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Mechanisms of Coal-Water Mixture
Combustion in Fluidized Beds

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The first quarter of FY 1990 was used to correct problems described in the previous progress report and to initiate a series of experiments on calcination and sulfation of coal-water-limestone mixtures (CWLM) in fluidized beds.

Acid condensation

The failure of an acid mist filter and Perma-Pure drier in the previous quarter made us sensitive to the possible occurrence of acid condensation in all of our experiments. To evaluate this possibility, we disassembled the gas sampling system after each test to inspect for condensation. Despite an expected dewpoint temperature well below room temperature, we regularly discovered small quantities of liquid at the exit of the Perma-Pure drier where the lines were no longer heat traced. From previous experience we have learned that a desiccant such as Drierite cannot be used to eliminate this fugitive moisture: SO₂ is also removed by the desiccant. To prevent this corrosive liquid from entering gas analyzers located downstream, we installed a small impingement filter in the line. Although the condensate collected in the filter can also absorb SO₂ from the gas stream, the surface area for this gas-liquid reaction is rather limited in the filter. Furthermore, titration of this liquid allows us to quantify the amount of SO₂ lost from the gas stream.

In practice, the amount of SO₂ removed by condensate is negligibly small compared to the gas stream concentration. A typical CWM test (43 % water) lasting 1.5 hrs yields only 3.2 ml of condensate with a pH of 2. Our calculations indicate that this represents a 0.0008% reduction in SO₂ concentration when burning CWM without sorbent and only a 0.003% reduction when burning CWM with sorbent. Accordingly, we can neglect this correction to SO₂ readings. After this determination, we were confident to proceed with our calcination and sulfation tests.

Calcination/Sulfation Tests

Hypothesis: CWLM has better sorbent utilization than dry coal and limestone.

Some researchers [1,2] suggest that addition of limestone directly to CWM can improve sorbent utilization compared to burning dry coal in a limestone bed. However, these two approaches to limestone addition have rarely been performed under comparable experimental conditions: observed differences might be attributable to differences in coals or combustion conditions used for the two methods of sorbent addition. Roberts et al. [3] have compared sorbent utilization for CWLM and dry limestone using identical feedstocks under the same combustion conditions. They found no differences in sorbent utilization. However, these tests were performed in a pressurized fluidized bed combustor which displays distinct desulfurization behavior [4] compared to atmospheric combustors of interest in our study.

Test: Coal and limestone were crushed separately in a hammermill fitted with a 1/16 inch screen. The cumulative size distribution of the limestone is given in Table 1. These were blended in proportions to give a Ca/S ratio of 2.0 with added water sufficient to give a solids loading of 57%. The resulting CWLM was burned in a six-inch deep sand bed at 1505 F.

Two dry sorbent tests were performed using 3/8 inch x 8 mesh dry coal to fire the combustor. Both dry sorbents were injected directly into a six-inch deep

sand bed using the pneumatic conveyance system described in a previous quarterly report. The first dry sorbent was the same crushed limestone used to prepare CWLM. We estimated that particles injected into the bed finer than 200 μ m would elutriate from the bed before they could significantly participate in desulfurization. This fine limestone was tested at a bed temperature of 1518 F.

A coarse limestone was prepared by double screening the product of a roller mill to 18 mesh x 35 mesh. The cumulative size distribution for this coarse limestone is compared to the fine limestone distribution in Table 1. We estimate that 99% of this material will not elutriate from the bed until significant attrition occurs. The coarse limestone test was performed at 1498 F.

Results: Fig 1. displays the results of these tests. The SO₂ reduction of 65% for the CWLM is significantly better than the 40% reduction obtained with the fine limestone. However, the 60% reduction obtained with the coarse limestone is comparable to the CWLM. These results suggest that fine limestone is trapped in CWLM agglomerates long enough to influence desulfurization. However, no advantage is indicated for CWLM compared to coarsely ground limestone when the bed is operated at 1500 F.

Hypothesis: Both calcination and sulfation occur within CWLM agglomerates.

The previous results clearly indicate some influence of agglomerate formation on desulfurization. Our previous work has shown that agglomerate residence time is only on the order of one minute [5]. It is not evident whether this is sufficient time for both calcination and sulfation to occur within the agglomerate or whether the environment within the agglomerate is favorable for both processes to occur.

Test: Basu [6] has shown that coal particles burn at temperatures as much as 360 F higher than the surrounding bed, depending on the size of the coal particles. Furthermore, it is well known that an optimal temperature (about 1550 F) exists for limestone utilization. This maxima occurs because both the extent of calcination and the rate of sulfation increase with temperature. Eventually a temperature is reached at which SO₂ reacts to form calcium sulfate before it can deeply penetrate the pores formed by calcination. Sulfate blocks the pores to additional SO₂ penetration and limestone utilization is reduced despite the favorable thermodynamics for calcination at elevated temperatures.

