

**INDUSTRY-GOVERNMENT-UNIVERSITY
COOPERATIVE RESEARCH PROGRAM FOR THE
DEVELOPMENT OF
STRUCTURAL MATERIALS FROM SULFATE-RICH FGD
SCRUBBER SLUDGE**

Final Report
September 1, 2000 to August 31, 2003

Prepared by Principal Investigators
Professors V. M. Malhotra and Y. P. Chugh

January 15, 2004

CBRC/DOE Grant Number: 99ECM01

Submitted by:
Department of Physics
Southern Illinois University at Carbondale
Illinois 62901

Disclaimers

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This research was also supported by the Illinois Department of Commerce and Economic Opportunity through the Office of Coal Development and the Illinois Clean Coal Institute. Neither Vivak M. Malhotra of Southern Illinois University at Carbondale nor any of his subcontractors nor the Illinois Department of Commerce and Economic Opportunity, Office of Coal Development, Illinois Clean Coal Institute, nor any person acting on behalf of either: (A) Makes any warranty of representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately-owned rights; or (B) Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report.

References herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, do not necessarily constitute or imply its endorsement, recommendation, or favoring; nor do the views and opinions of authors expressed herein necessarily state or reflect those of the Illinois Department of Commerce and Community Affairs, Office of Coal Development, or Illinois Clean Coal Institute.

Notice to Journalists and Publishers: If you borrow information from any part of this report, you must include a statement about the state of Illinois' support of the project.

ABSTRACT

The main aim of our project was to develop technology, which converts flue gas desulfurization (FGD) sulfate-rich scrubber sludge into value-added decorative materials. Specifically, we were to establish technology for fabricating cost effective but marketable materials, like countertops and decorative tiles from the sludge. In addition, we were to explore the feasibility of forming siding material from the sludge. At the end of the project, we were to establish the potential of our products by generating 64 countertop pieces and 64 tiles of various colors.

In pursuit of our above-mentioned goals, we conducted Fourier transform infrared (FTIR) and differential scanning calorimetry (DSC) measurements of the binders and co-processed binders to identify their curing behavior. Using our 6" x 6" and 4" x 4" high pressure and high temperature hardened stainless steel dies, we developed procedures to fabricate countertop and decorative tile materials. The composites, fabricated from sulfate-rich scrubber sludge, were subjected to mechanical tests using a three-point bending machine and a dynamic mechanical analyzer (DMA). We compared our material's mechanical performance against commercially obtained countertops.

We successfully established the procedures for the development of countertop and tile composites from scrubber sludge by mounting our materials on commercial boards. We fabricated more than 64 pieces of countertop material in at least 11 different colors having different patterns. In addition, more than 100 tiles in six different colors were fabricated. We also developed procedures by which the fabrication waste, up to 30-weight %, could be recycled in the manufacturing of our countertops and decorative tiles. Our experimental results indicated that our countertops had mechanical strength, which was comparable to high-end commercial countertop materials and contained substantially larger inorganic content than the commercial products. Our moisture sensitivity test suggested that our materials were non-water wettable and did not disintegrate on submerging the product in water for at least two months. Countertop polishing techniques were also established.

List of Figures

- Figure 1. The FTIR spectrum of the Poly-Deg polymer used to fabricate the countertop composites from CWLP scrubber sludge.
- Figure 2. The thermal characteristic of polymer used to fabricate the countertop composites from CWLP scrubber sludge. The positive peak signifies endothermic reaction, while the negative peak suggests exothermic reaction.
- Figure 3. This figure depicts how the concentration of polyester fiber content affected the mechanical strength of the countertop composites formed from sulfate-rich scrubber sludge. The composites were fabricated at 50°C.
- Figure 4. This figure depicts how the formation temperature affected the mechanical strength of the countertop composites formed from sulfate-rich scrubber sludge. These composites contained no fibers.
- Figure 5. How the density of the countertop-type composites, formed from scrubber sludge and polymer, was affected by the scrubber sludge-to-polymer ratio. These composites were formed via compressive molding technique. The straight-line drawn, which is the best-fit line, signifies the linear relation between the density and ratio.
- Figure 6. How the average flexural strength of the countertop-type composites, formed from scrubber sludge and polymer, was affected by the scrubber sludge-to-polymer ratio used. These composites were formed via conventional molding technique.
- Figure 7. This figure depicts the lack of linear relationship between density and the average flexural strength of the countertop-type composites, formed from scrubber sludge and polymer. These composites were formed via conventional molding technique.
- Figure 8. How the density of the countertop-type composites, formed from scrubber sludge and polymer, was affected by the scrubber sludge-to-polymer ratio. These composites were formed via a vacuum molding technique.
- Figure 9. How the average flexural strength of the countertop-type composites, formed from scrubber sludge and polymer, was affected by the scrubber sludge-to-polymer ratio used. These composites were formed via a vacuum molding technique.
- Figure 10. This figure depicts the lack of linear relationship between density and the average flexural strength of the countertop-type composites formed from scrubber sludge and polymer. These composites were formed via a vacuum

molding technique.

- Figure 11. This figure depicts how the concentration of polymer SAM-P2 affected the mechanical properties of the countertop composite formed from sulfate-rich scrubber sludge. The commercial countertop we tested gave an average strength of about 40 MPa.
- Figure 12. This figure depicts how the concentration of polymer SAM-P2 controlled the density of our countertop composites formed from sulfate-rich scrubber sludge.
- Figure 13. Countertops fabricated from scrubber sludge and waste material.
- Figure 14. Countertops formed from scrubber sludge and waste material.
- Figure 15. Countertops fabricated from scrubber sludge and waste material.
- Figure 16. This data reproduce the stress-strain curve for countertop materials fabricated from sulfate-rich FGD scrubber sludge and polymer Poly-Bul.
- Figure 17. This reproduces the stress-strain curve for countertop materials fabricated from sulfate-rich FGD scrubber sludge and Poly-Deg and polyester polymers. The scrubber sludge-to-polymer ratio was 1.02. The ratio between Poly-Deg and polyester was 4.3.
- Figure 18: The digital pictures of 1-inch thick countertops fabricated from sulfate-rich scrubber sludge.
- Figure 19. This figure reproduces the effect of post-curing and the polymer's particle size on the flexural strength of decorative tiles formulated from sulfate-rich scrubber sludge.
- Figure 20. This figure shows how the concentration of granules affected the flexural strength of our decorative tile composites
- Figure 21. Decorative tiles made from sulfate-rich scrubber sludge and waste or broken tiles.
- Figure 22. Stress versus strain curve for decorative tiles fabricated from sulfate-rich scrubber sludge.
- Figure 23. This digital picture shows four tiles mounted on a commercial Durock board.
- Figure 24. This figure shows thirty decorative tiles, which were mounted on a 3 feet by 2.5 feet Durock board.

Figure 25. Different color tiles, fabricated from sulfate-rich scrubber sludge, were mounted on a commercial Durock board.

Figure 26. Excellent bonding was observed between tiles, fabricated from sulfate-rich scrubber sludge, and commercial Durock board as can be seen here.

Figure 27. A siding sample of size 10" x 10" x 0.125" fabricated from sulfate-rich scrubber sludge.

Figure 28. Schematic of the pilot scale approach to fabricate FGD materials.

INTRODUCTION AND BACKGROUND

About 22 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 (5%) 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, January 1994).

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 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) or $\text{CaSO}_3 \cdot n\text{H}_2\text{O}$, depending upon the FGD technology used. The disposal of about 22 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], e.g.,

- 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 is 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 ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), 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 it is argued that our proposed countertop and tile materials are able to compete in the high-end gypsum product market, high-end tabletop market (e.g., Corian-type countertops), and tile markets and is able to capture 5% of the rapidly growing export market, this will translate into 5 million tons of sludge utilization. This potential market will generate 600 jobs (3% of the current 20,000 workers) with an annual turnover of 250 million dollars. Thus, the successful development of our proposed structural composite materials should not only generate new markets for coal combustion residues but should also strengthen the utilization of Midwestern coal.

Specifically, our materials will 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, 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 SO₂ 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 following were the objectives of this two-year project:

- 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 force with controlled temperature up to 350°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.
- to conduct explorative experiments to establish the feasibility of forming wood-substitute siding materials from sulfate-rich scrubber sludge.

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

- **TASK 1:** In this task we were to 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 our binders.
- **TASK 2:** Under this task, we focused on maintaining the highly twinned crystal growth behavior of scrubber sludge particles in our materials and yet allowing the impregnation of the polymer to form smooth textured composites. In addition, we attempted to alter physical and chemical parameters for the fabrication of composites so that enhanced mechanical strength of our decorative composites ensued.

- **TASK 3 and 4:** Under these tasks, the composites formed under task 1 and 2 were subjected to various mechanical performance tests and the ensuing data were analyzed.
- **TASK 5:** The economic analyses of our structural products was to be the focus of this task.
- **TASK 6:** The main objective of this task was to explore strategies of commercializing the products, which showed potential.

EXECUTIVE SUMMARY

The mandate of this project was to develop value-added materials from sulfate-rich scrubber sludge. Specifically, we established technology to fabricate cost effective but marketable materials like countertops, decorative tiles, and siding material from the sludge.

To accomplish the aforementioned goals, we conducted Fourier transform infrared (FTIR) and differential scanning calorimetry (DSC) measurements of the binders and co-processed binders to identify the curing behavior of our binders. Using our 6" x 6" and 4" x 4" high pressure and high temperature hardened stainless steel dies, we developed procedures to fabricate countertop and decorative tile materials. The composites, fabricated from sulfate-rich scrubber sludge, were subjected to various mechanical tests.

During the course of this project, the following was accomplished:

- 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.
- Our differential scanning calorimetry (DSC) measurements on as-received polymer suggested that the countertop composites should be formed at $T > 60^{\circ}\text{C}$ and not at $T < 55^{\circ}\text{C}$ as recommended by the supplier. In fact, this was born out subsequently after forming the composites at $T > 60^{\circ}\text{C}$.
- We evaluated how the fiber content in our countertop materials affected the strength of the formed composites.
- We studied how the orientation of the fibers within our countertop composites affected their mechanical strength. Our results suggested that though the 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.
- We probed how the formation temperature controlled the strength of the formed material, and we concluded that higher formation temperature ($T < 110^{\circ}\text{C}$) imparted better strength to the countertop material formed from sulfate-rich scrubber sludge.
- We also studied how the degree of cure affected the mechanical strength of our composite materials. It appeared that post-curing in fact decreased the strength of the countertop material.
- We formed countertop composites using conventional molding technique in which we varied the concentration of the sludge from 10-weight % to 50-weight %. However, sludge was treated to control its crystallization in our composite during molding. It appeared the flexural strength of our composites was comparable or better than the flexural strength of commercial products with similar filler concentration.
- We designed and built a vacuum die to form countertop composites under mild vacuum. Using this die, we formed countertop composites in which we varied the concentration of scrubber sludge. The concentration of the sludge in the composite

was varied between 50-weight % and 75-weight %. It appeared that we could use up to 65-weight % scrubber sludge in our composites and yet obtain comparable flexural strength to that of commercial products. However, it should be pointed out that it is believed the commercial products contain only 33 % inorganic phase.

- We explored whether countertop composite's resistance to scratching could be further enhanced by forming the composites from block copolymers. In this approach, we incorporated a polymer in addition to the polymer that was used to form countertops. Our results indicated that a second polymer, without degrading the strength of our countertops, could be added to further improve the scratch resistance of the countertop. In fact, 5-wt % of the second polymer could accomplish this without reducing the scrubber sludge crystallites in our materials.
- Our 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.
- Our experiments suggested that 2 wt % decorative granules could be incorporated in our tile composites without compromising the strength of the material.
- We 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. Our results suggested that sludge-derived tiles could be mounted on currently existing commercial backing boards.
- Our strength and fabrication measurements suggested that a significant amount of waste and broken countertops could be recycled.
- Our strength and fabrication measurements suggested that a significant amount of broken tiles could be used to design different patterns in our decorative tiles. This approach, we believe, would considerably reduce the waste and disposal costs of our fabrication process.
- The results from above-mentioned steps were harnessed to fabricate 4" x 4" x 0.2" countertop composites with 11 different colors and patterns.
- Using data obtained from previously listed steps, we upscaled our countertop composites to 6" x 6" x 0.2" sizes. At least four different colored countertop composites were fabricated. We have now successfully fabricated 64 pieces of countertop, thus, establishing the viability of forming countertop materials from scrubber sludge.
- We examined whether aging affected the strength of our countertops and tiles. The flexural strength measurements suggested that a year of aging did not affect the strength.
- We also tested the stability of our tiles in water. After continuous immersion in water for more than a month, we so far have not observed disintegration of the tile or swelling.
- 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.

- Our detailed economic analysis indicated that our countertop product would be approximately 10 times cheaper than the current high end “Corian-look-alike” countertops. The decorative tiles would cost about \$ 0.85 per tile.

EXPERIMENTAL PROCEDURES

CHARACTERIZATION

Sludge Sample: For the development of value-added materials, we used sulfate-rich scrubber sludge obtained from City Water Light & Power (CWLP) plant located in Springfield, Illinois. The sludge was in the form of wet sludge and was only air-dried prior to fabricating our decorative materials.

Fourier Transform Infrared Measurement: We collected transmission-Fourier transform infrared (FTIR) data, when required to ascertain how various fabrication parameters affected the structure of our materials. The spectra were collected using KBr pellet technique. The spectra were obtained on a Nicolet IR-44 FTIR spectrometer equipped with a DTGS detector and interfaced with a PC 286 computer. Typically, 100 single beam scans (interferograms) of the sample were collected. The reference interferograms were collected under identical conditions but without a sample in the beam. During this process, the spectrometer was continuously purged with dry nitrogen gas. With the use of the transformed single-beam sample and reference spectra, the spectra of the sample could be plotted as transmittance or absorbance. We used triangular apodization to transform the interferograms acquired at 4 cm^{-1} resolution. Therefore, the effective resolution of the spectra was approximately 6 cm^{-1} .

Differential Scanning Calorimetry Measurements: The thermal behavior of formulated decorative composites was monitored by conducting differential scanning calorimetry (DSC) measurements. The DSC data were acquired on a Perkin-Elmer DSC7 system, interfaced with a PC 486 computer using a Unix operating system. The DSC was calibrated for temperature and enthalpy. The temperature calibration was performed by the two-point method, using the melting transitions of indium (157°C) and zinc (420°C). The accuracy in temperature between 30°C and 410°C , based on our calibration procedure, was estimated to be $\pm 1^{\circ}\text{C}$. The enthalpy calibration was performed using indium heat of fusion as the standard. After the enthalpy calibration, the DSC data on zinc metal were re-recorded, and the observed enthalpy of the melting transition of zinc was consistent with the values reported in the literature. The conditions under which the instrument calibration was performed exactly matched the experimental run conditions, namely the scan rate of $5^{\circ}\text{C}/\text{min}$, nitrogen gas purge at 30 psi pressure. During both calibration and heating runs, the dry box assembly over the sample head was flushed with nitrogen gas to maintain thermodynamic equilibrium. Aluminum (Al) sample pans were used to record the DSC curves.

MIX OPTIMIZATION AND FABRICATION OPTIMIZATION

Fabrication of Countertop Materials: Generally, the following steps were executed for fabricating the composites from scrubber sludge:

- As a first step, the CWLP scrubber sludge was air dried for 3 to 4 days prior to forming the composites.

- The air-dried scrubber sludge particles were mixed with appropriate ingredients and thoroughly mixed using a high shear mixture to ensure the best achievable homogeneous distribution of the particles. Our observations suggested that well mixed homogenous-looking powder was a crucial step for successfully fabricating countertop composites from scrubber sludge.
- The sample mixtures were poured into either 4" x 4" or 6" x 6" hardened stainless steel dies. The samples were hot pressed at the desired pressure and temperature to form the primary composite skeleton.
- Various fibers were laid in the die in a random orientation. The fibers were sandwiched between the mixture of sludge particles so that our composite had a lamina configuration.
- We also fabricated composites where polyethylene fiber mesh was laid on the bottom of the die before the sample mixture was poured into the hardened stainless steel die. This approach resulted in countertop composites, which were suitable for mounting on existing non-polymer countertops, e.g., wood countertops or Formica countertops.
- After the mix had been poured into the stainless steel dies, the composite was formulated by hot-pressing the material at desired pressure and temperature. Typically, we cured our composites for 30 minutes.
- The successful curing was also crucial in the quality of the composites formed. We observed if the polymer was not fully cured or was not thoroughly mixed with the sludge then the material either stuck to the die or crumbled.
- The composites were cured in air.
- Two different polymers, i.e., Poly-Deg and Poly-Bul, were used to form our composite materials.

