

# Materials for Nuclear Waste Disposal and Environmental Cleanup

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## BORON AND LEAD BASED CHEMICALLY BONDED PHOSPHATES CERAMICS FOR NUCLEAR WASTE AND RADIATION SHIELDING APPLICATIONS

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### ABSTRACT

We present research about the development of a fast setting ceramic materials fabricated with boron oxide, and wollastonite powders with potential use for nuclear waste transport, disposal, stabilization, and radiation shielding applications. The boron oxide is mixed with calcium silicate and phosphoric acid in order to consolidate a ceramic by an acid base-reaction. These materials have high compression strength when compared with cements and with other available solutions for the treatment of nuclear wastes, and are suitable as fire resistant shielding materials. Nuclear attenuation experiments, compressive strength, x-ray diffraction, and scanning electron microscopy were used to characterize these materials. Our work indicates that a balance between lead oxide and boron oxide is needed to obtain a suitable hybrid material with good mechanical properties that can attenuate gammas and neutrons.

### INTRODUCTION

Chemically Bonded Phosphate Ceramics (CBPCs) are formed in low temperature conditions by mixing a base powder with phosphoric acid. The compound that forms from the cement like processing has the properties of an engineering ceramic with the advantage of being able to be formed with relative ease and low expense<sup>1,2,3</sup>. An additional advantage is that the compound can be formulated with additives that can enhance the properties of the ceramic without causing a major degradation of the structural properties. The high melting temperatures and the good thermal resistance allow this ceramic to be used as a firewall to prevent transformer explosions<sup>4</sup>. Based upon these principles the ceramic was examined with several different additives to determine the improvement of the linear attenuation coefficient for dry cask spent fuel storage and/or transportation cask for spent nuclear fuel.

Dry cask spent fuel storage involves storing spent nuclear fuel above ground and/or transporting it in casks that are lined with gamma and neutron shields<sup>5,6</sup>. One issue that arises with these casks is that while they are designed to withstand high temperatures for short periods of time, there have been examples of traffic accidents<sup>7,8</sup> that have resulted in temperatures and times exceeding the current safety design parameters. This research examines CBPCs with regards to neutron shielding in order to obtain preliminary data for an improved design of nuclear casks that can survive a traffic accident of similar nature to the new scenarios considered.

### EXPERIMENTAL PROCEDURE

#### Manufacturing

CBPC samples were fabricated by mixing an aqueous phosphoric acid formulation and natural wollastonite powder ( $\text{CaSiO}_3$ ) M200 (from Minera Nycoc; see Table 1). Also, boron oxide (from Alfa Aesar; see Table 2) was added to the mixture. For all samples, the 1.2 ratio liquid (phosphoric acid formulation) to powders (wollastonite +  $\text{B}_2\text{O}_3$ ) was maintained constant, see Table 3. The mixing process of the components was conducted in a Planetary Centrifugal Mixer (Thinky Mixer<sup>®</sup> AR-250, TM). First, wollastonite was mixed with the acidic liquid for 1 min, then, boron oxide was added and mixed for 1 min. All samples were dried for 2 days at 100°C in order to stabilize the weight.

Table 1. Chemical composition of wollastonite powder.

Composition	CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MnO	MgO	TiO <sub>2</sub>	K <sub>2</sub> O
Percentage	46.25	52.00	0.25	0.40	0.025	0.50	0.025	0.15

Table 2. Chemical composition of B<sub>2</sub>O<sub>3</sub> powder.

Composition	B <sub>2</sub> O <sub>3</sub>	SO <sub>4</sub>	Al <sub>2</sub> O <sub>3</sub>	Cl	H <sub>2</sub> O (insoluble)
Percentage	95.00	0.7	0.1	0.2	0.02

Table 3. Raw materials amounts in the samples fabricated.

Sample composition	Wollastonite (CaSiO <sub>3</sub> ) (g)	B <sub>2</sub> O <sub>3</sub> (g)	Total powders (g)	Phosphoric acid formulation (g)
CBPC	100	0	100	120
CBPC-2 B <sub>2</sub> O <sub>3</sub>	98	2	100	120
CBPC-10 B <sub>2</sub> O <sub>3</sub>	90	10	100	120
CBPC-15 B <sub>2</sub> O <sub>3</sub>	85	15	100	120
CBPC-20 B <sub>2</sub> O <sub>3</sub>	80	20	100	120

