VALUE-ADDED PRODUCTS FROM FGD SULFITE-RICH SCRUBBER MATERIALS

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ABSTRACT

Massive quantities of sulfite-rich flue gas desulfurization (FGD) scrubber materials are produced every year in the USA. In fact, at present, the production of wet sulfite-rich scrubber cake outstrips the production of wet sulfate-rich scrubber cake by about 6 million tons per year. However, most of the utilization focus has centered on FGD gypsum. Therefore, we have recently initiated research on developing new strategies for the economical, but environmentally-sound, utilization of sulfite-rich scrubber material.

In this exploratory project (Phase I), we attempted to ascertain whether it is feasible to develop reconstituted wood replacement products from sulfite-rich scrubber material. In pursuit of this goal, we characterized two different wet sulfite-rich scrubber materials, obtained from two power plants burning Midwestern coal, for their suitability for the development of value-added products. The overall strategy adopted was to fabricate composites where the largest ingredient was scrubber material with additional crop materials as additives. Our results suggested that it may be feasible to develop composites with flexural strength as high as 40 MPa (5800 psi) without the addition of external polymers. We also attempted to develop load-bearing composites from scrubber material, natural fibers, and phenolic polymer. The polymer-to-solid ratio was limited to ≤ 0.4. The formulated composites showed flexural strengths as high as 73 MPa (10,585 psi). We plan to harness the research outcomes from Phase I to develop parameters required to upscale our value-added products in Phase II.

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EXECUTIVE SUMMARY

In our pursuit to develop value-added wood substitute products from sulfite-rich FGD scrubber material, we collected samples of scrubber material from two different power plants. These power plants burned high-sulfur Midwestern bituminous coal and were fitted with wet FGD scrubbers. The scrubber samples had not undergone stabilization with fly ash and were in a wet cake form. The as-received, but air-dried, scrubber materials were subjected to chemical, vibrational, and thermal analyses. A series of composites were formulated from sulfite-rich scrubber material, natural fibers, and crop byproducts in which the scrubber material was the dominant ingredient. The composites were analyzed for their mechanical characteristics.

The following summarizes the experiments undertaken to achieve our objectives:

1. The wet cake was air dried and then subjected to arsenic (As), boron (B), cadmium (Cd), mercury (Hg), and selenium (Se) analyses. The concentration of As, B, Cd, Hg, and Se were < 4.8 mg/kg, 61 mg/kg, < 0.95 mg/kg, 0.28 mg/kg, and 6 mg/kg, respectively.
2. Because the potential re-emission of mercury from FGD scrubber materials, be they sulfate-rich or sulfite-rich, during their utilization is of concern, we are examining the mercury concentration in the wet scrubber material on a long term basis. We ascertained mercury concentrations in the scrubber material using EPA Method 7473. It appeared that the bulk of the mercury was associated with the solids in the as-received wet scrubber cake with scrubber water containing only < 3 μg/kg of Hg. The determined mercury concentration steadily increased for the scrubber material as a function of air drying time at ambient temperature. In fact, the mercury concentration increased by 80% in 90 days of air drying. This is because the presence of water dilutes the mercury concentration.
3. Spectroscopic measurements were undertaken on as-received, but air dried, scrubber materials from two different power plants. The results suggested that they were largely sulfite-rich scrubber products but did contain carbonate and organic impurities. In addition, the scrubber materials we examined contained free sulfate ions trapped in matrices. These impurities are unlikely to affect the performance of our products.
4. The thermal stability of the scrubber materials was determined by conducting differential scanning calorimetry (DSC) measurements at $25^{o}C < T < 510^{o}C$ on two different scrubber materials, obtained from two different power plants. The thermal analysis suggested that the scrubber materials were thermally stable up to ~ $420^{o}C$. At $T > 420^{o}C$, water molecules were released from the scrubber material. This behavior may inhibit sustaining fire in our wood substitute products.
5. In another set of experiments, we explored how various fibrous materials would affect the strength of wood substitute composites formed from sulfite-rich scrubber material. Four natural fibrous materials were chosen for this

purpose. The composites tested for their flexural strength provide strong evidence that the type of fibrous material chosen has a critical effect on the strength. The strength of the composites formulated from scrubber material and natural fibers ranged from 12.5 MPa (1813 psi) to 30 MPa (4350 psi).

6. We also explored whether byproducts derived from annual crops can alter the strength of the wood-substitute composites developed from sulfite-rich scrubber material. Three natural protein concentrates derived from three different crops were obtained and were tested. It appeared that 5 wt% natural proteins improved the strength of the composites from 2 MPa (290 psi) to 30 MPa (4350 psi). Enhanced concentration of natural proteins did not further increase the strength. It is worthwhile to point out those commercial wood products we tested in our laboratory, e.g., particle floor board, OSB, and sawdust board, had a flexural strength of 16 MPa (2320 psi), 25 MPa (3625 psi), and 29 MPa (4205 psi), respectively.
7. The incorporation of 2 inch size fibrous material substantially improved the brittle behavior, i.e., our products became much less brittle.
8. It appeared that formation pressure and temperature substantially affected the flexural strength of the composites formulated from sulfite-rich scrubber material. Moreover, the brittleness of our composites could be further reduced by incorporating burlap mesh as a core of the composite.
9. We investigated how the addition of cheap polymeric material along with lignin extracted from crop byproducts can affect the mechanical properties of the composites formulated from sulfite-rich scrubber materials. This was undertaken because the thrust of our research is to develop wood-substitute products, thus our products should be amenable to conventional wood tools, i.e., they can be cut with regular saws and can be routed using conventional routers besides being able to be nailed. The strength linearly increased from 3 MPa as the polymeric concentration increased. In fact, for 30 wt% polymeric material our products' flexural strength was in excess of 48 MPa (6960 psi). This should be contrasted with commercial plywood we tested whose strength was 40 MPa (5800 psi).
10. We explored whether it would be feasible to develop load-bearing composites from sulfite-rich scrubber materials. For the development of these composites, we used commercial polymers. However, the concentration of the polymer-to-solid ratio was limited to 0.4. We were able to obtain flexural strengths as high as 73 MPa (10,585 psi). The addition of the clay particles to our mixture did not improve the strength of our load-bearing composites. In fact, the larger the concentration of clay (< 8 wt%) in our composites the lower was the strength of the material. Our initial results also suggested that by incorporating cheap additives like lignin, we can further reduce the polymer concentration in our products without compromising the mechanical properties.

REPORT DETAILS

Introduction

According to the American Coal Ash Association [1], about 31,102,000 tons of flue gas desulfurization (FGD) byproducts were produced in the USA in the year 2005. Out of this, 11.98 million tons were FGD gypsum and 1.43 millions tons were dry scrubber material. On the other hand, sulfite-rich scrubber byproduct production was 17,700,000 tons in 2005. It is believed that 77% of the total FGD gypsum produced is consumed in wallboard, Portland cement, and agricultural applications. The rest of the FGD gypsum, i.e., about 2.71 million tons, is landfilled. In a pursuit to further expand the utilization of the FGD gypsum, additional value-added products are being developed, e.g., countertops, decorative tiles, and frictional materials [2-6].

The economical and environmentally-conducive management of sulfite-rich scrubber byproducts is much bleaker. Out of 17,700,000 tons of wet sulfite-rich scrubber material produced in 2005, only about 439,619 tons were used as structural fills/structural embankments and 245,471 tons for mining applications. The rest, i.e., 17,014,910 tons, was landfilled. Unlike FGD gypsum, which when sold can garner resources for the electric utilities, most power plants have to pay to dispose of sulfite-rich scrubber material. In fact, electric utilities paid to dispose of 2.08 million tons in 2000. Clearly, environmentally-friendly and economically-conducive utilization of sulfite-rich scrubber material is of utmost importance for coal burning electric utilities.

With a view to increase the utilization of the sulfite-rich scrubber material, we proposed to develop value-added structural products from it. More specifically, it was proposed that we would explore the feasibility of developing wood substitute composites from the sulfite sludge; and if the research seemed promising, then a more comprehensive research approach would be proposed for Phase II. This was to be accomplished by exploiting the physical and chemical properties of sulfite-rich scrubber materials, natural byproducts, and agricultural byproducts. To establish the preliminary viability of developing structural materials, we proposed five tasks.

Experimental Methods

Sample Procurement:

The sulfite-rich scrubber material was obtained from two different power plants, i.e., PP-A and PP-B. Both power plants are located in the Midwest and burn Midwest bituminous coal. The scrubber material was in the form of wet cake, and this material had not been fixated with fly ash. The natural and agricultural byproducts were either bought on the open market or obtained from the agricultural industry.

Trace Elemental Analysis:

The trace elemental analysis, i.e., arsenic (As), boron (B), cadmium (Cd), and selenium (Se), on the scrubber cake was conducted by a commercial and a certified, laboratory. The 6010B method in conjunction with ICAP was used to ascertain As, B, Cd, and Se concentrations in the scrubber material. The mercury (Hg) concentration on an air-dried (at 23°C) scrubber cake was also determined by the commercial laboratory using EPA 7471A method. In addition, we systematically evaluated how the total mercury concentration was affected when it was air-dried at ambient temperature. For our total mercury concentration measurements on scrubber cake, as well as on the water associated with the scrubber cake, we used EPA 7473 method using a Direct Mercury Analyzer (Milestone's DMA-80) instrument.

Differential Scanning Calorimetry (DSC) Measurements:

The thermal behavior of as-received scrubber materials was ascertained by subjecting them to DSC measurements at 30°C < T < 510°C. The DSC data were acquired on a Perkin-Elmer DSC7 system, interfaced with a computer using a Windows XP 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 420°C, based on our calibration procedure, was estimated to be ±1°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 10°C/min, nitrogen gas purge at 30 psi pressure. Also, during both calibration and heating runs, the dry box assembly over the sample head was flushed with dry air to maintain thermodynamic equilibrium. Aluminum (Al) sample pans in an unsealed mode generally were used to determine the thermal behavior of fibers and composites. This was achieved by pushing down the top sample pan cover gently onto the bottom pan containing the sample.

Fourier Transform Infrared (FTIR) of Scrubber Material:

Because the chemical phases of scrubber materials are an important parameter in the development of wood substitute composites, we used FTIR experiments to monitor the as-received wet, dried, and processed phases of the scrubber materials. To record transmission infrared spectra, we used a thin film approach. In this approach, slightly wet scrubber material was smeared on an infrared optical substrate. A second substrate was pressed down on the first substrate, and the substrates were slid at 45°, thus forming a thin film. When

required, we also used thin films of nujol mull, containing the ground sample, sandwiched between KBr windows to record our infrared spectra. The FTIR spectra were collected at 4 cm^{-1} resolution over the frequency range of 400 cm^{-1} to 4000 cm^{-1} using a Thermo Electron 670 FTIR spectrometer.

