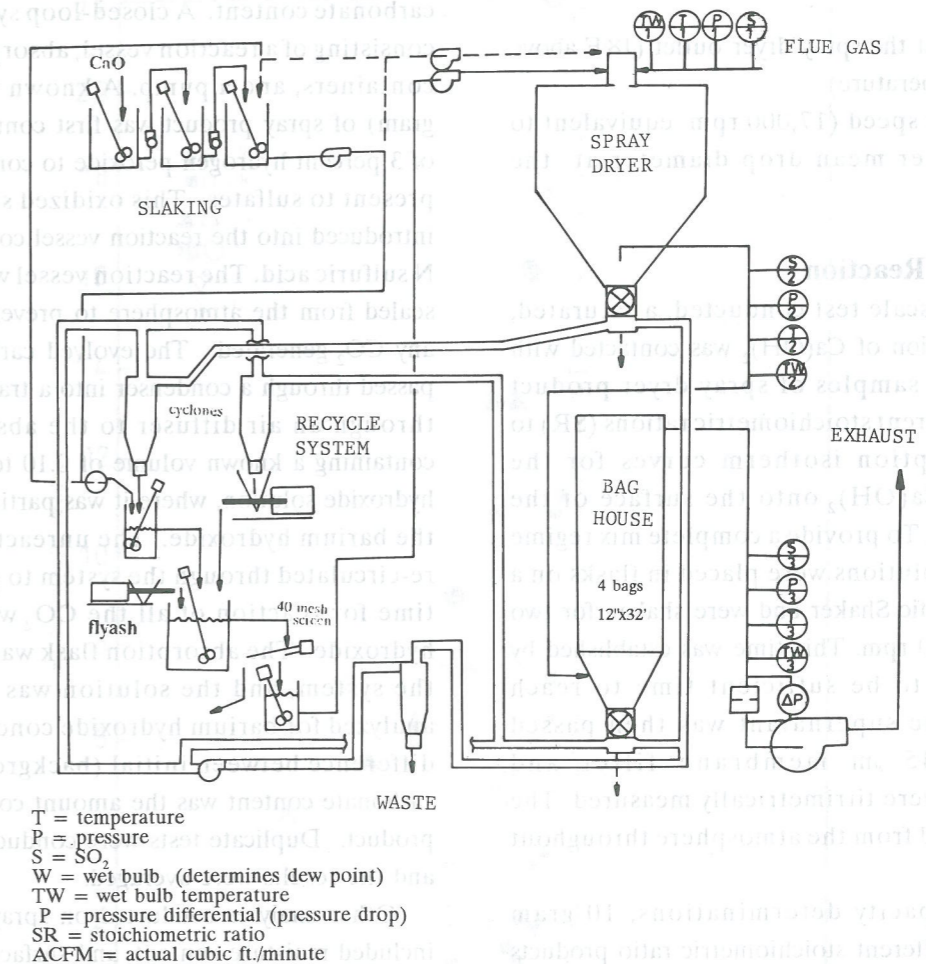
University of Tennessee FGD pilot plant confirmed the benefit of milling but did not attribute it to the exposure of unreacted lime, because analyses of products showed negligible amounts of unreacted $Ca(OH)_2$. One factor in this apparent inconsistency is the product size. Larger products may have a core of $Ca(OH)_2$ which remains unreacted because of the limited penetration of SO_2.

This study was designed to investigate the potential for accumulation of calcium hydroxide on a recycled product during the mixing prior to atomization. Experiments were conducted to simulate the conditions of the slurry portion of the pilot plant facility. Products added here were hypothesized to make more "surface" lime available by adsorbing calcium and thereby reduce the dependency on SO_2 penetration for complete lime utilization. Certain solids have the ability to separate gaseous or liquid components from a flue stream. This ability arises from the unbalanced forces existing on the surface molecules (6). Thus, adsorption is a surface phenomenon and is possibly due to either electrical forces, Van der Waals attraction, chemical reaction or condensation. For the first type, the presence of a charged site on the surface of the adsorbent attracts ions of adsorbate. In physical adsorption, intermolecular forces are at play to concentrate one substance on the surface of another. In chemical adsorption, the adsorbate and adsorbent molecules chemically react, the rate increasing the increase in temperature. Since an actual chemical reaction takes place in this type, no movement of molecules is possible within the interface or on the surface. (7). The scope of this study did not delineate the form of the adosrption but rather just its presence.

