Combustion Byproducts Recycling Consortium

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COMBUSTION BYPRODUCTS RECYCLING CONSORTIUM

Ashlines

a program of the National Mine Land Reclamation Center at West Virginia University in cooperation with the U.S. Department of Energy - National Energy Technology Laboratory www.netl.doe.gov

To promote and support the commercially viable and environmentally sound recycling of coal combustion byproducts for productive uses through scientific research, development, and field testing.

Tile, Countertops, and Structural Materials from Sulfate-Rich FGD Scrubber Sludge

V. M. Malhotra and Y. P. Chugh, PIs

One day, a family, maybe even yours, will return home each evening to a house covered in sulfate-rich, flue gas desulfurization (FGD) scrubber sludge materials. The kids will wash up in a bathroom lined with tiles made of scrubber sludge, while the adults prepare and serve the evening meal on a scrubber sludge countertop. And this will all be far more lovely than it sounds.

V. M. Malhotra and Y. P. Chugh, professors at the Southern University of Illinois at Carbondale, have completed a two-year project to develop technology for converting sulfate-rich, FGD scrubber sludge into value-added decorative building materials. The research was funded by the Combustion Byproducts Recycling Consortium (CBRC), the Illinois Department of Commerce

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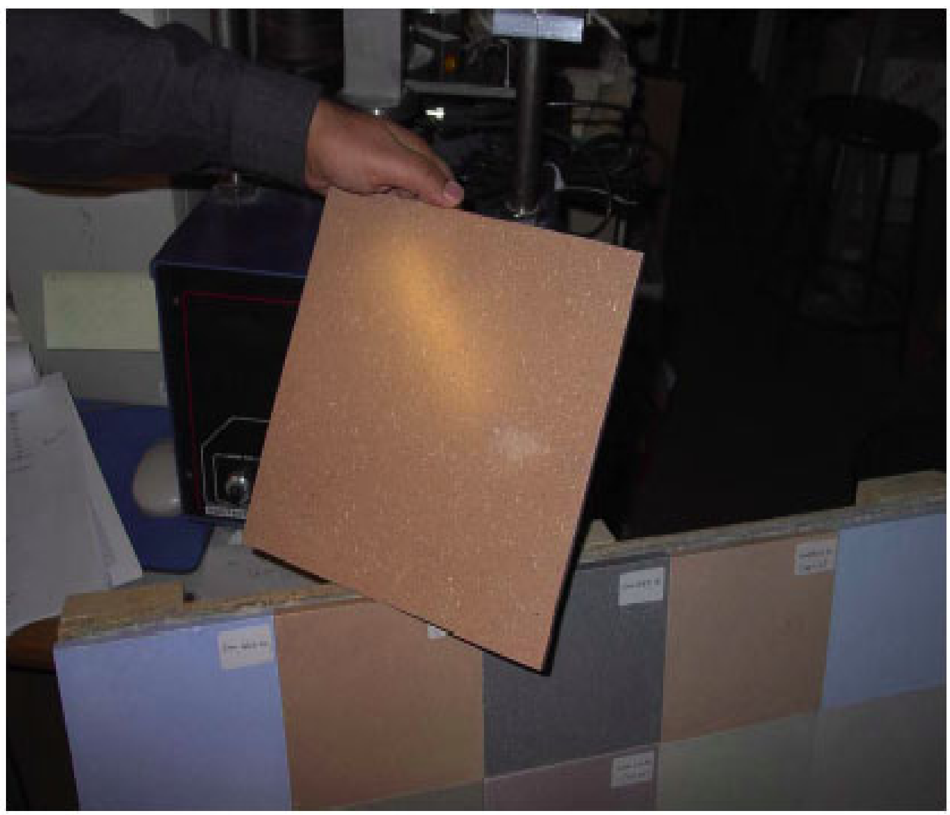


Sample of size 10″ x 10″ x 0.125″ siding fabricated from sulfate-rich scrubber sludge.

Tile, Countertops, and Structural Materials from Sulfate-Rich FGD Scrubber Sludge

(continued from page 1)

and Economic Opportunity through the Office of Coal Development, and the Illinois Clean Coal Institute.

Malhotra and Chugh sought to establish technology for fabricating cost-effective but marketable materials, like countertops and decorative tiles, from the sludge. In addition, they explored the feasibility of forming siding material from the sludge. By the end of the project, they generated several structural and decorative materials of various colors with potential market value.

Background

About 29 million tons of FGD scrubber sludge is currently produced in the U.S. Most of it is disposed of 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.