#### Characterization

For compression tests, samples were fabricated using glass molds of 12.7 mm diameter and 100 mm long. A diamond saw was used to cut cylinders of 28 mm length. Samples were ground (with silicon carbide papers of grit ANSI 400) using a metallic mold until flat, parallel, and smooth surfaces were obtained. The final length was 25.4 mm. Compression tests were conducted in an Instron<sup>®</sup> machine 3382. A set of 5 samples was tested for each composition of Table 3. The crosshead speed was 1 mm/min. For Scanning Electron Microscopy (SEM) examination (sample sections were ground using silicon carbide papers grit ANSI 240, 400 and 1200 progressively), samples were mounted on an aluminum stub and sputtered in a Hummer 6.2 system (15mA AC for 30 sec) creating approximately a 1nm thick film of Au. The SEM used was a JEOL JSM 6700R in high vacuum mode. X-Ray Diffraction (XRD) experiments were conducted using an X'Pert PRO (Cu K $\alpha$  radiation,  $\lambda=1.5406 \text{ \AA}$ ), at 45KV and scanning between 10° and 80°. M200, M400 and M1250 wollastonite samples (before and after the drying process) were ground in an alumina mortar and XRD tests were done at room temperature. The above characterization was conducted for the compositions summarized in Table 3. A similar set of experiments for PbO additions (instead of B<sub>2</sub>O<sub>3</sub>), was presented before<sup>6</sup>.

In order to determine the shielding effect of CBPCs a method for measuring the attenuation of neutrons was implemented. In order to allow for quick measuring of the attenuation coefficients a He-3 neutron detector was used. The He-3 detector gives a count of thermal neutrons over a set time period. This detector was connected to a lower level discriminator to reduce noise and a

scaler to obtain counts. A PuBe neutron source was used at the Missouri University of Science and Technology Research Reactor (MSTR). The production of neutrons from the PuBe sources occurs when the alpha particle released from the plutonium reacts with beryllium in the source producing neutrons according to the reaction shown in equation 1.



This produces neutrons with a wide energy range; the neutron energy spectrum for PuBe can be seen in Figure 1a.

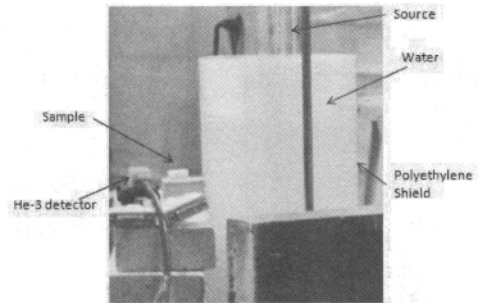
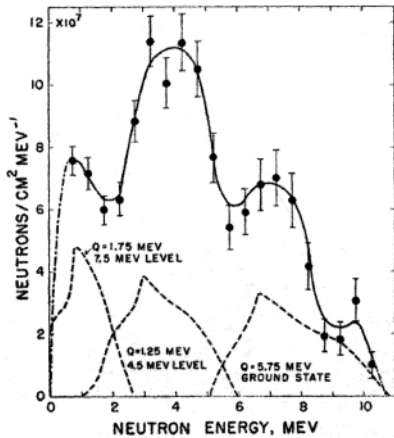


Figure 1 a) PuBe neutron energy spectrum<sup>9</sup>, and b) neutron attenuation setup

Since the spectrum of the PuBe source contains more fast neutrons than thermal neutrons a method for thermalizing the neutrons was used. The average distance for thermalizing a fast neutron in water is about 12.7 cm (estimated from the neutron age for fast neutrons  $\sim 27 \text{ cm}^2$ )<sup>10</sup>. The source was suspended in water in a container of low density polyethylene (borosilicate glass must be avoided) with a distance to the wall of 9 cm. The sample was placed on a platform with the edge of the sample 1 to 2 cm away from the polyethylene wall. The samples were then counted using a He-3 detector with 10 minute count rates with and without a 0.6 mm cadmium shield placed over it. When present, the cadmium shield absorbs all the thermalized neutrons traveling through the sample, and the difference measured with and without the Cd shield gives the neutron difference used to calculate the attenuation for the samples. A picture of the setup is shown in Figure 1b.

## RESULTS AND ANALYSIS

Figure 2 shows boron oxide ( $\text{B}_2\text{O}_3$ ) and wollastonite ( $\text{CaSiO}_3$ ) powders respectively. Wollastonite grains are needle like shaped while  $\text{B}_2\text{O}_3$  grains do not have specific shape.

