DURABLE PHOSPHATE-BONDED NATURAL FIBER COMPOSITE PRODUCTS

PATRICK K. DONAHUE; MATTHEW D. ARO

University of Minnesota Duluth Natural Resources Research Institute
5013 Miller Trunk Highway
Duluth, Minnesota, 55811, USA

ABSTRACT

The University of Minnesota Duluth Natural Resources Research Institute (NRRI) and the Wisconsin Business Innovation Corporation (WBIC) conducted a preliminary study to determine the feasibility of producing composite building products utilizing Ceramicrete®, an innovative chemically-bonded phosphate ceramic binder developed by the United States Department of Energy's Argonne National Laboratory (ANL), and waste pulp and paper mill residues. Specifically, the project was to demonstrate that waste pulp and paper mill residues can be added to Ceramicrete® to create durable building materials; to determine whether the products meet industry performance standards and consumer acceptance tastes; and to determine preliminary manufacturing costs and economic feasibility of producing the new value-added products. We are beginning an extensive three-year study to conduct the necessary technical and business/market developments tasks to bring the product concepts to commercialization.

KEYWORDS

inorganic cement; magnesium phosphate cement; inorganic binder; chemically bonded phosphate ceramic; inorganic-bonded composite building products

1. INTRODUCTION

Each year, millions of tons of waste pulp and paper mill residue are landfilled, land spread, or burned. In the United States, Minnesota and Wisconsin pulp and paper mills alone produce nearly 3,500 tons per day while nationwide 8.2 million wet tons are produced (NCASI, 1992). The driver of our project is the paper industry's waste disposal problem. The majority of residue is landfilled with an average tipping fee of $32.19/ton (Repa, 2001), but environmental regulations prevent new landfills from being sited as quickly as existing ones are being filled, making innovative disposal solutions more critical everyday. In addition, the number of U.S. landfills is steadily decreasing – from 8,000 in 1988 to 1,767 in 2002. (US EPA, 2006). As landfill prices rise and land spreading is similarly restricted, paper mills will turn to the next cheapest treatment – incineration – which will only increase the energy costs of residue disposal.

The WBIC and the NRRI propose to minimize industrial waste disposal through recycling and beneficial reuse. We propose an applied product development project to conduct the necessary tasks for production of durable phosphate-bonded building products, such as fire-rated architectural door core, door stile, and door rail material utilizing waste pulp and paper mill residue as a feedstock.

This development project aims at expanding on the results of the feasibility study presented in this paper. Our goal is to expand on this investigation and produce commercially-viable value-added composite products utilizing unique properties of Ceramicrete® with those of waste pulp and paper mill residues to develop durable and fire-resistant composite building products. The novel phosphate binders, originally developed for treatment of radioactive waste streams, are also useful as inorganic adhesives for production of wood composite building materials. Also, the addition of waste coal-fired power plant fly ash can be utilized to enhance the strength properties of these composites. These inorganic-bound pulp and paper mill residue composite products will also reduce maintenance costs due to improved durability, superior fire and water resistance, and greater resistance to biological degradation. The binders are rapid-setting and require no extra energy input to cure – thus, the building products cure quickly at room temperature.

The focus of our innovation is to think of the residue not as refuse but as a valuable resource. The solids portion of the residue is approximately 50 percent cellulose fiber and the other 50 percent is inorganic material such as clays, dies, and calcium carbonate. The residue has high moisture content, typically 40-65% on an oven-dry basis. Previous research at the NRRI has determined that these primary constituents of residue, especially clay, have potential for the production of fire-rated building products. There is an increasing shortage of wood fiber in the composite wood products industry and utilizing this readily available feedstock is an appealing alternative to virgin fiber. Our goals are to develop technology to produce more durable and environmentally friendly pulp and paper mill residue-based composites, reduce the environmental impact of the papermaking process by minimizing land filling of waste pulp and paper mill residue, and to design, develop, test, and demonstrate durable phosphate-bonded building products from a novel composite material.

2. MATERIALS

2.1 Pulp and Paper Mill Residue

This project utilized waste residues from Stora Enso's Kimberly, Wisconsin mill. The residues were kept chilled until ready to use to reduce the chances for rotting. The material was not processed in any way prior to board formation – no drying or screening activities were conducted.