Since only about five percent of wet scrubber sludge is utilized nationally, and the wallboard industry may be able to absorb only a portion of high-quality gypsum sludge, alternative utilization strategies must be developed to effectively utilize FGD wet scrubber sludge.

In 1989, 21.9 billion square feet of gypsum-based products were utilized in the U.S. along with 1.20 billion square feet of tile materials. The gypsum and tile business together generated about 4.7 billion dollars in 1994 (*U.S. Industrial Outlook 1994,* U.S. Department of Commerce).

FGD technology commonly uses sorbents such as $CaCO_3$ or CaO to scrub SO_2 gas from the flue gases generated by coal burning power plants. Although FGD technology is successful in reducing the SO_x emission, it generates a large quantity of solid residue, called FGD scrubber sludge. FGD residue is generally composed of $CaSO_4.2H_2O$ (gypsum) or $CaSO_3.nH_2O$, depending upon the FGD technology used.

The disposal of about 29 million tons of scrubber sludge is a serious economic problem for the coal utilities. A number of commercial applications of scrubber sludge have been proposed [1–9]. For example,

- road base construction,
- manufacture of wallboard,
- agriculture, and
- friction materials.

Notwithstanding the proposed applications, a large portion of it ends up in landfills. The limited utilization of the sludge has been due to fluctuations in its composition and properties.

The processes involved in manufacturing a commercial product using gypsum commonly employ higher pressures and temperatures. In fact, the hemihydrate phase ($CaSO_4.0.5H_2O$), called plaster, is used as the starting material because of its cementitious properties. A homogeneous paste of this plaster is prepared by mixing it with water in a definite proportion. The paste hardens to generate a highly porous material whose physical and engineering properties are strongly governed by

- the water-to-plaster ratio,
- the water temperature,
- impurities,
- additives and accelerators,
- mode of mixing, and
- extent of mixing.

Thus, the processing parameters have a profound effect on the shapes, sizes, and compaction of the gypsum crystals formed. In fact, most of the physical and engineering properties of these materials are governed by the microstructure of the hardened gypsum, because of the interlocking of the crystals [7–12].

If FGD scrubber sludge is to be used in the manufacturing of structural materials, then it is necessary to study how temperature, pressure, and other parameters affect the crystal growth habits of scrubber sludge, especially sulfate-rich sludge. In addition, technology is required to overcome the deleterious effects of organic and inorganic components, often present in scrubber sludge, in the fabrication of materials.

These organic and inorganic impurities/components are difficult, if not economically prohibitive, to separate from sludge. Hence, strategies are needed to form materials from FGD scrubber sludge, which are not affected by the presence of these impurities and/or components.

If the countertop and tile materials developed by this research project were able to compete in the high-end gypsum product market, high-end tabletop market, and tile markets, and were able to capture 5 percent of the rapidly growing export market, this would translate into 5 million tons of sludge utilization. This potential market would generate 600 jobs (3 percent of the current 20,000 workers) with an annual turnover of 250 million dollars. Thus, the successful development of the proposed structural composite materials should not only generate new markets for coal combustion residues but should also strengthen the utilization of Midwestern coal.

Specifically, the developed materials would benefit in the following ways:

- by reducing the cost of scrubber sludge disposal;
- by generating new structural material markets for coal combustion byproduct-based materials, specifically FGD residue;
- by providing the technological base for industry to locate in the Midwestern area, especially hard hit by the Clean Air Act, and, therefore, generating additional jobs in the region which currently do not exist;
- by converting FGD byproducts into marketable items, thus, converting byproducts into valuable, sellable raw material;
- by utilizing the wet scrubber sludge and the associated revenue generated, encouraging further use of scrubbers for SO_2 control; and
- by lowering the requirement to cut trees, thus preserving our forests.

Objectives

The goal of this project was to develop technology for the conversion of sulfate-rich scrubber sludge into value-added decorative materials; i.e., countertops, decorative siding, and decorative tiles. Specifically, the project had the following objectives:

- to design, assemble, and utilize high-temperature, high-pressure molding dies for fabricating large-size composites (up to 8-inch size) from FGD scrubber sludge (the experimental setup was to be capable of applying at least 200,000 lbs of force with controlled temperature up to 350^{o}C);
- to develop protocols and engineering procedures for the development and fabrication of value-added materials from sulfate-rich scrubber sludge;
- to enhance the mechanical strength of materials produced from sulfate-rich scrubber sludge (the fabricated composites' strength was to be compared with commercially available materials);
- to optimize the type of fibers used and their content for enhanced durability and textural appearance of the material;
- to establish procedures for different surface treatment so that our materials would not scratch under normal conditions;
- to fabricate our composites in at least six different colors and patterns; and
- to conduct explorative experiments to establish the feasibility of forming wood-substitute siding materials from sulfate-rich scrubber sludge.

