

DOE/METC/C-96/7211

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Conference Title:

1995 International Ash Symposium

Conference Location:

Lexington, Kentucky

Conference Dates:

October 23-25, 1995

Conference Sponsor:

University of Kentucky

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FEB 13 1996
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Composition and Chemistry of Particulates from the Tidd Clean Coal Demonstration Plant Pressurized Fluidized Bed Combustor, Cyclone, and Filter Vessel

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INTRODUCTION

In a Pressurized Fluidized Bed Combustion (PFBC)/cyclone/filter system ground coal and sorbent are injected as pastes into the PFBC bed (where combustion occurs); the hot gases and entrained fine particles of ash and calcined or reacted sorbent are passed through a cyclone (which removes the larger entrained particles); and the very-fine particles that remain are then filtered out, so that the cleaned hot gas can be sent through a non-ruggedized hot-gas turbine.

The 70 MWe Tidd PFBC Demonstration Plant in Brilliant, Ohio was completed in late 1990 and underwent a four-year test program as part of the Clean Coal Program of the U. S. Department of Energy (DOE).¹ The initial design utilized seven strings of primary and secondary cyclones to remove 98% of the particulate matter. However, the Plant also included a pressurized filter vessel, placed between the primary and secondary cyclones of one of the seven strings. Thus, for a slipstream of about one-seventh of the total PFBC exhaust gases, final particle removal occurred in the filter vessel.

Coal and dolomitic limestone (i.e., SO_2 sorbent) of various nominal sizes ranging from 12 to 18 mesh were injected into the combustor operating at about 10 atm pressure and 925 °C. The cyclone removed elutriated particles larger than about 0.025 mm, and particles larger than *ca.* 0.0005 mm were filtered at about 750 °C by ceramic candle filters. Thus, the chemical reaction times and temperatures, masses of material, particle-size distributions, and chemical compositions were substantially different for particulates removed from the bed drain, the cyclone drain, and the filter unit.

Accordingly, we have measured the particle-size distributions and concentrations of calcium, magnesium, sulfur, silicon, and aluminum for material taken from the three units, and also determined the chemical formulas and predominant crystalline forms of the calcium and magnesium sulfate compounds formed. The latter information is particularly novel for the filter-cake material, from which we isolated the "new" compound $\text{Mg}_2\text{Ca}(\text{SO}_4)_3$. To

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supplement these data, we also have modeled the gas-sorbent reactions in the pressurized bubbling-bed.

The scale of the Tidd facility allowed collection of data that should be representative of a full-scale commercial plant.

EXPERIMENTAL SECTION

Particulate samples were collected from the filter vessel of the Tidd PFBC Clean Coal demonstration plant in Brilliant, OH.¹ Portions of this material were variously used as received, heated (while open to the atmosphere) at 750 °C, or similarly heated at 925 °C. Leachates from these samples were prepared by extraction with water at 22 °C. The insoluble residues from these aqueous extractions also were analyzed. Powder-pattern and single-crystal X-ray diffraction data were obtained at room temperature. Additional information on compound concentrations, based on the different thermal stabilities of various compounds, was obtained by measurements of weight losses at various temperatures in an (atmospheric pressure) thermogravimetric analyzer (TGA), the DuPont 951/Thermo Analyst 2100. Size distributions for particles larger than 0.045 mm were obtained by standard dry sieving. For particles too small for sieving, aerodynamic particle-size distributions were measured with an Amherst Process Instruments Aerosizer; the stated effective range of this instrument is about 0.7 to 0.00002 mm. For water-insoluble fractions some size distributions also were obtained by a Coulter Multisizer II.

Elemental analyses for magnesium and calcium were performed variously by X-ray fluorescence (XRF), Perkin-Elmer 5000 atomic adsorption (AA) spectrometer, and Dionex Ion Chromatograph (IC); silicon and aluminum analyses also were by AA. A Leco SC-432 DR instrument and XRF were used for total sulfur, and the ASTM D 2492-84 method was utilized to distinguish the forms (pyritic, sulfite, and sulfate) of sulfur.

RESULTS

Satisfactory operation of the Tidd pressurized fluidized bed combustor (PFBC) was not obtained with limestone; however, satisfactory operation was obtained with various dolomites and dolomite particle sizes ranging from 12 to 18 mesh; smaller sorbent particle sizes gave better sorbent utilizations and overall bed performance.¹ Figure 1 illustrates the particle size distribution of the Plum Run dolomite sorbent used for the data of Figures 2-5.

Figure 2 illustrates a typical particle-size distributions for materials (obtained on May 5, 1994) from the PFBC bed-drain, the cyclone-drain, and the filter vessel, respectively. The area under the peak for each material represents 100% of that individual sample (i.e., the peak areas do not represent the relative amounts of material from each source).