Typical composition of residue from Stora Enso's mill in Kimberly, Wisconsin is listed in Table 1 (as supplied by Stora Enso).

Table 1 – Chemical composition of waste residue

Parameter	Result (mg/kg on dry weight basis)
Aluminum (as Al)	4600
Calcium (as Ca)	39000
Copper (as Cu)	13
Iron (as Fe)	750
Magnesium (as Mg)	1200
Manganese (as Mn)	29
Potassium	230
Sulfate (as SO_4)	300
Solids	52%
pH	7.9
Fiber length (avg.)	.584mm

2.2 Magnesium Phosphate Binder

The chemically-bonded phosphate ceramic (CBPC) binder utilized in this project was developed and patented by ANL. NRRI has a non-exclusive license agreement with ANL to research, make, use, and sell products utilizing the patented ANL technologies. The raw materials needed to produce this CBPC binder (called

Ceramicrete®) are magnesium oxide (MgO) and monopotassium phosphate (KH_2PO_4), however the literature reveals that various metal oxides and acid phosphate salts can be used for the production of these binders. Ceramicrete® is formed by the following acid-base reaction:

$$MgO + KH_2PO_4 + 5H_2O = MgKPO_4{*}6H_2O$$

Typically, 3 parts KH_2PO_4, 1 part MgO, and 2 parts water (by weight) is used to produce Ceramicrete®. Various additives can be used to retard the setting time of the binder; boric acid has been shown to work well. However, this project utilized no retardants. The KH_2PO_4 dissolves in water releasing phosphate ions and decreasing the pH of the solution. The MgO dissolves in this low pH solution and releases Mg^{2+} cations which react with the negatively charged phosphate ions to form a gel. As the hydration reaction continues more gel is formed and a crystalline lattice of $MgKPO_4{*}H_2O$ mineral is created that forms around unreacted MgO particles as well as pulp and paper mill residue fibers and any other fillers. The ceramic material that is formed is near neutral (pH of, generally, 6-8).

Pure Ceramicrete® has a compressive strength of 3,000-4,000 pounds per square inch (psi). When class C fly ash is added at 60% loading, the compressive strength increases to 8,000-12,000 psi (Jeong & Wagh, 2002). Thus, it appears that fly ash is an excellent way to increase strength of composite products bonded with Ceramicrete®.

For an in-depth discussion on CBPC technology please refer to the book Chemically Bonded Phosphate Ceramics written by ANL's Dr. Arun S. Wagh.

2.2.1 Energy Benefits

Production of Ceramicrete® requires 2.36 million BTU/ton (BCS, 2002) while Portland cement, a traditional inorganic-bonded composite wood product binder, requires 5.79 million BTU/ton to produce (PCA, 1990). Therefore, Ceramicrete® production consumes only 40.8% of the energy used in cement production. In addition, Ceramicrete® production requires only a fraction of the energy used in production of traditional wood composite product binders such as petroleum-based phenol formaldehyde and diphenylmethane diisocyanate resin. The low energy consumption of the phosphate binder production is due to surface mining of phosphate ore and low temperature chemical extraction of the phosphate values from these ores. Thus, Ceramicrete® has the potential to reduce energy dependence in the inorganic-bonded composite wood products industry. (Wagh, 2004:175).

2.2.2 Magnesium Oxide

Magnesium oxide is produced from the processing of natural magnesite minerals (magnesium carbonate) and dolomite (mixture of calcium and magnesium carbonates). It is extracted from these minerals or produced from magnesium-rich brines. Out of the candidate metal oxides used to produce CBPCs, MgO is the most suitable because it has moderate solubility (in between that of calcium oxide (CaO) and iron oxide (Fe_3O_4)) (Wagh, 2004:36). MgO is produced in different grades of reactivity based on the length of time and temperature it is calcined. Wagh reports that dead-burned MgO is most suitable for CBPC production (Wagh, 2004). Calcining the MgO reduces particle porosity, increases particle size, and, therefore, reduces effective surface area. These properties reduce the rate of dissolution of the MgO particles in acid solution thus producing a manageable rate of reaction. For this study, we utilized 'MagChem P98 PV,' a dead-burned MgO from Martin Marietta Magnesia Specialties of Raleigh, North Carolina, USA. This product had the following analysis: MgO, 97.7% min.; SiO_2, 0.8% max.; CaO, 1.1% max.; Fe_2O_3, 0.25% max.; Al_2O_3, 0.3% max.; and loss on ignition (LOI), 0.3% max. This material has the screen analysis depicted in Table 2. For in-depth technical information on the history, manufacture, and uses of MgO please see The Chemistry and Technology of Magnesia by Dr. Mark A. Shand.

