

FINAL TECHNICAL REPORT
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Project Title: **PAPERLESS FGD SCRUBBER SLUDGE
STRUCTURAL MATERIALS**

ICCI Project Number: 00-1/3.1C-1
Principal Investigator: Vivak M. Malhotra, Southern Illinois University at
Carbondale
Other Investigator: Samuel Amanuel, Southern Illinois University at Carbondale
Project Manager: Dr. Francois Botha, ICCI

ABSTRACT

The focus of this project is directed toward developing technology which would harness the natural resources of the State of Illinois in developing environmentally friendly, but marketable recyclable paperless byproduct structural (RPBS) composites. These would be formed from sulfate-rich scrubber sludge from the CWLP (City Water Light & Power, Springfield, Illinois) plant. In pursuit of this goal, two different types of RPBS materials were developed, i.e., conventional-strength paperless wallboard composite and high-strength paperless structural composite. The following experiments were undertaken: (a) We designed and built 10" x 10" x 0.2" and 12" x 12" x 1" dies for the fabrication of RPBS composites. (b) We extracted microfibrils and evaluated their physical structure using SEM technique. (c) X-ray diffraction (XRD) and Fourier transform infrared (FTIR) characterization of the crystallization behavior of sulfate-rich scrubber sludge under pressure as a function of the formation temperature was monitored. (d) High temperature oxidation behavior of sulfite-rich FGD scrubber sludge was studied at $50^{\circ}\text{C} < T < 1100^{\circ}\text{C}$ using the technique of differential thermal analysis (DTA) so that cheap but effective conversion of sulfite-rich sludge to sulfate-rich sludge could be accomplished. (e) A number of RPBS materials were formed using our 10" x 10" and 12" x 12" dies and were subjected to dynamic mechanical analyzer (DMA) and flexural strength measurements to probe the effects of the various variables on the strength of our conventional-strength paperless and high-strength paperless materials. We were successful in developing conventional-strength paperless wallboards, which were stronger than commercial papered wallboard materials. Moreover, our wallboards could directly be painted and could be repaired once mounted. On the other hand, our high-strength paperless structural material was 7.5 times stronger than commercial wallboard and could be mounted in water sensitive areas.

EXECUTIVE SUMMARY

Objectives: The main objectives of this project were:

- (a) To design and fabricate a 10" x 10" x 2" molding die for the formation of recyclable paperless byproduct structural (RPBS) composites.
- (b) To enhance the mechanical strength of our 8' x 6" x 0.2" and 10" x 10" x 0.2" paperless structural material by systematically changing water-to-scrubber sludge (w/s) ratio, formation temperature, and pressure.
- (c) To further enhance the mechanical integrity of our 8" x 6" x 0.2" and 10" x 10" x 0.2" RPBS materials, fabricated from sulfate-rich scrubber sludge, by incorporating naturally occurring additives.
- (d) To explore strategies for the air oxidation of sulfite-rich scrubber sludges into sulfate-rich sludges.

Introduction: About 22 million tons of FGD scrubber sludge are currently produced in the U.S. every year. Most of it is disposed in the landfills near power plants. In Illinois, Indiana, and Western Kentucky 6 million tons of wet scrubber sludge are currently produced. About 7,000 MW of additional capacity is expected to be wet scrubbed in the near future in response to the Clean Air Act Amendments of 1990; and this will further increase the amount of wet scrubber sludge produced annually. At present only about five percent (5%) of wet scrubber sludge is utilized nationally. Most of the FGD scrubber sludge, which had found some use in Portland cement, agriculture, and plaster, is sulfate-rich sludge. The wallboard industry is reluctant to use FGD by-product gypsum because of the impurities, both organic and inorganic, and variations in the product from batch to batch. However, for sulfite-rich scrubber sludge the utilization is much bleaker even though some use as structural fill and as aggregates has been suggested. Therefore, new additional utilization strategies must be developed to effectively utilize FGD wet scrubber sludge.