To meet the project objectives of developing decorative materials, the following six tasks were proposed:

- *Task 1*—Focus mainly on optimizing the mixes to be used for countertops, decorative tiles, and siding materials. Another important step in this task was to enhance cross-linking between sludge crystallites and the binders.
- *Task 2*—Focus on maintaining the highly twinned crystal growth behavior of scrubber sludge particles in the materials, yet allow the impregnation

(continued on page 4)

Tile, Countertops, and Structural Materials from Sulfate-Rich FGD Scrubber Sludge

(continued from page 3)

of the polymer to form smooth textured composites. In addition, an attempt at altering physical and chemical parameters for the fabrication of composites was made so that enhanced mechanical strength of the decorative composites ensued.

- *Tasks 3 and 4*—Subject the composites formed under tasks 1 and 2 to various mechanical performance tests and analyze the ensuing data.

- *Task 5*—Perform an economic analyses of the structural products.

- *Task 6*—Explore strategies for commercializing the products, which showed potential.

Summary and Conclusions

The following was accomplished during the course of this project:

- The FTIR measurements were conducted on the as-received polymer to identify the vibrational oscillators, which could be used to measure the concentration of the polymer and cured structure of the polymer in our countertop composites.

- The differential scanning calorimetry (DSC) measurements on as-received polymer suggested that the countertop composites should be formed at $T > 60^oC$ and not at $T < 55^oC$ as recommended by the supplier. In fact, this was born out subsequently after forming the composites at $T > 60^oC$.

- The researchers evaluated how the fiber content in the countertop materials affected the strength of the formed composites.

- They also studied how the orientation of the fibers within our countertop composites affected their mechanical strength. The results suggested that though a sandwich configuration gave the highest flexural strength, the incorporation of the fiber mesh at the bottom would facilitate the installation of the countertops on pre-existing countertops.

- The researchers probed how the formation temperature controlled the strength of the formed material and concluded that higher formation temperature ($T < 110^oC$) imparted better strength to the countertop material formed from sulfate-rich scrubber sludge.

- They also studied how the degree of cure affected the mechanical strength of the composite materials. It appeared that post-curing, in fact, decreased the strength of the countertop material.

- The researchers formed countertop composites using conventional molding technique in which they varied the concentration of the sludge from 10 to 50 weight-percent. However, the sludge was treated to control its crystallization in the composite during molding. It appeared the flexural strength of the composites was comparable or better than the flexural strength of commercial products with similar filler concentration.

- The researchers designed and built a vacuum die to form countertop composites under mild vacuum. Using this die, they formed countertop composites in which they varied the concentration of scrubber sludge. The concentration of the sludge in the composite was varied between 50 and 75 weight percent. It appeared that we could use up to 65 weight percent scrubber sludge in our composites and yet obtain comparable flexural strength to that of commercial products. However, it is believed the commercial products contain only 33 percent inorganic phase.

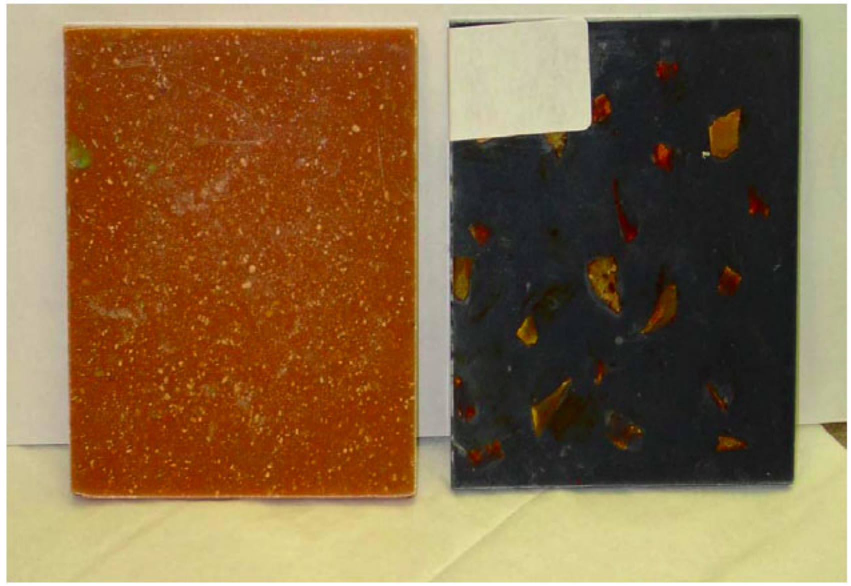
- The researchers explored whether the countertop composite's resistance to scratching could be further enhanced by forming the composites from block copolymers. In this approach, they incorporated a polymer in addition to the polymer that was used to form countertops. The results indicated that a second polymer could be added to further improve scratch resistance without degrading the strength of the countertops. In fact, 5 weight percent of the second polymer could accomplish this without reducing the scrubber sludge crystallites in the materials.

