

EFFECT OF PRESSURE ON PREPARATION OF SO₂ SORBENT FROM LEONARDITE AND ON SO₂ ADSORPTION BY LIMESTONE AND DOLOMITE AS DETERMINED FROM PRESSURE THERMOGRAVIMETRIC ANALYSIS

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ABSTRACT

Control of SO₂ with limestone or dolomite is state-of-the-art at the present time, but activated carbon in the form of low-rank coal char also has some promise. A process for production of the sorbent includes selection of temperature regime, pressure, activation gas, residence time, and additive. The effect of pressure on the behavior of sorbent during SO₂ removal from flue gas or during production of sorbent carbon is the parameter least found in the literature. Pressure thermogravimetric analysis (pTGA) provides a simple means of studying this effect.

In this study, a fully calcined and a partially calcined dolomite and limestone were tested for SO₂ sorbent characteristics under pTGA at 840°C at 160 psig. The stones were characterized by capacity and rate of sorption of SO₂.

A leonardite was carbonized at 480°C and activated at 800°C under nitrogen at ambient, 150, 300, and 450 psig. Each char was then exposed to a flowing gas mixture containing argon and SO₂. The char produced at lower pressures adsorbed more SO₂ than those produced at successively higher pressures as determined by TGA and confirmed by American Society for Testing and Materials (ASTM) total sulfur measurements.

INTRODUCTION

Combustion of coal provided approximately 55% of the available electric power in the United States in 1993 with the burning of approximately 814,000 tons (1) of coal. As the demand for electricity increases, the demand for coal will also increase, resulting in accelerated depletion of our coal supplies. At present, the quality of the coal mined to produce this electricity, in terms of pollutants such as sulfur, nitrogen, and heavy metals liberated to the environment, is relatively clean compared to much of the remaining minable coal reserves. Government, utilities, and researchers have been aware of the potential environmental consequences of burning "dirtier" coal for more than three decades and have been attempting to deal with the problem through application of known technology and development of newer, more efficient, less costly methods of emission control. Both precombustion and postcombustion methods have been attempted as means to remove potential pollutants from coal before they enter the environment. Industrially, precombustion cleaning of bituminous coal by physical means, e.g., float-sink, froth floatation, magnetic separation, has met with mild success, while cleaning by chemical means, e.g., molten caustic leaching, has been generally discounted as being too costly. Similarly, physical or chemical cleaning of low-rank coal results in excessive cost for the product.

For lack of economically and technically feasible precombustion cleaning methods, most environmental protection from the emissions from coal combustion is currently done by cleaning stack gas from the utility. Sorbents such as limestone (CaCO₃) and dolomite (CaCO₃-MgCO₃) are commonly used for scrubbing SO₂ from the gas. Well-known processes such as those of Pure Air's Advanced Scrubber, Chiyoda's CT-121 Scrubber, S-H-U wet limestone scrubber, LIFAC sorbent injection system, Bechtel's Confined Zone Dispersion Process, AirPol Gas Suspension Adsorption Process, the Babcock and Wilcox LIMB process, and Consolidation Coal's Coolside Process all make use of limestone in either the raw or calcined form as the sorbent for SO₂ emissions (2). Factors concerning the cleaning efficiency of the stones include partial pressure of SO₂, contact time, degree of calcination, surface area, temperature, and surface incidence of inert material. Each of these factors can be studied using thermal analysis techniques. Pressure thermogravimetric analysis is particularly useful for these studies since it allows the determination of the effect of all of these factors.

Similarly, preparation of sorbents such as activated carbon is affected by each of the properties above.

EXPERIMENTAL

Prior to testing, the dolomite and limestone samples were crushed in a hammer mill and then further reduced in size on a Braun mill. The samples were reconstituted by recombining sieve fractions and mixing thoroughly.

Two tests were performed on each of the two CaCO_3 -based samples using the pressure thermogravimetric analyzer (pTGA). The test methods used to determine SO_2 uptake from a mixed gas stream by each sample were as follows:

The samples were crushed in mortar and pestle to pass 20-mesh screen ($0.84 \text{ mm} = 840 \mu\text{m}$). The samples were classified into four size fractions by sieving. Class sizes were 250–840 μm , 150–250 μm , 75–150 μm and $< 75 \mu\text{m}$. To obtain test results which would represent sorption results characteristic of the bulk material, size fractions were recombined prior to pTGA testing.

Method 1. Approximately 20 mg of crushed reconstituted sample was loaded onto the sample pan of an SRE 1990/600 pTGA. The cover was replaced, and the sample chamber was pressurized to 160 psig with N_2 and the gas flow adjusted to nominally 100 mL/min. Heatup was approximately $100^\circ\text{C}/\text{min}$ to 840°C , and the sample was calcined at that temperature for up to 150 minutes. Nitrogen flow was then replaced by a synthetic sulfated combustion gas mixture containing 13% CO_2 , 3.5% O_2 , and 0.25% SO_2 (balance N_2), and flow was continued for at least 60 minutes. The tests were terminated and the system cooled down under flowing N_2 .