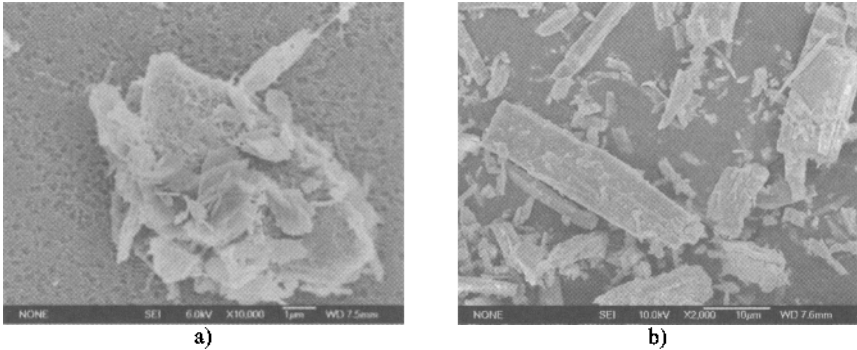


Figure 2 SEM images of the raw powders used to fabricate the CBPC, a) B<sub>2</sub>O<sub>3</sub>, and b) CaSiO<sub>3</sub>.

Figure 3 shows SEM images for the CBPCs fabricated. CaSiO<sub>3</sub>, CaHPO<sub>4</sub>·2H<sub>2</sub>O, BPO<sub>4</sub> and B<sub>2</sub>O<sub>3</sub> have been identified in the images. These results were confirmed by the XRD data as shown in Figure 4.

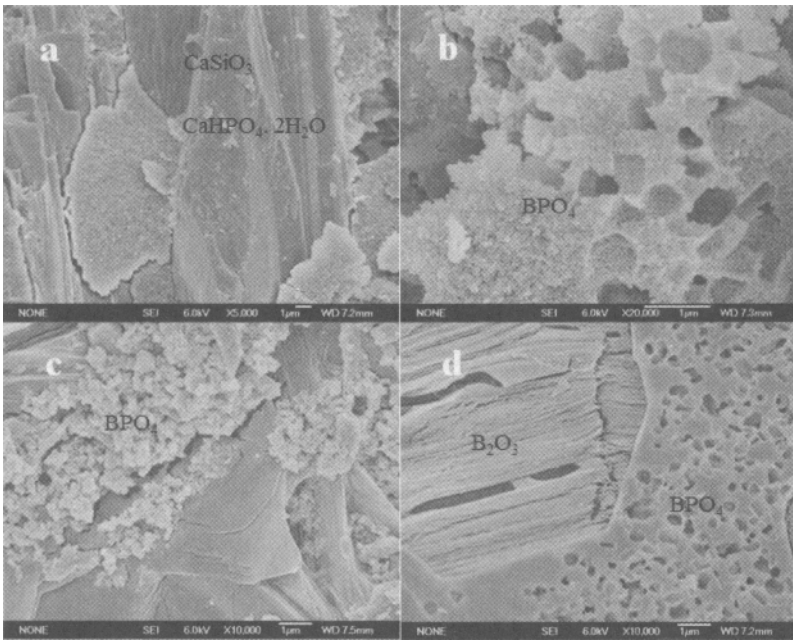


Figure 3 SEM images for the boron-based chemically bonded ceramics fabricated.

Figure 4 shows the XRD for the materials used (raw powders) and fabricated in this research (see Table 3).  $\text{CaSiO}_3$ ,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{BPO}_4$ , and  $\text{B}_2\text{O}_3$  are shown.  $\text{B}_2\text{O}_3$  is mostly amorphous. Brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) is the result of the reaction between  $\text{CaSiO}_3$  and  $\text{H}_3\text{PO}_4$ . Brushite and boron phosphate are the binding phases.

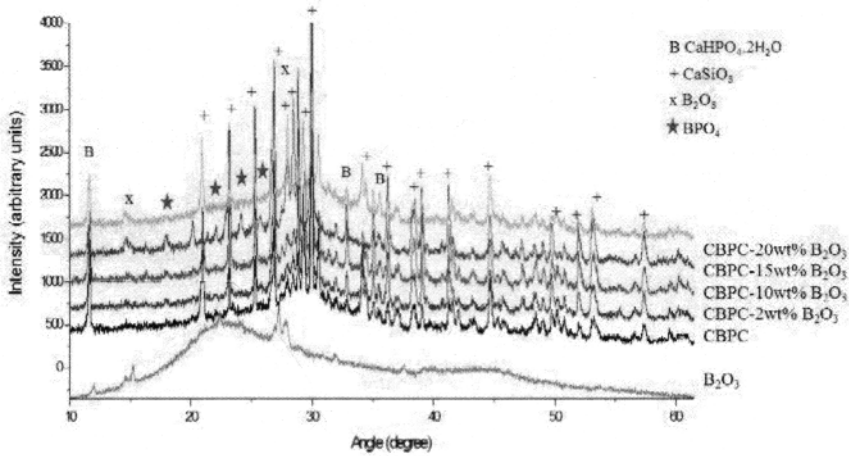


Figure 4 XRD for the raw powders and ceramics fabricated.