Brief Summary of Experiments Undertaken: In pursuit of our goal to develop technologies which convert sulfate-rich scrubber sludge into paperless structural materials, we undertook both fundamental and applied studies during this year. Specifically, we have targeted the development of two types of paperless materials, i.e., conventional-strength paperless wallboard material and high-strength structural material. In pursuit of the aforementioned goal, the following measurements were undertaken: (a) We designed and built 10" x 10" x 0.2" and 12" x 12" x 1" dies in the Department of Physics workshop. (b) We extracted microfibrils and evaluated their physical structure using SEM technique. (c) X-ray diffraction (XRD) and Fourier transform infrared (FTIR) characterization of the crystallization behavior of sulfate-rich scrubber sludge under pressure as a function of the formation temperature was monitored. (d) High temperature oxidation behavior of sulfite-rich FGD scrubber sludge was studied at $50^{\circ}\text{C} < T < 1100^{\circ}\text{C}$ using the technique of differential thermal analysis (DTA). (e) A number of RPBS materials were formed using our 10" x 10" and 12" x 12" dies and were subjected to dynamic mechanical analyzer (DMA) and flexural strength measurements to probe the

effects of the various variables on the strength of our conventional-strength paperless and high-strength paperless materials.

Summary of Outcomes : Specifically the following was concluded:

(1) The presence of microfibrils in the epidermis and of cellulose porous network in natural materials has the desired characteristic, which can be exploited to develop paperless wallboard materials.

(2) From the XRD and FTIR characterization studies we ascertained that: (a) Mainly two phases of calcium sulfate, i.e., gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), were present in materials formed at high pressure. For samples fabricated at $T < 130^\circ\text{C}$, gypsum phase was the dominant phase, while the materials formed at $T > 130^\circ\text{C}$ mainly contained hemihydrate. (b) Water-to-scrubber sludge (w/s) ratio had a significant effect on the crystal growth habits of the gypsum in our samples. For w/s ratio of 0.2, largely parallelogram (columnar) shaped gypsum crystals were formed, while for w/s ratio of 0.6, gypsum crystallites exhibited needle-like (acicular) shapes. The needle-shaped crystals showed orientational behavior within the material. (c) The crystal growth rate was found to accelerate at higher temperatures ($T < 130^\circ\text{C}$) leading to the formation of interlocking needles of gypsum crystallites. This interlocking of the crystallites led to the higher fracture strength observed in the case of the materials fabricated at 90°C as compared with those fabricated at 30°C . The abrupt fall in the fracture strength observed in case of the samples fabricated at 130°C could be associated with the dominance of hemihydrate phase in them. (d) At 30°C , the sample fabricated using w/s = 0.6 did exhibit slightly higher fracture strength as compared with the one fabricated with w/s = 0.2. However, the Thermal Mechanical Analyzer results clearly showed that if the samples were fabricated at slightly higher temperatures of around 90°C , then the materials had even higher fracture strength, irrespective of the w/s ratio used.

(3) Our high temperature oxidation measurements ($T < 1100^\circ\text{C}$) on sulfite-rich FGD scrubber sludge indicated that loosely bound water was lost from the sludge at around 157°C , however, the chemically bound water, i.e., $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$, was tenuously bound in the structure and required much higher temperatures ($> 350^\circ\text{C}$) before it was removed from sulfite-rich scrubber sludge. The exothermic reactions at 511, 710, and 878°C could be associated with the oxidation of CaSO_3 . However, it appeared that the major oxidation of the sulfite-rich scrubber sludge to sulfate-rich scrubber sludge occurred at around 700°C . Therefore, if the sulfite-rich scrubber sludge is to be used to make structural materials, then it must be oxidized at $T > 700^\circ\text{C}$.

(4) Water-to-sludge ratio had a profound effect on the mechanical strength of our paperless wallboards. In general, the higher the w/s ratio the lower was the flexural strength and density of the wallboard material fabricated from sulfate-rich scrubber sludge.

(5) The co-blending of the hemihydrate phase of the scrubber sludge and other metal sulfates improved the flexural strength of the paperless wallboard material.

(6) The incorporation of dilute paint during the crystallization process of the conventional strength wallboard resulted in a paperless material, which was smoother and stronger. Moreover, the material could be directly painted without any primer.

(7) Our high-strength paperless structural materials, fabricated from sludge, natural proteins, and microfibrils were stronger (about 30 MPa) than conventional papered wallboards (about 5 MPa).

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