

ADSORPTION OF SULFUR DIOXIDE FROM COMBUSTION GASES
ON A REGENERABLE MOLECULAR SIEVE

Colin Chriswell and Sai Gollakota

Ames Laboratory, Iowa State University, Ames, Iowa 50011

ABSTRACT

A new molecular sieve adsorption process is being developed for removal and recovery of sulfur dioxide from combustion gases. Desirable features of the process include:

- SO₂ accumulation is efficient at temperatures ranging from 50°C to >800°C, at pressures ranging from 1 to 30 atmospheres, and at SO₂ concentrations ranging from 500 ppm to 100%.
- Rates of adsorption are high, bed depth requirements are low, and back pressures are negligible.
- Sulfur dioxide is selectively adsorbed in the presence of major and trace constituents of combustion gases.
- Preliminary evaluation indicate the process will be competitive in costs with wet-lime scrubbing, but also it will be applicable to hot combustion gases that cannot be desulfurized by existing methods.

INTRODUCTION

Well-established, effective, but costly processes exist for flue gas desulfurization. Installation of wet-lime scrubbers on new coal-fired electric plants contribute about 15% to construction costs and consume about 4% of energy inputs to the plant (1). Less expensive alternatives are desirable, but because of the high cost involved, only well-proven techniques are considered for flue gas desulfurization.

Direct coal-fired gas turbines can produce electricity more economically than steam plants (2). Cleanup of high-temperature, high-pressure gases entering turbines is needed to prolong turbine life as well as to meet environmental requirements. Viable processes do not exist for removal of sulfur dioxide from gases at temperatures greater than 1000°F (550°C) and at pressures greater than 10 atmospheres.

During the 1960's, the U. S. Bureau of Mines demonstrated that sulfur dioxide could be removed from flue gases and recovered using molecular sieve adsorbents (3, 4). Union Carbide subsequently developed and commercialized a process called Purasieve S which used molecular sieves for recovering sulfur dioxide from gas streams (5). At temperatures of flue gases (100°-200°C) the molecular sieve processes were effective, capital and operating costs were low, and high-purity sulfur dioxide was recovered as a by-product. However, the processes were not accepted. Attrition rates for the relatively costly molecular sieves were too high. Their alumina skeletons were degraded by corrosive agents in the gas streams.

In 1978, Flanigan and co-workers at Union Carbide developed a new type of molecular sieve now known as silicalite (6). Silicalite is composed of pure silicon dioxide. It is resistant to corrosive agents except for hydrofluoric acid and strong alkalis and is stable to temperatures in excess of 1000°C (7).

Initial studies performed at the Ames Laboratory proved that sulfur dioxide was selectively and quantitatively adsorbed from stack gases and synthetic stack

gases on silicalite (7, 8). The effectiveness combined with the stability of silicalite suggested utility for combustion gas desulfurization.

The objectives of the present work at the Ames Laboratory are aimed towards hot gas cleanup. Studies being performed include the following areas:

- Evaluating the adsorption properties;
- Determining if trace gases are adsorbed;
- Elucidating conditions under which adsorbed sulfur dioxide is converted, in-situ, to sulfur trioxide;
- Determining efficient conditions for regeneration of silicalite and recovery of SO_2 ;
- Evaluating the economic feasibility of the overall process.

EXPERIMENTAL

Adsorbent and Gases - A granular molecular sieve, designated as S-115, was obtained from Union Carbide Corporation and used in all studies. Pure gases and synthetic stack gases were obtained from Matheson.

Adsorption Studies - The apparatus used in adsorption experiments is depicted in Figure 1. A synthetic stack gas at high pressure is mixed with nitrogen to obtain the desired SO_2 concentration. The gas is preheated to the desired temperature and passed through an adsorption bed. At temperatures below 650°C , the adsorbent is retained in stainless steel tubing and adsorption pressures are controlled by a regulator at the bed end. At temperatures greater than 650°C , the adsorbent is retained in quartz tubing and only low pressures (1 atmosphere) are used. Effluents from the bed pass through a 10-cm flow cell in a u.v. spectrophotometer (Varian, Cary D-219), and SO_2 concentrations are continuously monitored based upon absorbance at 284 nm.

