

Preparation and Characterization of Chemically Bonded Phosphate Ceramics (CBPC) for Encapsulation of Harmful Waste

W. A. Ibrahim, H. A. Sibak and M. F. Abadir*

Chemical Engineering Department, Faculty of Engineering, Cairo University

*magdi.abadir@yahoo.com

Abstract: A chemically bonded phosphate ceramic material has been prepared for the sake of encapsulating lead battery waste. In this paper the optimum conditions for the preparation of magnesium potassium phosphate compacts are determined and the formation of the final product assessed using XRD. The effect of applied pressure and pressing duration as well as the Mg:K molar ratio on the porosity and permeability of compacts was studied. It was found that a minimum porosity was achieved by using a molar ratio of Mg:K = 1:1 and that a pressing time of 10 minutes is sufficient to reach compacts of reasonably low permeability. Also, the compressive strength of compacts was found to increase linearly with curing time and to be much more affected by pressing time duration than by the magnitude of the applied pressure.

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1. Introduction

At present, hundreds of million of tons of diverse substances acting as source of harm to the human health, plant life, and useful microorganisms, are discharged to the aqua sphere. In a number of these places the concentration of harmful impurities is already impermissible and their level exceeds the maximum permissible concentration.

In this respect one of the most promising methods of abating the harmful effect of industrial waste is encapsulation in more or less impervious matrices prior to landfilling. Among these can be cited epoxy resins, polyethylene, polysiloxane, phosphate bonded ceramics, etc...⁽¹⁾

The preparation of chemically bonded ceramics relies on reacting a base with an acid to form a sparingly soluble salt. One of the most common of these materials is magnesium phosphate prepared by the reaction between magnesium oxide and orthophosphoric acid⁽²⁾. A common problem associated with the preparation of such material is the large exothermic heat associated with its formation. Such effect increases the solubility of the formed phosphate. To counter this effect several methods have been used: Wagh et al⁽³⁾ have studied the effect of firing MgO to high temperatures on its subsequent solubility in phosphoric acid. They found that heating up the oxide to 1300°C for three hours had for effect to form sintered products of low solubility. Also, Sarkar⁽⁴⁾ and Wagh et al⁽³⁾ have used boric acid as retardant and found that it has a positive effect on decreasing the solubility of the formed phosphate salt. The incorporation of a second cation with Mg further decreases the solubility of the

formed salt. Wagh et al⁽⁵⁾ have prepared a potassium magnesium phosphate ceramic through the following reaction:



On the other hand, Ivengar and El Tabbaa⁽⁶⁾ synthesized a magnesium potassium phosphate cement as an alternative to Portland cement. Testing revealed a dense microstructure, high early-age strength development and low volume expansion of the developed cement.

More recently Xing et al⁽⁷⁾ have studied the effect of varying the magnesium to potassium ratio on setting time. They found that an increase in this ratio entailed shorter setting time and higher compressive strength. They interpreted their findings in the light of XRD results.

The use of such cements for stabilization of harmful ions such as Cu⁺⁺, Zn⁺⁺, Ni⁺⁺ has been studied by several authors^(8,9,10). The general approach was to encapsulate the heavy metal compounds in situ while the cement was setting. These authors then studied the leaching behavior of metallic ions using different analytical techniques.

The present paper aims at preparing a magnesium – potassium phosphate cement and studying the effect of process parameters on properties related to efficient encapsulation such as porosity, permeability and compressive strength.

2. Experimental

2.1. Raw Materials

The starting materials used in this work were: magnesium hydroxide, as source of Mg⁺⁺ ions, potassium dihydrogen phosphate, as source of K⁺⁺

ions, phosphoric acid and boric acid, used as setting retardant. Table 1 shows the source and purity of

such materials.

Table 1: Starting raw materials

Name	Formula	M.W.	Source	Purity %
Magnesium hydroxide	Mg(OH) ₂	58.03	Asma dye* company.	95
Potassium Di hydrogen phosphate	KH ₂ PO ₄	136.03	Adwic.**	98 min.
Boric Acid	H ₃ BO ₃	61.83	Adwic.**	99 min.