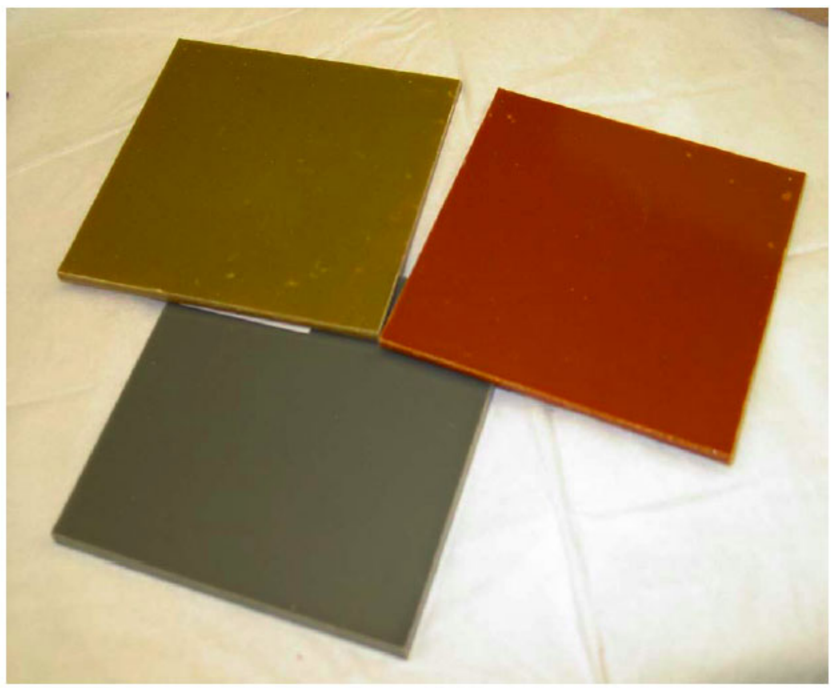
- Flexural strength measurements on the decorative tiles indicated that the particle size of the polymer had a crucial effect on the strength of the material; i.e., the smaller the particle size of the polymer the larger was the flexural strength of the composite.

- Experiments suggested that 2 weight percent decorative granules could be incorporated in the tile composites without compromising the strength of the material.

- The researchers have completed the fabrication of 64 decorative tiles from scrubber sludge. Four of the tiles were mounted on a commercial backing board using commercial adhesive. Results suggested that sludge-derived tiles could be mounted on currently existing commercial backing boards.

- Strength and fabrication measurements suggested that a significant amount of waste and broken countertops could be recycled.





Countertops fabricated from scrubber sludge and waste material.

- Strength and fabrication measurements suggested that a significant amount of broken tiles could be used to design different patterns in the decorative tiles. The researchers believe this approach would considerably reduce the waste and disposal costs of the fabrication process.