Materials And Methods

Pilot Plant: The University of Tennessee dry flue gas desulfurization (FGD) pilot plant is a 1000 ACFM spray dryer/fabric filter SO_2 removal system which utilizes a $Ca(OH)_2$ slurry which is atomized into a seven foot diameter spray dryer via a Stork Bowen rotating disk atomizer capable of speeds of 11,000 to 19,000 rpm. (See figure 1) The flue gas was extracted from one of three stoker-fired boilers via a suction fan located downstream of the pilot plant facility. The SO_2 concentration upstream of

T = temperature
P = pressure
S = SO_2
W = wet bulb (determines dew point)
TW = wet bulb temperature
P = pressure differential (pressure drop)
SR = stoichiometric ratio
ACFM = actual cubic ft./minute

the spray dryer was controlled by injection of gaseous SO_2 from liquid SO_2 cylinders. An adjustable dilution air inlet damper was used to control the temperature of the flue gas upstream of the spray dryer.

Flue gas extracted from the boiler entered the spray dryer concentrically around the atomizer. A set of vanes around the atomizer imparted an angular downward motion to the flue gas. This provided an optimum condition for mixing, reaction, and drying of the water-based $Ca(OH)_2$ slurry with the flue gas. The product-laden flue gas then entered the hopper of the baghouse. Product and fly ash were collected in the bottom of the spray dryer and on the fabric filters. Rotary valves located on the hoppers of the spray dryer and baghouse were used to remove the solids.

Calcium hydroxide slurry was prepared by slaking of quicklime at a 3.5/1 mass ratio of water to lime, followed by dilution to the appropriate concentration. Titration with 3N HCL was used to measure the available hydroxide alkalinity from which the lime concentration was determined. To accomplish recycle tests, a predetermined mass of product was added to the lime slurry in such a way that a 4/1 mass ratio of product to lime (as CaO) was produced. A mixing period of greater than thirty minutes was provided before injection to the atomizer. The SO_2 concentrations at the inlet and outlet of the spray dryer(see Figure 1 - Ports S1 and S2) were monitored by a Lear Siegler SM800 SO_2/NO analyzer. The operating parameters of a typical test were as follows:

1. Inlet temperature range (300 ± 10°F)
2. Inlet SO_2 concentrations (1000 - 1200 ppm)

3. Flue gas volumetric flow rate (1000 ACFM)

4. Lime slurry preparation temperature (200 - 210°F)

5. Final diluted slurry concentration (0.3 - 0.8 lb. CaO/gallon H$_2$O)

6. Temperature at the spray dryer outlet (18°F above the wet bulb temperature)

7. Atomizer disc speed (17,000 rpm, equivalent to 75-85 micrometer mean drop diameter at the conditions tested

Complete Mix Reaction

In the bench scale test conducted, a saturated, particle-free solution of Ca(OH)$_2$ was contacted with 0.10 to 40 gram samples of spray dryer product generated at different stoichiometric rations (SR) to generate adsorption isotherm curves for the adsorption of Ca(OH)$_2$ onto the surface of the reacted products. To provide a complete mix regime of contact, the solutions were placed in flasks on a Brunswick Scientific Shaker and were shaken for two hours at 200 - 250 rpm. This time was established by trial and error to be sufficient time to reach equilibrium. The supernatant was then passed through a 0.45 μm membrane filter and concentrations were titrimetrically measured. The flasks were sealed from the atmosphere throughout the experiment.