The peak in the size distribution for bed-drain material occurred near 1.4 mm, which accounted for almost one-third of the bed material; and the width of the size distribution at peak half-height was about 1.8 mm. The presence of particles (≥ 2.4 mm) larger than those in the sorbent feed stock indicates that some clunker formation occurred around coal-paste agglomerates, caused by melting of fuel minerals during localized temperature excursions in

the bed.

Also illustrated by Figure 2 is the corresponding size distribution of the ash and spent sorbent obtained from the drain of the primary cyclone ahead of the filter vessel. For this material a much narrower size distribution was obtained; the peak in the size distribution occurred near 0.05 mm, and particles of this size accounted for about two-thirds of the cyclone capture. The width of the size distribution at half-height was narrower, only about 0.03 mm. Each sieve size of the cyclone and bed materials in Figure 2 was separately analyzed for calcium, magnesium, sulfur, silicon, and aluminum; and the weight (as the oxide) of each element in each size-range, divided by the total weight of the sample before sieving, was plotted vs. the sieve size. These data for the bed-drain material are plotted in Figure 3; as well as the bed-drain particle size distribution replotted from Figure 2. The calcium utilization measured for the bed-drain material was 50%.

Figure 4 illustrates for the cyclone-drain material the same kind of data that was plotted in Figure 3 for material from the bed drain. For the cyclone-drain material the concentrations of magnesium, calcium, and sulfur were essentially independent of particle size for sizes less than 0.1 mm. The calcium utilization of the cyclone-drain material was 58%, compared to 50% for the bed-drain material. Because the sulfation reaction tends to occur at the surface of the sorbent and the particle-sizes were smaller in the cyclone than in the bed, these calcium utilizations are in accord with qualitative expectations.

The X-ray diffraction patterns of the bed-drain and cyclone-drain materials showed their CaSO_4 to be in the orthorhombic crystalline form.

Aerodynamic particle-size distributions for filter-cake materials are illustrated by Figure 5 (same data as in Figure 1, but plotted in different units) and Figure 6, which show, respectively, the distributions with, and without, the cyclone in place. Removal of larger-sized particles by the cyclone produced a slightly asymmetrical size-distribution centered at about 0.004 mm with a width at half-height of about 0.005 mm (Figure 5). When the cyclone was removed (about one year later, Figure 6), this same 0.004 mm peak was again observed; but a much broader and higher peak of larger particles also was observed.

In contrast to the calcium utilizations found for the bed-drain (50%) and cyclone-drain (58%) materials, the "calcium utilization" (assuming that all $\text{SO}_4^{=}$ were present as CaSO_4) measured for the filter-cake was 160%. The impossibility of this value indicated that not just calcium sulfate was present, but that some form of magnesium sulfate must be forming in the filter vessel, also. The occurrence of a sulfation reaction in the filter vessel was later confirmed by measurements of the SO_2 concentrations in the inlet and outlet gases.² The latter measurements showed that the filter-vessel reaction reduced the SO_2 concentration by 42%. The X-ray powder pattern of the filter-cake material of Figure 5 contained the characteristic lines of orthorhombic CaSO_4 , the same crystalline form as the bed-drain and cyclone-drain materials. In addition, the powder pattern exhibited the lines of a compound reported in the literature^{3,4} to be $\text{Mg}_3\text{Ca}(\text{SO}_4)_4$.

The solubility of orthorhombic CaSO_4 in water is very low; and we were able to extract the magnesium-calcium sulfate in question from the filter-cake with water at 22 °C. (This was confirmed by the disappearance of the " $\text{Mg}_3\text{Ca}(\text{SO}_4)_4$ " lines from the solid residue left by the aqueous extraction.) Elemental analyses of the leachate indicated the correct formula was $\text{Mg}_2\text{Ca}(\text{SO}_4)_3$. The latter stoichiometry was confirmed by the compound density⁵ (obtained from single-crystal X-ray diffraction measurements of the unit cell dimensions) and by the crystal structure (also determined from single-crystal X-ray diffraction data⁶) The filter-cake material contained about 37 wt% $\text{Mg}_2\text{Ca}(\text{SO}_4)_3$, as measured by direct chemical analysis.

ACKNOWLEDGEMENTS

We thank M. Mudd, W. Rinehart, J. Hoffman, and others at American Electric Power for providing plant access and samples; G. Wang for Figures 5 and 6; and L. Carpenter and R. Dennis of METC for assistance in obtaining samples. G.J. Haddad is a National Research Council Associate. This work was funded by Fossil Energy, U.S. Department of Energy.

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Figure 1. Particle-size distribution for Plum Run dolomite used for the data of Figures 2-5.

Figure 2. Particle-size distributions for bed-drain, cyclone-drain, and filter cake materials obtained from the Tidd plant on May 5, 1994.

Figure 3. Weight percents (of the total sample) of Ca, Mg, S, Si, and Al found in various sieved fractions of the bed-drain material, and wt % of the total sample represented by each sieve size.

Figure 4. Same as Figure 3, but for Ca, Mg, and S in the cyclone-drain material.

