

SULFUR CAPTURE CAPACITY OF LIMESTONES IN COMBUSTION GASES: EFFECT OF THERMALLY INDUCED CRACKING

Ye Liu, Joel L. Morrison and Alan W. Scaroni
The Pennsylvania State University
402 Academic Activities Building
University Park, PA 16802

Keywords: limestone; thermally induced cracking; sulfation capacity.

INTRODUCTION

Limestones and dolostones can be used in coal-fired, fluidized bed power plants as sorbents to capture SO₂ from the combustion gases. The physical properties of calcined sorbents, especially pore size distributions, and the relationship between these properties and subsequent sulfur capture behavior have been subjects of extensive study¹⁻⁴. In general, calcines of limestones and calcines of dolostones differ not only in chemical composition, but more importantly in physical structure, and this is manifested as a difference in sulfation behavior. Prediction of the development of pore volume and characteristics upon calcination, is usually based on the chemical composition of the starting sorbents¹⁻³. These models predict that limestones and dolostones will have different pore structures during and after calcination. They also predict that two limestones or two dolostones with the same chemical compositions will have the same pore structures after calcination.

However, there are numerous examples to show that the pore structures of calcined sorbents differ significantly from those predicted from chemical properties^{1,5}. The reasons for this, and the effect this has on sulfation behavior are not well understood.

The work presented here is a study of the sulfur capture capacities of two limestones with high CaCO₃ contents (99.4 and 98.5, respectively). The limestones are therefore chemically similar, however, they are petrographically different. Significant differences existed between the physical properties of the calcines and in their sulfation behavior. An explanation for the differences is presented.

EXPERIMENTAL

Two limestones with high CaCO₃ contents were collected from different quarries in Pennsylvania (from the Linden Hall and Annville formations). Their physical and chemical properties are given in Table 1.

Calcination and sulfation experiments were conducted in a Perkin-Elmer Series 7 thermogravimetric analyzer (TGA). The reactive gas flow consisted of 15 volume % CO₂, 4% O₂, 2,000 ppm SO₂ and the balance N₂. The flow of 125 standard cubic centimeters per minute (SCCM) was controlled by Brooks Electronic mass flow controllers and was passed downwards over the sample, which was held in a platinum pan of 5 mm diameter. From 4 to 10 mg of sample were used for each run, depending on the particle size. Before starting the rapid heating, the system was thoroughly purged with the reactant gas. To simulate the practical situation in a fluidized bed combustor where sorbent particles are introduced into a high temperature gaseous environment, the samples were heated at the maximum setting of 200 °C/min. to the final temperature of 875°C.

Surface area measurements were performed on an Autosorb-1 gas adsorption system (Quantachrome Corporation) using nitrogen as the adsorbate. The pore size distributions were obtained using an Autocan mercury porosimeter (Quantachrome Corporation).

Morphological analyses were performed on an EM-30 Environmental Scanning Electron Microscope (ESEM) (ElectroScan). Unlike the traditional SEM, the ESEM is capable of examining specimens without coating. In addition, the examination can be conducted on a hot stage where the specimen can be heated up to 1000° C.

RESULTS AND DISCUSSION

It is generally accepted that at atmospheric pressure and high temperature, it is the CaO formed by the thermal decomposition of CaCO₃ that reacts with SO₂ and O₂ according to:



instead of the direct sulfation of limestone by:



Figure 1 illustrates typical TGA profiles of the Linden Hall and Annville samples in a simultaneous calcination and sulfation test. The profiles consist of two characteristic portions. At first, the weight loss due to calcination by reaction (1) dominates. Sulfation starts, however, as soon as CaO is formed. This has been confirmed previously by comparing data obtained with and without SO₂ in the calcining gas⁶. During active calcination, the sulfur uptakes were about 5 % (on a S/Ca molar ratio basis) and 10 % for the Linden Hall and Annville samples, respectively, for the particle size of 60x100 mesh. In the second portion of the TGA trace, the sample weight increases with time due to the occurrence of sulfation. The sulfur uptake by reaction (2) is initially rapid, then gradually decreases as pore plugging occurs⁷.