For total capacity determinations, 10 gram samples of five different stoichiometric ratio products were contacted with nine 300 ml. solutions of Ca(OH)$_2$. Products were placed in the flasks, 300 ml saturated solutions of Ca(OH)$_2$ were added, reaction flasks were sealed from the atmosphere, and were shaken for 3 to 4 hours. Solutions were vacuum filtered through a 0.45 μm membrane filter and the concentration of a portion of it was measured. The rest of the supernatant was then discarded and new saturation solutions were added, flasks were sealed from the atmosphere, and were shaken for 3-4 hours. This procedure was repeated nine times. For the last one there was no measurable Ca(OH)$_2$ adsorption by products, an indication of exhaustion of capacity. The difference in initial and final concentrations for each set was summed to get total capacity. Double-endpoint titrations were conducted to prevent any misleading interpretations.

Carbonate Analysis

Spray dryer products generated at different stoichiometric ratios were also analyzed for calcium carbonate content. A closed-loop system was set up consisting of a reaction vessel, absorption flask, trap containers, and a pump. A known weight (0.3-0.5 gram) of spray product was first contacted with 3 ml of 3 percent hydrogen peroxide to convert any sulfites present to sulfates. This oxidized sample was then introduced into the reaction vessel containing warm 6 N sulfuric acid. The reaction vessel was immediately sealed from the atmosphere to prevent the escape of any CO$_2$ generated. The evolved carbon dioxide was passed through a condenser into a trap flask and then through an air diffuser to the absorption vessel containing a known volume of 0.10 to 0.15 N barium hydroxide solution, where it was partially reacted with the barium hydroxide. The unreacted portion was re-circulated through the system to provide enough time for reaction of all the CO$_2$ with the barium hydroxide. The absorption flask was removed from the system, and the solution was titrimetrically analyzed for barium hydroxide concentration. The difference between initial (background) and final carbonate content was the amount contributed by the product. Duplicate tests were conducted with sample and the results were averaged.

Other analyses conducted on spray dryer products included moisture content, and surface area. Moisture content was determined as the difference between the weight of the product before and after drying at 103°C and dessication. The surface area was measured by a Micrometrics Model 3300 surface area analyzer which was a modified B.E.T. technique.

Results and Discussion

In order to observe the behavior of FGD products completely mixed conditions, a series of reactors were set up for contacting saturation solutions of Ca(OH)$_2$ and products. The spray dryer product properties and the complete mix adsorption capacities are shown on Table I. A graph of Ca(OH)$_2$ adsorbed as a function of Ca(OH)$_2$ concentration is shown in Figure 2.

As shown in the figure, the adsorptive capacity of the products dramatically increased at near saturation concentrations. Based on this observed behavior at

