FINAL TECHNICAL REPORT
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Project Title: **MATERIALS FROM FGD SULFITE-RICH SCRUBBER BYPRODUCTS: NEW APPROACHES**


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ABSTRACT


Massive quantities of sulfite-rich FGD scrubber material are produced in the nation. In Illinois, 296,000 tons of sulfite-rich scrubber materials were produced in the year 2000. Almost all of it ended up in landfills, whether disposed of on site or in paid landfill areas. Unlike sulfate-rich scrubber byproduct, there are not many established uses for the sulfite-rich scrubber material. Thus, economically conducive and environmentally sound management of sulfite-rich scrubber material is of utmost importance to Illinois coal-burning electric utilities. In this one-year preliminary project, we explored the potential of using sulfite-rich scrubber material for making molds for the fabrication of metal products, pottery products, and sanitaryware products. Moreover, we also explored the effective, but cheap, oxidation strategies of converting landfilled sulfite-rich scrubber material into sulfate-rich material. Our results indicated that it is feasible to make molding dies for tableware products from sulfite-rich scrubber material though the results were not as encouraging for the sanitaryware products. The strength of the molding material for sanitaryware products, formulated from sludge and FBC fly ash, did not exceed 5 MPa. The air oxidation at $30^oC < T < 450^oC$ was not effective in converting sulfite-rich scrubber material into sulfate-rich scrubber material, though we did develop a different oxidation approach, which seems to be effective in converting sulfite material into sulfate material.


**Pages 1 to 26 contain proprietary information.**

## EXECUTIVE SUMMARY

### OBJECTIVES:

The following were the main objectives of our project:

1. To characterize the sulfite-rich scrubber material from the SIPC power plant.
2. To establish handling parameters for the incoming scrubber material.
3. To build technological parameters for the development of high-strength but porous dies for sanitaryware and tableware manufacturing.
4. To generate a technology for economically oxidizing incoming wet sulfite scrubber material from SIPC power plant.
5. To develop metal-casting dies from oxidized sulfite-rich scrubber material.

Five specific tasks were proposed to accomplish our goals:

- Task 1: To collect scrubber sludge samples from the SIPC power plant and to characterize the as-received scrubber material,
- Task 2: to develop molds and dies from sulfite-rich scrubber material, FBC fly ash, and proprietary resin,
- Task 3: to develop economical oxidation strategies,
- Task 4: to conduct mechanical and chemical testing on molds and dies, and
- Task 5: to undertake initial economic analysis.

### BACKGROUND:

The environmental concerns associated with burning high-sulfur coal by electric power utilities have been recognized, and considerable efforts have been directed towards mitigating the emission of $SO_2$. One of the approaches, which has gained considerable success in reducing $SO_2$ emissions, is wet flue gas desulfurization (FGD) technology. In wet scrubbers, the flue gas enters a large vessel fitted with a spray tower, where it is sprayed with a water-limestone ($CaCO_3$) or water-lime (CaO) slurry. Typically, the concentration of lime or limestone in the slurry is approximately 10%. The calcium in the slurry reacts with $SO_2$ in the flue gas to form calcium sulfite ($CaSO_3$), i.e.,

$$SO_2 + CaCO_3 = CaSO_3 + CO_2.$$

In practice, however, air in the flue gas causes some oxidation of calcium sulfite, and the final product is a wet mixture of calcium sulfite and calcium sulfate, i.e.,

$$Ca(SO_3)_x.Ca(SO_4)_y.zH_2O.$$

According to the American Coal Ash Association, about 25.6 million tons (23.01 million metric tons) of FGD byproducts were produced in the United States in the year 2000. Out of 25.6 million tons of FGD byproducts, 7.3 million tons were FGD gypsum byproduct. On the other hand, sulfite-rich scrubber byproduct's production was 17.9 million tons in 2000. It is believed that 70% of the total FGD gypsum produced is consumed in wallboard, Portland cement, and agricultural applications. The rest of the FGD gypsum—i.e., about 2.2 million tons is landfilled.

