

TITLE: Chemistry of Coal-Related Microparticles DATE: 11 November, 1991

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### BACKGROUND

The objective of this research is to develop and apply novel single microparticle techniques to perform simultaneously thermogravimetric analysis and Raman/fluorescence spectroscopies on microparticles of coal (macerals) and sorbents (CaO) used for coal desulfurization. The combination electrodynamic balance/spectrometer system is being used to chemically characterize macerals from different ranks of coal and to explore the chemistry and chemical reaction rates associated with processes involving such microparticles. Rate processes will be examined at elevated temperatures by heating the particles electromagnetically, and a significant part of the research involves the design, construction and utilization of a microparticle heating system.

### WORK COMPLETED

Work has continued on the hardware and software related to the infrared particle heating system and the feedback controller needed for temperature and heating rate control. An extensive study of the chemical reaction between levitated CaO particles and a humid SO<sub>2</sub>/air stream at ambient temperatures was completed, and a paper based on this study was submitted for publication.

The reaction between SO<sub>2</sub> and the sorbent CaO was followed by recording Raman spectra of the electrodynamically levitated microparticle as the reaction proceeded. At ambient temperatures no reaction was detected in the absence of water vapor, but in the presence of a humid gas stream a two-stage reaction was observed. Initially, the hygroscopic CaO particle absorbed water as indicated by an increase in mass. Figure 1 shows the increase in levitation voltage, which is directly proportional to the particle mass, for four different particles. Two of the particles were exposed to humid air alone and two were levitated in a stream containing SO<sub>2</sub>. We note that the curves tend to approach an asymptotic limit of approximately a 50% mass increase.

Raman spectra obtained during the experiment show the formation of Ca(OH)<sub>2</sub> as the absorbed water reacts with CaO. Figure 2 displays the increase in the Raman peak associated with the hydroxyl stretching mode of Ca(OH)<sub>2</sub> for (a) a 60 μm particle calibration particle of Ca(OH)<sub>2</sub> and for (b) a 100 μm reacting particle of CaO levitated in a humid stream of SO<sub>2</sub>/N<sub>2</sub>. The formation of the hydroxide is clearly demonstrated in this figure. If the chemical reaction between CaO and H<sub>2</sub>O went to completion, the mass increase would be 32.11%. Thus, Figure 1 indicates that there is excess water taken up in the pores of the particle.

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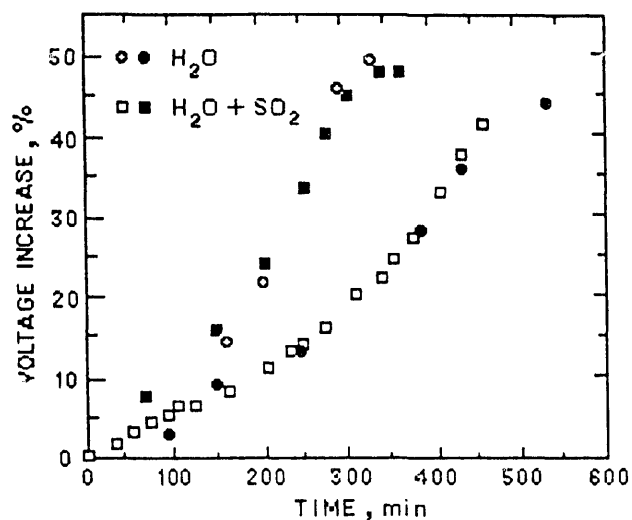


Figure 1. The mass increase of levitated CaO particles with and without SO<sub>2</sub> in the gas stream flowing past the particle.

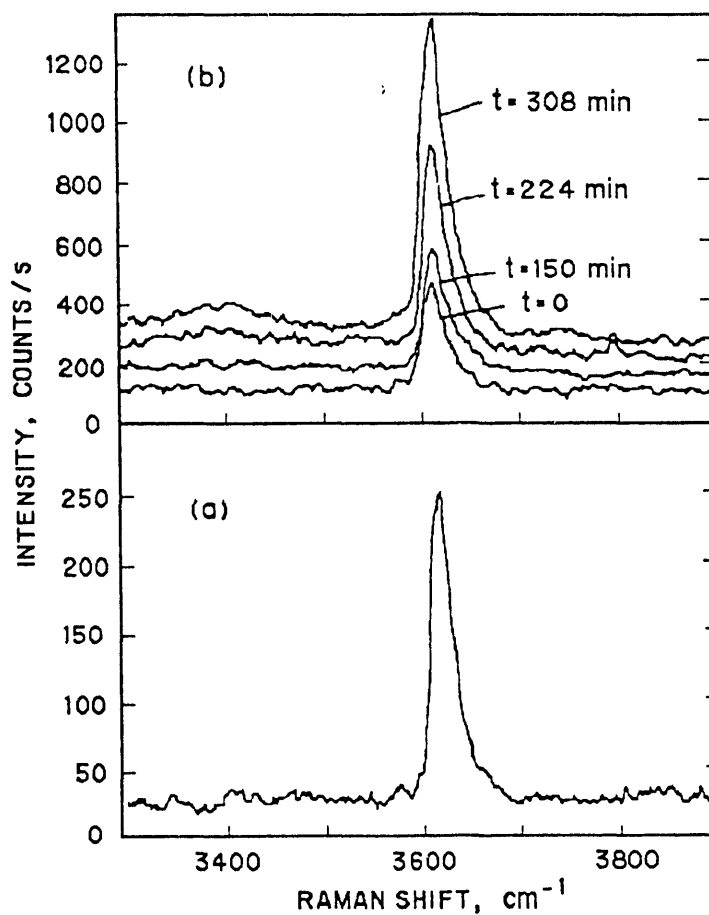


Figure 2. A comparison between the Raman spectrum for the hydroxyl stretching mode of (a) a 60  $\mu\text{m}$  reference particle of Ca(OH)<sub>2</sub> and (b) a 100  $\mu\text{m}$  particle of CaO reacting with water vapor and SO<sub>2</sub>.