Figure 2: Isotherm Curves of Spray Dryer Products and Their Total Adsorptive Capacity from Adsorption Column and Complete Mix Reactors
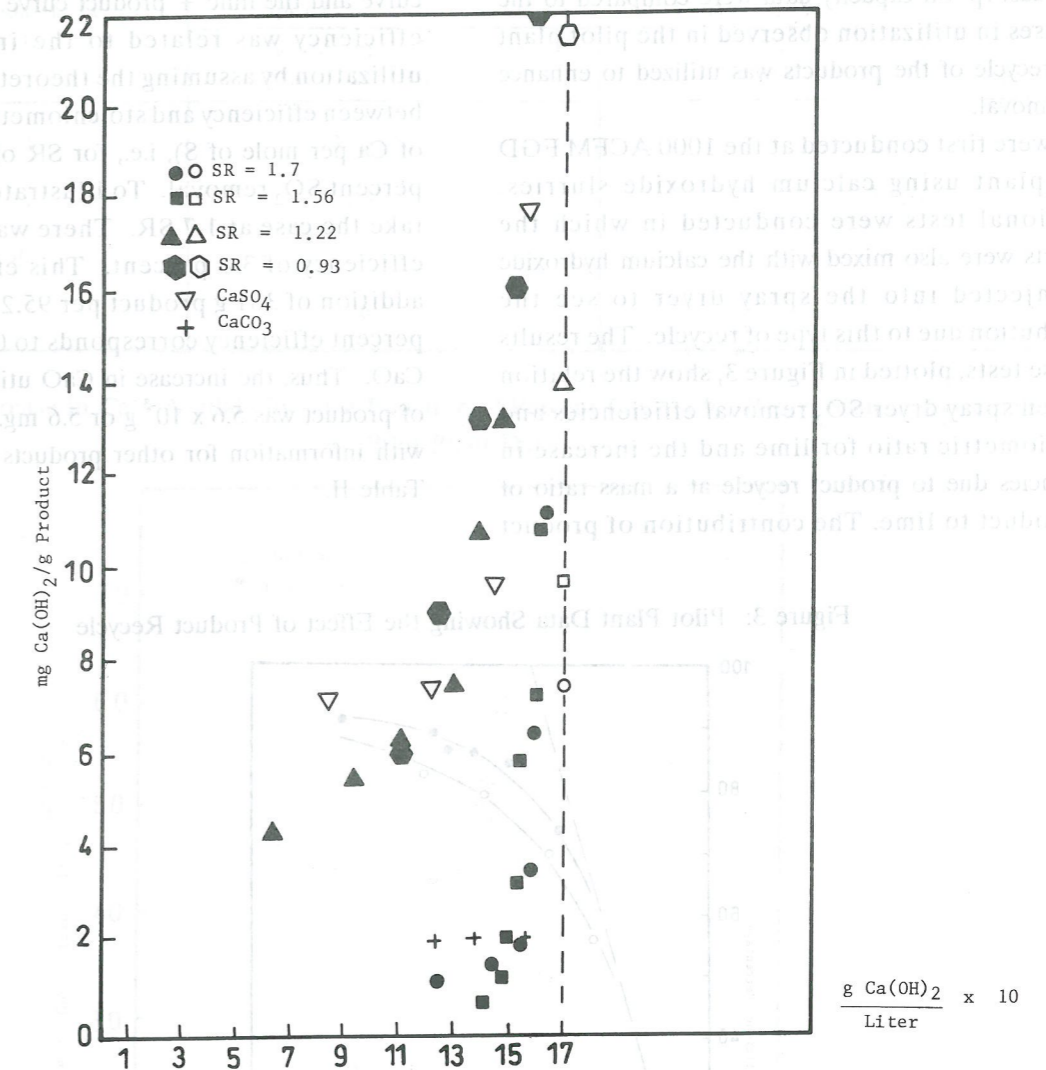
Table I: Properties of Spray Dryer Products Used in the Experiments

Product ID Number	Stoichiometric Ratio*	Spray Dryer Efficiency %	Surface Area m^2/g	CaCO$_3$ Content %	Moisture Content %	Absorptive Capacity mg Ca(OH)$_2$/g product
28	0.93	69.0	15.61	20.6	4	22.5
18	1.22	79.3	21.39	36.0	9	14.0
3	1.56	82.1	20.95	22.1	5	9.5
5	1.70	85.8	11.87	60.2	2	7.1

*Stoichiometric Ratio = mole Ca injected/mole inlet SO$_2$

the saturation concentration, a second set of test were conducted to simulate a consistant saturation concentration. Saturated solutions of Ca(OH)$_2$ (1.65 g Ca(OH)$_2$/liter) were contacted with the products repeatedly until no more Ca(OH)$_2$ was adsorbed by the products. Total capacities obtained as such are

termed "total capacities for complete mix conditions" and are shown by the open symbols in Figure 2. The above adsorption capacity data were compared to the increases in utilization observed in the pilot plant when recycle of the products was utilized to enhance SO_2 removal.

