VALUE-ADDED PRODUCTS FROM FGD SULFITE-RICH SCRUBBER MATERIALS

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Industrial Collaborators: Southern Illinois Power Cooperative and Duke Energy
Grant No.: DE-FG26-06NT42689
Performance Period: February 1, 2006 to April 10, 2007

ABSTRACT

OBJECTIVES: According to the American Coal Ash Association, about 29.25 million tons of flue gas desulfurization (FGD) byproducts were produced in the USA in 2005. Out of 29.7 million tons, 17.7 million tons were sulfite-rich scrubber materials. At present, unlike its cousin FGD gypsum, the prospect for effective utilization of sulfite-rich scrubber materials is not bright. In fact, almost 17 million tons are leftover every year. In our pursuit to mitigate the liability of sulfite-rich FGD scrubber materials' disposal, we are attempting to develop value-added products that can commercially compete. More specifically, for this three year project, we have the following overall objectives: (1) To thoroughly characterize sulfite-rich scrubber materials, from two different power plants burning different coals, and natural byproducts for their variabilities in physical and chemical properties. (2) To evaluate the chemical stability of the scrubber products, especially under our material fabrication conditions. (3) To optimize the fabrication conditions for the development of wood substitute materials from sulfite-rich scrubber material. (4) To establish manufacturing conditions for the fabrication of load-bearing lumber material from sulfite-rich scrubber materials. (5) To evaluate the long-term stability of our products. (6) To generate technology transfer parameters so that products can move from laboratory to pilot-scale manufacturing. The focus of the project during the first year was directed toward objectives 1 and 2, while in the current phase we are pursuing objectives 3 and 5.

ACCOMPLISHMENTS TO DATE: The major efforts during the last 14 months were focused on: (a) identifying the drying behavior of the sulfite-rich scrubber materials so that fabrication parameters could be optimized, (b) elucidating the thermal characteristics of the scrubber materials by undertaking differential scanning calorimetry (DSC) measurements at $30^oC < T < 510^oC$ and thermal gravimetric (TGA) and differential thermal analysis (DTA) measurements at $50^oC < T < 725^oC$, (c) ascertaining the structural characteristics of the as-received scrubber materials and how potential manufacturing steps would alter the structural parameters, (d) determining the total mercury concentration in the scrubber materials and exploring whether there was any potential of mercury re-emission during value-added product manufacturing, (e) analyzing the natural byproduct additives' structural and thermal behavior by conducting *in-situ* high temperature diffuse reflectance Fourier transform infrared (IHTDR-FTIR) at $25^oC < T < 450^oC$, and (f) formulating wood substitute composites from sulfite-rich scrubber materials. The following summarizes our experimental outcomes: (1) Gravimetric measurements suggested that water was rapidly lost at ambient temperature from the scrubber cake for the first 24 hours, and thereafter there was a dramatic decrease in the rate of water evaporation. However, for our product manufacturing, 24 hours of scrubber cake drying would be adequate. (2) The XRD diffraction of the as-received, but air-dried, scrubber cakes from two different power plants indicated peaks at 11.7^o, 16.1^o, and 16.7^o, thus, suggesting the scrubber cakes to be a mixed phase of $CaSO_3.0.5H_2O$, $CaSO_3.4H_2O$, and

$(CaSO_4)_x.(CaSO_3)_{1-x}.nH_2O$. (3) Our DSC, TGA, and DTA measurements indicated that the products developed from the sulfite-rich scrubber materials would be stable as long as the temperature was < 400^{o}C. (4) The total mercury concentrations in sulfite-rich scrubber material should be determined at least after 14 days of air drying (T < 30^{o}C) time. Our results also suggested that while the scrubber material from one power plant showed large standard deviation of mercury concentration, indicating inhomogenous distribution of mercury that was not the case for scrubber material obtained from another power plant. The higher pressures inhibited the mercury emission from the sulfite-rich scrubber materials even though the samples were subjected to temperatures as high as 250^{o}C. (5) The detailed thermal measurements, i.e., TGA and DTA analyses at 50^{o}C ≤ T ≤ 1250^{o}C, on the scrubber materials suggested that there were four main thermal events by which scrubber materials from both power plants decomposed. Consistent with the DSC results, TGA and DTA measurements also reinforced our suggestion that in our wood-substitute composites, the scrubber material would not decompose at T < 400^{o}C. Above 400^{o}C, half water molecule was lost from the hannebachite crystallites, thus this might retard the flammability of our composites. (6) The exposure of sulfite-rich scrubber material to high-pressure (ambient pressure ≤ P < 3000 psi) and high-temperature (25^{o}C < T < 250^{o}C) resulted in the compression of hannebachite crystallites though they maintained their platelet-like shape. However, it was noticed that higher pressures, i.e., P > 1100 psi, and higher-temperatures, i.e., T > 200^{o}C, generated a considerable number of fines. (7) A series of wood substitute composites were formulated from sulfite-rich scrubber material, natural fibers and proteins, and other additives and flexural strength of as high as 85 MPa (12325 psi).

FUTURE WORK: During the next twenty-two months, the following research activities are planned:

- To generate scientific and engineering parameters needed for demonstrating the feasibility of fabricating wood substitute composites from sulfite-rich scrubber material. This will be accomplished by generating 6” x 6” materials.
- To develop load-bearing lumber materials from sulfite-rich scrubber and natural waste materials. This will be demonstrated by fabricating 10” x 10” products.
- To produce procedural and technical parameters needed to upscale our products for pilot scale manufacturing.

LIST OF PAPERS:

(1) G. Markevicius, R. D. West, V. M. Malhotra, F. B. Botha, and C. E. Miller**,** “Mercury Behavior in FGD Sulfite-rich Scrubber Materials at Elevated Temperatures and Pressures”
ACS Fuel Div. Preprints 52(1), 170-172 (2007).
(2) G. Markevicius, S. Jones, V. M. Malhotra**,** F. B. Botha, and C. E. Miller, “Characteristics of Sulfite-Rich Scrubber Materials and Potential Value-Added Materials from Them”, World of Coal Ash Conference, Covington, KY, May 7-10 (2007).

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