Breakthrough Curves - Adsorption studies result in breakthrough curves as depicted in Figure 2. Interpretation of these plots of SO_2 concentrations in effluent gases vs. volume of gas passing through an adsorption bed is performed using established techniques (9, 10). Data obtained are: capacity - the amount of sulfur dioxide accumulated per gram of silicalite; adsorption rate; and minimum bed depth - the bed depth required for efficient adsorption.

Adsorption Capacity - Adsorption capacity determined from breakthrough curves is confirmed by determining the total sulfur content of spent silicalite using a total sulfur analyzer (Fisher).

Desorption of Sulfur Dioxide - Conditions for desorption of sulfur dioxide were determined by thermogravimetric analysis (TGA) of spent silicalite. An aliquot of spent silicalite was placed in a thermal analysis unit (DuPont) and weight was measured vs. temperature under a controlled atmosphere. In addition, studies were performed using a total sulfur analyzer in which sulfur dioxide evolution was determined at discrete temperatures.

RESULTS AND DISCUSSION

Adsorption Parameters. The capacity of silicalite as a function of adsorption temperature is given in Figure 3. As can be seen, below $\sim 350^\circ\text{C}$, the amount of sulfur dioxide accumulated decreases as temperature increases. This is expected. Above 350°C , however, there is an increase in capacity. This indicates a change in adsorbent structure or a different adsorption mechanism, perhaps chemisorption. X-ray diffraction analysis and Fourier Transform Infrared

Spectroscopic studies of spent silicalite reveal no evidence of chemisorption or of structural changes. Thus, the mechanism for adsorption at high temperature has not yet been determined. Even in the absence of a mechanism for high-temperature adsorption, the fact that sulfur dioxide is accumulated at temperatures in excess of 500°C make silicalite uniquely suited for cleanup of hot gases.

For hot gas cleanup, adsorption must also be effective at high pressures. As shown in Figure 4, at 500°C, the capacity of silicalite actually increases by a factor of about two when pressure is increased from one to ten atmospheres. Previous studies indicated that sulfur dioxide is adsorbed on silicalite as a liquid (8). The beneficial effects of pressure are consistent with liquefaction.

As shown in Figure 5, capacity increases as SO₂ concentration increases. With pure sulfur dioxide, the capacity is limited only by the pore volume of the adsorbent. The increase in capacity with increasing SO₂ concentration is of great practical significance for the desulfurization of combustion gases. Combustion of high-sulfur coals, which would lead to higher sulfur dioxide concentrations in gases, would not require proportionally larger desulfurization units.

The rate of adsorption has been found to vary from 6×10^{-4} cm³/gm-m to 22×10^{-4} cm³/gm-m over the conditions studied. High adsorption rates are typical of molecular sieves. Critical bed depth requirements have been found to vary from <1 to 4 cm. This is a consequence of the high adsorption rates. Back pressures created by a 3-m bed depth will be 0.1 psi. This is low, but even lower back pressures could be obtained readily because the required bed depth is less than 0.04 m. Back pressure is of great importance because of the cost of moving massive volumes of gas created in combustion against even small back pressures.

Adsorption of Trace Constituents - Work on the adsorption of trace constituents of combustion gases on silicalite is in progress. This work is of importance because irreversible adsorption of even a trace constituent of a combustion gas on silicalite would lead to a long-term decrease in capacity available for sulfur dioxide accumulation. No gases studied previously are retained as well as is sulfur dioxide. Thus, no problems are anticipated.

In-Situ Conversion of SO₂ to SO₃ - Previous work (8) has shown that sulfur dioxide can be converted to sulfur trioxide during adsorption or desorption on silicalite. Conditions for conversion were not defined. In the present work, conversion has been observed only at temperatures in excess of 650°C with stainless steel containers or in excess of 800°C with quartz containers. Detailed studies have not yet commenced.

Regeneration of Silicalite and Recovery of Sulfur Dioxide - Initial studies on the regeneration of silicalite indicate that thermal desorption in an oxidizing atmosphere results in recovery of capacity. As shown in Figure 6, TGA studies show that the temperature required for desorption of sulfur dioxide is determined by the temperature at which it was adsorbed. This phenomena has not yet been explained.

Preliminary Economic Evaluation - Silicalite is usable for removing sulfur dioxide from hot combustion gases and no other viable process exists, thus silicalite adsorption is the most economical process available. Sufficient data are not yet available for rigorous cost evaluations, but comparisons can be made with wet-lime processes used for flue gas desulfurization. Capital costs for

silicalite adsorption are likely to be much lower than for lime processing. The back pressure of silicalite is less than one-tenth that from lime scrubbers which eliminates the need for blowers. The gas is desulfurized without cooling which eliminates the need for reheaters.