Tests were first conducted at the 1000 ACFM FGD pilot plant using calcium hydroxide slurries. Additional tests were conducted in which the products were also mixed with the calcium hydroxide and injected into the spray dryer to see the contribution due to this type of recycle. The results of these tests, plotted in Figure 3, show the relation between spray dryer SO_2 removal efficiencies and stoichiometric ratio for lime and the increase in efficiencies due to product recycle at a mass ratio of 4/1 product to lime. The contribution of product

recycle was calculated from Figure 3 by taking the difference in the efficiency between the lime-only curve and the lime + product curve. This increase in efficiency was related to the increase in CaO utilization by assuming the theoretical relationship between efficiency and stoichiometric ration (moles of Ca per mole of S), i.e., for SR of 1.0 there is 100 percent SO_2 removal. To illustrate the procedure, take the case at 1.7 SR. There was an increase in efficiency of 3.8 percent. This effect was due to addition of 381 g product per 95.2 g CaO. The 3.8 percent efficiency corresponds to 0.038 SR or 2.1 g CaO. Thus, the increase in CaO utilization per gram of product was 5.6×10^{-3} g or 5.6 mg. This data along with information for other products are presented in Table II.

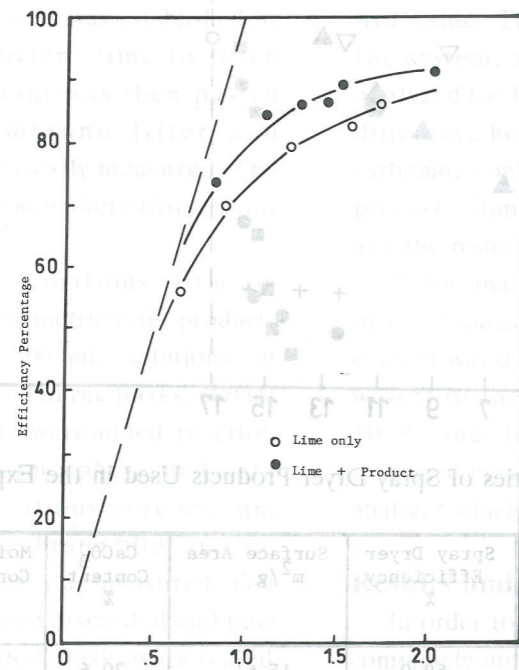**Figure 3: Pilot Plant Data Showing the Effect of Product Recycle**

Table II: Calculation of Increased SO_2 Reaction Produced by Product Recycle

Stoichiometric Ratio	Increase in Efficiency Due to Recycle %	Corresponding Values		Increase in Line Located per Product Added (mg/g)
		CaO Utilization (g)	Product Added (g)	
0.93	8	4.47	207	21.6
1.22	6	3.36	273	12.3
1.56	5	2.80	349	8.0
1.70	4	2.10	381	5.6

Table III: Comparison of Pilot Plant Data and Bench-Scale Absorption Experiments

Stoichiometric Ratio	Specific Increased Lime Utilization, mg. CaO/g product	
	Based on Pilot Plant Testing	Based on Laboratory Absorptive Testing
0.93	21.6	22.5
1.22	12.3	14.0
1.56	8.0	9.5
1.70	5.6	7.1