Composite Formulation:

Generally, the following steps were executed for fabricating the composites from scrubber sludge:

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

(b) The air-dried scrubber sludge particles were mixed with appropriate ingredients and thoroughly mixed using a high shear mixer to ensure the best achievable homogeneous distribution of the particles.

(c) The sample mixtures were poured into a 2.25 inch diameter hardened stainless steel die. Various fibers were laid in the die either in a random orientation, crisscrossed, or perpendicular to the axis of the die.

(d) The mixture was hot pressed at the desired pressure and temperature to form the primary composite skeleton.

(e) The primary composite structures were then cured for 30 minutes before removing the sample. We cured our composites in air.

Strength Testing:

To evaluate how various variables affected the mechanical strength of our composites, we tested the samples for their flexural strength and flexural modulus. We used a band saw to cut rectangular strips of the sample having nominal thickness of about 0.2 cm, width of 0.95 cm, and length of 5.8 cm. To accomplish the flexural strength measurements, a three point bending system was designed from equipment obtained from ELE International. This system is a 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 (σ) 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 quadruplet; thus, the data presented are the average of these four values.

Results and Discussion

Chemical Analysis of Scrubber Material:

If value-added wood substitute products are to be developed from sulfite-rich scrubber material, then the fate of certain elements, which potentially could be toxic, needs to be monitored. Therefore, we air dried scrubber cake prior to determining the concentration of As, B, Cd, Hg, and Se. The results are summarized in Table 1 for the scrubber material obtained from PP-A.

Table 1. The chemical analysis on as-received but air-dried sulfite-rich scrubber cake (PP-A).

Element/Metal	Concentration (mg/kg)	Reporting Limit (mg/kg)
Arsenic (As)	< 4.8	4.8
Boron (B)	61	24
Cadmium (Cd)	< 0.95	0.95
Mercury (Hg)	0.280	0.016
Selenium (Se)	6.0	4.8

It is worth pointing out that we observed considerable variation in the mercury concentration in the scrubber material from week to week, though overall the mercury concentration was never lower than 200 μg/kg. Whether the mercury will be emitted during the composite formulation needs to be examined. As a first step toward that goal, we explored how air drying the scrubber material would affect its mercury concentration. We air dried the scrubber cake up to 60 days and monitored the mercury concentration along with the water associated with the scrubber cake. The mercury concentration in scrubber water was extremely low, i.e., 1.6 μg/kg. However, as can be seen from Fig. 1, the mercury concentration steadily increased as the sample was progressively dried. After one day of air drying, the Hg concentration in the scrubber material increased from 211 to 252 μg/kg. This concentration further increased to 360 μg/kg after 60 days of air drying. Because sulfite-rich scrubber material has a strong tendency to hold water and because mercury concentration in the associated water is very low (1.6 μg/kg), therefore, the mercury concentration is expected to increase as the water contribution to the overall weight decreases. Whether some mercury volatizes from the scrubber cake at ambient temperature during air drying is not currently known.

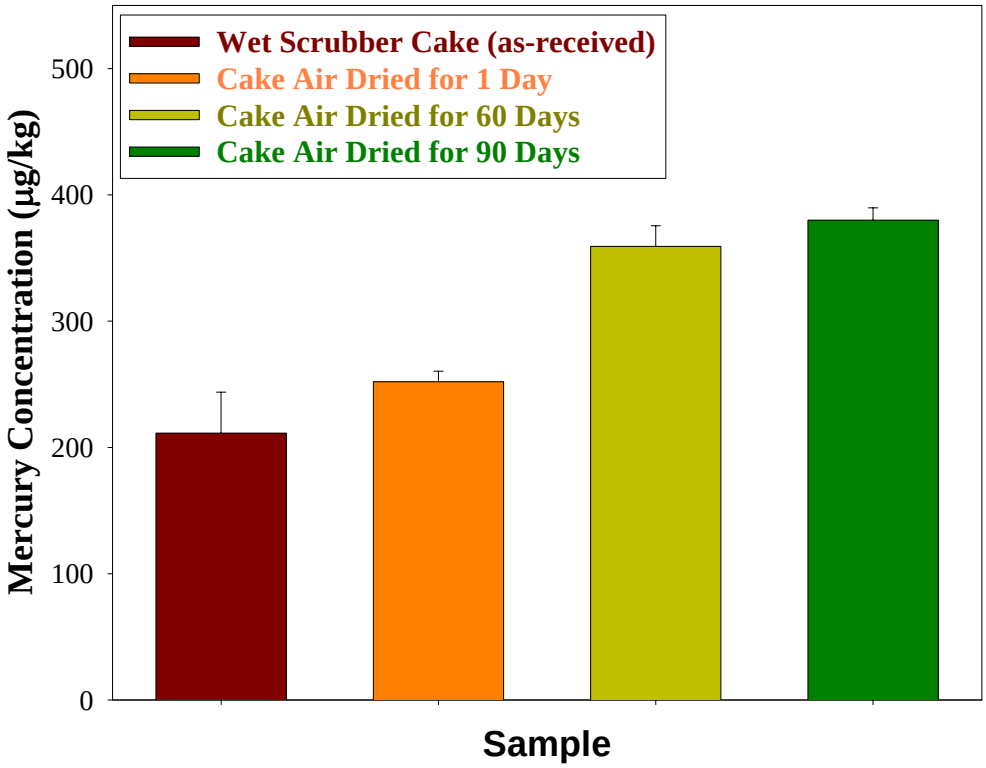

***Figure 1**. The effect of air drying (24°C) on the mercury concentration in the sulfite-rich scrubber material obtained from PP-A.*

Thermal Analysis of Scrubber Materials:

It is known that sulfite-rich scrubber materials are difficult to dewater. The formation of wood substitute products by combining scrubber material and natural byproducts requires careful monitoring of the role of water in the formulation of the composites. Therefore, to understand the drying behavior, we subjected the sulfite-rich scrubber materials obtained from two different power plants to differential scanning calorimetry (DSC) measurements at 25°C < T < 510°C. Prior to subjecting the samples to DSC measurements, the scrubber cakes were air-dried for 72 hours at ambient temperature. The results are shown in Fig. 2. We did not observe any endothermic peak at around 100°C, suggesting that air drying removed most of the bulk water from sulfite-rich scrubber material. We did observe weak endothermic peaks at 150°C and 361°C for scrubber material obtained from Plant PP-A. No thermal events were observed at 45°C < T < 400°C for scrubber material obtained from PP-B. The cause of the thermal events at 140°C < T < 375°C most likely suggests the presence of impurities in the sulfite-rich scrubber obtained from PP-A. Both scrubber materials showed strong endothermic peaks at ~ 450°C with a weak shoulder at around 420°C. The strong endothermic peak observed at around 450°C is associated with the decomposition of $CaSO_3.0.5H_2O$ into its anhydrous phase, thus, releasing water molecules [7]. Therefore, it is reasonable to argue

that the thermal decomposition of wood substitute products, developed from sulfite-rich scrubber material, could retard the fire in our products.

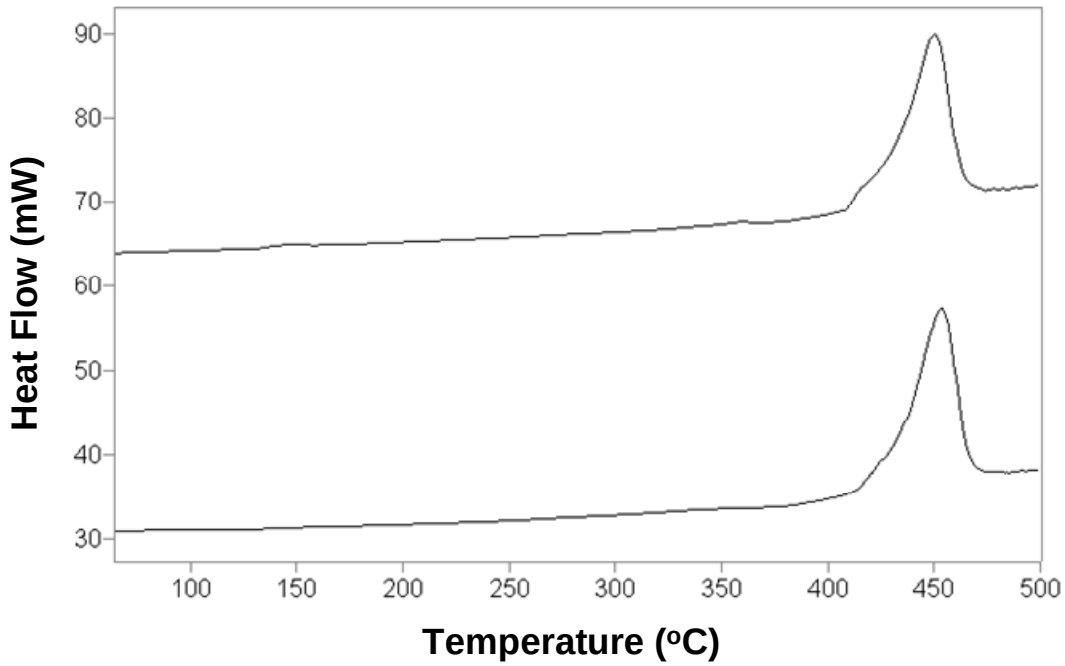

Figure 2: *The observed DSC thermographs from sulfite-rich scrubber materials. The top curve is for Plant PP-A, while the bottom curve depicts the thermal behavior observed for the scrubber material obtained from Plant PP-B.*

Vibrational Spectra of Scrubber Materials:

Figure 3 reproduces the observed infrared spectra of scrubber materials obtained from PP-A and PP-B. Table 2 lists the frequencies of the observed oscillators from the two scrubber materials. It is worth noting that the spectra from the two scrubber materials are largely similar, if not identical. The oscillators at 3380 cm^{-1} and 1624 cm^{-1} can be assigned to the stretching and bending modes of H_2O, respectively. The oscillators at around 986, 950, 875, 650, 610, 521, 489, and 448 cm^{-1} are typically observed from hydrated $CaSO_3$. However, medium intensity bands observed for both scrubber materials at around 1494 and 1430 cm^{-1} can not be attributed to calcium sulfite. These bands are more likely associated with either calcite and/or dolomite. The presence of calcite or dolomite in the scrubber material should not be surprising because lime or limestone slurries are typically used in FGD scrubbing technologies. The presence of weak bands at around 720 cm^{-1} further supports our argument that both sulfite-rich scrubber materials contained un-reacted carbonates. However, the presence of carbonates is unlikely to affect the performance of our wood substitute composites.