Table 2 – Screen analysis of MagChem P98 PV

Screen size (Tyler equivalent)	% passing
16 mesh	100
30 mesh	99.8
50 mesh	98
100 mesh	91
200 mesh	75
325 mesh	60

2.2.3 Monopotassium Phosphate

Monopotassium phosphate is an acid phosphate produced by reacting phosphoric acid with a chloride or carbonate of potassium. It is commonly used as a food ingredient and as fertilizer material for plant growth. The KH_2PO_4 used in this project was purchased from AerChem, Inc. of Bloomington, Indiana, USA and has the following analysis: P_20_5, 51% min.; K_2O, 34% min.; F, 10 ppm max; and As, 3 ppm max. It appears that acid phosphates with a P_2O_5 content of 50-60% may be candidates for the production of CBPCs (Wagh, 2004:32).

2.2.4 Aggregates

To reduce the amount of Ceramicrete® binder required for product production (thus reducing product cost) we have examined various fillers. The most beneficial filler is fly ash. The spherical cenospheres in the fly ash are light and increase the compressive strength of the product. It appears that class C or class F ash can be used; theoretically, using whichever grade fly ash is available in the surrounding geographical area makes the most sense. However, class C fly ash (which absorbs slightly more water) may cause the Ceramicrete matrix to set slightly faster than class F due to the higher CaO content. In addition to acting as a filler or 'extender,' the amorphous silica in fly ash is somewhat soluble in the acid phosphate solution, thus fly ash actually contributes to the generation of more binder in the mix, thus producing a stronger product (Wagh, 2004:38). Similarly, it has been discovered that fly ash may physically fill the voids of the CBPC paste which may increase strength of the final product. Also, near the contact surface between fly ash particles and $MgKPO_4*6H_2O$ mineral there is evidence that Mg ions diffuse in to the fly ash particle surface and silicon and aluminum found in fly ash disperse in to the $MgKPO_4*6H_2O$ mineral and a non-crystalline layer is formed around the fly ash particles. It has been reported this layer around the fly ash particles creates a strong bond between the fly ash particles and $MgKPO_4*6H_2O$ (Zhu & Zongjin, 2005).

We have determined that hammer milled aspen oriented strand board (OSB) flakes added to the mix significantly increases the bending strength of the samples. The fibers in the waste residue are very short, thus we speculate that adding OSB flakes can be a simple method for increasing bending strength.

Regular sand can be used as an aggregate to increase toughness. Also, in certain applications, the addition of wollastonite ($CaSiO_3$) may be desirable. $CaSiO_3$ is a mineral with a narrow and elongated geometry – this geometry allows $CaSiO_3$ to increase the flexural strength of a product if so desired.

For this project, fly ash and OSB flakes were the only aggregates used. Bags of fly ash were collected from Duluth Steam in Duluth, Minnesota, USA. The bags were kept sealed until ready to use. This fly ash is not of structural concrete grade (i.e. Class C or Class F); however it appears that several types of ashes can be used successfully. The OSB flakes were supplied by Potlatch Corporation of Cohasset, Minnesota, USA.