The following parameters were found to be crucial for the formation of countertops:

- the order in which ingredients were added prior to mixing,
- mode of mixing,
- length of mixing,
- the dispersion of the mixture in the die,
- die temperature, i.e., whether the die was pre-heated or its temperature was ramped along with the mixture.

Fabrication of Decorative Tiles: In general, the following procedure was adopted to formulate our decorative tiles from sulfate-rich scrubber sludge:

- Initially we converted gypsum phase of the scrubber sludge into a hemihydrate phase prior to forming decorative tiles at high temperature and high pressures. However, our experimental results suggested that it would be more economical to directly use wet sludge to form decorative tiles without losing any structural performance. Therefore, most of our tiles were formed from wet scrubber sludge.

- We prepared mixture blends of wet scrubber sludge and polymer Poly-MI. The as-received polymer, i.e., Poly-MI, was in small granular form. Initially, we attempted forming our tiles using this granular polymer. The results were poor and erratic. The formed composite was dusty. However, these problems were overcome when we ground the as-received polymer. The commercial supplier of the polymer suggested it should not be ground. However, our actual experimental observations suggested that far superior tiles were produced when we reduced the particle size of the polymer to $< 10 \mu\text{m}$.
- The blended polymer-MI and wet sludge were hot pressed in our stainless steel dies at $T > 90^\circ\text{C}$ and force $> 1000 \text{ lbs}$. Design patterns were accomplished by directly coloring the sludge prior to blending. The tiles were formed in 4" x 4" x 0.2" and 6" x 6" x 0.125" sizes.

MECHANICAL PERFORMANCE

Strength Measurements: To test the mechanical performance of our countertop and tile composites we tested the mechanical performance by undertaking 3-point bending test. We used a diamond circular saw to cut rectangular strips of the sample having nominal thickness of about 0.2 cm and width of 0.95 cm from our 4" x 4" or 6" x 6" tiles or countertops. To accomplish the flexural strength measurements, a three point bending system was designed from equipment obtained from ELE International. This system is a highly reliable, precision system for evaluating the mechanical properties of materials. The system is designed to test materials under either tension or compression mode. We designed and built our own load cells to carry out the measurements in the three point bending mode. The span length was fixed at 5.1 cm. The sample was supported by two cylinders below and one cylinder above the center of the specimen. A force was applied directly above the center of the specimen. A deflectometer was mounted directly below the center of the specimen to measure the deflection as the force was applied. Using the standard method, the flexural strength was ascertained, i.e.,

$$\sigma = \frac{3Fl}{2bh^2},$$

where F , l , b , and h are the load at failure, span length, width, and the thickness, respectively. The flexural strength measurements were made in triplicate; thus, the data presented are the average of these three values.

We computerized our data collection by interfacing the ELE mechanical testing system with a Pentium IV based computer. The collected mechanical data were transferred to an in-house written software, which converted the data into graphic strain-stress curves.

RESULTS AND DISCUSSION

CHARACTERIZATION

To develop countertop materials from scrubber sludge, two polymer samples were obtained, i.e., Poly-Deg and Poly-Bul. The as-received polymers were further chemically processed so that they would interact with the sludge crystallites. The decorative tiles were fabricated using polymer-MI.

The FTIR spectrum of the Poly-Deg polymer is depicted in Fig. 1. From the careful analysis on the infrared spectrum, the following vibrational modes were identified which could be used to track the interaction between the polymer and the sludge, i.e., 2996, 2950, 1736, 1722, 1194, and 1154. If there was interaction between the polymer and sludge, then C = O and C – O vibrations' intensity might shift and/or there might be a frequency shift of these oscillators, etc.

Figure 2 depicts the observed thermal behavior of as-received Poly-Deg polymer. The main thermal events, along with their heat of reaction, are listed in Table 1. As can be seen from the figure, there are three major thermal events for the polymer used to form our countertop type materials. An initial endothermic reaction was observed at 78°C that may indicate the expulsion of volatiles from the polymer. However, the main curing reaction for this polymer was observed at 120°C. Interestingly, the composite formation temperature suggested by the manufacturer was below 80°C. This leads us to believe it is imperative that thermal data on the as-received polymer must be collected before the composite formation is undertaken. Our DSC results suggest that a higher degree of cross-linking would be achieved if the composites were formed at $T > 80^{\circ}\text{C}$. This in fact was born out as shown later.

Table 1
Thermal behavior of the polymer used to form countertop composites.

Temperature (°C)	Reaction	ΔH (J/g)
78	Endothermic	+ 5.2
86	Endothermic	very weak
88	Exothermic	- 0.4
120	Exothermic	- 64
158	Exothermic	- 1.5

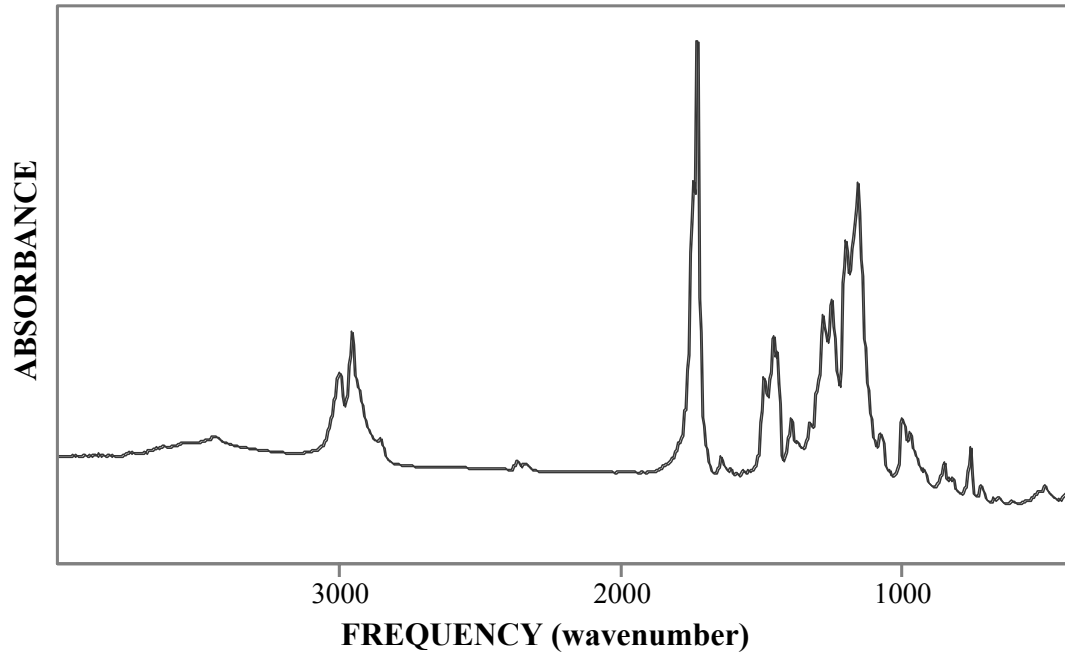


Figure 1. The FTIR spectrum of the Poly-Deg polymer used to fabricate the countertop composites from CWLP scrubber sludge.

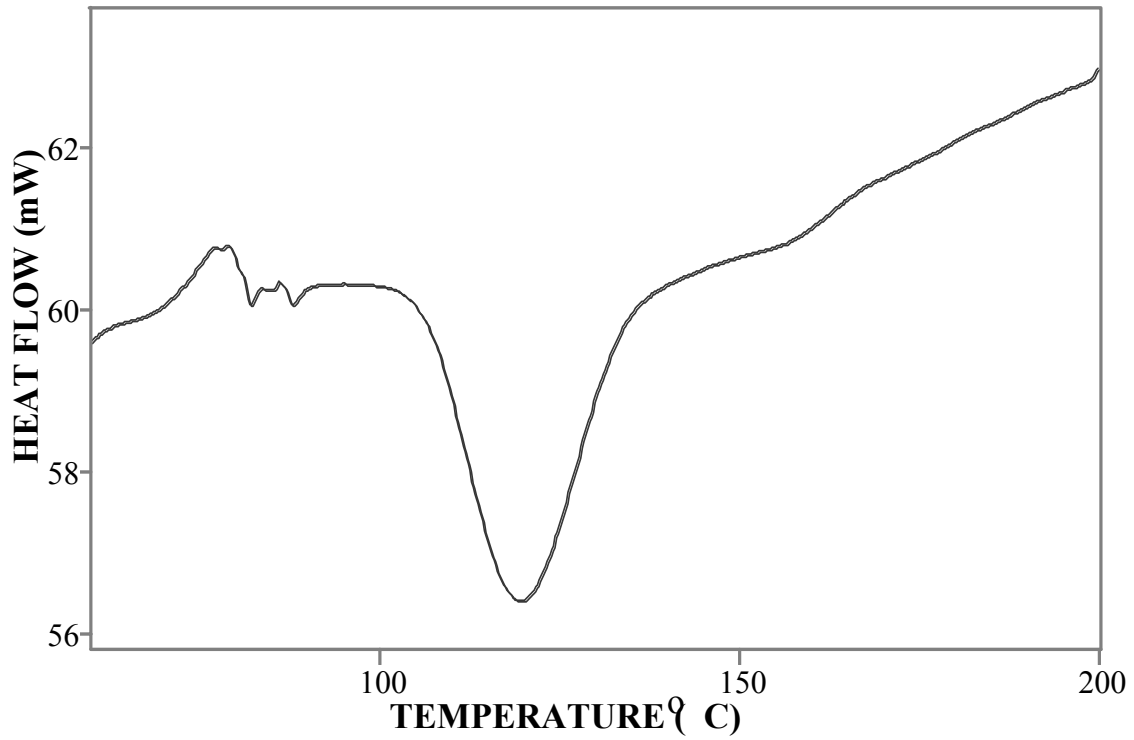


Figure 2. The thermal characteristic of polymer used to fabricate the countertop composites from CWLP scrubber sludge. The positive peak signifies endothermic reaction, while the negative peak suggests exothermic reaction.

COUNTERTOP MATERIALS FABRICATION OPTIMIZATION AND TESTING

Effects of Fibers: We undertook experiments to probe how the concentration of polyester fibers affected the strength of countertop materials fabricated from scrubber sludge. To answer this, we formed our countertop composites from dried scrubber sludge, polymer, and polyester fibers. The fiber concentration was varied from 0 to 3.08-wt %. The composites were fabricated in a 4-inch by 4-inch die at 50°C. After the material was formed, the countertop was ejected from the die and was cut with a band saw into 2-inch strips for undertaking three-point bending tests to determine the flexural strength. Four strips for each sample fabricated were tested for the flexural strength. How the concentration of the polyester fibers affected the flexural strength is depicted in Fig. 3. The flexural strength data reported in Fig. 3 are the average of four measurements. Two important observations were that (1) the countertop depicted brittle failure whether it contained any fibers or not and (2) the fibers had only a marginal impact on the flexural strength of the formed composite.

Effect of Formation Temperature: The issue of formation temperature effect on the curing behavior was addressed by forming countertop materials at 50°C, 80°C, and 100°C. The countertop composites at these temperatures were formed in a 4-inch by 4-inch die using a 30-ton capacity press fitted with heated and temperature controlled platens. The formed composites were subjected to flexural strength measurements using our three-point bending machine. The four measurements were collected for each formation temperature. The results are summarized in Fig. 4. Clearly, the formation temperature had a significant effect on the curing behavior and thus, on the flexural strength of the material. Higher formation temperatures lead to higher strengths.

Effect of the Concentration of Scrubber Sludge: We also examined how the scrubber sludge-to-polymer ratio controlled the mechanical strength of our countertop composites. To answer this question, we formed composites using a 2.25-inch diameter die in which the scrubber sludge-to-polymer ratio was varied from 0 to 1. After the samples were cured, their density was ascertained. Figure 5 clearly shows the density of the composite increased as the scrubber sludge-to-polymer ratio increased. In fact, an excellent linear dependence was observed. This was to be expected as the concentration of the scrubber sludge increased in the composite since sludge has a higher density than polymer.

Figure 6 depicts how the average flexural strength was affected by the concentration of the sludge in the composite. Surprisingly, the strength increased when scrubber sludge was incorporated into the polymer. Our initial results suggest that adding 45-weight % scrubber sludge into our composite did not markedly affect the strength of our countertop composites. To compare the mechanical strength of our countertop composites with commercially available Corian material, we obtained Corian samples with various color additives. The Corian samples were subjected to flexural measurements identical to those used for our samples. The flexural strength of Corian samples, depending on the additives, varied between 40 MPa to 60 MPa. It is believed that Corian samples have a composition that contains up to 33 % fillers. The rest

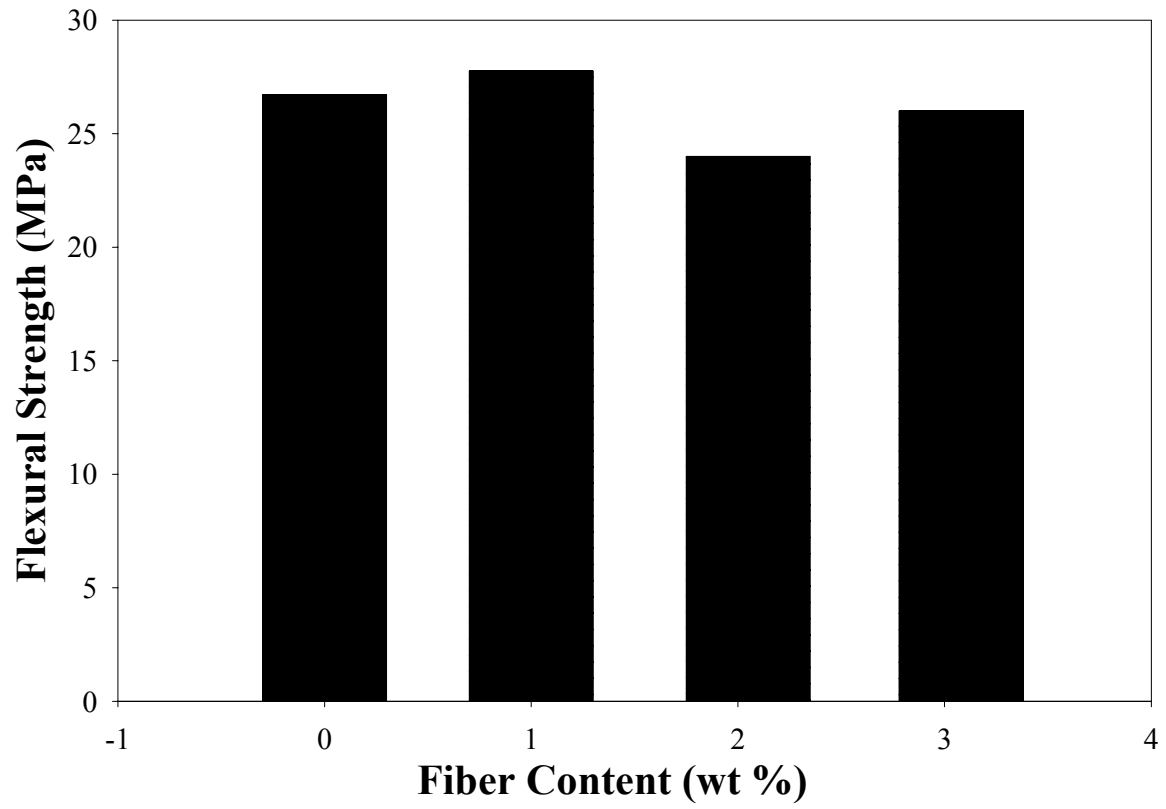


Figure 3. This figure depicts how the concentration of polyester fiber content affected the mechanical strength of the countertop composites formed from sulfate-rich scrubber sludge. The composites were fabricated at 50°C.