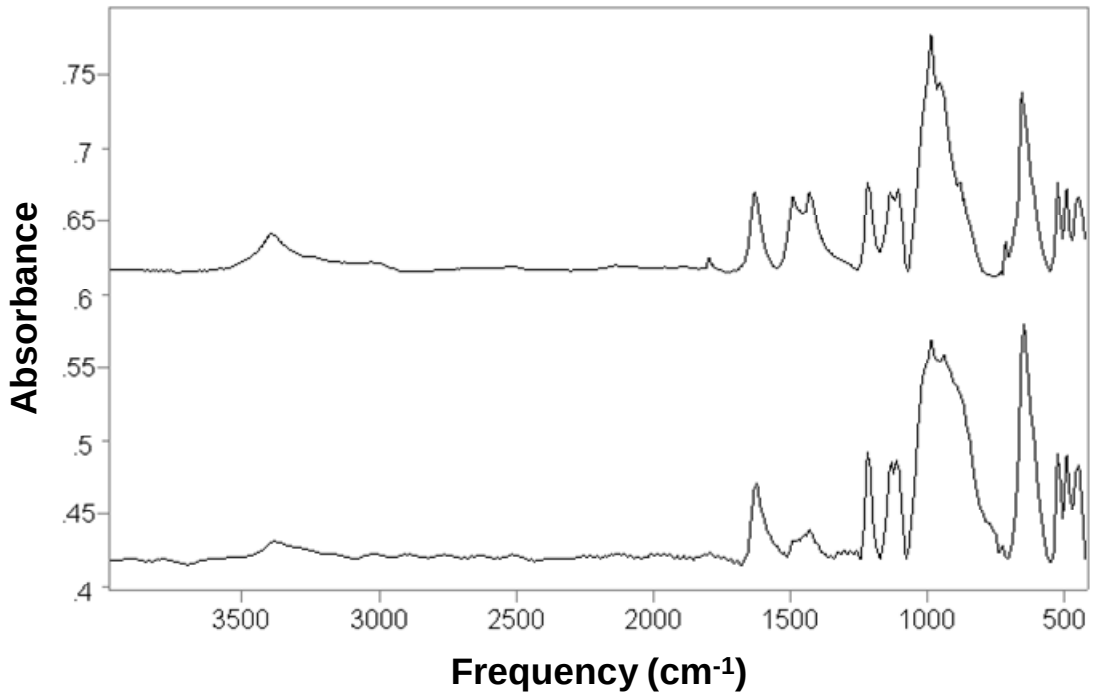

Figure 3. *Comparative infrared spectra of scrubber materials obtained from Plant PP-A (top curve) and Plant PP-B (bottom curve).*

The vibrational band observed at around 1790 cm^{-1} for the scrubber material obtained from PP-A suggests organic impurity. No such vibrational mode was observed for scrubber material obtained from PP-B. The PP-A uses adipic acid to make the scrubbing process more efficient. However, adipic acid produces strong vibrational bands at 1700, 1300, and 1190 cm^{-1} consistent with the presence of carboxylic acid groups. The presence of a band at 1790 cm^{-1} is unlikely to be associated with – COOH groups. At present, it is not clear which organic species this vibration belongs to though it mostly likely is associated with – C = O vibration.

The infrared bands observed at around 1210, 1132, and 1107 cm^{-1} suggest the presence of sulfate in the sulfite-rich scrubber material. It may be tempting to associate these bands with calcium sulfate or FGD gypsum. Typically, we have observed a doublet at 1140 and 1114 cm^{-1} due to the presence of FGD gypsum. This doublet could be associated with a stretching (ν_3) mode of SO_4^{2-}. The presence of a triplet at 1210, 1132, and 1107 cm^{-1} for both scrubber materials rather suggests free sulfate ions, i.e., the ions which are trapped within a matrix, thus, are not exposed to crystalline perturbations.

Table 2. The observed infrared bands for the scrubber material obtained from Power Plant A (PP-A) and Power Plant B (PP-B).

Power Plant A Frequency (cm^{-1})	**Power Plant B** Frequency (cm^{-1})	**Comments#** **(intensity, width)**
3388	3380	m, b
1796	1796	w, sp
1629	1624	m, sp
1492	1494	m, sp
1433	1430	m, sp
1214	1213	m, sp
1133	1132	m, sp
1105	1107	m, sp
	1012	vs, b
985	986	vs, sp
949	937	vs, b
881	875	s, b
710	721	w, sp
651	648	s, b
610	611	m, sh
521	521	m, sp
490	489	m, sp
449	446	m, sp

vs: very strong, s: strong, m: medium, w: weak, b: broad, sh: shoulder, sp: sharp

Effects of Natural Fibrous Material on Composites:

We explored how various fibrous materials would affect the strength of wood substitute composites formed from sulfite-rich scrubber material. Based on our past experience, we chose industrial hemp, jute, kenaf, and wheat straw as our fibrous additives. Because in this experiment we were interested in exploring the effects of additives rather than maximizing the use of scrubber material, we mixed scrubber material and the additives in a 1:1 ratio. The room temperature air-dried scrubber material was thoroughly mixed with the fibrous additives. To this mixture, we added protein-C to establish a protein-to-mixture ratio of 0.07. To the scrubber material-natural fiber additive-protein mixture, water was added to initiate gelling reaction, if any. This mixture was subjected to compressive molding under a pressure of 2.72 MPa. The formed composites were ejected from the 2.2” die, cooled to room temperature, and cut for flexural strength measurements.

Figure 4 reproduces the flexural strength and bulk density of the composites formulated using commercial hemp, jute, kenaf, and wheat straw as additives. As can be seen, the wheat straw made the strongest material, i.e., strength of about 32 MPa (4640 psi). It is worthwhile to point out that this strength is comparable to the strength of commercial plywood. Another issue we

explored was whether the layout of the fibers would affect the strength of the materials fabricated from sulfite-rich scrubber sludge. For this experiment, we chose jute fibers. These fibers were randomly mixed, were laid out in a crisscross manner, and were laid perpendicular to the axis of the die. Interestingly, the random mixing gave the best flexural strength as can be seen in Fig. 5.

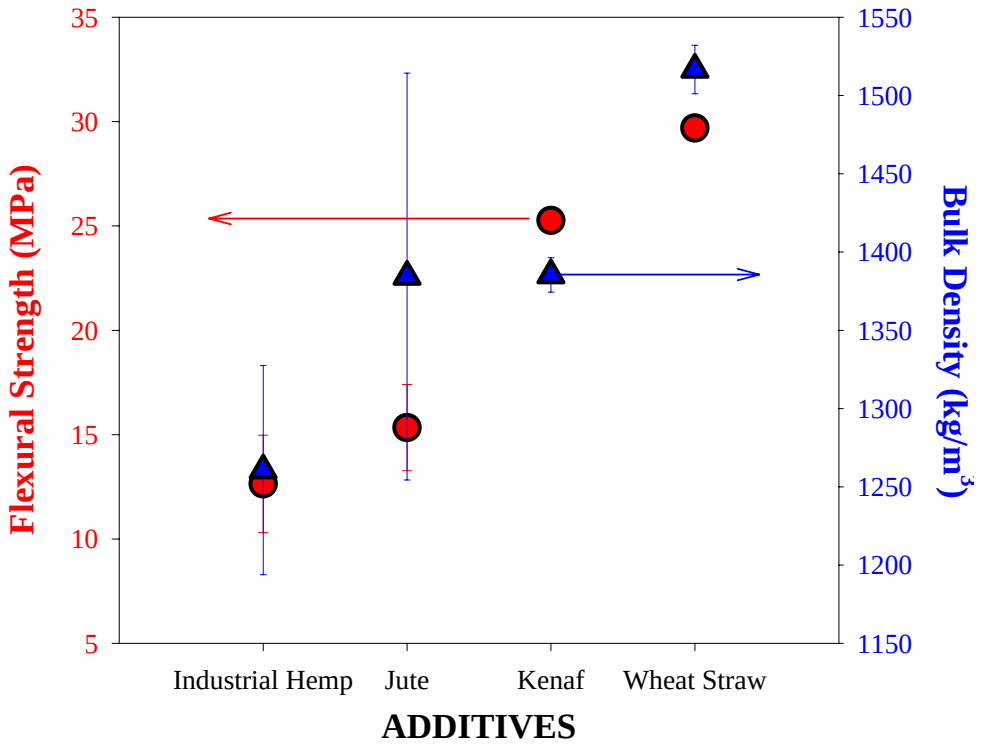

***Figure 4**. This figure depicts how fibrous additives affected the strength of wood substitute composites made from sulfite-rich scrubber material.*

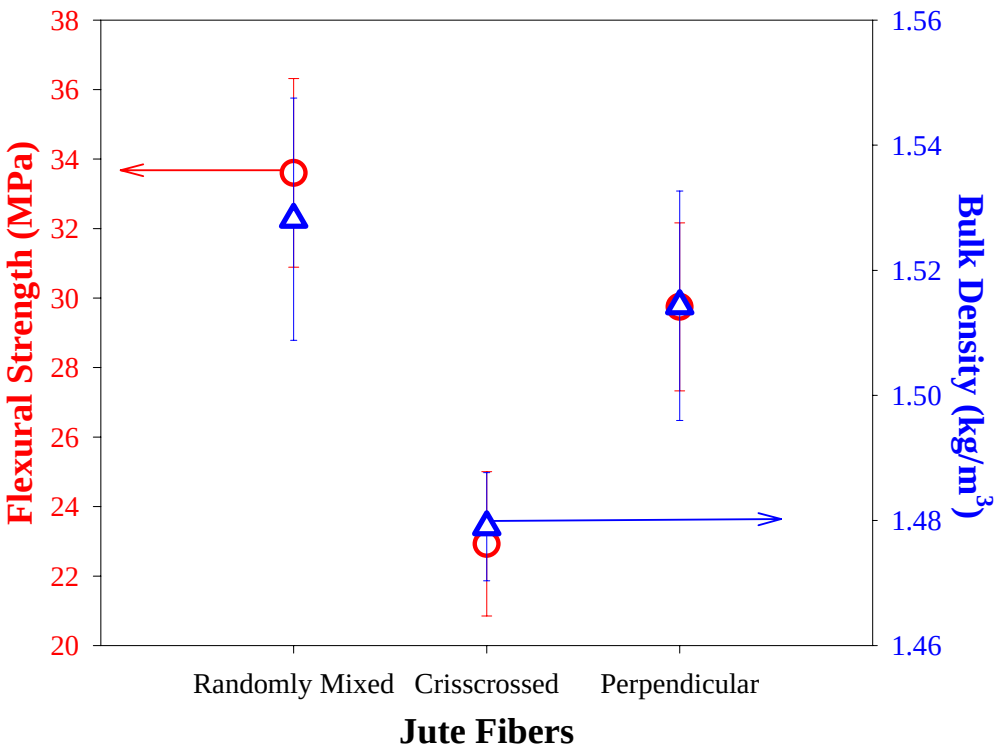

Figure 5. *How the fiber orientation affected the strength and the bulk density of the composites formulated from sulfite-rich scrubber material.*

Effects of Natural Polymers and Proteins:

We extracted various proteins from agricultural byproducts to formulate our wood substitute composite materials. Three different proteins were extracted, i.e., protein-C2, protein-S1, and protein-W. We used these proteins to formulate composites from sulfite-rich scrubber material. Moreover, we systematically varied the concentration of protein-C2 and protein-S1 in our composites to ascertain the optimum protein-to-solid ratio which gave the best flexural strength.