3. METHODS

3.1 Board Formation

As stated earlier, the waste residues were kept chilled until ready to use. Since pulp and paper mill residues are typically encrusted with inorganic material, mostly calcium carbonate ($CaCO_3$) and clay, dispersion of the agglomerated fibers in the Ceramicrete® mix is a processing complication. We have learned that KH_2PO_4 acts as a natural fiber dispersant which helps to disintegrate the residue clumps. We have also experimented with different water soluble polymer dispersing agents including carboxy-methyl-cellulose (CMC). CMC has the ability to disperse pulp fibers and promote inter-fiber bonding via its carboxy-methyl groups. In addition, CMC may penetrate the fiber network which increases the fiber surface availability for bonding (Giri et al., 1998). It appears that CMC rapidly hydrates the cellulose fibers in the pulp and paper mill residue and reduces the viscosity of the agglomerates which promotes dispersion (Klingenberg et al., 2000). Other experiments were conducted using EKASoft 509HA pulp and paper mill fluff pulp debonder from EKA Chemicals. For this project, KH_2PO_4 was the only dispersant used.

To make the boards, KH_2PO_4 was premixed with water for five minutes in a five quart planetary-style mixer. Waste residue at approximately 53% moisture content (oven-dry basis) was mixed with the KH_2PO_4 and water for ten minutes to help disentangle the residue clumps. MgO and fly ash were added to the mixer and mixed for 15 minutes. All mixing was done at approximately 30 rotations per minute.

The mixture was transferred to a 6.5 in. X 6.5 in. box mold and cold-pressed at room temperature to 0.75 in. thickness for two hours. The samples set firm in approximately 45-75 minutes. The samples were then cured for 96 +/- 12 hours in the NRRI walk-in conditioning room at approximately 70 deg. F and 70 percent relative humidity (RH). The samples were then trimmed to 6 in. X 6 in. and 3 in. X 3 in. samples. The sides of both samples were sanded smooth using a Dynabrade rotary sander. The samples were then equilibrated at 75 deg. F and 50% RH in the NRRI Mechanical Testing Laboratory for 48 hours before testing.

The following waste residue:Ceramicrete® ratios were used in this study: 0.63, 0.79, 0.92, and 1.1. The materials needed to make the boards are presented in Table 3. Five repetitions of each residue:Ceramicrete® ratio was produced.

Table 3 – Amount of materials in each of the boards

Weight (g)							
	MgO	**KH_2PO_4**	**Fly ash**	**Residue**	**Water**	**OSB Flakes**	**Fly ash:binder ratio**
Board 1	100	300	100	250	300	75	0.25
Board 2	87.5	262.5	150	275	250	75	0.43
Board 3	75	225	200	275	250	75	0.67
Board 4	62.5	187.5	250	275	250	75	1.00

3.2 Testing Methods

The physical and mechanical properties of the boards were evaluated according to American Society for Testing and Materials (ASTM) D1037-99.

4. RESULTS

4.1 Density

Figure 1 shows the densities of the four boards. Board 4 had the highest residue:Ceramicrete® ratio (1.1) and had the lowest density. This is due to the fact that the board contained less binder, which is much denser than the cellulose fibers in the residue. Board 3 had the highest density; this could be due to better compaction of the mixture components.

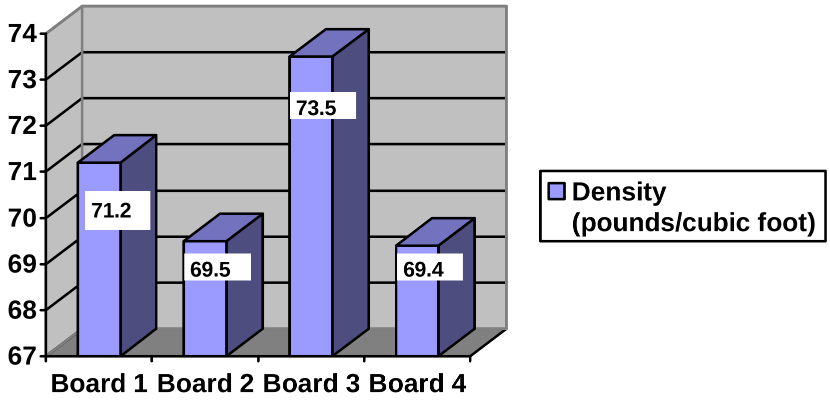

Figure 1: Board density

4.2 Water Absorption

Figure 2 shows the water absorption of each board. The absorption is calculated as the percentage increase in weight of the boards after a 24-hour water soak. Board 4 had the greatest water absorption. This board had the least amount of binder and, as expected, exhibited the greatest water absorption since there is less binder matrix encapsulating the cellulose fibers, which have inherently high water absorption rates. Alternately, high binder content produces more $MgKPO_4*6H_2O$ mineral during hydration resulting in better bonding between fibers. This produces a less porous product that absorbs less water (Delgado et al., n.d.). The highest density board, Board 3, had the lowest water absorption.