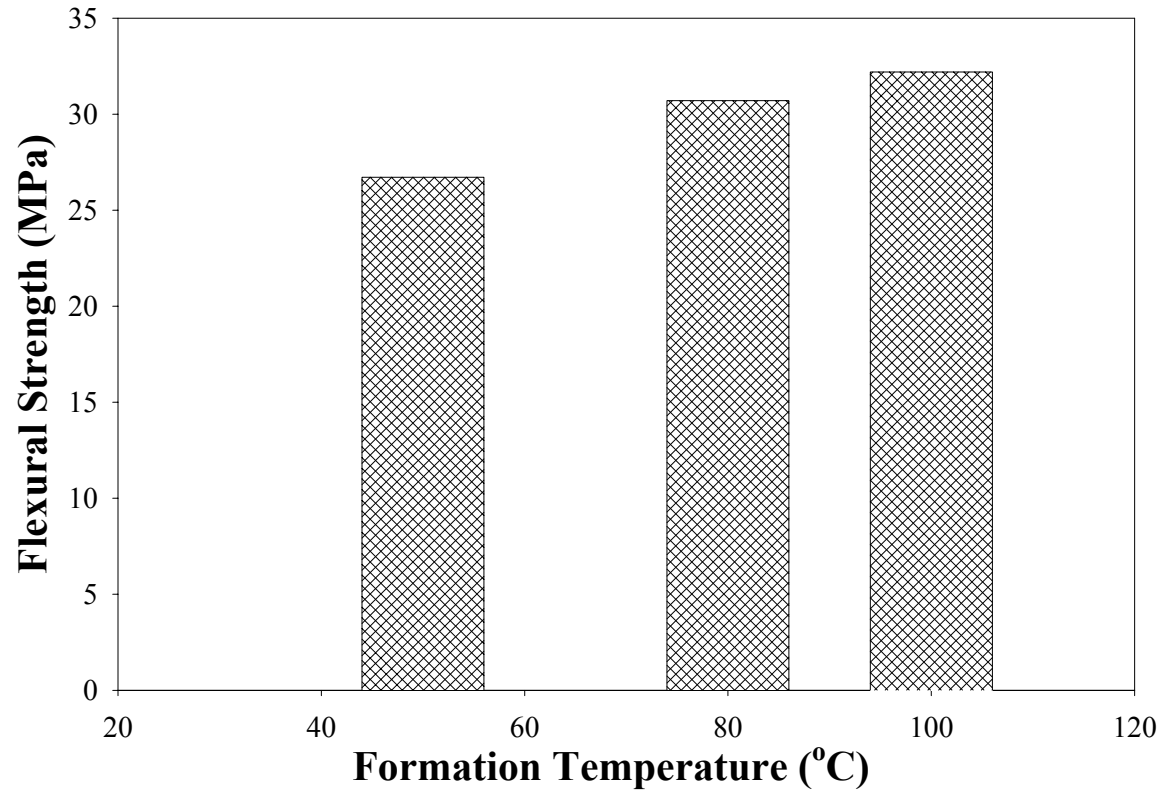


Figure 4. This figure depicts how the formation temperature affected the mechanical strength of the countertop composites formed from sulfate-rich scrubber sludge. These composites contained no fibers.

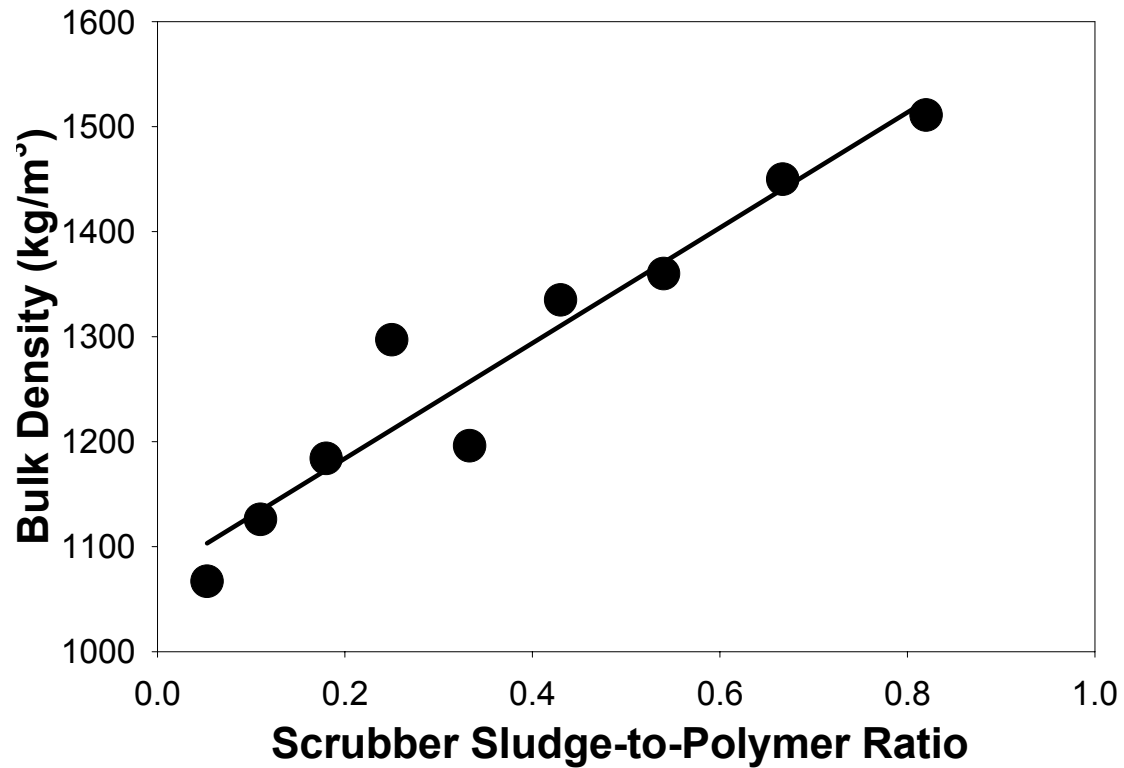


Figure 5. How the density of the countertop-type composites, formed from scrubber sludge and polymer, was affected by the scrubber sludge-to-polymer ratio. These composites were formed via compressive molding technique. The straight-line drawn, which is the best-fit line, signifies the linear relation between the density and ratio.

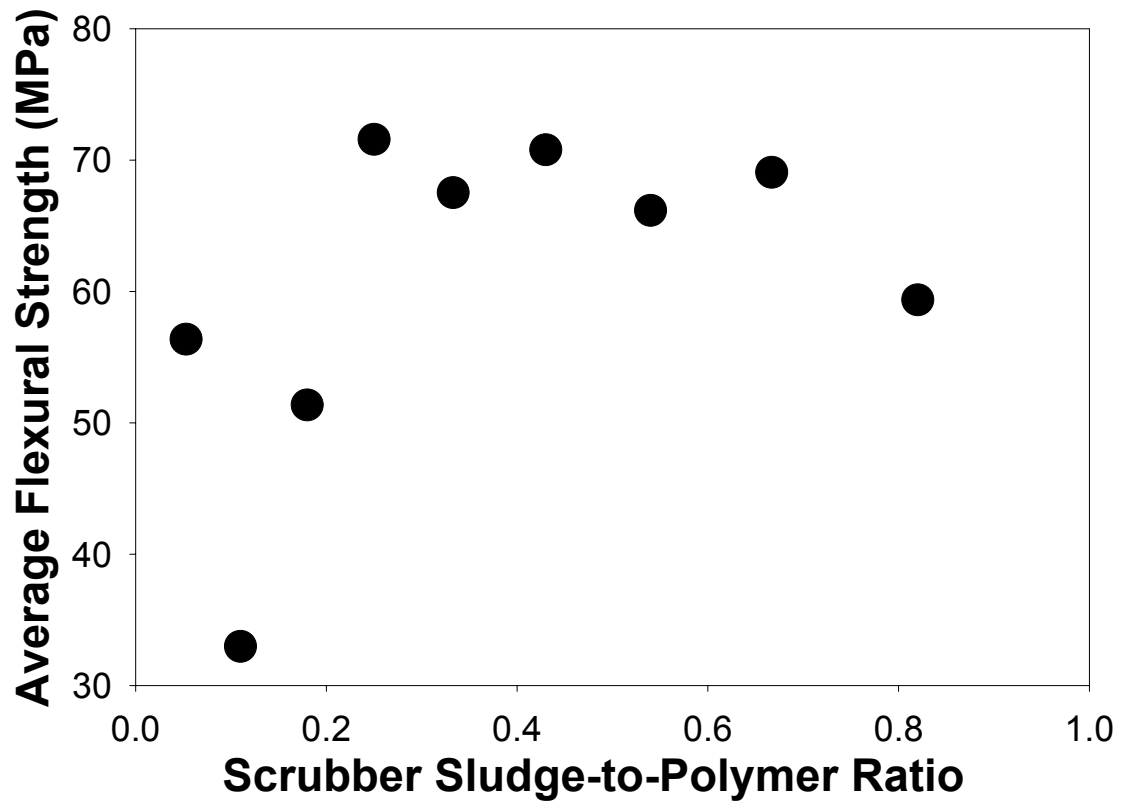


Figure 6. How the average flexural strength of the countertop-type composites, formed from scrubber sludge and polymer, was affected by the scrubber sludge-to-polymer ratio used. These composites were formed via conventional molding technique.

is propriety DuPont polymer. Our countertop composite with 33 % scrubber sludge additive gave an average flexural strength of ~ 67 MPa. Clearly, our results suggest that our composites may have comparable or better performance than high-end countertop materials. However, additional measurements are needed to reach a definite conclusion. It is interesting to note that we did not find a linear dependence between the density and the flexural strength of our countertop composite as can be seen from Fig. 7.

Effect of the Concentration of Scrubber Sludge (Vacuum Route): Since we are interested in forming countertop composites in which we can maximize the concentration of the scrubber sludge without compromising the desired mechanical properties, we are exploring other experimental strategies besides conventional molding. We undertook experiments to evaluate how vacuum molding rather than conventional molding would affect the mechanical strength of our countertop composites. For this purpose, we designed and built a 2-inch diameter die where we can subject the sample to vacuum when under molding pressure. We formed a series of countertop composites where the concentration of scrubber sludge was varied from 50-weight % to 75-weight % under mild vacuum. The results are summarized in Figures 8, 9, and 10. As the concentration of the sludge increased in our composite from 50-weight %, the flexural strength of the composite decreased. Since it is believed that the high-end commercial polymer countertops have a maximum filler concentration of 33 %, we cannot compare our values with the commercial product. However, it appears we can at least use up to 65-weight % scrubber sludge in our composites and still retain flexural strengths comparable to commercial products.

Effect of Colors on the Strength: One of the deliverables at the end of this two year project was a 4-feet by 4- feet panel containing 6" x 6" x 0.2" and 4" x 4" x 0.2" sized countertop composite samples. This effectively implies about 64 samples will be needed to cover the panel. We fabricated 18 countertop composite samples of size 6-inch by 6-inch by 0.2-inch. These samples were prepared in five different colors, i.e., brown, yellow, green, orange, and blue. Six samples were picked at random and were subjected to flexural strength measurement using a three-point bending test experiment. The flexural strength results are summarized in Table 2.

Table 2

The flexural strength of countertop composites fabricated from sulfate-rich scrubber sludge and Poly-Deg polymer.

SAMPLE ID	COLOR ADDITIVE	Flexural Strength (MPa)
BV424	None	36
BV426	None	44
BV427	Orange	37
BV428	Blue	32
BV429	Green	31
BV430	Brown	39
High-end commercial countertop	White	41

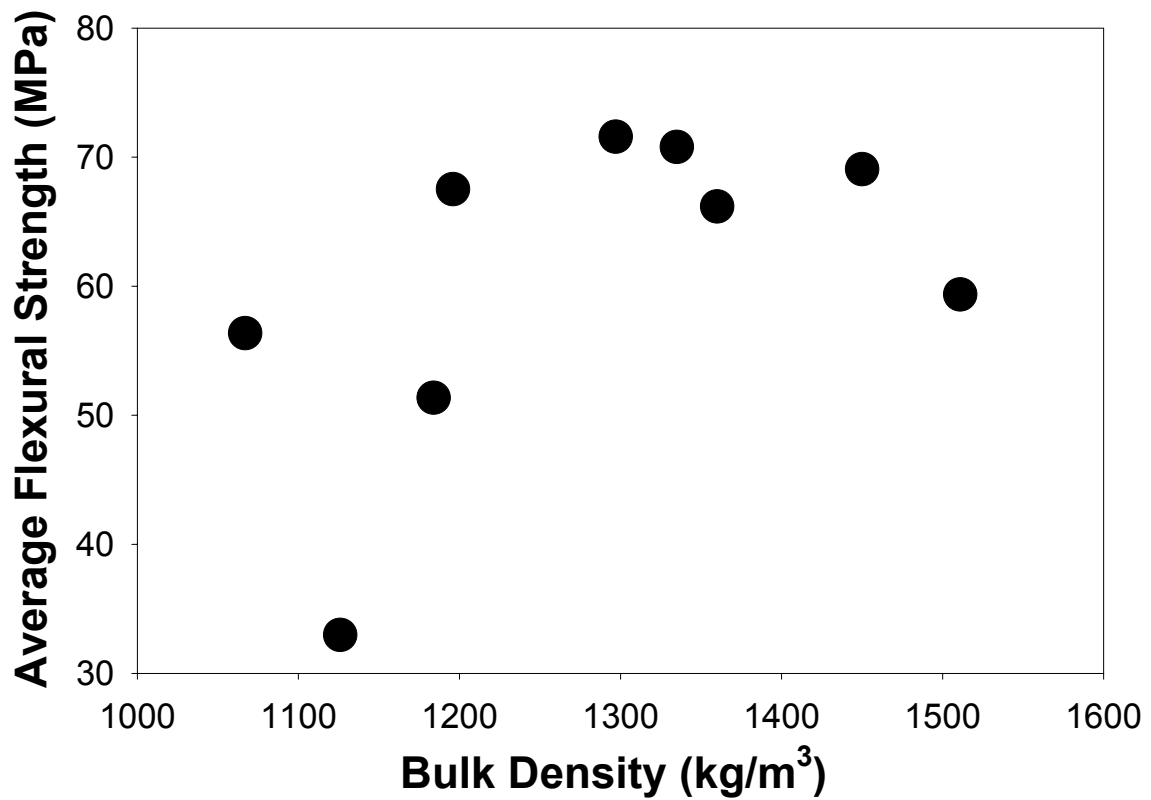


Figure 7. This figure depicts the lack of linear relationship between density and the average flexural strength of the countertop-type composites, formed from scrubber sludge and polymer. These composites were formed via conventional molding technique.