Figure 6 reproduces how the protein-C2 concentration affected the flexural strength and bulk density of the composites. As can be seen, protein-C2 had a strong influence on the strength of the composite, i.e., without any protein in the mix the strength of the material was very marginal. However, when 2 g of protein-C2 was added, the strength dramatically improved from ~ 0.3 MPa (44 psi) to ~ 30 MPa (4350 psi). However, no further benefit was observed as we increased the protein-C2 concentration in the sample. In fact, for the protein-C2 concentration of 6 g or higher, the strength decreased and so did the density.

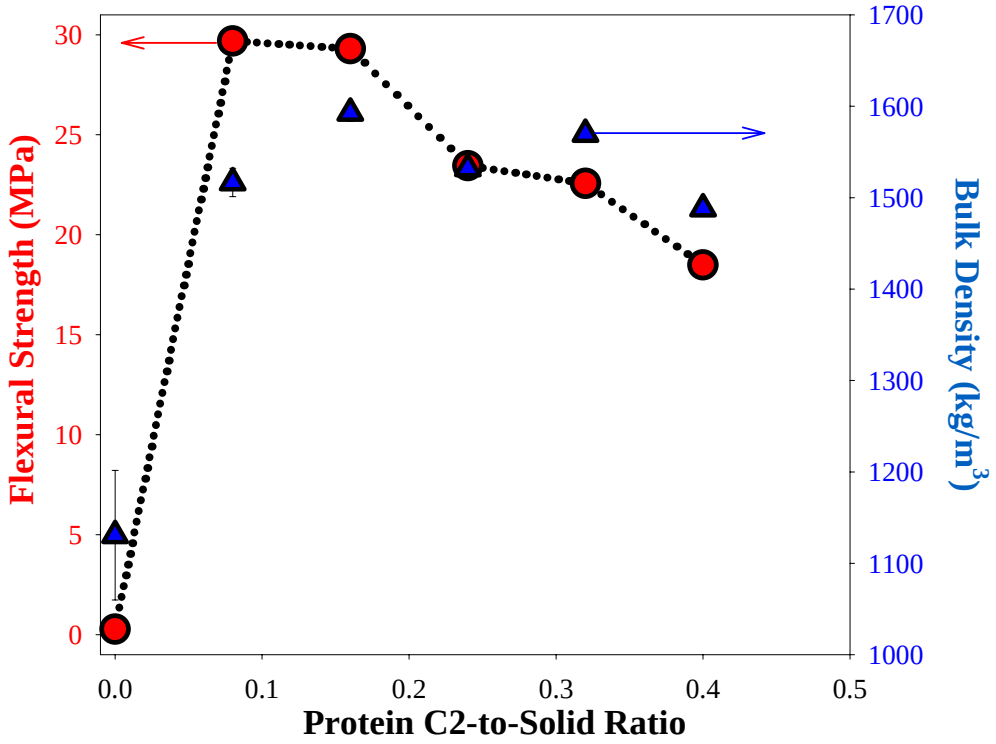

Figure 6. *This figure depicts how protein-C2 concentration affected the strength of wood substitute composites made from sulfite-rich scrubber material.*

Because the sulfite-rich scrubber materials are typically obtained in the form of wet cake, we explored to what extent drying would be required to formulate our wood substitute composites. We first air-dried our sulfite-rich scrubber cake at ambient temperature (23°C) for 3 days and then added various concentrations of water into the scrubber material prior to forming the composites. Figure 7 shows how the water content in the sample altered the strength of our wood substitute composites. Even though the density of the sample decreased as the water content of the mixture increased, there was also a decrease in the flexural strength of the composite. It may appear that the presence of water in our mix had a deleterious effect on the strength of the composites; but when we dried the cake at 125°C, the strength dropped to < 2 MPa (290 psi). Therefore, it appears that water plays a crucial role in the formation of wood substitute composites, i.e., too much water lowers the strength and too little water has a catastrophic effect on the strength. In the future we plan to identify the optimum quantity of water required to formulate our wood substitute composites from sulfite-rich scrubber material.

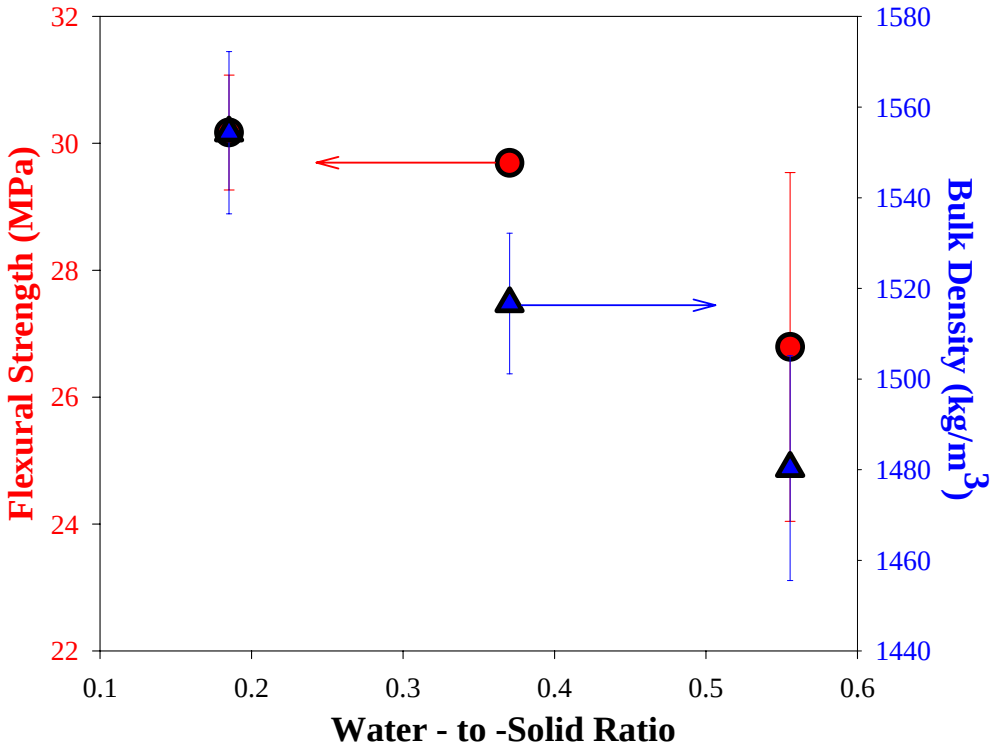

Figure 7. *This figure depicts how water concentration affected the strength of wood substitute composites made from sulfite-rich scrubber material and protein-C2.*

A second protein, i.e., protein-S1, was also used to formulate our wood composites. Figure 8 depicts how the concentration of protein-S1 affected the mechanical properties of the composites formulated from sulfite-rich scrubber material. Just like protein-C2, the addition of protein-S1 also dramatically improved the strength of the composite. In addition, the strength dependence on the concentration of protein-S1 showed a behavior similar to that observed for protein-C2 though the maximum strength achieved for protein-S1 was less than that observed for protein-C2. In view of the results presented in Figs. 6, 7, and 8, it is reasonable to argue that the maximum strength benefit was achieved when the concentration of natural proteins in our mix was less than 10 wt%.

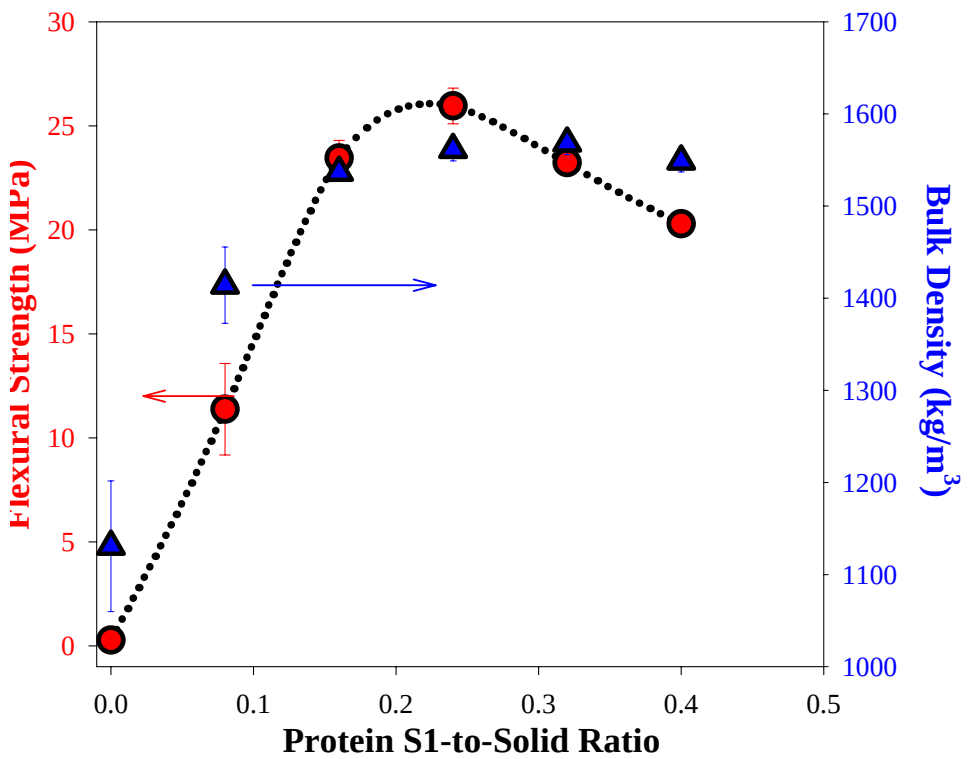

Figure 8. *This figure depicts how protein-S1 concentration affected the strength of wood substitute composites made from sulfite-rich scrubber material.*

One of the drawbacks of the above-shown mixes was that though the materials fabricated were stronger than commercial reconstituted wood products, our products tended to be much more brittle as shown in Fig. 9. To overcome the brittle behavior, we added 2”-sized fibrous wheat straw particles in our composites. As can be seen from Fig. 10, the addition of 2” fibrous particles considerably reduced the brittle character of composites derived from sulfite-rich scrubber material. However, an undesired consequence was lower flexural strength of the composites.