Method 2. Approximately 20 mg of crushed reconstituted sample was loaded onto the sample pan of the SRE 1990/600 pTGA. The cover was replaced, and the sample chamber was pressurized to 160 psig with a gas mixture containing 13% CO_2 and 3.5% O_2 (balance N_2) and the gas flow adjusted to nominally 100 mL/min. Heatup was approximately $100^\circ\text{C}/\text{min}$ to 840°C , and the sample was held at that temperature for up to 90 minutes (for half-calcination). The synthetic sulfated combustion gas mixture containing 13% CO_2 , 3.5% O_2 , and 0.25% SO_2 (balance N_2) was then introduced, and the tests were completed as in Method 1.

The effect of pressure on the sorption capacity of activated char prepared from a North Dakota leonardite was studied. The sample was carbonized at 480°C under N_2 at each of four pressures: 450 psig, 300 psig, 150 psig, and ambient pressure. Each sample was activated under N_2 at 800°C at its respective pressure. The resulting activated char was tested for SO_2 adsorption capacity. Each sample analyzed for SO_2 capacity was then analyzed for total sulfur content.

RESULTS AND DISCUSSION

The results of sieving the crushed dolomite and limestone samples are shown in Table 1. Over 75% of the limestone consisted of particles less than 75 microns in size compared with ~57% of the dolomite under the same crushing conditions.

From the results of the sieve fractions, it can be assumed that the limestone would have greater surface area, although not measured in this study, than that of the dolomite since it has a much larger fines fraction. Therefore, the former should have the greater capacity for SO_2 adsorption than the latter. However, from the results of SO_2 uptake in Table 2, it appears that that is not true. In addition, the rate of uptake of SO_2 should also be more rapid on that with the larger surface area, but instead the rates are nearly the same for the fully calcined samples and are identical for the half-calcined samples. If the difference between rates and capacities of the two samples were consistent, differential decrepitation of the materials might explain the apparent contradiction. However, this does not appear to be the case since the rates of uptake are the same while the capacities differ. The presence of the MgCO_3 in the dolomite may be the best explanation for the higher sorptive capacity of the dolomite. Assuming limestone to be CaCO_3 and dolomite to be CaCO_3 - MgCO_3 , there are more metal ions per unit mass in dolomite than in limestone resulting in the potential for more available SO_2 receptor sites. The presence of the MgCO_3 may catalyze the calcination and thus activate the surface more effectively. Additional data are needed to confirm this as a reason for the observed difference in SO_2 sorption between the dolomite and the limestone samples.

The SO_2 adsorbed on the activated char shown in Table 3 indicates that preparation of activated char from leonardite under pressure results in decreased activity toward SO_2 . This is supported by the total sulfur measurements made on the residual activated char after it has adsorbed the SO_2 . The decrease in SO_2 adsorption results from the loss of active sites on the char. The apparent pressure dependence may be due to heavy tar formation at the openings of pores resulting in a loss in total surface area and, consequently, the loss of active sites for SO_2 sorption.

CONCLUSIONS

- Both the fully calcined and half calcined dolomites tested were better SO₂ sorbers than the corresponding calcined forms of the limestone tested.
- Although their capacities for SO₂ differed, the rates at which the dolomite and limestone adsorbed were similar for the fully calcined forms and identical for the half-calcined forms.
- Crushing the stones resulted in a significantly different distribution of size fractions.
- Activated char produced from North Dakota Leonardite under increased pressure had lower activity toward SO₂ than that produced at ambient pressure, probably because of pore plugging by tar unable to boil away.

REFERENCES

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2. U.S. Department of Energy (DOE). "Clean Coal Technology: The Investment Pays Off," Report No. DOE/FE-0291 (Revised), July 1995.

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TABLE 1
Sieve Fractions from Limestones and Dolomite

	Particle Size, μm				
	250-840	150-250	125-150	75-125	<75
Dolomite	0.1	0.7	10.3	31.4	56.8
Limestone	0.1	0.4	3.3	19.5	75.5

TABLE 2
Comparison of Fully Calcined and Half-Calcined Limestone
and Dolomite Toward SO₂ Adsorption

Abbr.	Calcination wt%	Ads. Total wt%	Ads. CO ₂ wt%	Ads. SO ₂ wt%	SO ₂ Ads. CO ₂ Eq. wt%	Ads. SO ₂ %/min.
Fully Calc.						
Doio.	-40.9	34.4	20.4	14.0	15.0	0.22
Lime	-32.6	39.5	31.0	8.5	8.0	0.19
Half-Calc.						
Doio.	-8.3	11.6	--	11.6	14.2	0.16
Lime	2.2	10.5	--	10.5	10.3	0.16

TABLE 3
Effect of Pressure on SO₂ Sorption by Activated Char
Prepared from North Dakota Lignite

pTGA, psig	SO ₂ Adsorbed on Activated Char, wt%	Total S in Spent Char, wt%
450	7.4	4.8
300	7.3	4.7
150	8.1	5.2
Ambient	8.7	6.0