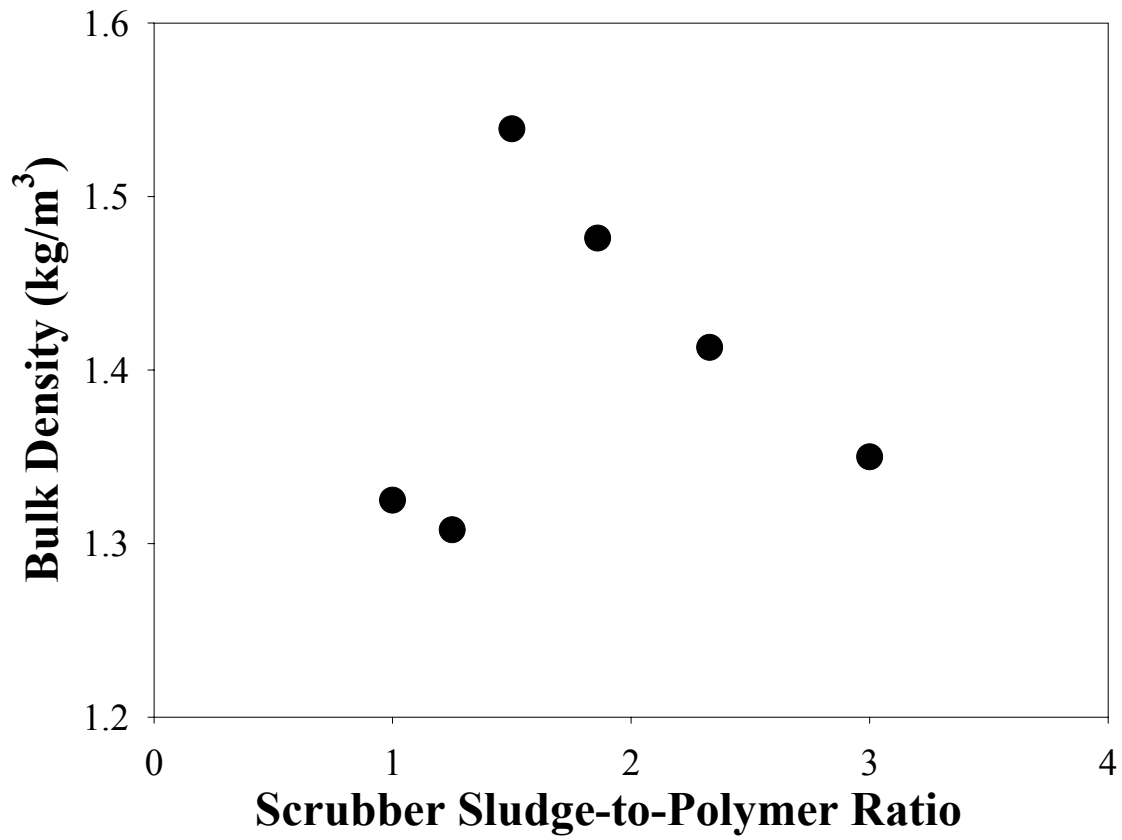


Figure 8. How the density of the countertop-type composites, formed from scrubber sludge and polymer, was affected by the scrubber sludge-to-polymer ratio. These composites were formed via a vacuum molding technique.

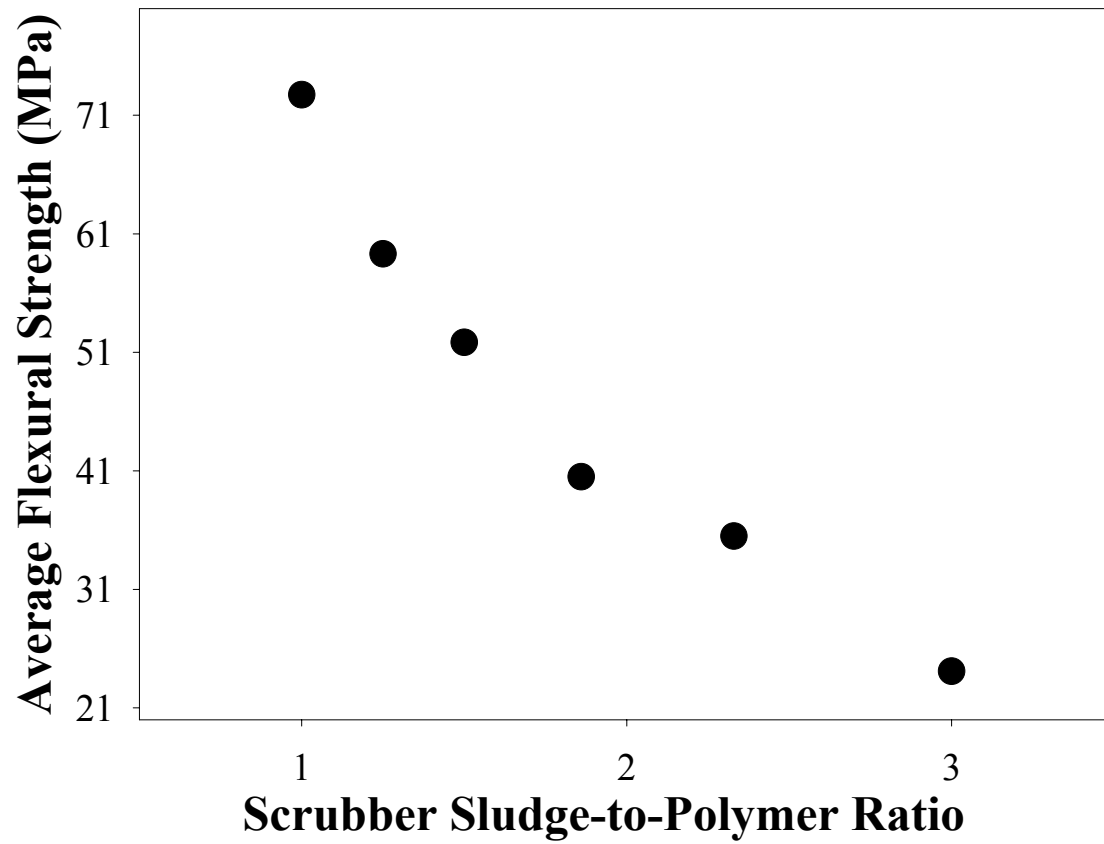


Figure 9. How the average flexural strength of the countertop-type composites, formed from scrubber sludge and polymer, was affected by the scrubber sludge-to-polymer ratio used. These composites were formed via a vacuum molding technique.

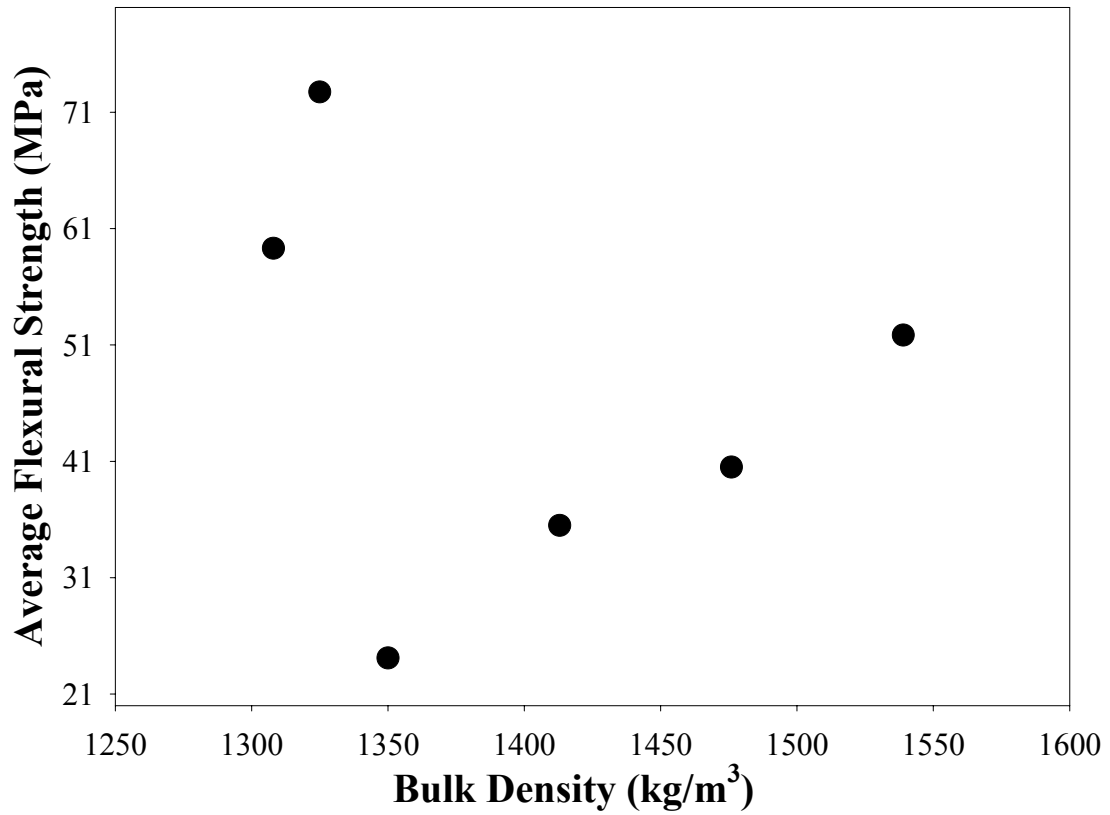


Figure 10. This figure depicts the lack of linear relationship between density and the average flexural strength of the countertop-type composites formed from scrubber sludge and polymer. These composites were formed via a vacuum molding technique.

Co-Blending of Polymers: Having established our ability to form countertop materials of different colors, we then focused our attention towards enhancing the textural and surface characteristics of our countertop materials. To enhance the scratch resistance of our countertops, we explored whether incorporating an additional polymer into the polymer used to form the countertops would further improve the scratch resistance of our material, i.e., by forming composites from polymer mixtures. The countertop composites formed from co-blended polymers were tested for their mechanical strength. The results are reproduced in Figs. 11 and 12. One of our goals in developing these materials was to improve the surface texture of our materials by using a different polymer in conjunction with our Poly-Deg polymer.

We have observed that adding a small amount of polyester polymer (SAM-P2) into our previous formulations can substantially improve the surface textures of the countertops. Moreover, co-blending the polymers did not decrease the strength as long as the concentration of SAM-P2 was limited to less than 5 wt %. It should be noticed that the commercial countertops we tested have a flexural strength of about 40 MPa, and our copolymer formed composites have a strength of 41 MPa. The newly introduced polymer did not influence the formation technique that so far had been developed. In addition, this polymer could be incorporated within the material under the same conditions, i.e., temperature and pressure, as the previous polymer.

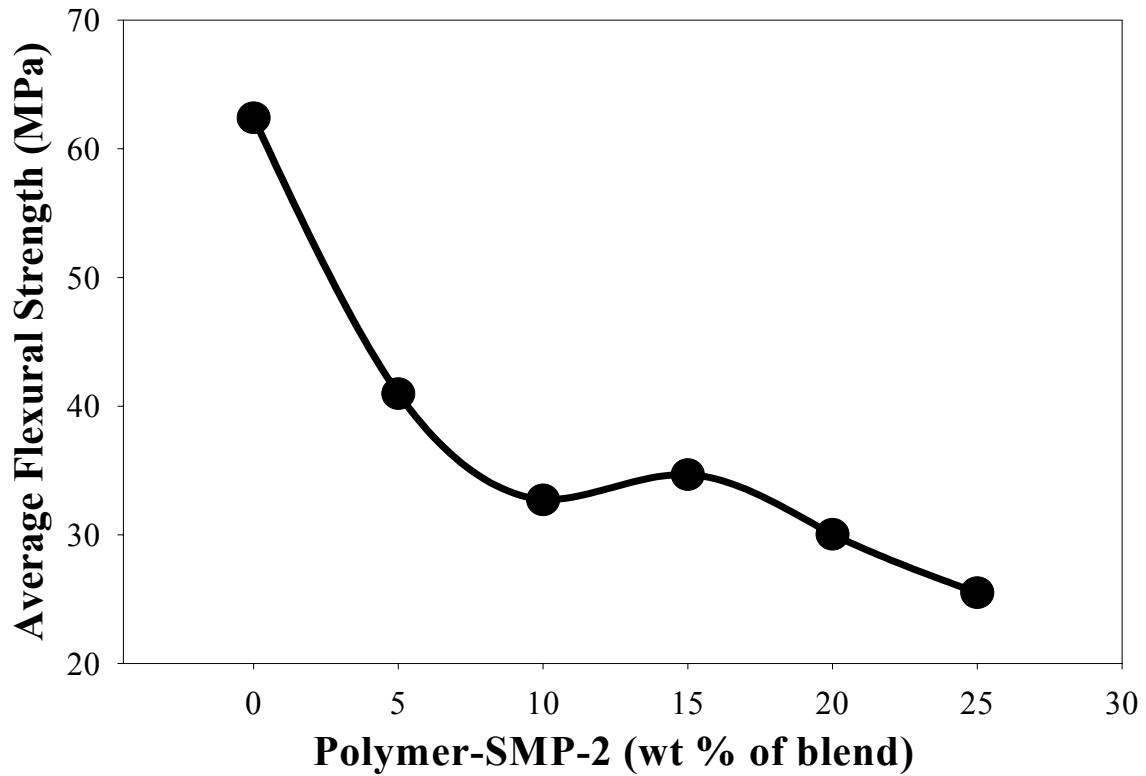


Figure 11. This figure depicts how the concentration of polymer SAM-P2 affected the mechanical properties of the countertop composite formed from sulfate-rich scrubber sludge. The high-end commercial countertop we tested gave an average strength of about 40 MPa.

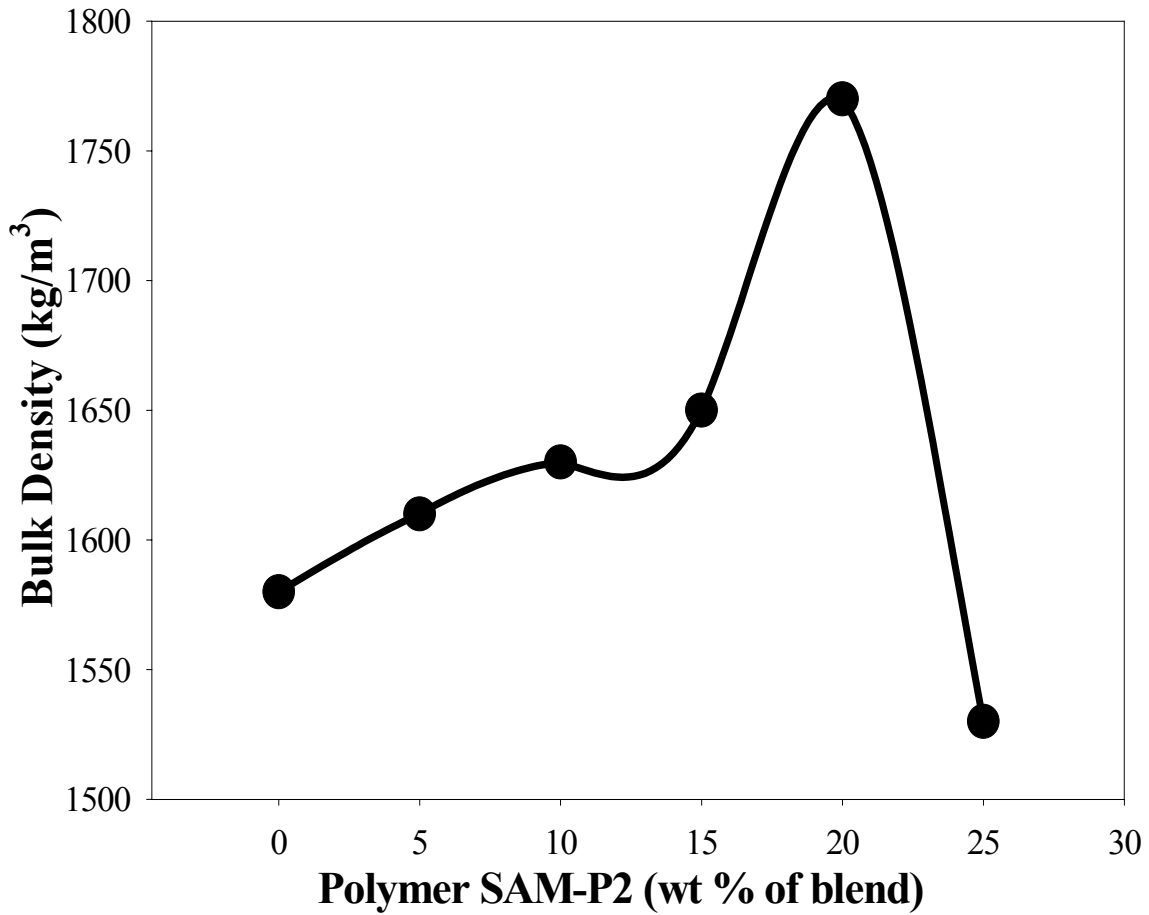


Figure 12. This figure depicts how the concentration of polymer SAM-P2 controlled the density of our countertop composites formed from sulfate-rich scrubber sludge.