Because, as described above, the addition of 2”-sized wheat straw particles achieved a reduction in the brittle characteristics of the scrubber material derived composites, the substantially lower flexural strength made the material less desirable. Typically, during composite formulations, we had used random distribution of cellulose fibers in the mix. It was felt that maybe a layup approach might produce materials with less brittleness but higher strength. Therefore, we inserted a burlap mesh as the core of our composites. The burlap was unlikely to be wetted by the scrubber material. To ensure a good bond between the burlap mesh and scrubber material, we added (< 1 wt%) either liquid phenolic or phenolic powder at the burlap mesh and scrubber material interface. It was noticed that during the composite formulations most of the liquid phenolic escaped from the die when pressure was applied. However, that was not the case for powder phenolic.

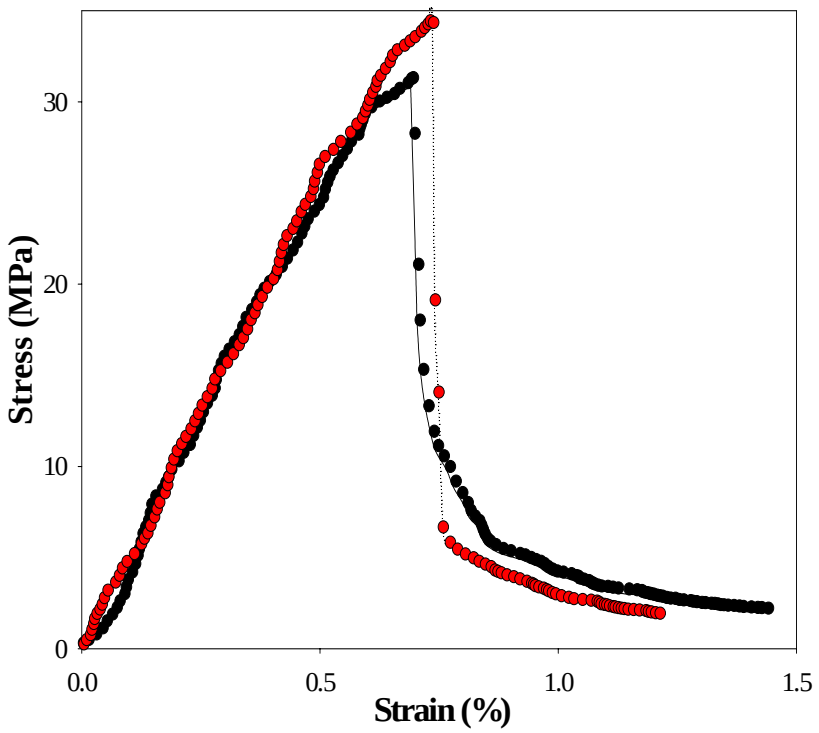

Figure 9. *Stress-strain behavior of wood substitute composites formulated from scrubber material and natural protein-W1.*

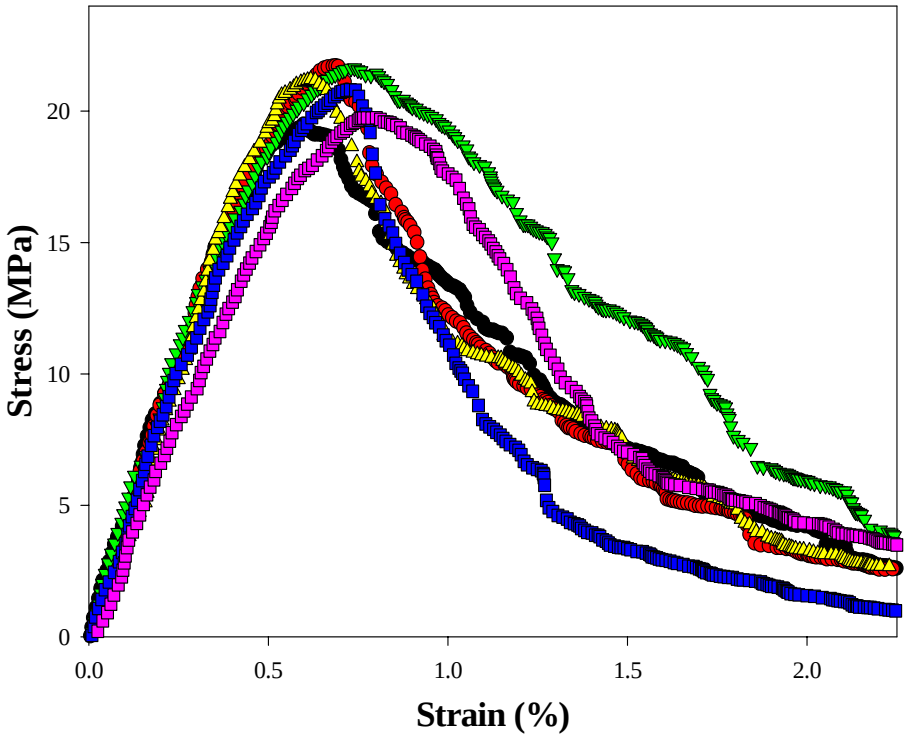

Figure 10*. Stress-strain curve for composites formulated from scrubber material, 2”-sized fibrous wheat straw particles, and natural protein-W1.*

Figure 11 depicts the stress versus strain curves for the composites formulated from sulfite-rich scrubber material, wheat straw, and burlap at the core of the composite. Unlike the brittle behavior observed when the burlap was not added, we observed a substantial improvement in the brittle characteristics of our composites. Not only did the materials become relatively less brittle but there was also a considerable improvement in the strength of the composites. For example, we typically observed strength of about 25 MPa (3625 psi) when we used no burlap in the core and strength of about 38 MPa (5510 psi) when burlap was in the core of the composite. Figure 12 shows the mechanical properties of the composites which were formed using burlap at the core of the composite. It is interesting to note that when we used phenolic powder at the scrubber material-burlap interface, not only did the strength improve but there was also a measurable reduction in the bulk density of the composites.

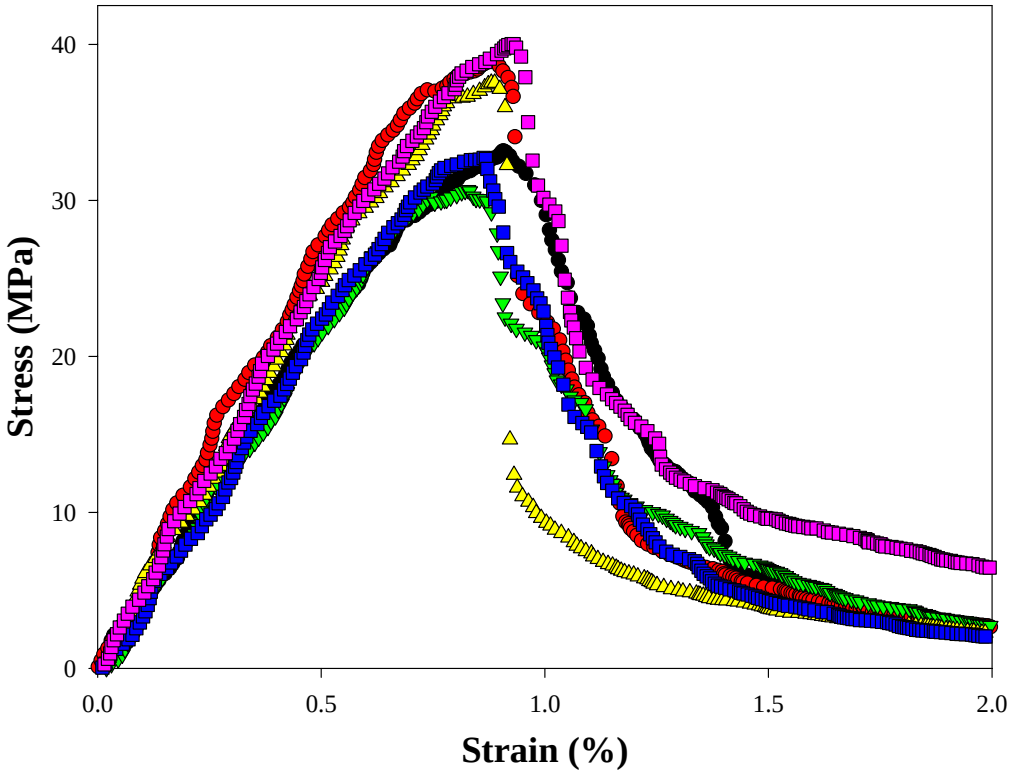

Figure 11*. The mechanical behavior of composites formulated from sulfite-rich scrubber material, wheat straw, protein-C2, and burlap at the core.*

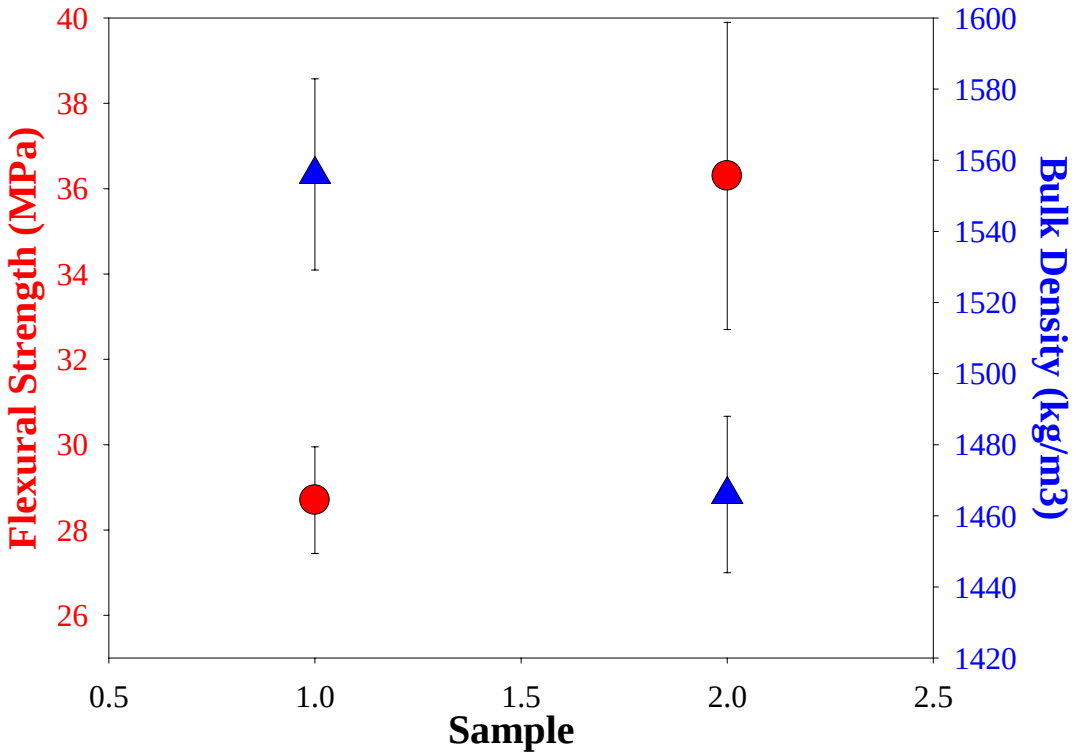

Figure 12*. The flexural strength and bulk density of the composites formulated from scrubber material with burlap at the core of the composite. In Sample 1, we used liquid phenolic at the scrubber material-burlap interface, while we used powder phenolic in Sample 2.*