Despite similar chemical compositions, for the size fraction of 60x100 mesh, the performance of the Annville sample was much better than that of the Linden Hall sample. This can be related to the larger pore volume in pores greater than 1 μm for the Annville calcine, as shown in Figure 2. Ulerich et al.⁴ found higher sulfation capacities for calcines with larger pores even though the pore volume and surface area may have been lower than those of calcines with smaller pores. The larger pores facilitate rapid sulfur capture and produce high sulfur capture capacity due to the more rapid transport of SO_2 to the interior of sorbent particles and because the pore plugging effect is minimized.⁷

The particle size dependency of the sulfur capture capacity for the Linden Hall and Annville samples is given in Figure 3. The S/Ca molar ratio was calculated from the following equation:

$$\text{S/Ca (molar ratio)} = \frac{[W_i - W_0(1 - \text{LOI})] / 80}{W_0 \text{CaCO}_3\% / 100}$$

where:

- W_i : Sample weight during sulfation reaction at time t_i ,
- W_0 : Initial sample weight,
- LOI: Loss on ignition,
- 80: Molecular weight of SO_3 (see reaction 2)
- 100: Molecular weight of CaCO_3 .

The sulfur capture capacity of the Linden Hall sample increases significantly as the particle size decreases. In a 200 minute run, the S/Ca molar ratio increased from 0.07 for 20x25 mesh particles to 0.47 for 200x270 mesh particles; in comparison, the sulfation performance of the Annville sample had a relatively weak dependence on particle size. As the particle size was changed over the same range, the S/Ca molar ratio only increased from 0.24 to 0.36.

Consequently, for the larger particle size, the Annville sample was superior to the Linden Hall sample, while for the smaller particle size, the opposite was the case. This dependency of performance on particle size is important from a practical viewpoint in that a conclusion that one sample is superior to another based on a test of one particular particle size fraction may not be valid for other particle sizes. In terms of the pore size distributions of the 60x100 mesh particles, it is understandable that for larger particles, the Annville sorbent displayed better performance because of the larger pore volume in larger sized pores. For the Linden Hall sample, the pore plugging effect prevents the interior surface from being accessible to SO_2 and O_2 . However, in the case of smaller particles, the above reasoning is not applicable.

The Linden Hall and Annville limestones are chemically similar but geologically different. The Linden Hall is a fine-grained (micritic) limestone and the Annville has undergone recrystallization producing a coarse-grained texture. Their detailed petrographic characterizations are described elsewhere⁵. The petrographic properties of carbonate rocks and their relationship to SO_2 sorption were studied by Harvey and Steinmetz^{8,9}. The grain size was found to be an important indicator of sulfation capacity. Among the carbonate rocks tested (including limestone, dolostone, marble and chalk), in general, the finer the grain size of the rock, the higher the sulfation capacity. However, the limestone samples tested exhibited increasing sulfation capacity with increasing grain size⁹. More recently, Zarkanitis and Sotirchos found that fine-grained Greer limestone had a stronger sulfation dependency on particle size than Georgia marble which consisted of coarse calcitic grains⁷. Morrison et al.⁵ showed using ESEM the occurrence of cracking within the Linden Hall and Annville samples during particle heat up. Extensive cracks developed among the grain boundaries for the Annville sample. For the Linden Hall sample, some particles contained only one or two randomly oriented fractures within the fine-grained structure. The conditions used for these experiments were low pressure (3 torr water vapor) and low heating rate (10 $^\circ\text{C}/\text{min}$).

Figure 4 presents ESEM photographs of Linden Hall and Annville samples, calcined in the TGA in the absence of SO_2 . For the Annville sample with larger grains, extensive cracks occurred along the grain boundaries of the 45x60 mesh particles (Figure 4a). As the particle size was decreased to 200x270 mesh, which is of the order of the grain size, there was essentially no fracturing within the grains, as shown in Figure 4b. Few fractures developed in the Linden Hall particles, as typified by the particles shown in Figures 4c and 4d. It should be noted that the surface structure of the calcined Linden Hall particles is much more porous than that of the Annville particles.

The occurrence of cracking in the larger particles of the Annville limestone benefits the sulfur capture process. It also facilitates rapid calcination. Figure 5 shows the ratio of the time to 50% calcination (t_{50}) between the Linden Hall and Annville samples as a function of particle size. For the 200x270 mesh particles (mean size = 63 μm), the calcination rate of the Annville sample is lower than that of the Linden Hall sample. However, for the 60x100 mesh particles (mean size = 193 μm), the calcination rate of the Annville sample is greater than that of the Linden Hall sample. It is hypothesized that the fractures facilitate the rapid evolution of CO_2 produced by the decomposition of CaCO_3 , thereby decreasing the CO_2 pressure inside the particle, and this increases the calcination rate.