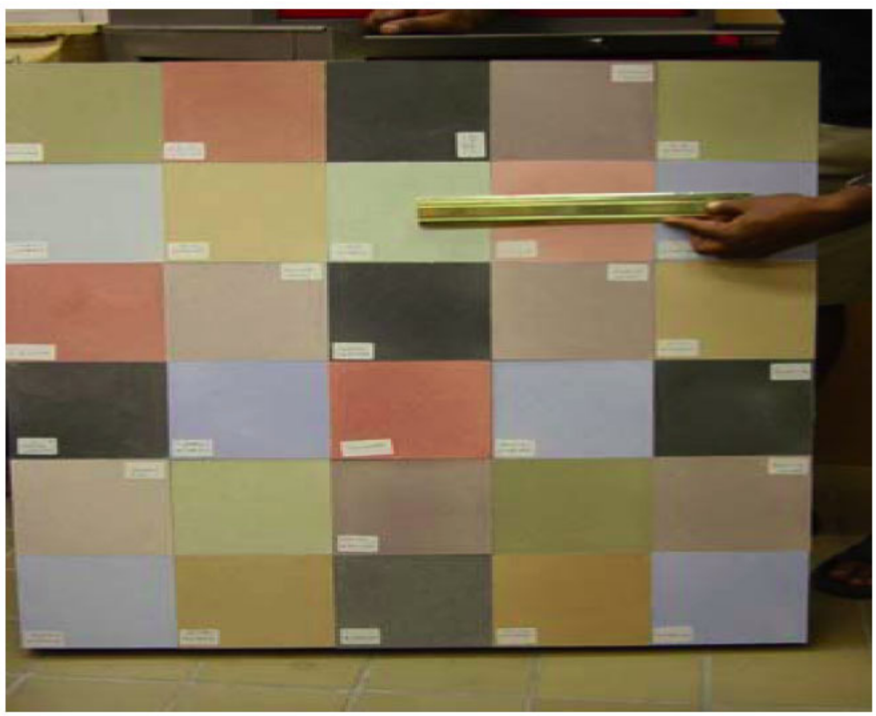
(continued on page 6)

Tile, Countertops, and Structural Materials from Sulfate-Rich FGD Scrubber Sludge

(continued from page 5)

- The researchers fabricated 4″ x 4″ x 0.2″ countertop composites in 11 different colors and patterns.
- The countertop composites were upscaled to 6″ x 6″ x 0.2″ size. At least four different colored countertop composites were fabricated. The researchers have now successfully fabricated 64 pieces of countertop, thus establishing the viability of forming countertop materials from scrubber sludge.
- The researchers examined whether aging affected the strength of the countertops and tiles. The flexural strength measurements suggested that a year of aging did not affect the strength.
- Stability of the tiles in water was also tested. After continuous immersion in water for more than a month, disintegration of the tile or swelling has not been observed.
- The leachate obtained from countertop and decorative tile using the ASTM D3987 procedure suggested that the concentration of selenium and arsenic were below the detection limits.
- The detailed economic analysis indicated that the countertop product would be approximately 10 times cheaper than the current high-end countertops. Decorative tiles would cost about $0.85 per tile.

Decorative tiles made from sulfate-rich scrubber sludge and waste or broken tiles.



Different color tiles fabricated from sulfate-rick scrubber sludge were mounted on a commercial Durock board.

Acknowledgements

This research was supported with funding from the CBRC, the Illinois Department of Commerce and Economic Opportunity through the Office of Coal Development, and the Illinois Clean Coal Institute.

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For more information about this project (#99ECM01) or to view the final report, please visit the CBRC Web site at **http://wvwri.nrcce.wvu.edu/programs/cbrc/**. Or contact the CBRC at **cbrc@wvu.edu.**

Request for Preproposals

The Combustion Byproducts Recycling Consortium (CBRC), a program of the National Mine Land Reclamation Center in cooperation with the U.S. Department of Energy National Energy Technology Laboratory, has announced a request for preproposals. Applications are due by **4:30 p.m. EST, July 31, 2005**

Each year, over 100 million tons of solid byproducts are produced by coalburning electric utilities in the U.S.. One of the CBRC's objectives is to develop and demonstrate technologies to address issues related to the recycling of byproducts associated with coal combustion processes. A goal of CBRC is that these technologies, by the year 2010, will lead to an overall ash utilization rate from the current 34 to 50 percent.

For more information on the CBRC program and for the preproposal application procedures and forms, please access the CBRC Web site at: **http://wvwri.nrcce.wvu.edu/programs/cbrc**, or contact the CBRC at West Virginia University at (304) 293-2867 or at **cbrc@wvu.edu**.

Calendar of Events

August 17–19

Coal-Gen 2005, Revival of the Fittest
San Antonio, Texas

Presented by PennWell

Contact: Registration Department
1421 S. Sheridan Road
Tulsa, OK 74112-6600 USA
Fax (888) 299-8057
coal-gen@pennwell.com,
www.coal-gen.com

August 31–September 1

Coal Combustion Product Optimization
Denver, Colorado

www.euci.com/conferences/august_05/coal_combustion_0805.php

September 18–22

22nd Annual International Pittsburgh Coal Conference "Coal, Energy, and the Environment"
Pittsburgh, Pennsylvania

Contact: (412) 624-7440
pcc@engr.pitt.edu
www.engr.pitt.edu/pcc

December 4–7

International Congress Fly Ash INDIA 2005
New Delhi, India

Contact: flyash.conference@gmail.com, www.flyashindia.tifac.org.in

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