Energy costs for silicalite adsorption will be comparable or less than those for lime scrubbers. Energy required for blowers and gas reheating is eliminated, but energy is needed for desorption of sulfur dioxide. For a worst-case scenario (regeneration at 400°C above adsorption temperature, no heat recovery, low-sulfur coal) approximately 640,000 BTU would be required to regenerate silicalite used to remove SO₂ from gases produced by one ton of coal. This would amount to less than 3% of the energy input.

Slurry disposal costs associated with wet-lime scrubbing are eliminated with silicalite adsorption and modest credits for sulfur dioxide sales are accrued. Because disposal costs are highly site specific and sulfur dioxide prices are volatile, the magnitude of the advantage for silicalite adsorption cannot be evaluated for general cases.

Adsorbent costs for silicalite adsorption or sulfur dioxide are likely to be higher than for lime scrubbing. The costs associated with lime scrubbing include the cost of lime, the availability of limes, and indirectly the costs associated with lime disposal. With silicalite, the predominant cost will be adsorbent attrition. Previous studies with silicalite indicate attrition rates of far less than 0.5% per adsorption/regeneration cycle are obtainable (11). In the present work, attrition rates have not yet been determined. If attrition is less than 0.1% per cycle, adsorbent costs will be comparable with the cost of lime. Determining low attrition rates requires repeated, time-consuming work that is in progress.

CONCLUSIONS

Adsorption of sulfur dioxide on silicalite molecular sieve provides an effective means for removing sulfur dioxide from hot combustion gases. Preliminary data indicate the process will be economically viable. Continued studies to define regeneration conditions precisely and to determine adsorbent attrition rates are in progress.

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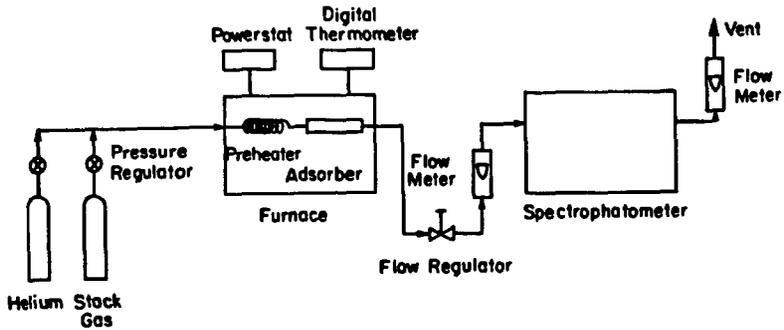


Figure 1. Schematic of apparatus used for SO₂ adsorption from hot, high-pressure gases.

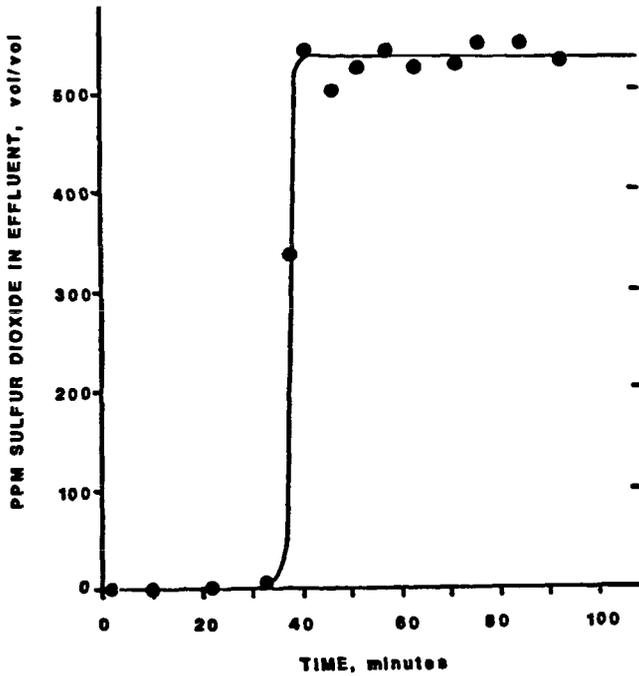


Figure 2. Typical breakthrough curve resulting from SO₂ adsorption on silicalite molecular sieve.