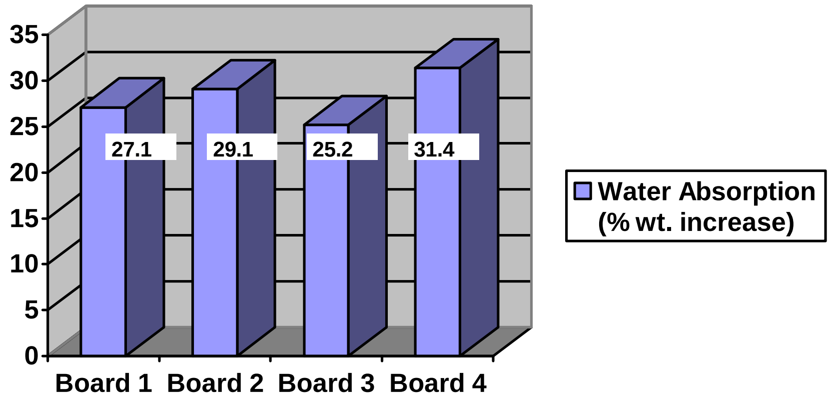

Figure 2: Water absorption

4.3 Thickness/Volume Swelling

Figure 3 shows the percentage thickness and volume swelling of the boards after a 24-hour water soak. Board 3 showed the lowest percent increase in thickness and volume. The high density of this Board makes for more difficult penetration of water; thus swelling of the fibers is reduced. Board 4 has the highest percentage volume increase since, most likely, it has the lowest density which allows for greater penetration of water; thus fiber swelling is increased.

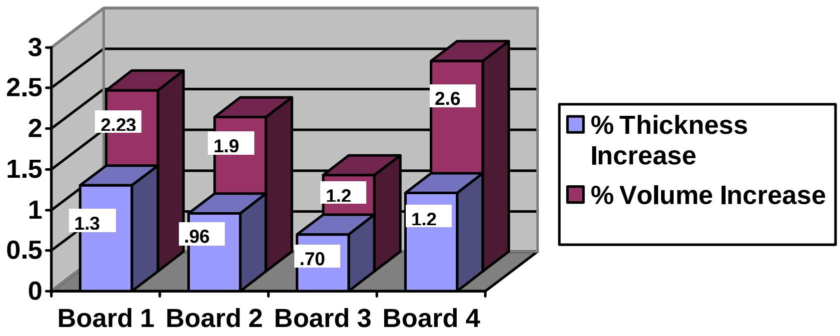

Figure 3: Percentage thickness and volume swelling

4.4 Modulus of Rupture

Figure 4 shows the modulus of rupture (MOR) in pounds per square inch (psi). The values show that Board 2 is, on average, stronger than the other boards. Board 2 has the second highest loading of binder but the second lowest loading of fly ash. This possibly suggests that a fly ash:binder ratio of 0.40-0.45 may be beneficial for increasing MOR.

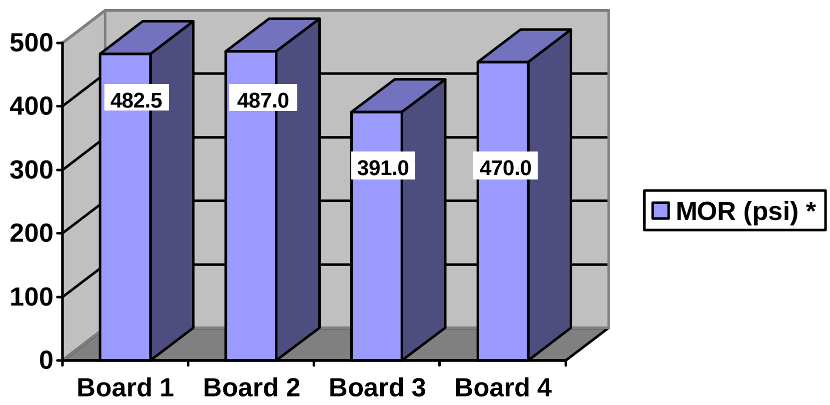

Figure 4: Modulus of rupture (*properties were obtained from specimens with short spans, so some small reduction due to shear effects may be presumed)