Waste Recycling (countertop): Even though originally we had not proposed to explore whether the waste generated during the countertop fabrication could be utilized or recycled, it became apparent that economic considerations would dictate that we do so. Therefore, we explored the following:

- Whether waste or broken countertops could be recycled.
- Whether common organic solvents could reduce the particle size of the waste countertop material so that they could be used as decorative material for our countertops.
- Whether cryogenic grinding could reduce the particle size of the wasted material rapidly and cheaply.

We were able to reduce our old countertop samples with the help of common solvents, such as acetone. However, we had two concerns regarding this procedure. First, we were not able to control the shape, size, and strength of the samples once they were dipped into the common solvents. Second, the amount of solvent required to break down the samples was substantial. This would generate a large amount of solvent waste. Therefore, the solvent approach was abandoned.

Since the solvent approach did not produce the desired results, we attempted to reduce the particle size of old countertops or discarded countertop materials using a cryogenic grinding approach. In this method, the samples were first immersed in liquid nitrogen before they were ground. It appeared that this approach would be successful in reducing the waste countertop to smaller sizes, but this approach might not be economical either.

To fabricate the countertops using the waste material, we first crushed the old material using a grinder designed and built in the Physics Department workshop. This grinding machine has been motorized using a high torque electric motor. In addition, small hoppers were built for feeding the chunks of old samples in the grinder. The ground samples were then mixed with scrubber sludge using a high shear mixer prior to carrying out the countertop fabrication.

Using the smaller sized countertop waste, we initially studied if the countertops, which were damaged or broken during the fabrication process, could be recycled. We were able to develop materials from the old or broken materials. In fact, the recycled materials not only were used as fillers but were also used to create different patterns. Figures 13, 14, and 15 show various countertop materials, which were fabricated using the recycled material.

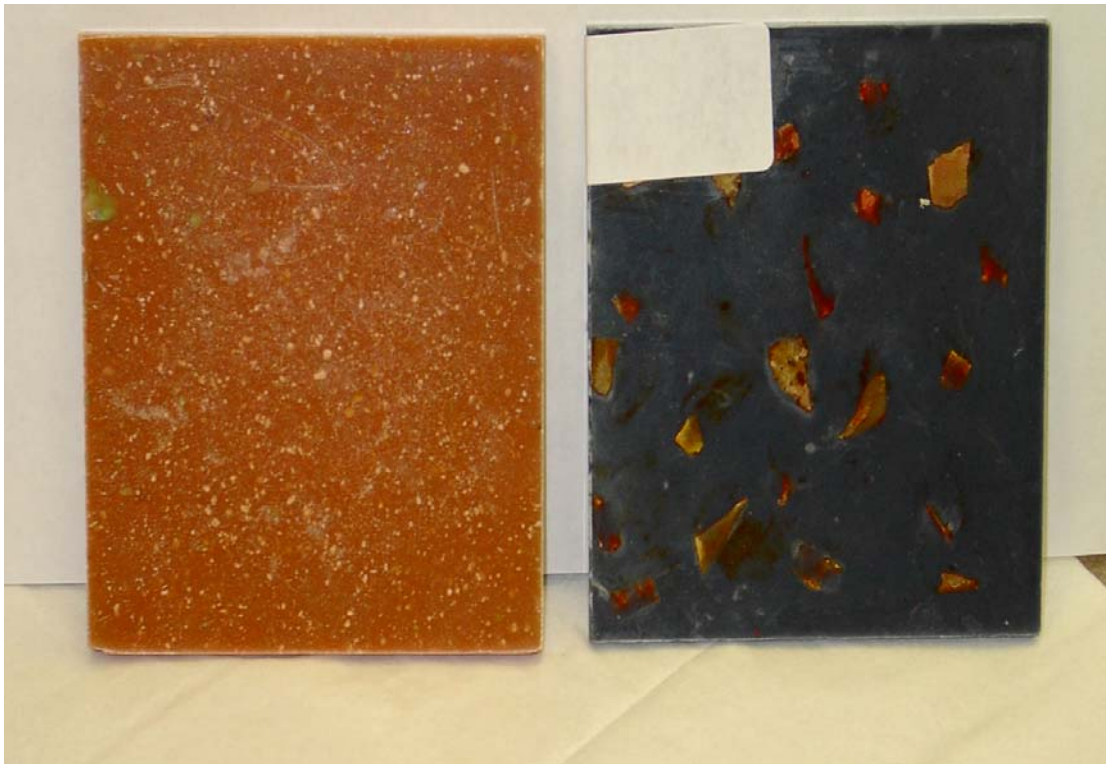


Figure 13. Countertops fabricated from scrubber sludge and waste material.

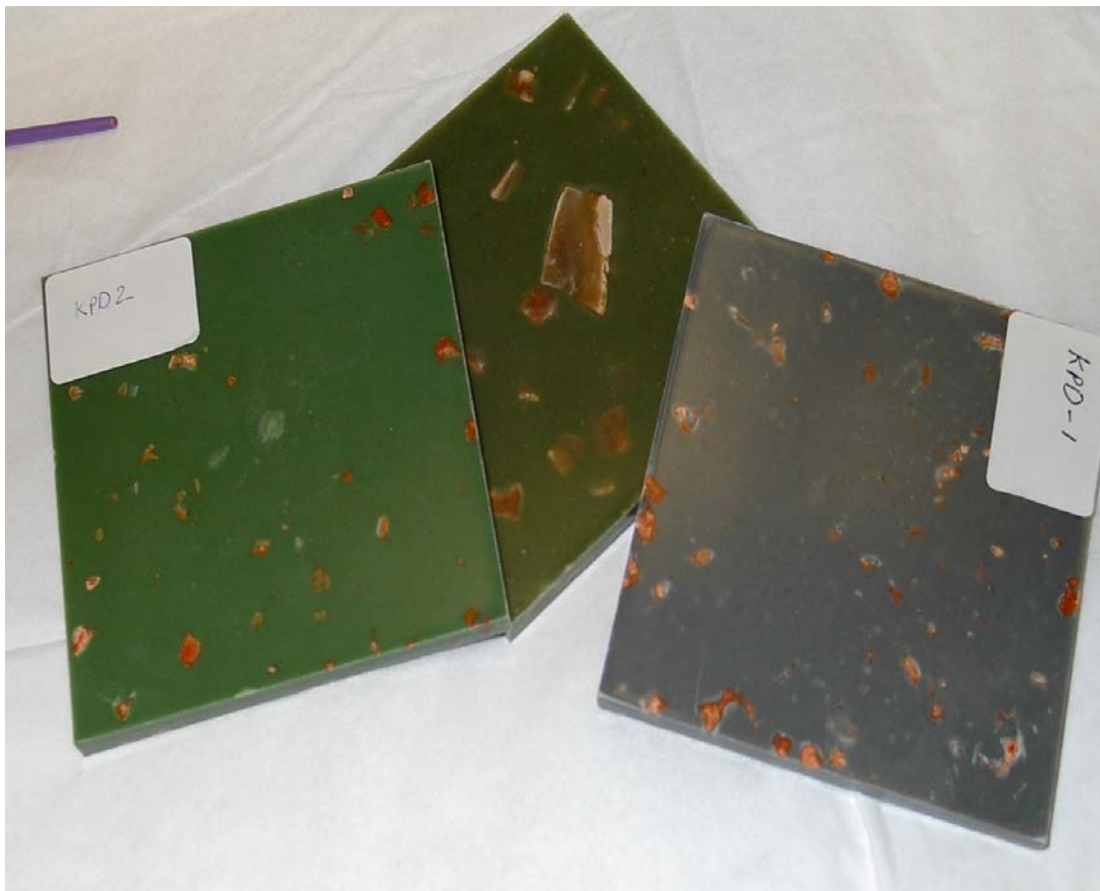


Figure 14. Countertops formed from scrubber sludge and waste material.

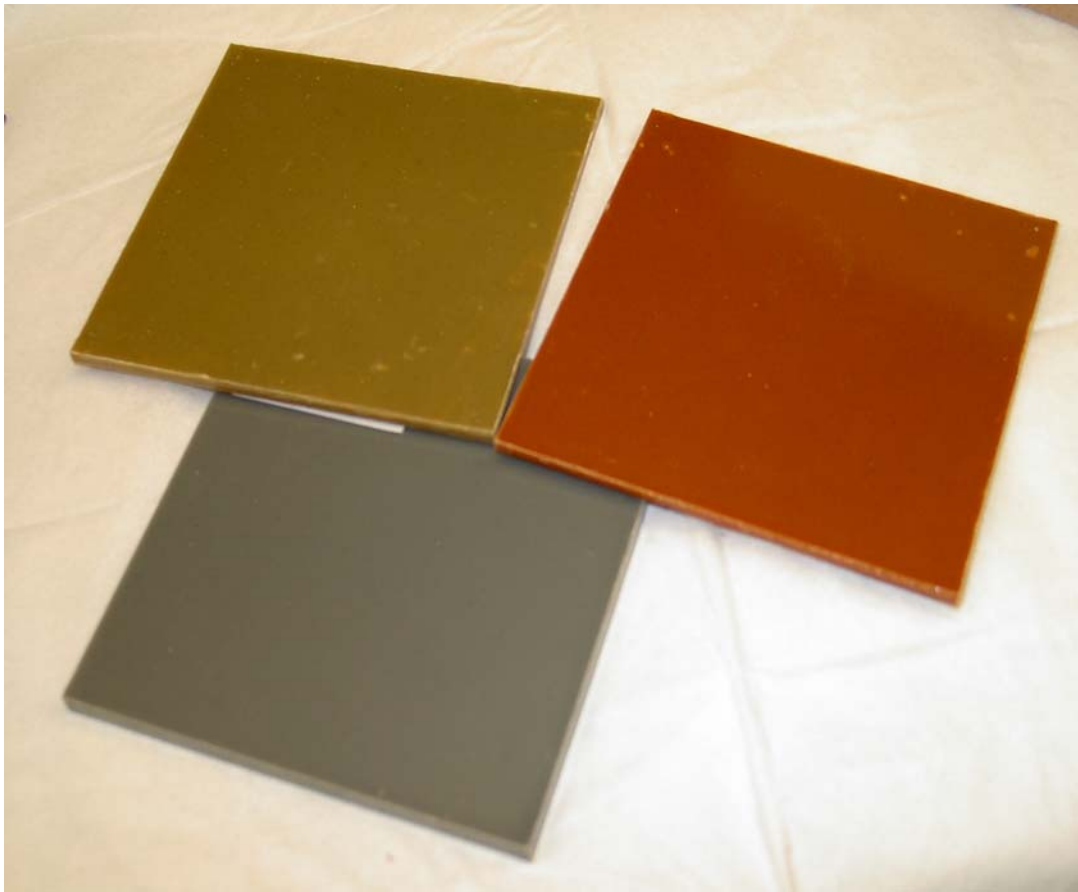


Figure 15. Countertops fabricated from scrubber sludge and waste material.

A number of countertop samples were fabricated using as-received but air-dried scrubber sludge and waste material. The formed materials were subjected to three-pointing bending tests to ascertain their flexural strength. The data are reproduced in Table 3. As can be seen from the data presented in Table 3, the incorporation of the waste materials did produce variability in the strength of the countertops. However, this variability, both in density and in average flexural strength, is within uncertainty associated with mechanical fabrication process.

TABLE 3
The effects of waste countertop and formation load on the flexural strength of countertops formed from scrubber sludge.

Scrubber Sludge (kg)	Old Countertop (kg)	Polymer Poly-Deg (kg)	Polyester (kg)	Load (lbs)	Density (kg/m ³)	Average Flexural Strength (MPa)
18.5	2	13.4	3	5000	1726	47.30
18.5	2	13.4	3	5000	1756	55.08
18.5	2	13.4	3	7500	1710	51.14
18.5	2	13.4	3	7500	1696	45.47
18.5	2	13.4	3	7500	1663	53.30
18.5	2	13.4	3	7500	1625	51.74

COUNTERTOP'S MECHANICAL PERFORMANCE

Polishing Countertops: The principle investigator visited a commercial Corian countertop facility to see the effectiveness of our product. In addition, the investigator discussed in detail the potential of our product with commercial installers and how we can adopt their polishing techniques. To further enhance the texture and feel of our product, we adopted the polishing procedure used in solid countertop surface industry, i.e.,

- the fabricated countertops were first ground to a smooth surface with a rotatory grinder using a 625 grit sized sand paper, and
- then the ground surface was further buffed and polished.

When we adopted this procedure, we found this procedure to be very effective in polishing out countertops. In fact, it allowed us to save countertop which would have been typically discarded because of surface defects.

Joining of Two Countertops: One of the important issues for the successful development of countertop materials from scrubber sludge was their ability to be joined, i.e., whether two pieces of the countertops could be put together to form a single, larger sample. To test this, we conducted experiments to explore whether two different color countertops, fabricated from sulfate-rich scrubber sludge, could be joined using the parent polymer. Indeed, we were successful in joining two countertop materials, and

during the last six months we have monitored the joined pieces for any kind of dimensional and mechanical instability. So far, we have not observed either dimensional or mechanical failure.

The other issue we dealt with was joining two countertop pieces when the joint was not transparent. The joint material was designed from sludge and polymer, thus, was not transparent. A joint line could be seen where two pieces were put together. Therefore, we attempted to join the countertops using the pure polymer from which they were originally fabricated. This joined the two pieces together without any apparent joint line. However, our experiments did suggest that the strength of the joint was not high, and it was easy to break the material at the joint-line. This was also true for commercial solid surface countertops having joints.

Effect of Age on Strength: To evaluate how age affected the strength of our material, we subjected the countertops fabricated a year ago to strength measurements. Three-pointing bending arrangement was used for these tests. The results are reproduced in Figure 16. The average flexural strength of our tested countertop material was about 31.5 MPa. This data are within the uncertainty of the strength measurements conducted last year. Therefore, it is reasonable to argue that time, at least a year, did not affect the strength of our material.

Polymer Comparison: We used two different types of primary polymers to fabricate our countertop composite materials, i.e., Poly-Bul and Poly-Deg. It should be mentioned the price of Poly-Deg was less than half that of Poly-Bul. We tested the countertops made from these two polymers to see whether there were any differences in the strength. For this, we tested year old samples. The results are reproduced in figures 16 and 17. While the countertops made from Poly-Bul had an average strength of about 32 MPa, the average strength of countertops made from Poly-Deg had strength of 38 MPa. It should be noticed that countertops made from Poly-Deg were denser than those made from Poly-Bul. It is worthwhile to point out that curing odor associated with Poly-Deg was greater than that associated with Poly-Bul.

Fabrication of 64 Countertop Pieces: In addition to exploring the recycling techniques and polishing approaches for our countertop materials, we finished fabricating sixty-four (64) countertop materials of 4" x 4" and 6" x 6" sizes. These countertops were fabricated in different colors and patterns as shown in Fig. 18. We chose to fabricate 1-inch thick decorative countertops. This thickness was chosen since typical high-end commercial countertops are about 1-inch thick.