Mei et al. [7] were the first to suggest that sorbent utilization might be degraded if limestone is incorporated into CWM that is burned at conventional FBC temperatures. They reasoned that the limestone will calcine and sulfate at the temperature of the burning CWLM agglomerate rather than at the lower bed temperature. If this is indeed the case, we should be able to show that the optimum temperature for desulfurization when burning CWLM in a sand bed should be significantly below the optimum temperature for dry coal burned in a limestone bed. The hypothesis was tested by repeating the experiments performed for the first hypothesis over a range of temperatures.

Results: Data is presented in Fig. 2 as percent reduction in SO₂ as a function of temperature. No discernable peak emerges for the fine limestone when

burning dry coal although this result may simply reflect the scarcity of data around 1550 F where the peak is expected. By contrast, the data for CWM with added fine limestone clearly peaks at 1460 F, nearly 100 F lower than expected for combustion of dry coal in limestone beds. A similar comparison between CWM with added fine limestone and dry coal with coarse limestone injected separately is given in Fig. 3. The coarse limestone data shows a broad peak between 1500 and 1550 F. Furthermore, it appears that the dry coal burned with coarse limestone will have better sorbent utilization than the CWLM at temperatures above about 1525 F.

We repeated these tests for CWLM with a Ca/S ratio of 1.0. These results are in Fig. 4. The location of the peak is difficult to discern for the limited data, but clearly the optimal temperature is below 1460 F. We conclude that there is good evidence that both calcination and sulfation occur within the agglomerate.

Test: An additional test of the previous hypothesis is to recover CWLM agglomerates from the fluidized bed and subject them to chemical analysis. If significant calcination and sulfation occur in agglomerates, we should detect CaO and CaSO₄ in addition to carbonate. Agglomerates can be recovered by the quench test described in previous progress reports. We have performed such a test but have not yet analyzed the agglomerates.

We must yet answer why the maximum SO₂ capture for CWLM is greater than the maxima for either fine or coarse limestone injected dry into a sand bed. Several possibilities are under investigation.

Hypothesis: The intimate contact of coal and limestone in the agglomerate is responsible for the improved utilization.

Test: CWLM and coal-limestone briquettes should show comparable limestone utilization. These tests are in progress.

Hypothesis: The gasification environment of a fluidized bed burning CWLM favors more complete calcination.

This hypothesis is based on the premise that a gasification environment exists around the calcining limestone. Equilibrium calculations that treat the combustor as a well-stirred reactor do not support this notion: sufficient oxygen exits to yield a very low partial pressure for CO. However, the emulsion phase of a fluidized bed, in contrast to the bubble phase, may be substoichiometric during combustion [8]. Furthermore, several models of burning coal particles suggest that local concentrations of CO can be very high [9]. Accordingly, high water vapor concentrations might promote the water-shift reaction:

and a gasification environment can be envisioned in either the emulsion phase or the boundary layer surrounding the burning agglomerates. We have not devised a method for directly testing for such localized gasification conditions.

The high CO₂ concentrations under gasification conditions will slow the calcination reaction

by shifting equilibrium to the left. Slower calcination might be expected to allow the rate of poor plugging by sulfation to overtake calcination, resulting in lower limestone utilization. However, two other processes may occur which reduce the net rate of sulfation under local gasification conditions. First, H₂ and CO can decompose CaSO₄ to CaO [10]. Accordingly, calcination might proceed to completion before sulfation began to plug pores. Furthermore, under high partial pressures of SO₂ or H₂S, as might exist in burning agglomerates, CaS is the stable sorbent product [10]. The smaller molar volume of this solid compared to CaSO₄ might avoid premature pore plugging. This compound is quickly converted to sulfate upon exposure to oxidizing conditions.

Test: We avoid fundamental questions as to the existence of local gasification conditions and the effects of such conditions on calcinations by simply evaluating the effect on water addition on sorbent utilization. Two tests will be performed. The first will inject water into the combustor when burning dry coal with dry limestone in a sand bed. This test will evaluate the importance of gasification conditions in the emulsion phase. The second test repeats the previous coal-limestone briquette tests but with water injected into the bed. This test will evaluate the importance of local gasification conditions around burning coal-limestone agglomerates (here simulated by briquettes).

Hypothesis: Increased residence time of fine sorbent is responsible for improved sorbent utilization observed in the first test we reported.

Test: Formulate CWLM with coarse limestone. If the hypothesis is true, peak SO₂ reduction should be the same as for dry coal burned with coarse limestone in a sand bed since residence times will be comparable.

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Figure 1

COMPARATIVE PLOT FOR DRY COAL AND CWM

$$C_0/5 = 1/2$$

Figure 2 % SULFUR SORPTION Vs. BED TEMPERATURE

Figure 3 % SO₂ SORPTION Vs. BED TEMPERATURE

Figure 4 % SULFUR SORPTION Vs. BED TEMPERATURE
Ca/S=2/1; COARSE SORBENT

Figure 5 % SULFUR SORPTION Vs. BED TEMPERATURE