The Raman spectra show that the formation of  $\text{Ca}(\text{OH})_2$  is followed by reaction with  $\text{SO}_2$  to form  $\text{CaSO}_3 \cdot n\text{H}_2\text{O}$ , where  $n=1/2$ . It is known that at elevated temperatures  $\text{CaSO}_4$  is formed by the reaction between  $\text{CaO}$  and  $\text{SO}_2$ , and it is clear from our study that the low-temperature reaction proceeds via the formation of  $\text{Ca}(\text{OH})_2$ .

Raman spectra obtained at various times during the reaction are presented in Figure 3 and show the formation of the hemihydrate of  $\text{CaSO}_3$ . If the reaction between the original  $\text{CaO}$  had gone to completion to form the hemihydrate of  $\text{CaSO}_3$ , the mass increase would be 130.3%. Thus, the mass increases indicated by Figure 1 indicate that complete reaction of  $\text{CaO}$  did not occur. It is likely that pore-plugging occurred, and this prevented  $\text{SO}_2$  from reaching unreacted  $\text{CaO}$  within the particle.

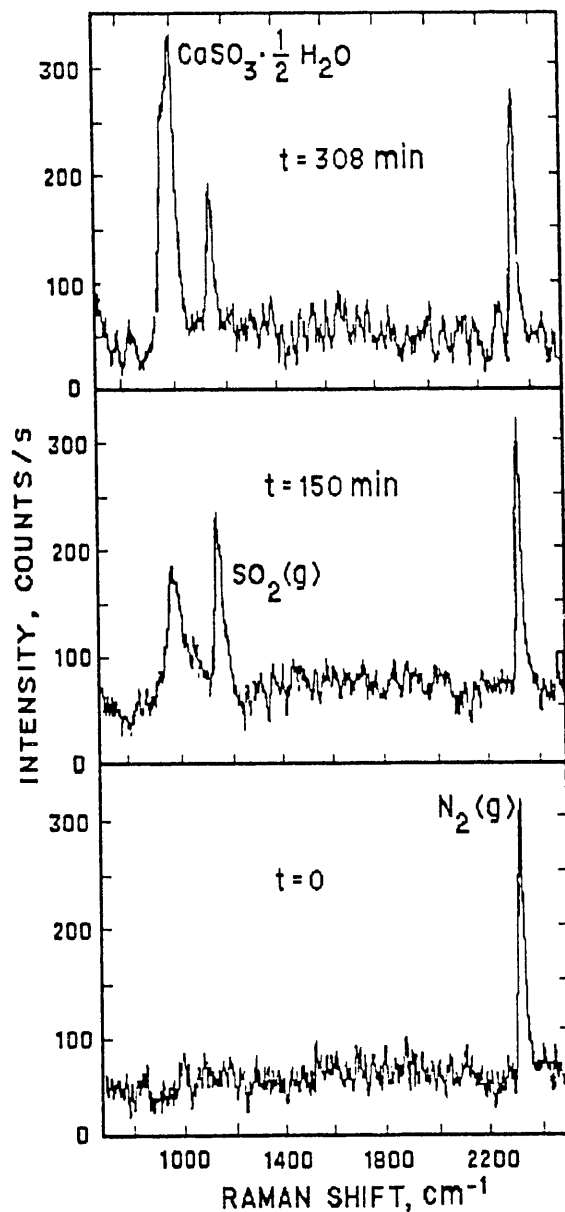


Figure 3. Raman spectra showing the formation of  $\text{CaSO}_3 \cdot n\text{H}_2\text{O}$  for  $n=1/2$  as the reaction proceeds between a  $\text{CaO}$  particle and a humid stream of  $\text{SO}_2/\text{N}_2$ . The peaks corresponding to gas phase  $\text{SO}_2$  and  $\text{N}_2$  are also labeled.

### PLANS FOR THE NEXT QUARTER

Completion of the construction and testing of the particle heating system and its feedback control apparatus is anticipated. Spectroscopic measurements of macerals will be extended to higher temperatures as the particle heating system is tested. Sorbent/SO<sub>2</sub> reactions will also be examined at elevated temperatures.

### PUBLICATIONS DURING THIS QUARTER

Rassat, S. D., and Davis, E. J., "Chemical Reaction of Sulfur Dioxide with a Calcium Oxide Aerosol Particle," submitted to *J. Aerosol Sci.*.

Buehler, M. F., Allen, T. M., and Davis, E. J., "Microparticle Raman Spectroscopy of Multicomponent Aerosols," *J. Colloid Interface Sci.* **146**, 79-89 (1991).

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