The importance of the occurrence of fractures within the particles during heat up to the subsequent sulfation behavior is supported by the sulfur distributions within the Linden Hall and Annville particles. The sulfur distribution maps, obtained from a Camera SX50 microprobe, are shown in Figure 6. For the Linden Hall sample, sulfur is concentrated in an outer layer around the particles, while for the Annville sample, sulfur penetrated into the particles and is distributed

along the grain boundaries. Reaction took place at the external surface of the Linden Hall particles, gradually closing the pores and blocking the pathway to the particle interior. This leads to significant intraparticle diffusion effects in the vicinity of the external surface. For the Annville sample, however, SO₂ penetrated into the particle interior through fractures along the grain boundaries and reaction occurred at the external surfaces of grains, which leads to intragrain diffusion effects.

CONCLUSIONS

This investigation examined the dependency of the sulfur capture capacity of two high CaCO₃ content limestones on particle size. The extent of sorbent utilization is dependent on the extent of sulfur penetration into the particles or sulfur penetration into the individual grains which comprise a single particle. The occurrence of cracking within particles had a strong impact on the sulfur capture behavior, since it produced significant accessible surface area.

The petrographic properties of sorbents play an important role in determining calcination and sulfation behavior. It has been shown that the cracking pattern is related to grain size, grain-grain interlocking and particle size. The present experiments indicated that cracking occurred between grains rather than within grains, i.e. no cracking occurred in a particle consisting of a single grain. The Annville sample with the larger grains showed a greater cracking tendency. The Linden Hall sample with smaller grains withstood the imposed stress better.

ACKNOWLEDGMENTS:

Financial support for this work was provided by the Pennsylvania Energy Development Authority and the Pennsylvania Aggregates and Concrete Association. Ronald Wincek is thanked for his help in modifying the TGA.

REFERENCES

- 1 Vogel, G. J., Johnson, I., Lee, S. H., Lenc, J. F., Lescarret, S. A., Montagna, J., Nunes, F. F., Shearer, J. A., Snyder, R. B., Smith, G. W., Swift, W. M., Teats, F. G., Turner, C. B., Wilson, W. I., Jonke, A. A. "Supportive Studies in Fluidized Bed Combustion", Argonne National Laboratory, ANL/CEN/FE-77-3, Annual Report, July 1976-June 1977.
- 2 Haji-Sulaiman, M. Z. and Scaroni, A. W. *Fuel*, 1991, **79**, 169
- 3 Rubiera, F., Fuertes, A. B., Pis, J. J., Artos, V. and Marban, G. *Thermochimica Acta*, 1991, **179**, 125
- 4 Ulerich, N. H., O'Neill, E. P. and Keairns, D. L. *Thermochimica Acta*, 1978, **26**, 269
- 5 Morrison, J. L., Liu, Y., Romans, D. E., Pisupati, S. V., Scaroni, A. W. and Miller, S. F. *Proceedings of SO₂ Capture Seminar "Sorbent Option and Considerations"*, National Stone Association, Cincinnati, Ohio, September 19-21, 1993
- 6 Romans, D. E., Liu, Y., Pisupati, S. V. and Scaroni, A. W. *Proceedings of 7th International Conference on Coal Science*, International Energy Agency, Banff, Canada, September 11-17, 1993
- 7 Zarkanitis, S and Sotirchos, S. V. *AIChE Journal*, 1989, **35**, 821
- 8 Harvey, R. D. *Environ. Geology Notes, Illinois State Geological Survey*, **38**, 1970
- 9 Harvey, R. D. and Steinmetz, J. C. *Environ. Geology Notes, Illinois State Geological Survey*, **50**, 1971

TABLE 1 Properties of the Linden Hall and Annville limestones

Limestone	Linden Hall	Annville
BET Surface area (N_2 , m^2/g)	0.215	0.155
Porosity (vol. %)	1.0	1.8
Loss on Ignition (wt%)	43.4	43.2
CaO (wt%)	55.7	55.2
MgO (wt%)	0.41	0.54
SiO_2 (wt%)	0.69	0.74
Al_2O_3 (wt%)	0.31	0.35
Fe_2O_3 (wt%)	0.07	0.05
Other minor oxides (wt%)	0.22	0.12
Total (wt%)	100.8	100.2