Figures 13 and 14 show the scanning electron microscopic (SEM) pictures of the composites formulated from scrubber material with burlap at the core of the composites. It can be seen that no major cracks, fractures, or fissures were present in the composites formulated from sulfite-rich scrubber material. We also did not observe any gaps between the straw fibers and sulfite-rich crystallites. It appeared that polymer readily infiltrated into the burlap mesh, and this can be clearly seen from Fig. 14. Therefore, it is argued that the brittle behavior of sulfite-rich derived structural composites can be considerably modified by incorporating a burlap mesh at the core of the composite.

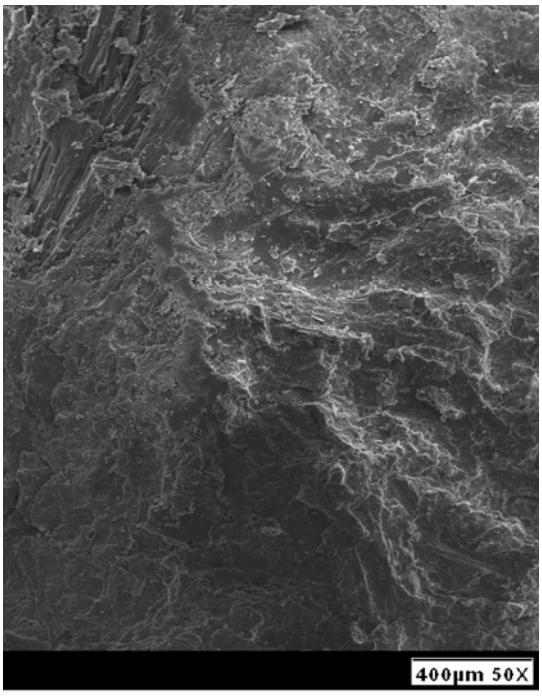

Figure 13. *SEM picture of the composite formulated from sulfite-rich scrubber material, wheat straw fibers, and protein-C2. The burlap mesh was incorporated at the core of the composite.*

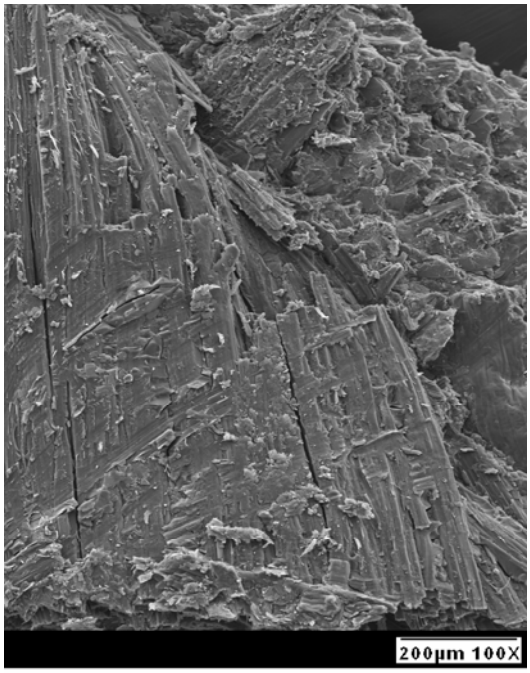

Figure 14. *SEM picture of the composite formulated from sulfite-rich scrubber material, wheat straw fibers, and protein-C2. The burlap mesh was incorporated at the core of the composite. The penetration of the polymer into the mesh can clearly be seen.*

Effects of Formation Temperature and Pressure:

Besides the ingredients used to formulate composites from FGD sulfite-rich scrubber material, the composite formation temperature and formation pressure would play important roles in controlling the mechanical properties of the formed composites. Therefore, we subjected our ingredients to variable temperature and variable pressure to ascertain how these variables affected the strength of our composites. Figure 15 shows how the formation pressure affected the mechanical properties of composites formulated from sulfite-rich scrubber material, wheat straw, and protein-C2. These composites were formed at 180°C. As the formation pressure increased from 2 MPa to 4.5 MPa, the flexural strength of the composites increased from ~ 22 MPa to 23.5 MPa, i.e., about a 7% increase. On the other hand, on increasing the pressure the density of the composites also increased.

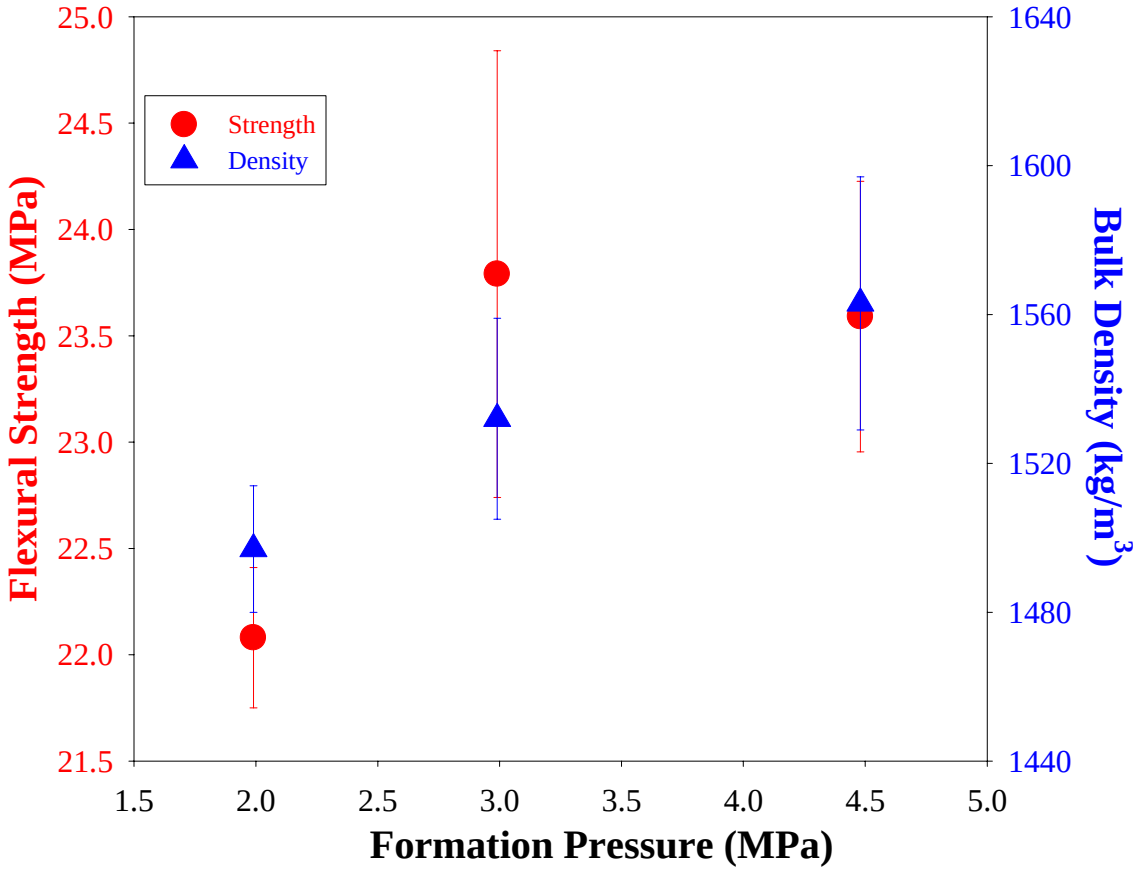

Figure 15. *The effect of formation pressure on the mechanical properties of composites formulated from sulfite-rich scrubber material, wheat straw, and protein-C2.*

How the formation temperature affected the mechanical properties of the composites formed from sulfite-rich scrubber material, wheat straw, and protein-S1 is depicted in Fig. 16. This series of composites was fabricated under a pressure of 2.59 MPa. As the formation temperature increased from 180°C to

210°C, it appeared that the flexural strength of the composite also increased. However, the increase was only marginal, i.e., the strength increased from 24 MPa to 26 MPa. Unfortunately, the increase in the strength also resulted in an increase of bulk density. To reach definitive conclusions, additional measurements are required where not only pressure and temperature are systematically varied for the composite formulation but the composites' ingredients are also changed to determine how these changes affect the mechanical properties. These measurements are planned in Phase II of this research.