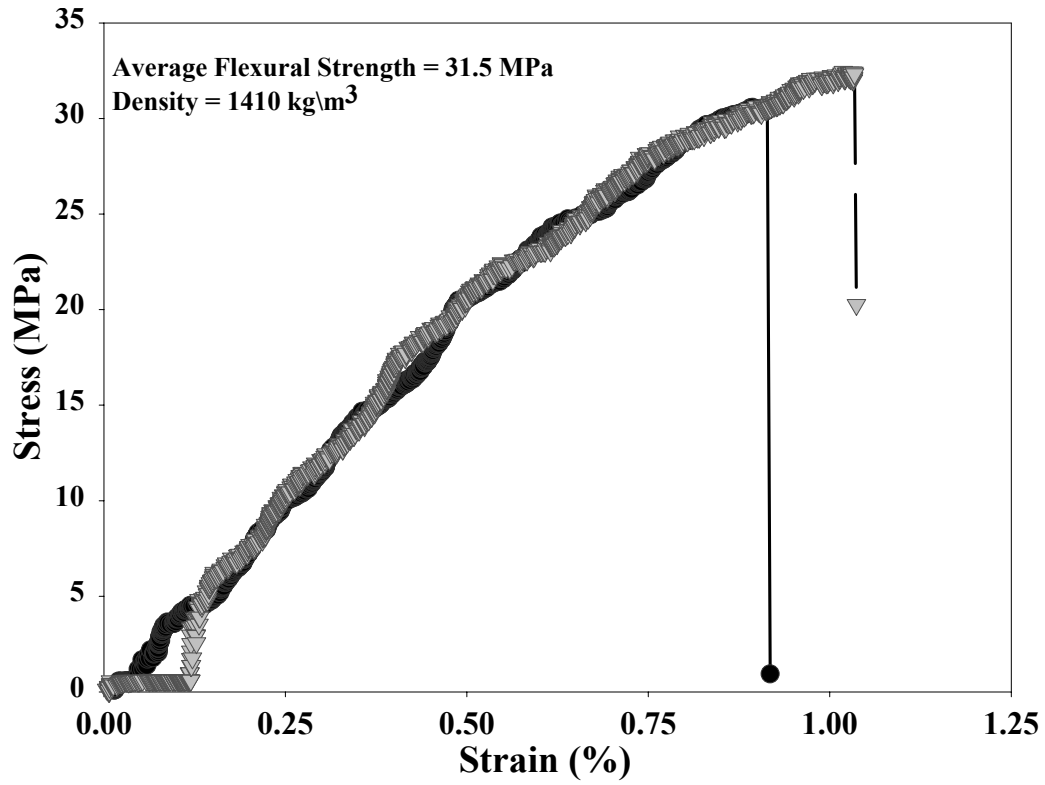


Figure 16. This data reproduce the stress-strain curve for countertop materials fabricated from sulfate-rich FGD scrubber sludge and polymer Poly-Bul.

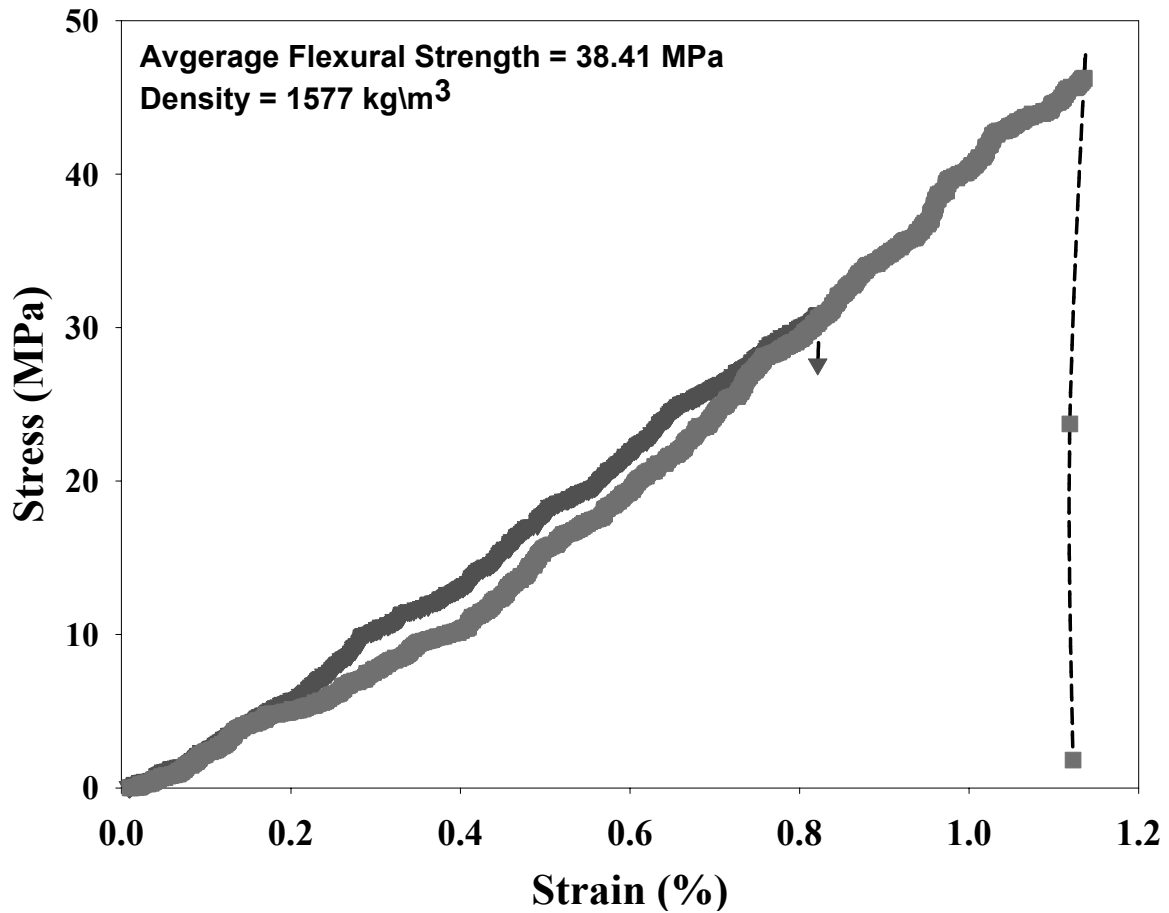


Figure 17. This reproduces the stress-strain curve for countertop materials fabricated from sulfate-rich FGD scrubber sludge and Poly-Deg and polyester polymers. The scrubber sludge-to-polymer ratio was 1.02. The ratio between Poly-Deg and polyester was 4.3.

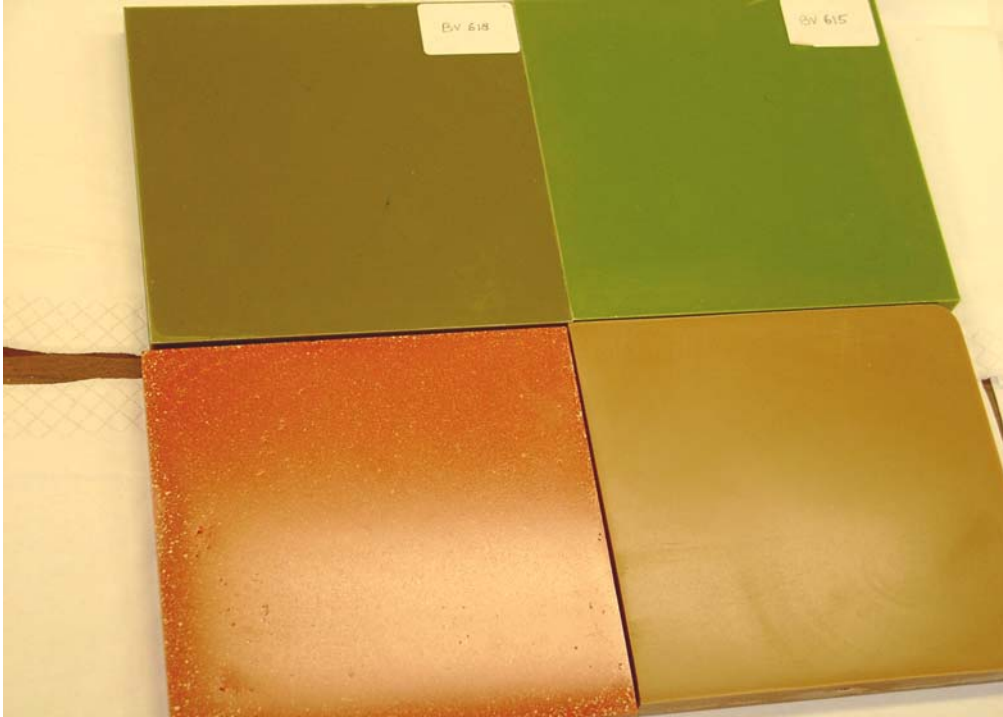


Figure 18: The digital pictures of 1-inch thick countertops fabricated from sulfate-rich scrubber sludge.

DECORATIVE TILE MATERIALS FABRICATION OPTIMIZATION AND TESTING

Decorative Tiles: We made substantial progress in the development and fabrication of the decorative tiles from sulfate-rich scrubber sludge during this project. These include:

- Ability to change design patterns on the decorative tiles with ease and without compromising their mechanical properties.
- Ability to vary the thickness of the materials without any mechanical or design problems.

Furthermore, we have identified the means to speed up the fabrication of these materials by changing some of the working conditions. By changing these conditions, we were able to reduce the time of fabrication by four fold. In this report, we will refer to these materials as Tiles-IV, which were fabricated using our recently modified approach, and we will refer to the previous samples as Tiles-I. Tiles-I were fabricated by conventional compressive molding technique. The results are summarized below:

- a. The flexural strength of Tiles-IV was slightly lower than the flexural strength of Tiles-I. However, the rate of fabrication for Tiles-IV was four times more than Tiles-I.
- b. We tested Tiles-IV for their flexural strength by applying load in different directions. The tiles exhibited the same strength in all directions. Thus, we argue that our tile materials are isotropic suggesting well-dispersed additives in the tile composite.
- c. The density of Tiles-IV materials was comparable to the density of the Tiles-I materials.
- d. The flexural strength of Tiles-IV samples varied with the density of the materials. The higher the density the higher was the flexural strength of the material.
- e. The specific flexural strength, on the other hand, did not decrease with the density of the materials.
- f. For comparison purpose, we post-cured Tiles-IV samples and compared the flexural strength of the post-cured samples with the samples, which did not undergo post-curing. Our results suggested that post-curing did not enhance the flexural strength of the tiles. This is clearly depicted in Figure 19. Therefore, we did not undertake post-curing of our tiles because it added additional cost to the manufacturing process without adding any strength benefits. The new approach we are using is promising. The fact that post-curing did not have a significant effect leads us to believe that we were able to fully cure the materials, even though we have reduced the time of fabrication. As a result, we believe reducing the time of fabrication by four times will reduce the cost of production by a significant amount. We are further testing the properties of these materials, and we are planning to study the effect of pigmentation and the effects of decorative patterns on the properties of these materials in the future.
- g. Another important parameter we examined was how the particle size of the partially cured polymer-M1 affected the strength of the formed composites. To accomplish this task, we fabricated composites from coarse polymer particles, i.e., as-received polymer and finely ground polymer, i.e., $< 45 \mu\text{m}$. In addition, we

formed composites in which we used coarse and fine particles in 1:1 ratio. To minimize the cost of grinding, we obtained a meat grinder and attached pulleys and gears to it so that the grinder could be motorized. Results are summarized in Figure 20. Clearly, the size of the polymer particle plays a crucial role in determining the eventual strength of the composite. In fact, the finer particle sized polymer increased the strength of our composites by almost 47 % relative to coarser particles.

EFFECT OF GRANULES: We also examined how the incorporation of granules, added to create different patterns on the decorative tiles, affected the mechanical properties of the tiles. The flexural strength results are summarized in Table 4 and Figure 20.

Table 4.
Effect of decorative granules on the strength of the tiles.

SAMPLE	M-polymer (%)	Scrubber Sludge (%)	Granules (%)	Density (g/cm ³)	Flexural Strength (MPa)	Specific Flexural Strength (MPa cm ³ /g)
BV 497	100	0	0	1.48	92.95	62.80
BV 498	48	48	4	1.63	43.69	26.80
BV 499	50	48	2	1.62	52.78	32.58
BV 500	50	50	0	1.65	41.71	25.28

The main experimental features are summarized:

- It is interesting to note that adding 2% of the granules (BV 499) in the sample actually increased the flexural strength when compared to the sample where no granules were added (BV 500). This means that the granules have better linkage with the matrix.
- Even though our granules are polyester polymer based, they do not act as binders. When we increased the amount of granules from 2% to 4% by reducing the binder by 2-wt %, the flexural strength decreased.
- The density of the materials did not change by various variables used as reported in Table 4. However, the combined effect of the above two resulted in lowering the specific flexural strength.

Waste Recycling (tiles): We undertook experiments to determine whether the broken or waste material obtained during the fabrication of tiles could be recycled. A number of tiles were fabricated from CWLP scrubber sludge using broken or damaged tiles. The experimental conditions were the same as used for developing the decorative tiles. We were able to load 45-55 % by weight of the old samples without reducing the mechanical strength of the materials significantly. Figure 21 depicts some of the decorative tiles,

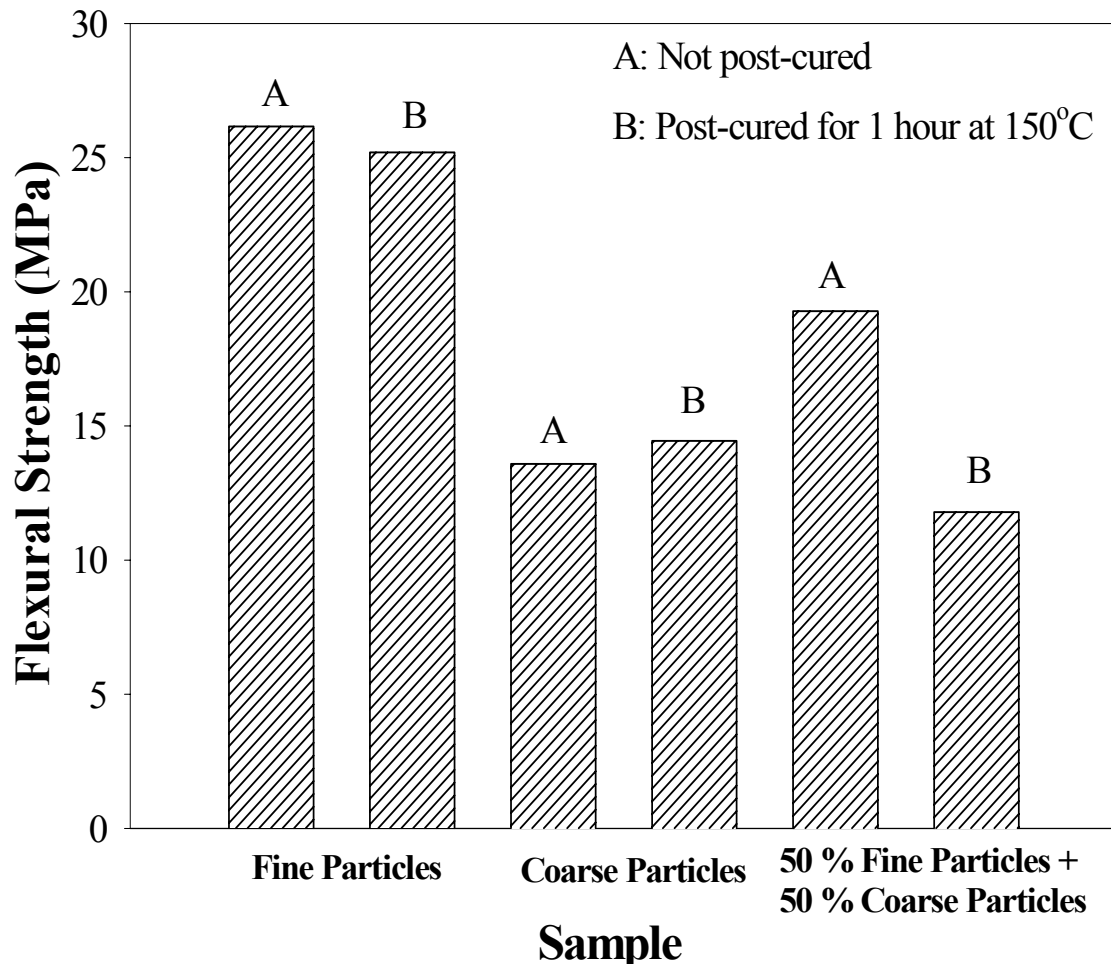


Figure 19. This figure reproduces the effect of post-curing and the polymer's particle size on the flexural strength of decorative tiles formulated from sulfate-rich scrubber sludge.