4.5 Screw Withdrawal

The ability of a product to withstand screw pull is important in certain applications. The screw withdrawal strength of each board is depicted in Figure 5. It appears that residue content has little effect on screw withdrawal strength.

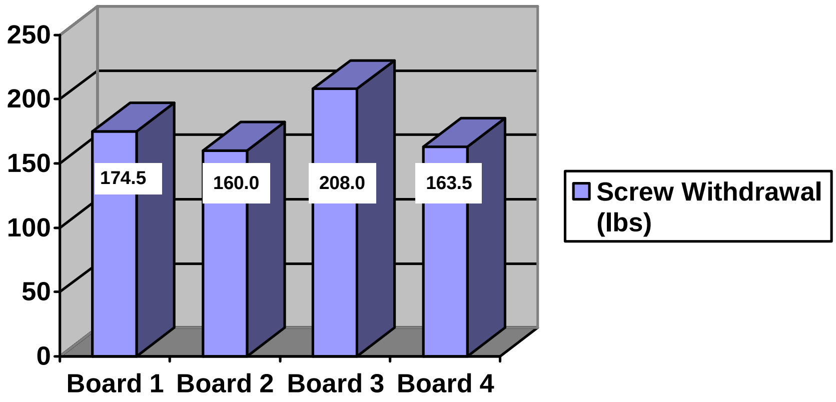

Figure 5: Screw withdrawal

4.6 Internal Bond

The ability of a panel product to withstand tension forces is important for certain applications. Figure 6 gives the internal bond values of the boards in psi. The internal bond strength of the boards increased until the fly ash loading exceeded approximately 24%. Board 3 had the highest internal bond while Board 4, with the lowest binder content, had the lowest internal bond. The data also suggests that internal bond strength decreases when the fly ash:binder ratio is greater than approximately 0.67.