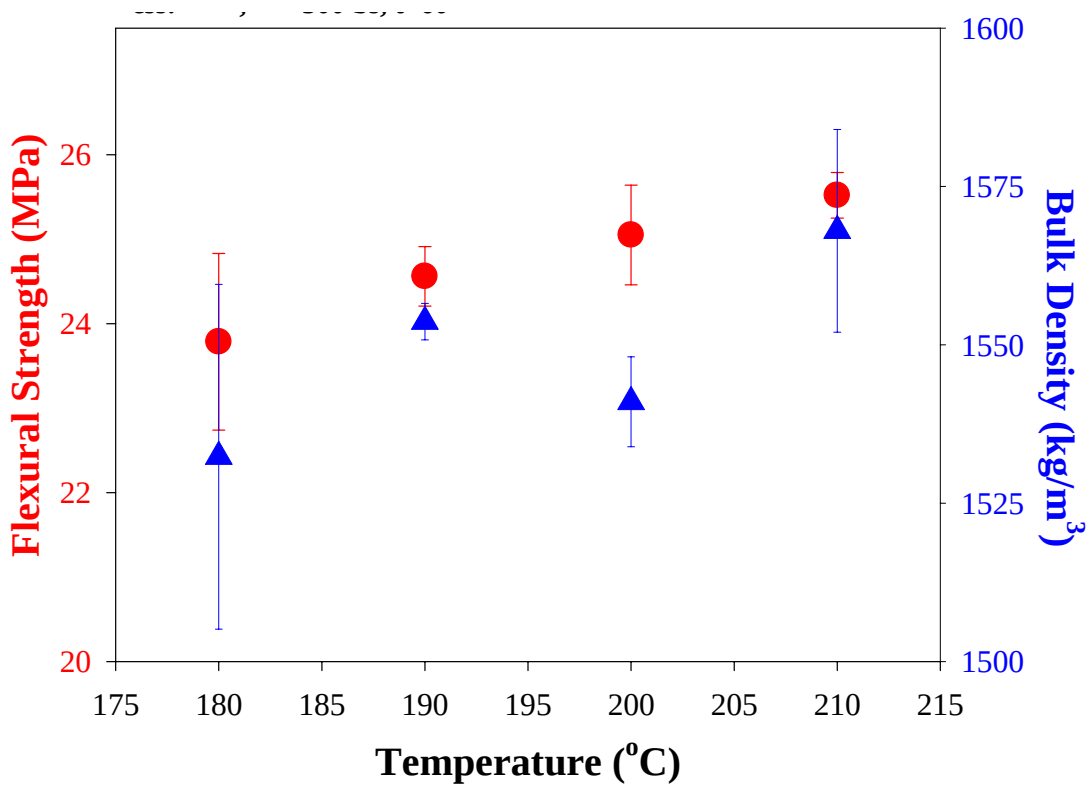

***Figure 16**. The effect of formation temperature on the mechanical properties of composites formulated from sulfite-rich scrubber material, wheat straw, and protein-S1. The formation pressure was 2.59 MPa.*

<u>LOAD-BEARING MATERIALS</u>:

In pursuit of developing value-added products from sulfite-rich scrubber materials, another product we have targeted is load bearing artificial lumber material (LBALM). This product is being developed using commercial polymers, e.g., phenolic resin. Because we want to minimize the use of petroleum-based polymers in our products, we intend to reduce the concentration of phenolic in our LBALM by partially replacing polymer with plant-derived lignin. However, our initial attempts were directed towards optimizing the polymer concentration needed to achieve our strength goals. Various concentrations of the phenolic were used though polymer-to-solid ratio was limited to 0.45. The temperature of

the composite formulation and compressive pressure used were fixed for all the samples. How the polymer concentration affected the flexural strength and bulk density is shown in Fig. 17. As the concentration of polymer increased, the strength of the material linearly increased. It is worth pointing out that the strength of our composites exceeded the strength of commercial plywood when the ratio of polymer-to-solid was < 0.4.

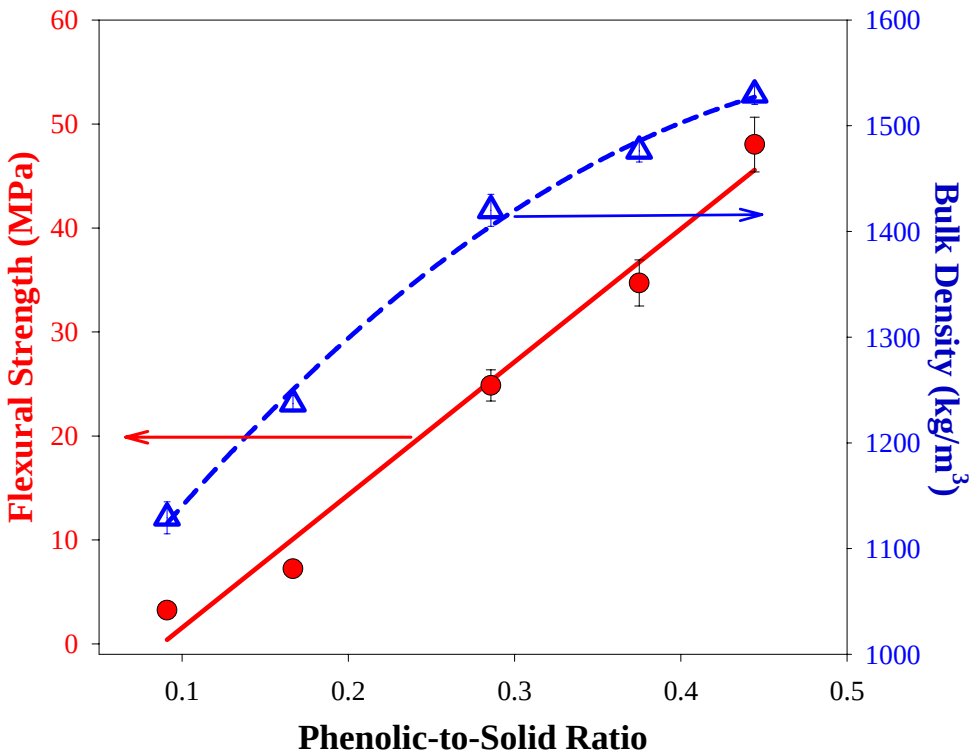

***Figure 17**. This figure depicts how phenolic concentration affected the strength of wood substitute composites made from sulfite-rich scrubber material.*

An important economic strategy for keeping our LBALM product relatively cheaper than the commercial, polymer-lumber materials on the market is to limit the amount of polymer in our product. Because polymer is the most expensive ingredient in polymer lumbers, e.g., artificial lumber developed from polymer and fly ash, it makes sense to limit the polymer concentration in our products without compromising the strength characteristics. In lumber materials, developed from fly ash, generally the polymer content is as high as 70 wt% [8,9]. Therefore, during this project, we explored the feasibility of:

- enhancing the strength of our composites by incorporating clay particles in our product while limiting the polymer concentration to 17 wt%, and
- exploring whether phenolic polymer could be partially replaced by natural lignin material.

Figure 18 reproduces how the incorporation of clay additive to our mixture affected the strength of the composite materials. The clay chosen was Cloisite 15A. The clay particles were mixed with sulfite scrubber material, cellulose-

derived fibrous material, and phenolic. As we were interested in limiting the concentration of the polymers in our load-bearing materials, we used phenolic-to-solid ratio of 0.14. The composites were formulated at 150°C. As the concentration of the clay particles increased, the flexural strength of the composites decreased. In fact, the strength was linearly, but inversely related, with the concentration of clay particles in our mixture.

On raising the composite formulation temperature to 175°C, there was no modification in the behavior of the flexural strength as a function of clay content. This can be clearly seen in Fig. 19. Again, the strength decreased as the clay content increased. However, it is worth noting that when the composite formulation temperature, with 0 wt% clay content, was raised to 175°C from 150°C, the strength of the composites derived from sulfite-rich scrubber material not only increased from 55.5 MPa (8047 psi) to 60 MPa (8700 psi) but their bulk density also decreased. Both are desirable traits for our composites. Generally, it has been argued that the incorporation of additives like clay particles enhances the strength of composites. Because we did not observe any increase in flexural strength, it was felt that to reach a definite conclusion, composites should be formulated from a different phenolic polymer but with much higher polymer-to-

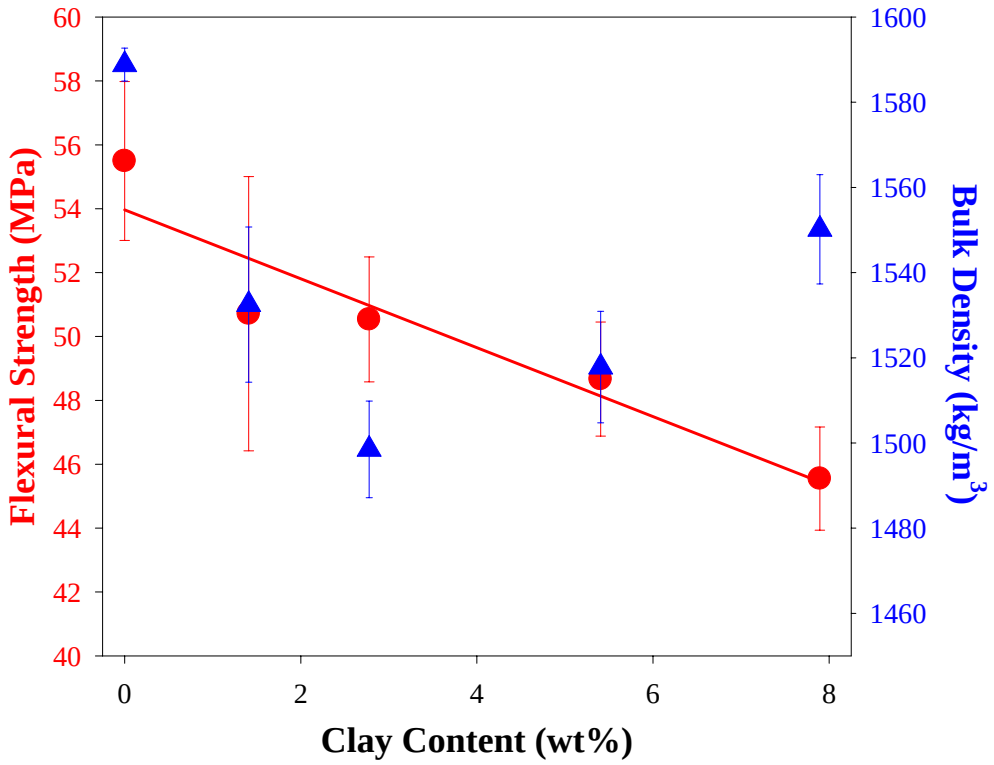

Figure18. *How clay concentration affected the mechanical properties of composites formulated at 150°C from sulfite-rich scrubber material, cellulose-derived fibrous material, and phenolic polymer. The polymer-to-solid ratio was 0.14.*