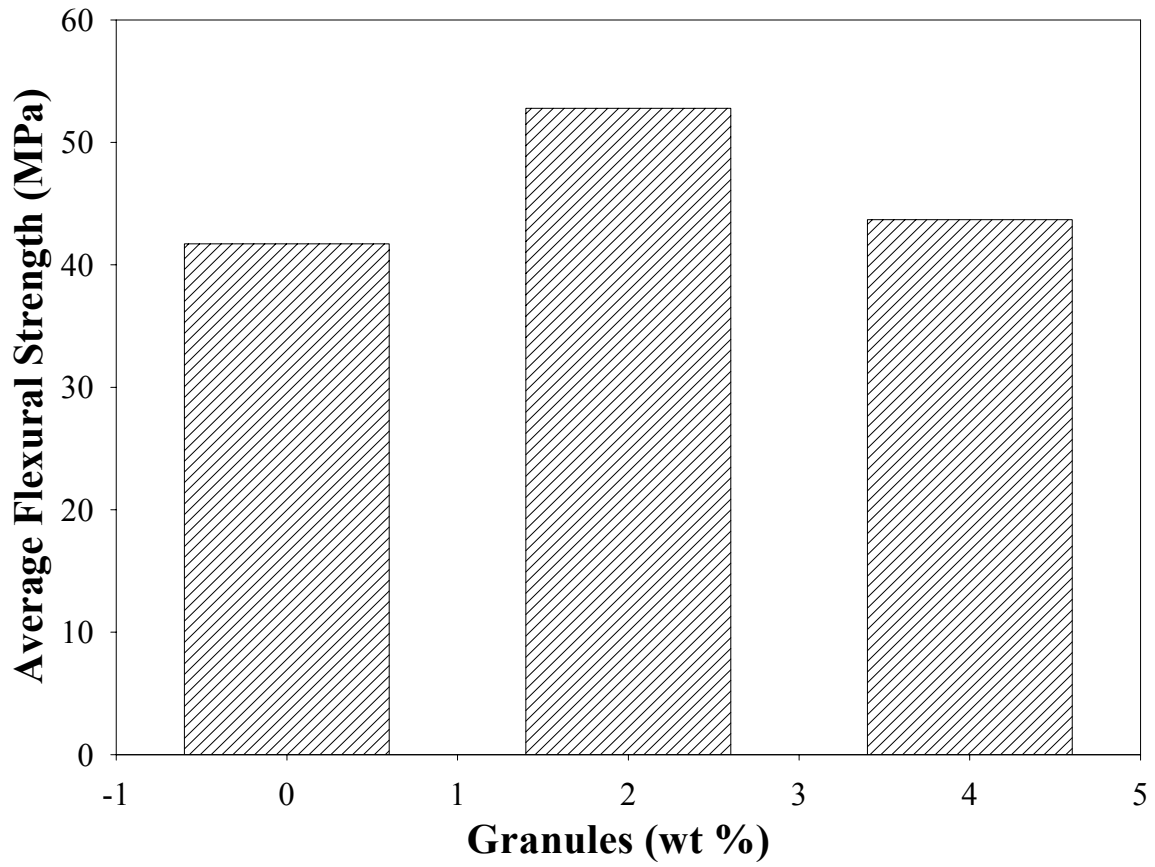


Figure 20. This figure shows how the concentration of granules affected the flexural strength of our decorative tile composites.

which were fabricated using recycled material. Tiles were subjected to mechanical tests to evaluate how the waste material's loading affected the strength of the tiles. The results are summarized on the following page in Table 5 and Table 6.

TABLE 5

The effect of waste loading on the mechanical performance of the tiles (series BV535 to BV539).

% Loading of Broken Tiles	Density (kg/m ³)	Average Flexural Strength (MPa)
10	1563	35.5
20	1538	35.9
30	1503	18.6
40	1470	9.3
50	1453	12.9

TABLE 6

The effect of waste loading on the mechanical performance of the tiles (series BV540 to BV545).

% Loading of Broken Tiles	Density (kg/m ³)	Average Flexural Strength (MPa)
25	1506	76.1
35	1472	75.4
45	1507	62.6
55	1461	41.6
65	1453	28.2
75	1382	6.5

Effect of Water on Tiles: We also examined the effect of water on the stability of the tiles fabricated from sulfate-rich scrubber sludge. There was a concern that our tiles may warp if exposed to water. We tested this by immersing our tile in standing water, i.e., the tile was completely under water. The stability of tile was checked every week for two months. We did not observe any warping in two months time, therefore, the experiment was discontinued after two months.



Figure 21. Decorative tiles made from sulfate-rich scrubber sludge and waste or broken tiles.

Effect of Age on Strength: The decorative tiles, which were fabricated from sulfate-rich scrubber sludge a year ago, were subjected to strength testing to gauge whether aging had any effect on the strength of our tiles. Three-point bending measurements were conducted on the tiles using a Universal Testing Machine. The stress-strain curves for our samples are depicted in Figure 22. The average strength of the tiles was 52.5 MPa, and the density of the tiles was 1620 kg/m³. These results suggest that aging (for a year) did not affect the strength of our materials.

Fabrication of 64 Tiles: One of the important goals of our project was to produce about 64 tiles to establish the feasibility of fabricating decorative tiles from sulfate-rich scrubber sludge. We have completed this task. The tiles were fabricated in different colors and were mounted on 3 feet by 2.5 feet commercial boards.

Mounted Tiles: The aforementioned tiles were mounted on commercial boards to evaluate their economic and commercial viability. Initially, we successfully mounted our tiles on a 12" x 12" commercial Durock board with the help of a commercially available adhesive, i.e., Mapei TYPE I. After mounting the samples, they were placed vertically for two months to test if the samples would peel either due to their own weight, fatigue failure of the adhesive, or lack of strong bonding between the tiles and the commercial board. The mounted samples are shown in Fig. 23. After seven months of regular observation, we did not see any detectable peeling. The samples are still intact to this date.

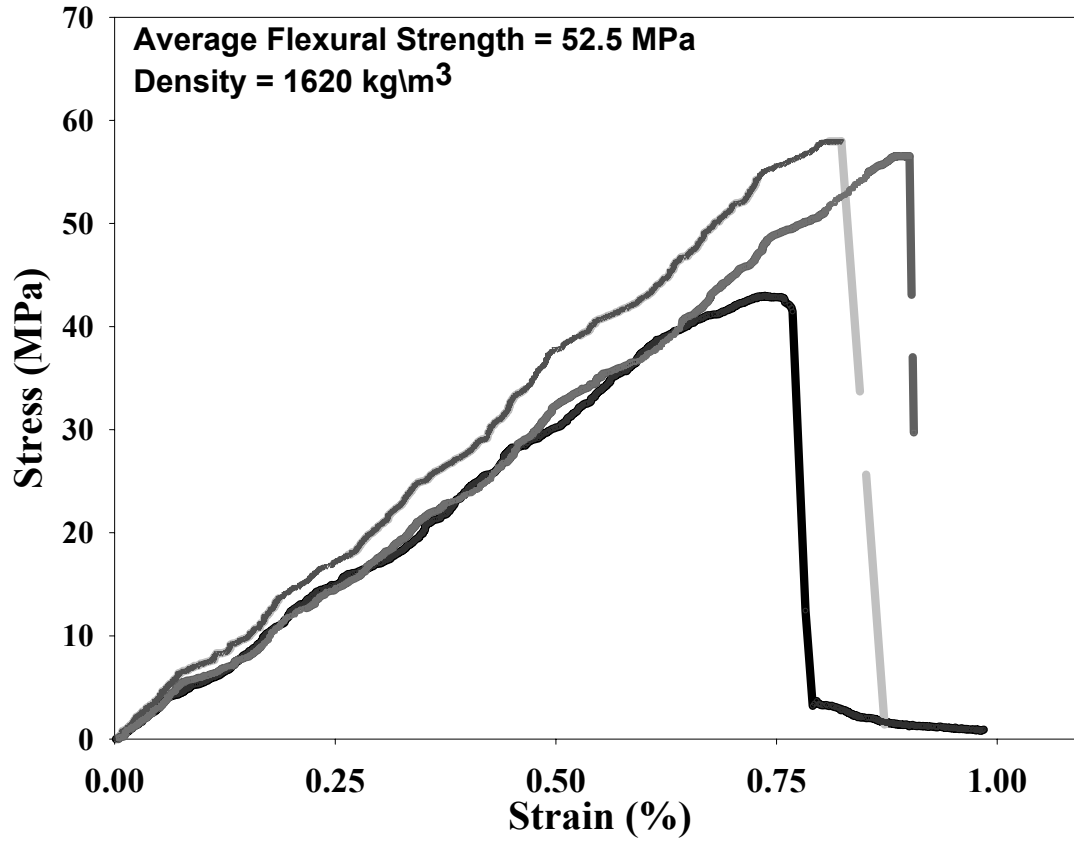


Figure 22. Stress versus strain curve for decorative tiles fabricated from sulfate-rich scrubber sludge.

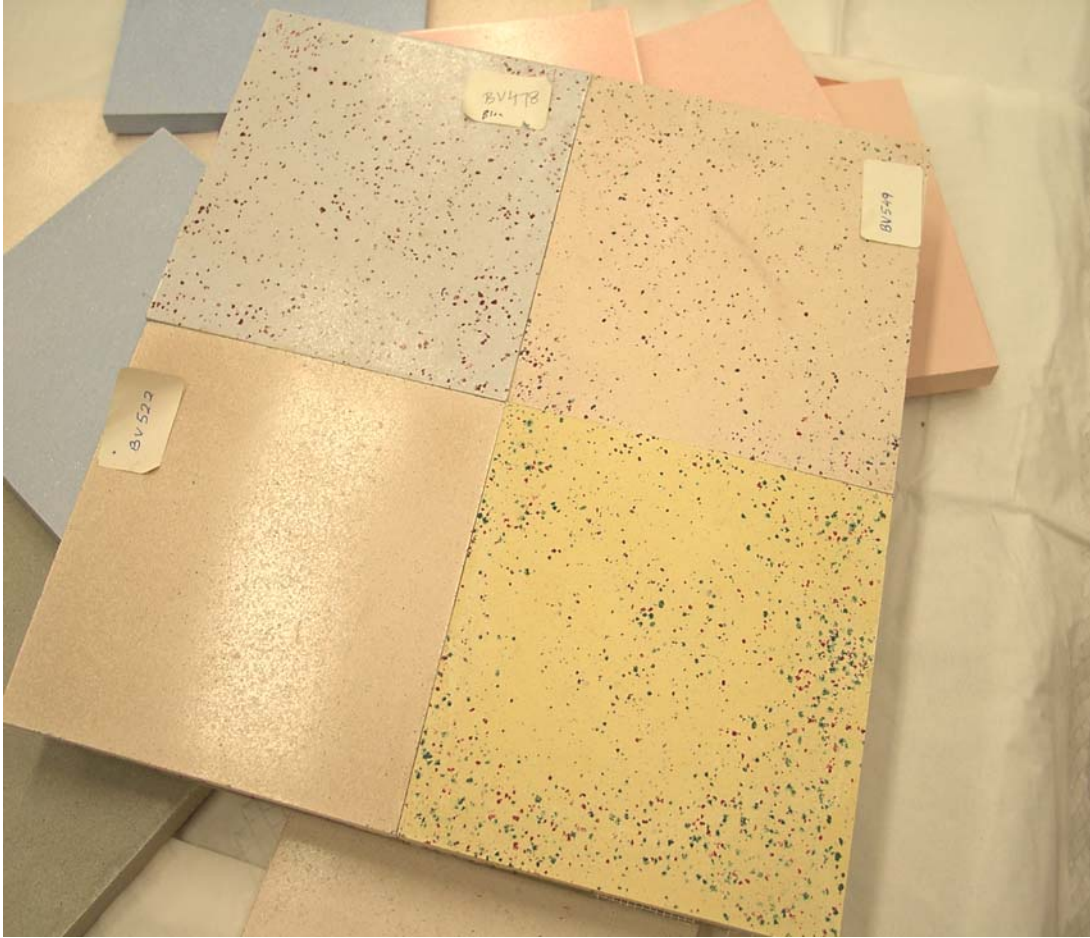


Figure 23. This digital picture shows four tiles mounted on a commercial Durock board.

Buoyed by our success to mount our tiles on a Durock 12" x 12" board, we attempted affixing decorative tiles on a 3 feet by two and half feet Durock underlayment board. Again, we used adhesive Mapei TYPE I for mounting our tiles. However, during the mounting process, we realized that commercial Durock board did not have enough modulus or strength to support any weight without adequate reinforcement. Therefore, we reinforced the Durock with plywood and wood strips of two inches by four inches. The Durock was mounted on the plywood using a readily available commercial adhesive, i.e., thinset mortar. Unfortunately, the mortar had to be mixed with water to set, and the plywood was dimensionally unstable with respect to variation in moisture content. The plywood swelled, and expanded when it was exposed to moisture. The plywood shrunk and also contracted when it lost its moisture. As a result, the Durock experienced uneven distribution of stress, and warped. The tiles that were mounted on the Durock also experienced uneven distribution of stress and hence did not stay intact. We should have waited longer before mounting the tiles on the Durock, until the curing of the thinset was complete and the plywood had dehydrated. We tried remounting our tiles using the experience gained above.

The remounted tiles are shown in Figs. 24, 25, and 26. The board, fitted with tiles, has not shown any defects or failures emerging either in the tiles or in the bonding between the tiles and the board so far.



Figure 24. This figure shows thirty decorative tiles, which were mounted on a 3 feet by 2.5 feet Durock board.



Figure 25. Different color tiles, fabricated from sulfate-rich scrubber sludge, were mounted on a commercial Durock board.



Figure 26. Excellent bonding was observed between tiles, fabricated from sulfate-rich scrubber sludge, and commercial Durock board as can be seen here.

Siding Material: We also conducted experiments to explore whether siding material could be fabricated from sulfate-rich scrubber sludge. Unlike decorative tiles and countertops, the performance requirements for siding material are substantially different. Therefore, siding materials must be able to withstand large variations in temperature and UV radiation. We attempted to form these materials in 10 inch by 10 inch by 0.125 inch size as shown in Figure 27. It appears, in principle, it is possible to form siding material from scrubber sludge, however, the actual development will require a stand alone project.

Leaching Behavior: Another important issue dealt with was whether the long-term exposure to water would have a deleterious environmental effect and whether long term exposure to water would compromise the strength of the material. We did not observe any strength reduction of our countertop material even when the sample was submerged in water for six months. The countertop and decorative tile samples were also sent to a commercial laboratory for ASTM D3987 shake extraction test. The ASTM D3987 test was undertaken to evaluate whether arsenic and selenium metals could pose a problem during the disposal phase of these materials. The results are summarized below in Table 7.

Table 7. The arsenic and selenium leachate obtained from countertop and decorative tile using the ASTM D3987 test

Sample	Arsenic (mg/L)	Selenium (mg/L)	Reporting Limit
Countertop	< 10	< 10	10
Decorative Tile	< 10	< 10	10

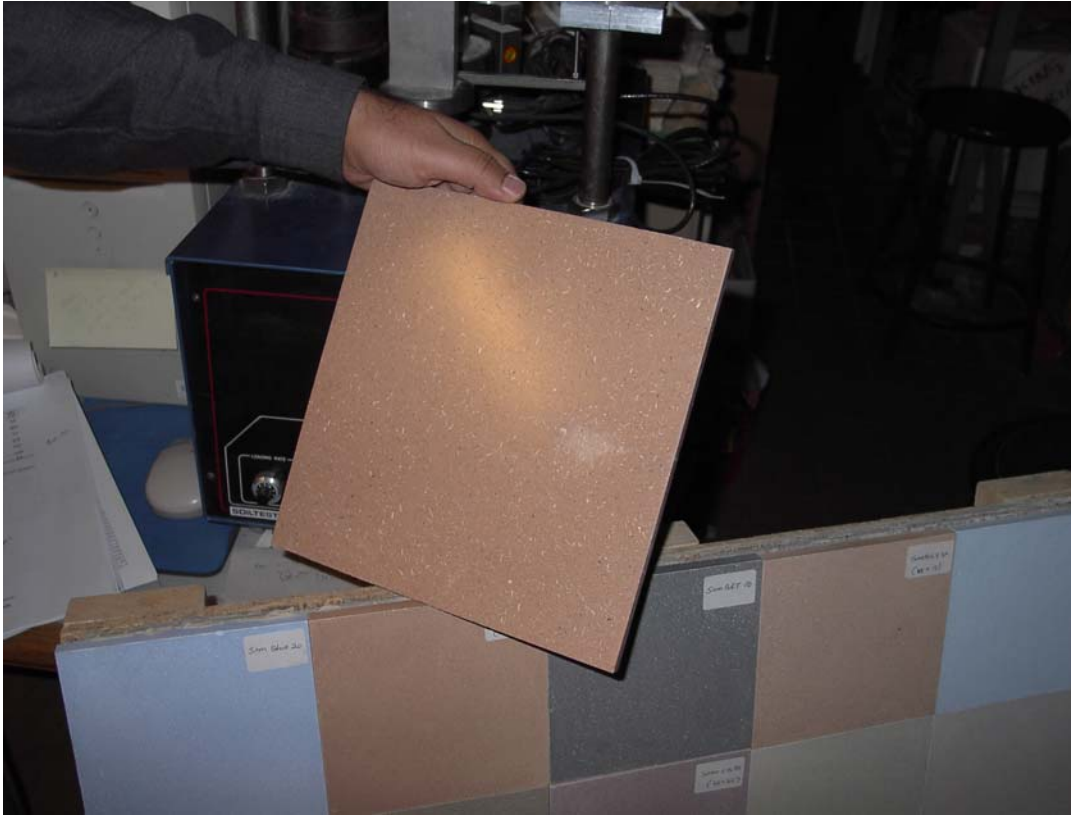


Figure 27. A siding sample of size 10" x 10" x 0.125" fabricated from sulfate-rich scrubber sludge.