Figure 4: Increase in CaO Availability as a Function of Percent $CaCO_3$ for Bench-Scale Experiments and Pilot Plant Data
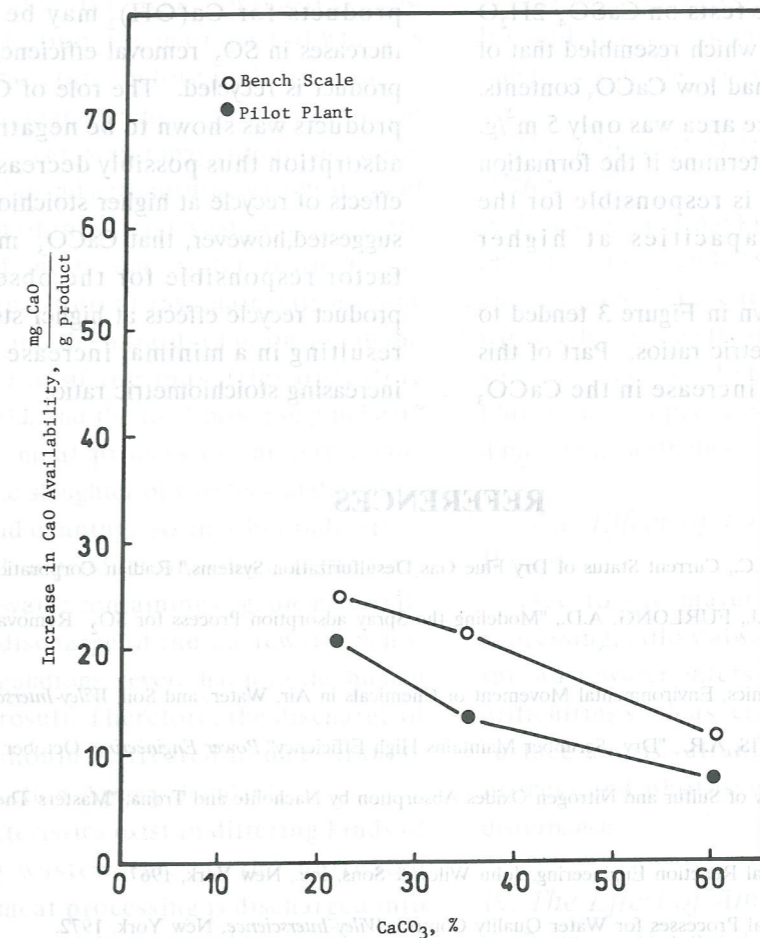
A comparison of the bench-scale adsorption data and pilot plant product recycle data shown in Table III indicates that adsorption could have been responsible for the observed increases in SO_2 removal efficiencies due to product recycle. The bench-scale adsorption capacities are generally higher than the pilot plant increase in CaO availability by up to 21 percent. This 21 percent difference corresponds to only 1 percent efficiency. Considering the scatter of data on both the product recycle and lime-only curves in Figure 3, a one percent error in efficiencies is well within the limits of accuracy.

The adsorption capacities of the recycle products studied in the bench scale and the pilot plants tests also showed a tendency to decrease as the stoichiometric ratio was increased as shown in Figure 4. One possible explanation for this decreased capacity per gram of product was the increased $CaCO_3$ content of the products observed at higher stoichiometric ratios. Adsorption tests were conducted on commercial grade $CaCO_3$ and $CaSO_4$ $2H_2O$ to support the above hypothesis. In the case of the $CaCO_3$, the adsorption capacity was significantly lower than that of the recycle products (see Figure 2). However, the surface area of the pure $CaCO_3$ was only $1 m^2/g$ compared to 15-20 m^2/g for the products. This may have contributed significantly to the decreased capacity. The tests on $CaSO_4$ $2H_2O$ showed adsorption capacities which resembled that of the recycled products which had low $CaCO_3$ contents. In this later case, the surface area was only 5 m^2/g. Further study is needed to determine if the formation and presence of carbonate is responsible for the decreased adsorption capacities at higher stoichiometric ratios.

The efficiency curves shown in Figure 3 tended to converge at higher stoichiometric ratios. Part of this could have been due to the increase in the $CaCO_3$ content and subsequent decrease in adsorption capacity, but some of it may also have been due to short-circuiting in the spray dryer. Also, if there was not enough residence time in the spray dryer, no matter how much lime was injected, no increase in SO_2 removal efficiencies would have been observed beyond a certain point. As shown in Table III, as the stoichiometric ratio was increased, there was an increase in differences between pilot plant and bench-scale adsorptive capacities. This would be expected if there is any short-circuiting since the effect of such a parameter would become more and more pronounced at higher stoichiometric ratios.

The results of this investigation support the hypothesis that the adsorption capacity of spray dried products for $Ca(OH)_2$ may be responsible for increases in SO_2 removal efficiencies found when the product is recycled. The role of $CaCO_3$ formation in products was shown to be negative with regards to adsorption thus possibly decreasing the beneficial effects of recycle at higher stoichiometric ratios. It is suggested, however, that $CaCO_3$ may not be the only factor responsible for the observed decrease in product recycle effects at higher stoichiometric ratios, resulting in a minimal increase in efficiency with increasing stoichiometric ratio.

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