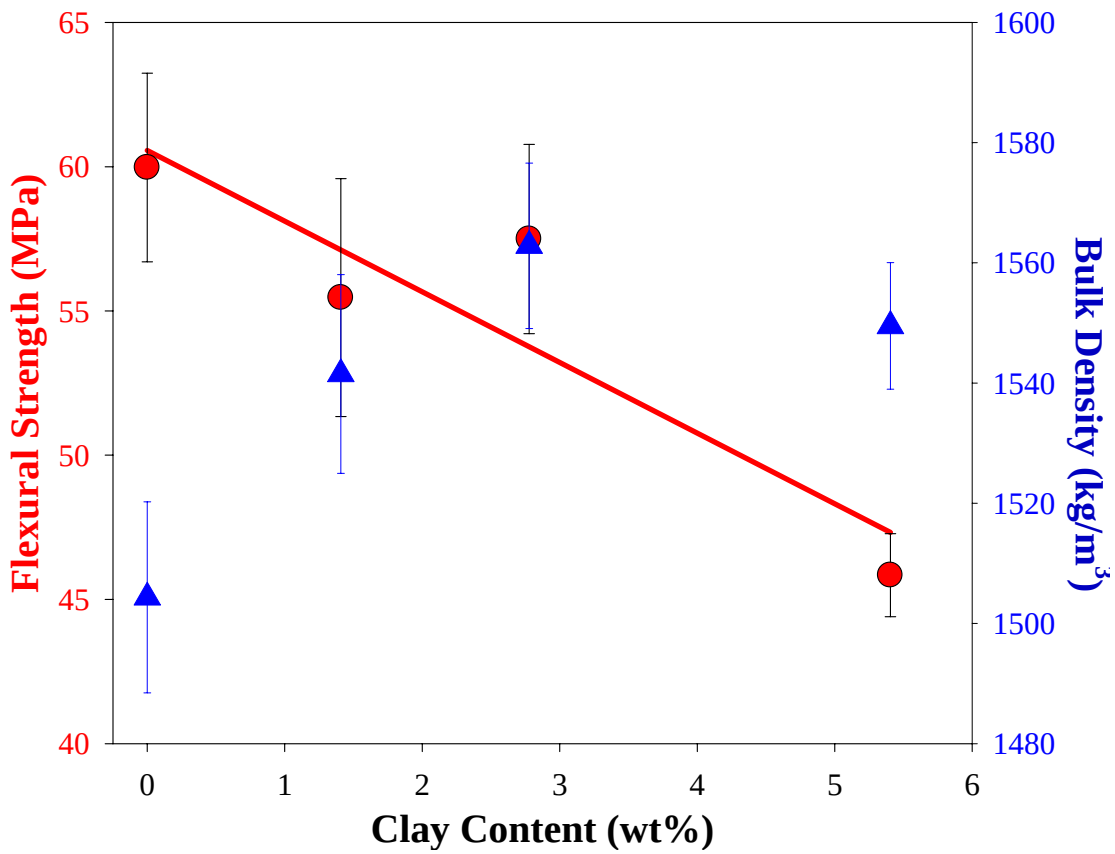

Figure 19. *How clay concentration affected the mechanical properties of composites formulated at 175°C from sulfite-rich scrubber material, cellulose-derived fibrous material, and phenolic polymer. The polymer-to-solid ratio was 0.14.*

solid ratio. We obtained phenolic samples from Buehler and formulated composites using polymer-to-solid ratio of 0.4. Again, we varied the concentration of Cloisite 15A clay in our composites. In addition, we hot-pressed pure phenolic to ascertain its strength without any additives. Figure 20 reproduces the results. As can be seen from this figure, when inorganic additives were added to pure phenolic, its flexural strength decreased and its bulk density increased. This is to be expected. However, we again observed that as the clay content increased in our composites, their strength decreased. Therefore, it is reasonable to argue that the addition of clay particles has no beneficial effects on the strength of our products, i.e., clay particles did not play any binding role for the load-bearing lumber materials. Our experiments also suggested that we could replace 50% of the polymer additive with natural lignin material and still could achieve the desired strength of our LBALM. This is clearly shown in Fig. 21.

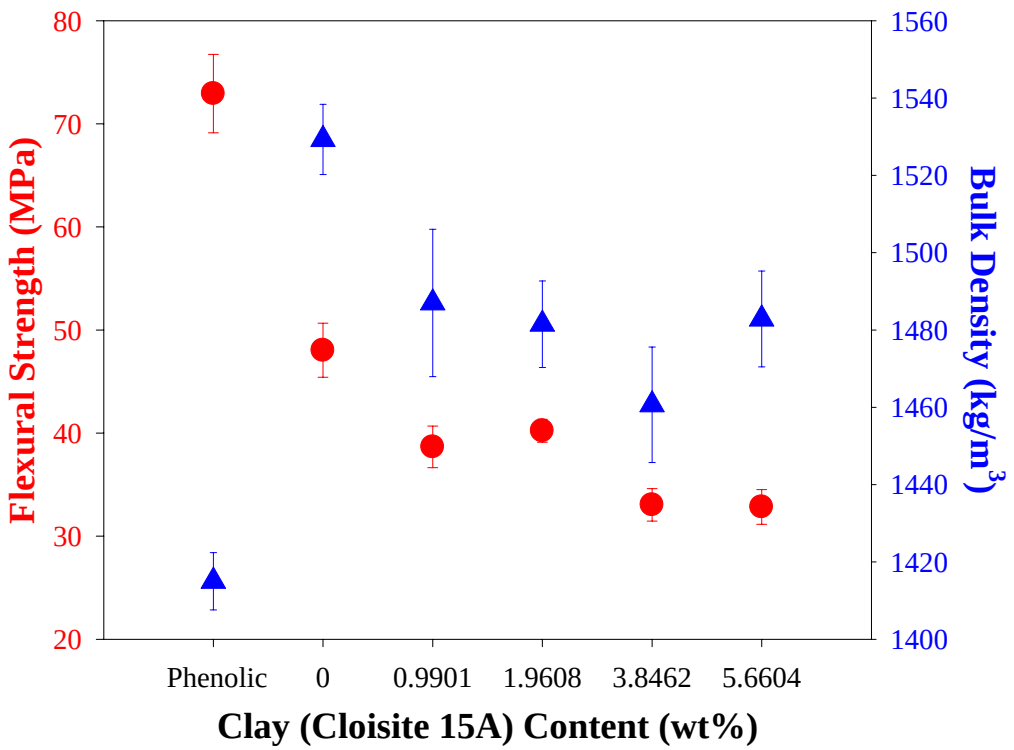

Figure 20. *How clay concentration affected the mechanical properties of composites formulated at 150°C from sulfite-rich scrubber material, cellulose-derived fibrous material, and phenolic polymer. The polymer-to-solid ratio was 0.4.*

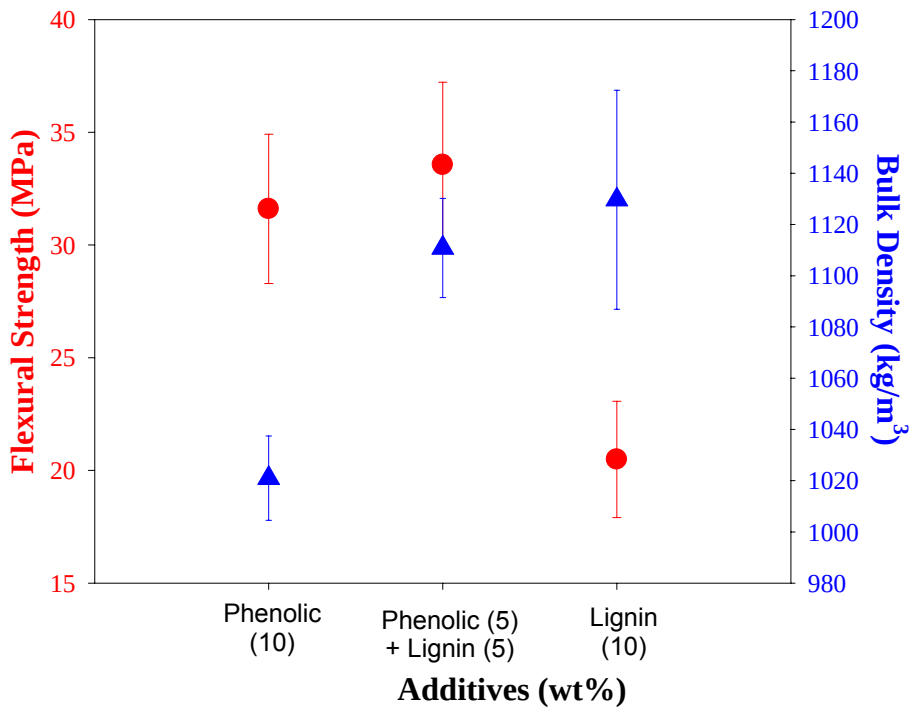

Figure 5. This data suggest that when 50% of the polymer additive was replaced with a cheap ingredient like lignin, the strength of the composite formulated from sulfite-rich scrubber material improved.

Summary and Conclusions

In October 2004, we initiated research in which we attempted to develop value-added products from sulfite-rich scrubber materials. The emphasis was on the fabrication of wood substitute materials, e.g., plywood, floor particleboard, and lumber. In pursuit of these goals, we explored how the physical and chemical properties of scrubber material and natural byproducts could be exploited to mitigate the problem of managing the huge production of sulfite-rich scrubber materials every year. The following was concluded:

1. The as-received sulfite-rich scrubber material showed considerable variation from week to week in its mercury content.
2. The determined mercury concentration steadily increased as a function of air drying time at ambient temperature. In fact, the mercury concentration increased by 80% in 90 days of air drying. This is because the presence of water dilutes the mercury concentration in the scrubber material.
3. The thermal analysis suggested that the scrubber materials were thermally stable up to ~ 420°C. At T > 420°C, water molecules were released from the scrubber material. This behavior may inhibit sustaining fire in our wood substitute products.
4. The infrared spectroscopic analysis of the scrubber materials suggested that they are largely sulfite-rich scrubber products but do contain carbonate and organic impurities. In addition, the scrubber materials we examined

contained free sulfate ions trapped in matrices. These impurities are unlikely to affect the performance of our products.

5. Four types of natural fibers were evaluated for the production of wood substitute products, and it appeared that one of them gave the best strength characteristics.
6. The introduction of natural proteins into the scrubber material dramatically improved the mechanical properties as long as the protein's concentration did not exceed 10 wt%.
7. To date, we have tested three different natural proteins, and the wood substitute products developed from them and scrubber material exceed the mechanical strength of commercial products like sawdust board, OSB, flooring particleboard, and particleboard. It is worthwhile to point out that no commercial polymers were used in our products unlike commercial products.
8. The incorporation of 2 inch size fibrous material substantially improved the brittle behavior, i.e., our products became much less brittle.
9. Our results suggested that it may be feasible to develop strong, load-bearing materials from sulfite-rich scrubber materials and polymers. However, the incorporation of clay additives did not have any beneficial effects on the strength or bulk density of the composites.
10. The concentration of the polymers in our load-bearing lumber composites derived from sulfite-rich scrubber material could be further reduced by adding cheap lignin to the mix.
11. It appeared that on increasing the composite formulation pressure, the overall flexural strength of the composite increased. However, the increase in the strength was only 7% when the formation pressure increased from 2 MPa to 4.5 MPa.
12. The temperature at which composites were formulated affected the flexural strength of composites derived from sulfite-rich scrubber material. In fact, the strength linearly scaled with temperature at $175^{o}C < T < 215^{o}C$.
13. Incorporating burlap mesh as a core of our composite decreased the composites' brittleness.

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