ECONOMIC ANALYSIS:

A comprehensive engineering economic analysis of the manufacturing of the countertops and decorative tiles was undertaken. Various parameters, such as production scale, product characterization, waste generation and disposal costs, capital cost requirements, production equipment costs, and operational costs, were considered. The overall pilot scale approach to fabricate our materials is depicted in Figure 28. The economic analysis results are summarized below for countertops and decorative tiles in Table 8 and 9, respectively.

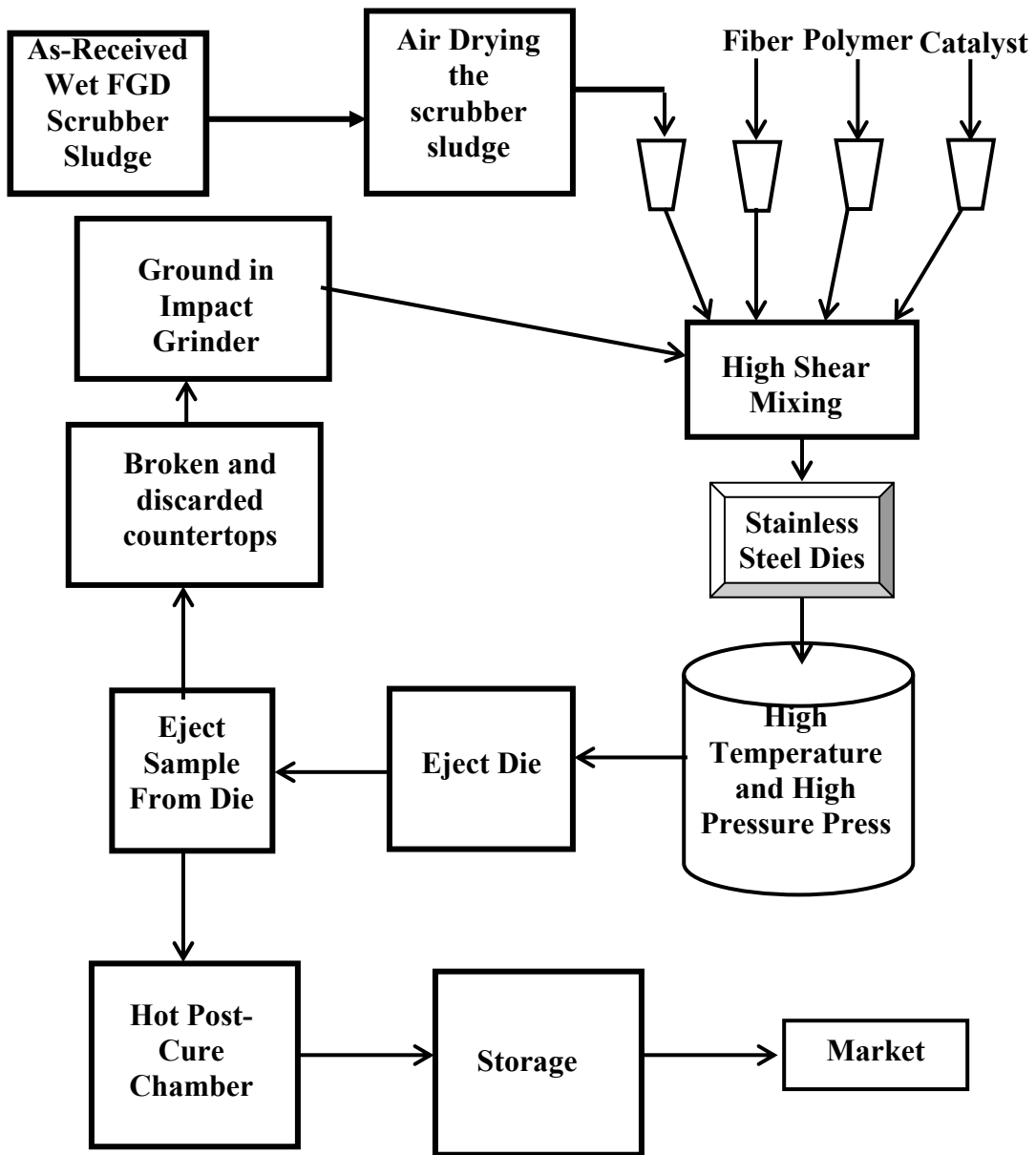


Figure 28. Schematic of the pilot scale approach to fabricate FGD materials.

Table 8. **Engineering Economics for Making Countertops****Assumptions:**

Life of the project	10 years
Amount of scrubber sludge (as-received) processed/year	378 tons
Type of Composite Product -- Tile (8" x 10" x 0.25")	
No. of days per year	300

Capital Costs:

Material handling systems (hoppers, screw feeds)	\$20,000
Flue gas drying system	\$10,000
Bens, conveyors, dust control systems	\$10,000
Mixers	\$30,000
Fabrication and production facilities	\$125,000
Curing Chamber	\$10,000
1500 Sq. ft. facility	\$20,000
Fork lift system	\$50,000
Other costs	\$25,000
 Total Capital Cost	 \$300,000

Because the same facilities will also be used for manufacturing decorative tiles, the capital cost consequently will be reduced by half for the countertops.

Modified Total Capital Costs	\$150,000
Interest rate	8%
Capital cost/year (150,000 x 0.149)	\$22,350

Costs:

<i>Size of countertop</i>	2' x 3' x 0.75"
Volume of countertop	0.375 cu. ft.
Density of the product	93.7 lbs/cu. ft.
Weight of each countertop	35 lbs
Waste (10%)	3.5 lbs
Total weight	38.5 lbs

Material Cost:

Cost of scrubber sludge [@ \$1/ton] per countertop	\$0.01
Cost of polymer [@1.45/lb] per countertop	\$25.1
Cost of fiber [@1.50/lb] per tile	\$2.90
 Total material cost	 \$28.0

Supplies:

Mold release per sample	\$0.10
Mold cost per mold	\$300.00
Number of molds = 3	
Number of countertops per year = 25200	
Mold maintenance (5% of total mold cost) = $300 \times 0.05 \times 3$	\$45.00
Mold maintenance cost per unit (=45/25200)	\$0.02
Hydraulic oil cost per unit (=500/25200)	\$0.02
All supplies (mold release etc.) per countertop	\$0.14

Maintenance:

Maintenance cost (10% of the capital cost) per countertop	\$0.60
---	--------

Power Cost:

Electric (0.1 kWh) per countertop	\$0.10
Heating (\$100/month)	\$0.05

Labor:

Labor cost (2 person @\$15/hour and 0.5 supervisor @\$30,000) per countertop	\$3.00
--	--------

<i>Estimated production cost:</i>	\$31.90
--	---------

Capital cost per countertop	\$0.90
------------------------------------	--------

Operating fund cost per countertop (60 days of operating funds = \$18,000)	0.71
---	------

Estimated total production cost per countertop	\$33.51
---	---------

Estimated Selling price per countertop	\$300 to \$400
---	----------------

Based on the analysis above, it is clear that countertops will have much greater than 20% rate of return.

Table 9. **Engineering Economics for Decorative Tiles****Assumptions:**

Life of the project	10 years
Amount of scrubber sludge (as-received) processed/year	378 tons
Type of Composite Product -- Tile (8" x 10" x 0.25")	
No. of days per year	300

Capital Costs:

Material handling systems (hoppers, screw feeds)	\$20,000
Flue gas drying system	\$10,000
Bens, conveyors, dust control systems	\$10,000
Mixers	\$30,000
Fabrication and production facilities	\$125,000
Curing Chamber	\$10,000
1500 Sq. ft. facility	\$20,000
Fork lift system	\$50,000
Other costs	\$25,000

Total Capital Cost	\$300,000
--------------------	-----------

Because the same facilities will also be used for manufacturing countertop products, the capital cost consequently will be reduced by half for the tiles.

Modified Total Capital Costs	\$150,000
Interest rate	8%
Capital cost/year (150,000 x 0.149)	\$22,350

Costs:

Size of tile	8" x 10" x 0.25"
Volume of tile (including 10% waste)	0.013 cu. ft.
Density of the product	84.2 lbs/cu.ft

Material Cost:

Cost of scrubber sludge [@ \$1/ton] per tile	\$0.01
Cost of polymer [@0.25/lb] per tile	\$0.10
Cost of fiber [@0.05/lb] per tile	\$0.01
Cost of other ingredients [@0.01/lb] per tile	\$0.01
Total material cost	\$0.13
All supplies (mold release etc.) per tile	\$0.01
Maintenance cost per tile	\$0.10

Power cost per tile	\$0.01
Labor cost per tile	\$0.20
Die cost per tile	\$0.05
Capital cost per tile	\$0.20
Operating fund cost per tile	\$0.05
Estimated production Cost per Tile	\$0.85
Estimated Selling price per tile	\$5.00 to \$6.00
(These tiles are decorative wall tiles rather than floor tiles.)	

Based on the analysis above, it is clear that decorative tile product will have much greater than 20% rate of return.

POTENTIAL COMMERCIALIZATION

Both investigators visited the CWLP, Springfield power plant with the intend of exploring whether a pilot scale manufacturing facility could be located at the power point itself. The negotiations are ongoing.

SUMMARY AND CONCLUSIONS

The mandate of this project was to develop value-added materials from sulfate-rich scrubber sludge. Specifically, we were to establish technology for fabricating cost effective but marketable materials like countertops, decorative tiles, and siding material from the sludge. During the course of this project, the following was accomplished:

- 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.
- Our differential scanning calorimetry (DSC) measurements on as-received polymer suggested that the countertop composites should be formed at $T > 60^{\circ}\text{C}$ and not at $T < 55^{\circ}\text{C}$ as recommended by the supplier. In fact, this was born out subsequently after forming the composites at $T > 60^{\circ}\text{C}$.
- We evaluated how the fiber content in our countertop materials affected the strength of the formed composites.
- We studied how the orientation of the fibers within our countertop composites affected their mechanical strength. Our results suggested that though the 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.
- We probed how the formation temperature controlled the strength of the formed material, and we concluded that higher formation temperature ($T < 110^{\circ}\text{C}$) imparted better strength to the countertop material formed from sulfate-rich scrubber sludge.
- We also studied how the degree of cure affected the mechanical strength of our composite materials. It appeared that post-curing in fact decreased the strength of the countertop material.
- We formed countertop composites using conventional molding technique in which we varied the concentration of the sludge from 10-weight % to 50-weight %. However, sludge was treated to control its crystallization in our composite during molding. It appeared the flexural strength of our composites was comparable or better than the flexural strength of commercial products with similar filler concentration.
- We designed and built a vacuum die to form countertop composites under mild vacuum. Using this die, we formed countertop composites in which we varied the concentration of scrubber sludge. The concentration of the sludge in the composite was varied between 50-weight % and 75-weight %. It appeared that we could use up to 65-weight % 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 % inorganic phase.
- We explored whether the countertop composite's resistance to scratching could be further enhanced by forming the composites from block copolymers. In this approach, we incorporated a polymer in addition to the polymer that was used to form countertops. Our results indicated that a second polymer, without degrading the strength of our countertops, could be added to further improve the scratch resistance

of the countertop. In fact, 5-wt % of the second polymer could accomplish this without reducing the scrubber sludge crystallites in our materials.

- Our 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.
- Our experiments suggested that 2 wt % decorative granules could be incorporated in our tile composites without compromising the strength of the material.
- We 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. Our results suggested that sludge-derived tiles could be mounted on currently existing commercial backing boards.
- Our strength and fabrication measurements suggested that a significant amount of waste and broken countertops could be recycled.
- Our strength and fabrication measurements suggested that a significant amount of broken tiles could be used to design different patterns in our decorative tiles. This approach, we believe, would considerably reduce the waste and disposal costs of our fabrication process.
- We fabricated 4" x 4" x 0.2" countertop composites in 11 different colors and patterns.
- We upscaled our countertop composites to 6" x 6" x 0.2" size. At least four different colored countertop composites were fabricated. We have now successfully fabricated 64 pieces of countertop, thus, establishing the viability of forming countertop materials from scrubber sludge.
- We examined whether aging affected the strength of our countertops and tiles. The flexural strength measurements suggested that a year of aging did not effect the strength.
- We also tested the stability of our tiles in water. After continuous immersion in water for more than a month, we so far have not observed disintegration of the tile or swelling.
- 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.
- Our detailed economic analysis indicated that our countertop product would be approximately 10 times cheaper than the current Corian and Corian-look-alike countertops. Decorative tiles would cost about \$ 0.85 per tile.

REFERENCES

- [1] "Request for Proposals for Research and Development of Illinois Coal", Illinois Clean Coal Institute, Carterville, Illinois, 1999.
- [2] Chou, M. -I M.; Bruinius, J. A.; Li, Y. C.; Rostam-Abadi, M., Lytle, J. M. Prep. Pap.-Am. Chem. Soc. Div. Fuel Chem. **40(4)**, 896 (1995).
- [3] P. J. Henkels, P. J.; Gaynor, J. C. Prep. Pap.-Am. Chem. Soc. Div. Fuel Chem. **41(2)**, 569, 1996.
- [4] Pauken, D. G. *Proc.*: Twelfth International Sympos. On Management & Use of Coal Combustion Byproducts (CCBs), Vol. 3, pp 91-1 - 91-13, Orlando, Florida, 1997.
- [5] Luckevich, L. M. "Making and marketing Flue Gas Desulfurization Gypsum" in 'Procd. 12th Inter. Sympos. on Coal Combustion By-Products Management and Use, Orlando, Florida, **2**, pp 67-1 to 67-7, 1997.
- [6] Malhotra, V. M., Valimbe, P. S., and Wright, M. A., *Fuel* **81**, 235 - 244 (2002).
- [7] Malhotra, V. M., Amanuel, S., and Botha, F., "Novel Paperless Structural Composites from Wet FGD Scrubber Sludge" Proceed. 27th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, Florida, USA, 2002, pp 991 - 1001.
- [8] Valimbe, P. S., and Malhotra, V. M., *Fuel* **81**, 1297 – 1304 (2002).
- [9] Malhotra, V. M., Amanuel, S., Pleasure, C., and Botha, F., "Structural Composites from FGD Sulfate-Rich Scrubber Sludge", *Fuel* (2003).
- [10] Dalui, S. K.; RoyChowdhury, M.; Phani, K. K.; *J. Mat. Sci.*, **31**, 1261, 1996.
- [11] Kelley, S. P.; Valimbe, P. S.; Malhotra, V. M.; Banerjee, D. D.; *Am. Chem. Soc. Prep., Div. Fuel Chem.*, **42(3)** 962, 1997.
- [12] Valimbe, P. S.; Malhotra, V. M.; Banerjee, D. D.; *Am. Chem. Soc. Prep., Div. Fuel Chem.*, **40(4)**, 776, 1995.