The economical and environmentally conducive management of sulfite-rich byproduct is much more bleak. Out of 17.9 million tons of sulfite-rich scrubber material produced in 2000, 3.03 million tons were disposed of as wet byproduct, 12.01 million tons were disposed of in landfills as dry byproduct, and only 0.636 million tons were used for any meaningful purpose at coal-burning electric utility sites. Unlike FGD gypsum, which when sold can garner resources for the electric utilities, most power plants have to pay to dispose of sulfite-rich scrubber material. As the cost of landfilling continues to escalate, the management problem is not just one of economy; it also presents environmental challenges due to the long-term concerns associated with calcium-sulfite landfills. Therefore, it is clear that economically and environmentally friendly uses of the sulfite-rich sludge are needed. In pursuit of this, we are developing technology to convert wet sulfite-rich scrubber sludge into:

- molding materials for the manufacture of sanitaryware products,
- fabrication dies for commercial pottery manufacturing, and
- metal-casting molds for products such as auto parts and other engineered metal.

## EXPERIMENTAL METHODS

In pursuit of our goal of converting sulfite-rich scrubber material into molding dies for tableware and sanitaryware products, we first characterized the incoming scrubber product using differential scanning calorimetry (DSC), X-ray diffraction (XRD), Fourier transform infrared (FTIR) and microscopic measurements. A number of experiments were conducted to formulate our molding materials from scrubber material, water, FBC fly ash, natural fibers, and natural polymers. The formed materials were subjected to mechanical tests to evaluate their suitability for molding materials.

## SUMMARY OF RESULTS

The outcomes are summarized below:

1. Differential scanning calorimetry (DSC) measurements revealed that as-received sulfite-rich scrubber material was largely composed of the sulfite phase. These measurements also suggested that as-received sludge had three types of water, i.e., loosely bonded water which evaporated at 140$^{o}$C and strongly bonded water which resisted vaporization until temperatures exceeded 386$^{o}$C and 417$^{o}$C, respectively.
2. The X-ray data suggested that in addition to $CaSO_3$, some calcium sulfate phase was also present. The FTIR results supported this conclusion.
3. Microscopic analysis of the as-received scrubber material showed the presence of black particles of various sizes in the scrubber material. Initially it was suspected that these particles might be the parent coal. However, vibrational analysis carried out on the handpicked black particles discounted that suspicion. Our

FTIR analysis of these particles suggested that they were actually composed of $CaCO_3$, $CaSO_3$, and some unknown organic phase.

4. Attempts were made to develop tableware molding materials from fixated sulfite-rich scrubber sludge and from a petroleum-based polymer. The flexural strength ranged, depending upon the concentration of the polymer, from 10 MPa to 30 MPa for the green composites. The concentration of the polymer was limited to < 25 wt%. As expected, the concentration of the polymer strongly influenced the strength. However, 4 to 5 wt% polymer gave enough strength for the product to be used for tableware molds. Natural fibers were also incorporated in the mold material so that during the firing additional pores would develop.
5. We also developed green structures for tableware molding material using cheap natural polymers and natural fiber material. This is expected to not only make disposal of molding material environmentally friendly but also considerably reduce the cost of manufacturing the molding dies. By controlling the variables such as water and natural polymers, we were able to attain a strength of about 10 MPa, thus, our product was much stronger than plaster-based molds. This was accomplished with only 3.5 wt% natural polymer.
6. We expended resources in developing sanitaryware molding materials from air dried sulfite-rich scrubber material and FBC fly ash. Irrespective of the variables tested, e.g., solid-to-water content, water's temperature, fly ash concentration, etc., none of the products displayed strength greater than 2 MPa. This strength was inadequate for sanitaryware molding material.
7. Drying the sulfite-rich scrubber material considerably improved the strength of the molds made for sanitaryware manufacturing, thus raising the possibility of using sulfite-rich scrubber material for sanitaryware molds.
8. Economic analysis suggested that there may be considerable demand for the molding material.
9. Our results suggested that air oxidation of fixated or pure sulfite-rich scrubber material at $30^oC < T < 450^oC$ was not effective. The infrared and DSC measurements indicated no sulfates were formed.
10. We did succeed in developing a method, which seems to be effective in converting existing sulfite-rich scrubber material into FGD gypsum. However, this research is ongoing.

**The remainder of this report contains proprietary information and is not available for distribution except to the sponsor of this project.**