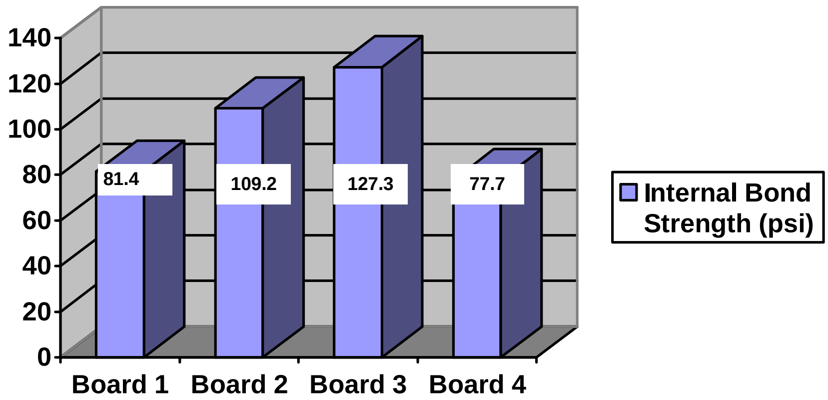

Figure 6: Internal bond strength

5. FUTURE WORK

The NRRI and WBIC expect to undertake a three-year study with the goal of conducting the necessary technical and business/market developments tasks to bring these preliminary product concepts to commercialization. The feasibility of producing laboratory bench-scale Ceramicrete®-bonded waste pulp and paper mill residue composite products has been demonstrated by the NRRI. Therefore, the first year of this project will be devoted to refining the previously-developed formulations – including researching alternative, lower-cost chemical selection for production of Ceramicrete® binder. These investigations will include defining product properties and evaluating processing characteristics. This information is crucial to scale-up production of the products and to optimize processing parameters. We also expect to conduct the necessary tasks to form a For-Profit technology transfer center that will conduct market development and research activities and, in subsequent years, be able to conduct pilot-scale product trials using various waste residue feedstocks. During the second year, medium- and pilot-scale prototypes will be produced and tested for the standards requirements at the NRRI. The technology transfer center will also conduct ongoing market and financial feasibility analyses for various products at various locations. During the third year, the focus will be on pilot-scale testing, energy economics of production, and quantification of the environmental and economic benefits for the industry and consumers. The work of all three years will be in close collaboration with the participating industrial partners, culminating in demonstration and implementation of the technology through sub-licensing agreements from the For-Profit technology transfer center.

6. CONCLUSIONS

A mixture of waste residue, Ceramicrete®, fly ash, water, and other additives can be consolidated under pressure to produce rigid and rapid-setting inorganic-bonded panel products. These products require no hot-pressing or drying of the waste residue feedstock. Physical and mechanical properties including density, water absorption, thickness/volume swell, screw withdrawal, internal bond strength, and bending strength/MOR were determined. All properties except MOR met or exceeded the minimum requirement for LD-1 grade particleboard. Preliminary market assessment shows there is potential for these products to be utilized as interior door core and door stile and rail material.

A market and product development meeting was held in Wisconsin with several Wisconsin-based door manufacturers with the goal of garnering industry support for the new potential door components. Our samples received very good reviews. It was determined that our products have the most potential for fire-rated stile and rail components due to the higher density and inorganic material content.

Due to the preliminary nature of this study, the authors recommend testing of other properties that are important to the use of panels in building components.

7. ACKNOWLEDGEMENTS

Funding for this project was provided by the Wisconsin Business Innovation Corporation/Northwest Regional Planning Commission; Wisconsin Department of Natural Resources; the University of Minnesota Initiative for Renewable Energy and the Environment; Minnesota Power; Stora Enso; and the FiberClay Council. The authors wish to thank Argonne National Laboratory, CityForest Corporation, and Sappi Fine Paper for material donation and project support.

8. REFERENCES

BCS, Incorporated. 2002. "Energy and Environmental Profile of the U.S. Mining Industry." Chapter 8, "Phosphates."

Delgado, T. S., Lamason, C. R. G., and Fernandez, E. C. "Cement-bonded Boards From Wastewater Treatment Sludge of a Recycled Paper Mill." Proceedings of a Workshop: Cement-Bonded Composites in the Asia-Pacific Region (2000).

Jeong, S. Y. and Wagh, A. S. 2002. "Chemically Bonded Phosphate Ceramics: Cementing the Gap Between Ceramics and Cements." Argonne National Laboratory.

NCASI. 1992. "Solid Waste Management and Disposal Practices in the U.S. Paper Industry." Technical Bulletin 641. NCASI. New York.

Portland Cement Association. 1990. U.S. Cement Industry Fact Sheet.

Repa, E. W. 2001. Waste Age. The Tip Off. Online. Accessed: August 22, 2006. <http://www.wasteage.com/mag/waste_tip_off/>

Klingenberg, D., Scott, T. C., Simonsen, J., and Zauscher, S. 2000. "Beneficial use of pulp and paper industry residuals: Extrusion for the manufacture of building panels." National Council for Air and Stream Improvement; Technical Bulletin No. 814.

United States Environmental Protection Agency (US EPA). Municipal Solid Waste - Basic Facts. Modified: February 22, 2006. Online. Accessed: August 23, 2006. <http://www.epa.gov/epaoswer/non-hw/muncpl/facts.htm>.

Wagh, A. S. 2004. Chemically Bonded Phosphate Ceramics. Elsevier. United Kingdom.

Giri, M., Rochefort, W. E. S., and Simonsen, J. 1998. "The novel technique of extrusion of pulp using carboxy-methyl-cellulose (CMC): Effect of CMC characteristics on pulp rheology." 70th Annual Meeting of The Society of Rheology. Paper IR4.

Zhu, D. and Zongjin, L. 2005. "Study of High Early Strength Cement based on Fly Ash, Magnesia and Phosphate." Materials Technology. 20-3: 129-192. 1066-7857.