Figure 5. Aerodynamic particle-size distribution for unagglomerated material collected (May 5, 1994) from the filter vessel.

Figure 6. Aerodynamic particle-size distribution for unagglomerated material collected from the filter vessel, after the cyclone had been removed from service.

Figure 1. Particle-size distribution for Titan Run sludge used for the data of Figures 2 & 3

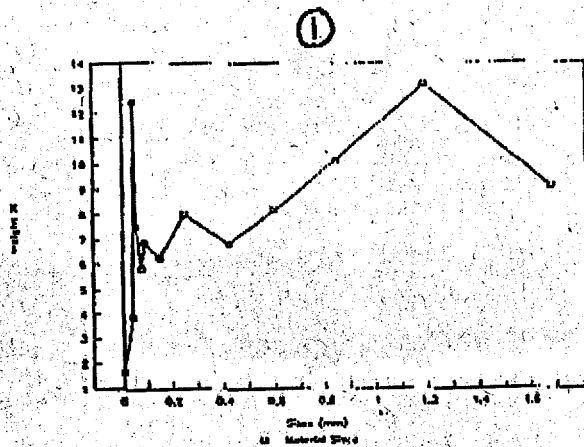


Figure 4. Same as Figure 3, but for Ca, Mg, and S in the cyclone-debris material.

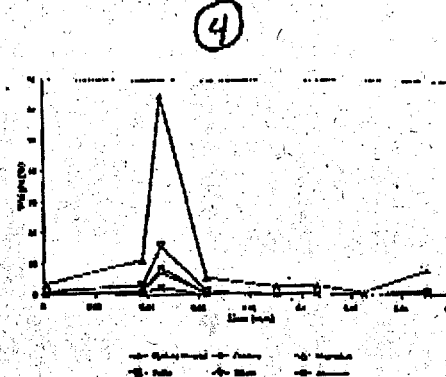


Figure 2. Particle-size distributions for bed-drain, cyclone-debris, and filter cake materials obtained from the Tidd plant on May 3, 1994.

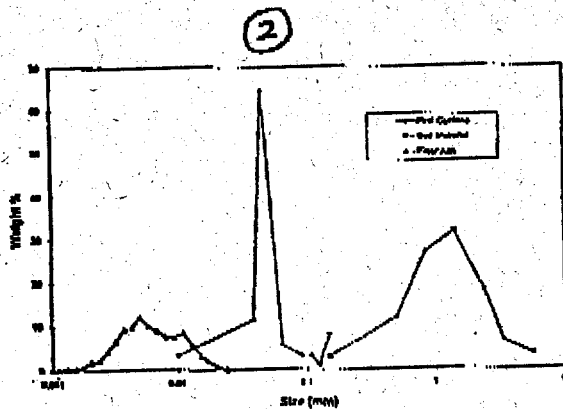


Figure 5. Aerodynamic particle-size distribution for unagglomerated material collected (May 3, 1994) from the filter vessel.

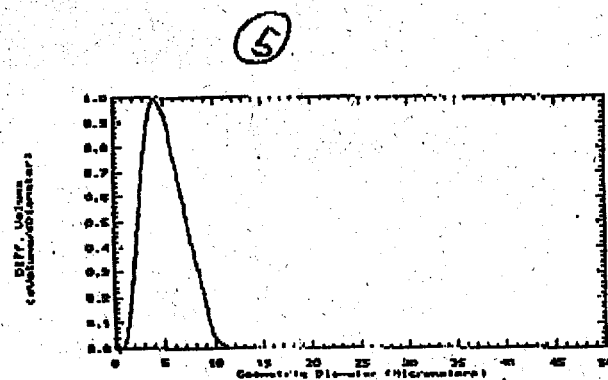


Figure 3. Weight percent (of the total sample) of Ca, Mg, S, Si, and Al found in various sieved fractions of the bed drain material, and wt % of the total sample represented by each sieve size.

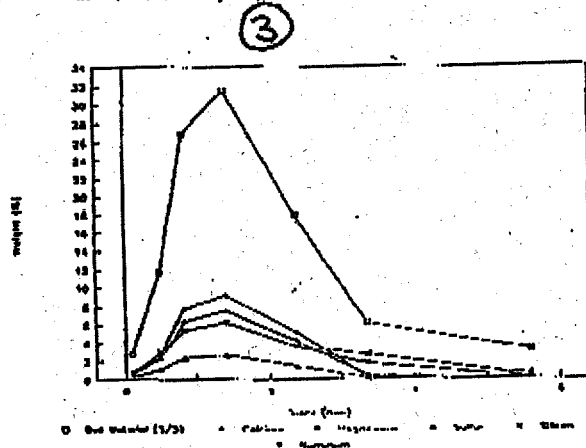


Figure 6. Aerodynamic particle-size distribution for unagglomerated material collected from the filter vessel, after the cyclone had been removed from service.