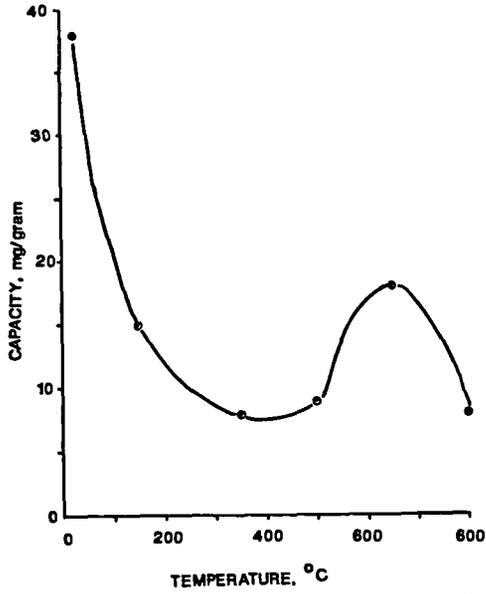


Figure 3. Adsorption capacity of silicalite for SO_2 as a function of adsorption temperature.

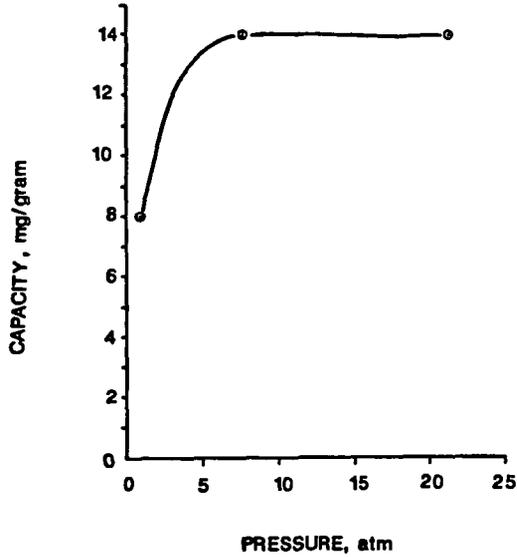


Figure 4. Adsorption capacity of silicalite for SO_2 as a function of adsorption pressure.

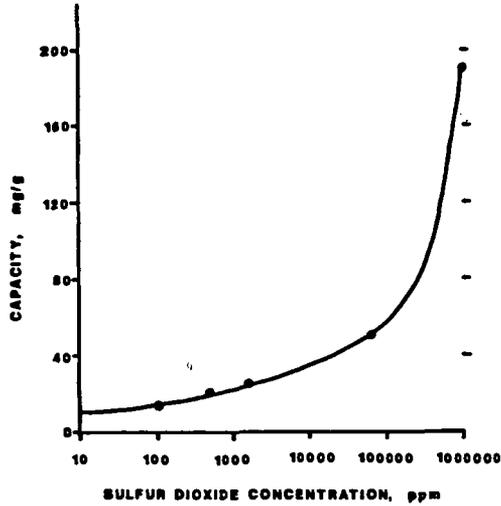


Figure 5. Adsorption capacity of silicalite for SO_2 as a function of SO_2 concentration in influent gas.

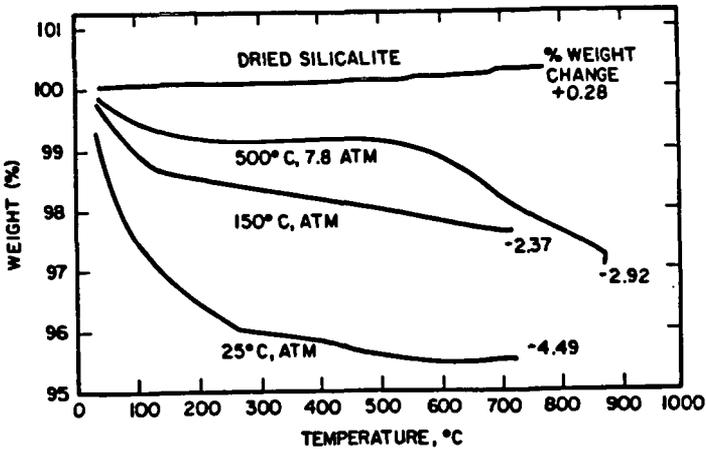


Figure 6. Thermogravimetric analysis and silicalite adsorbents containing SO_2 adsorbed under identified conditions.