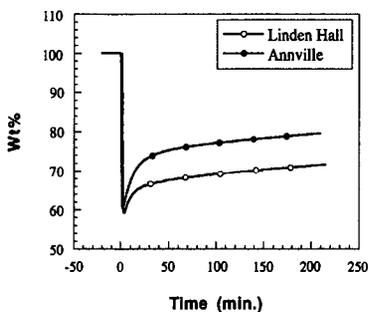


Figure 1 TGA profiles during simultaneous calcination and sulfation of 60x100 mesh sorbent particles

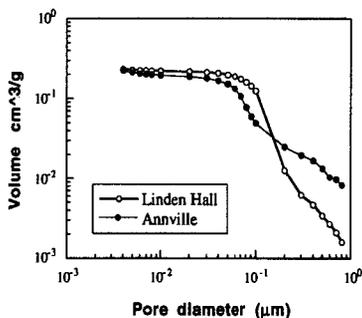


Figure 2 Pore size distributions of calcined 60x100 mesh sorbent particles

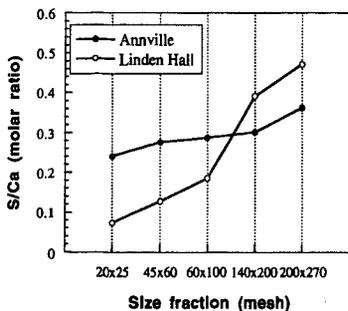


Figure 3 Dependency of sulfur uptake capacity on particle size for a 200 min test

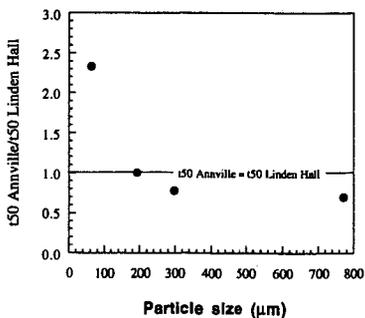
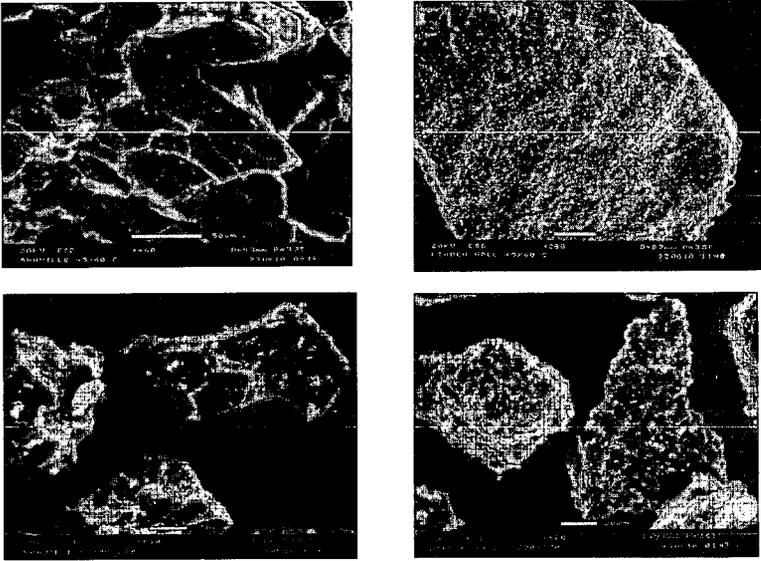


Figure 6 Dependency of the relative calcination time on particle size



a (above) Annville 45x60 mesh
 b (bottom) Annville 200x270 mesh

c (above) Linden Hall 45x60 mesh
 d (above) Linden Hall 200x270 mesh

Figure 4 ESEM photographs of calcined Annville and Linden Hall samples

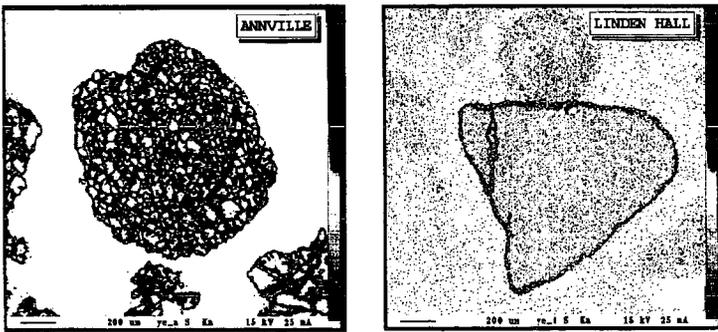


Figure 5 Sulfur distribution maps of sectioned Annville and Linden Hall sulfated particles