Figure 5 shows the compressive strength for the CBPCs with  $\text{B}_2\text{O}_3$  contents. The standard deviation was bigger for the sample with 10%  $\text{B}_2\text{O}_3$ . As the  $\text{B}_2\text{O}_3$  contents increases, the compressive strength decreases.

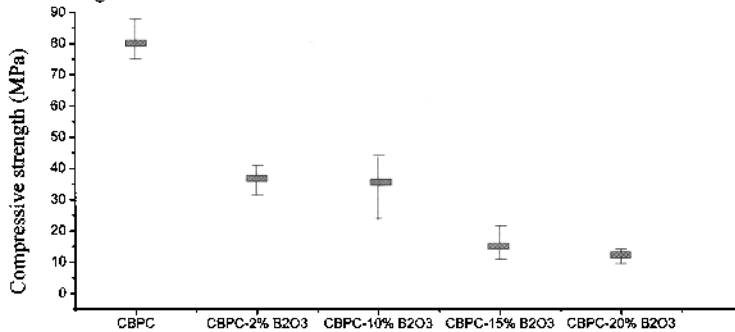


Figure 5 Compressive strength for the boron-based chemically bonded ceramics fabricated.

Results for the neutron attenuation experiment for several different CBPCs are summarized in Table 4.

Table 4: Thermal Neutron Attenuation Values for CBPCs

	Thickness (cm)	Linear Attenuation (cm <sup>-1</sup> )	Error
20% Boron	2.774	0.089	0.017
0%	1.664	0.060	0.018
50% PbO	1.284	0.045	0.023
Boron oxide	1.308	0.068	-

From the results the addition of boron improved the attenuation of CBPCs by 48% for thermal neutrons. However the addition of PbO caused a decrease in attenuation by 25%. The CBPCs compared well to boron oxide during the testing being only 11% lower. The CBPC also compares favorably when it was combined with boron oxide showing a definite increase in thermal neutron attenuation for both materials. However, these results still have large error values and further testing on neutron attenuation with a more intense source is recommended.

One of the reasons for the relatively large errors is due to the continued thermalization of neutrons within the sample, i.e. the sample is not only blocking neutrons but is still thermalizing them. Another possible error is that the source location has small variations in its position. This happens because the source had to be repositioned several times over the course of the experiment to guarantee a safe working environment for the experimenter (i.e. ALARA). Missouri S&T has a new neutron generator in the process of being licensed. Utilizing a neutron generator as a source of neutrons will alleviate the safety problems, since the generator can be started and stopped at will as opposed to the PuBe neutron source.

#### DISCUSSION

The reaction generating brushite is shown in equation 2. CaHPO<sub>4</sub>·2H<sub>2</sub>O is a calcium phosphate that under time and temperature can lose the bonded water molecule and transform to a more stable phase, monetite, CaHPO<sub>4</sub>.

In the acidic formulation used, boron oxide is dissolved and boric acid (H<sub>3</sub>BO<sub>3</sub>) is generated. Then, the reaction of boric acid and phosphoric acid can generate boron phosphate (BPO<sub>4</sub>) as found experimentally. We suggest the reaction generating BPO<sub>4</sub> in equation 3,



As B<sub>2</sub>O<sub>3</sub> presence increases, the compressive strength is decreased. This can be associated with two factors. The first one is likely due to a weak reaction of saturation of boron ions in the acidic solution. The second one is that when the residual boron oxide content increases, there is more possibility to have agglomeration of these particles. The agglomeration produces a poor liquid impregnation, which decreases the compressive strength.

#### CONCLUSION

The addition of boron oxide to CBPC shows significant improvement in neutron attenuation for the ceramic. A previously prepared sample with PbO however, demonstrated a significant drop in neutron attenuation. For applications of this ceramic as a shielding material, a balance



between boron oxide and lead oxide needs to be determined in order to function as an effective radiation shield. In this regard further testing on the ceramic with more variation in regards to boron content will be performed.

#### ACKNOWLEDGMENTS

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