* Alexandria, Egypt

** Lake Forest, CA, US

2.2. Characterization and Testing

The following techniques were used for phase identification and testing of the prepared specimens:

All samples and chemicals used in the preparation of solutions were weighed using an analytical balance of (Sartorius) with a sensitivity of 10⁻²g. Intimate mixing was performed using "J. P. Selecta" magnetic stirrer.

Phase identification was performed using Philips type PW 1373 X-Ray diffractometer.

The true density (ρ_T) of the formed C.B.P.C. was determined using ISO 5018 – 1983 standard⁽¹¹⁾. This method relies on the commonly used density flask technique. In the present case, water was used as the liquid medium.

Compacts were formed by pressing the cement using several levels of uniaxial pressure ranging from 4.5 to 34.5 MPa. The molds used were cylindrical with 2" in diameter. The pressing duration was varied from 5 to 15 min. The pressed specimens were then cured for time periods reaching 28 days.

The bulk density (ρ_B) of pressed C.B.P.C. specimens was determined using by dividing the weight of the formed sample W by the volume of the same sample V_B cm³ using the standard method ISO 5017 – 1998⁽¹²⁾.

$$\rho_B = W / V_B \quad (1)$$

Total porosity was calculated following the determination of both types of density using the following definition:

$$\text{Total Porosity} = 1 - (\rho_B / \rho_T) \quad (2)$$

Permeability was determined using the Darcy equation:

$$\kappa = \frac{Q \cdot \mu \cdot \Delta x}{\Delta P} \quad (3)$$

Where:

Q is the superficial (or bulk) fluid flow rate through the medium (m³/s)

κ is the permeability of the medium (m²)

μ is the viscosity of the fluid (Pa.s)

ΔP is the applied pressure difference (Pa)

Δx is the thickness of the medium (m)

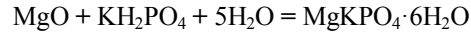
Permeability was determined for cylindrical specimens of diameter = 2" and height of at least 2" following the method suggested by Pal et al⁽¹³⁾. This test was only performed on pressed specimens. A three specimen sample was tested and the average value recorded.

Compressive strength was measured with an InstronTM machine used in compression mode delivering a uniaxial load. Specimens tested were of 2" diameter and 2" in height following ISO 10059 – 1992⁽¹⁴⁾.

3. Results and Discussion

3.1. Mixing of cement ingredients

Mixing of MgO and KH₂PO₄ was performed using excess water than that required for the reaction:



Setting time was found to increase with the percent excess water added, as expected. A reasonable period of time is necessary to allow for the formation of the mixed phosphate and for proper molding of specimens. When no retardant was used, the maximum available time for mixing before setting sets in did not exceed 4 minutes whatever level of excess water was used. This duration was not sufficient since preliminary experiments have shown that it takes at least 20 minutes to achieve proper formation of the mixed salt. That is why, boric acid was added as retardant. Fig. 1 shows the relation between available mixing duration and the percent excess water for two levels of boric acid addition for a Mg:K molar ratio of 1:1 and a mixing speed of 100 rpm.

Using higher mixing speeds yielded lower setting time while lower mixing speeds were ineffective in achieving homogenization.

This figure shows that the use of 5% boric acid with any amount of excess water failed to yield setting times less than 20 minutes. Consequently, it was necessary to add 10% boric acid with 50% excess water.

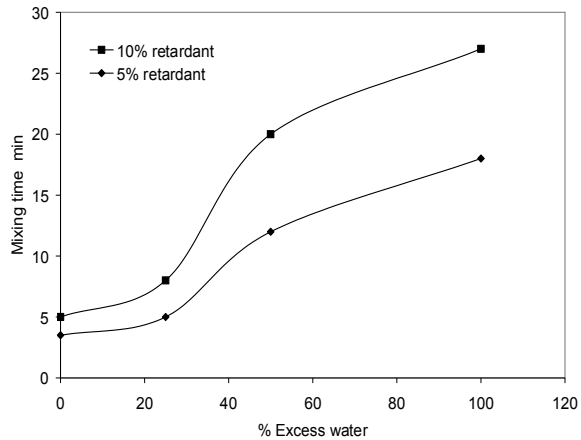


Fig.1: Effect of excess water on mixing time (Mg:K = 1, mixing speed = 100 rpm)

On the other hand, Fig. 2 shows the effect of varying Mg:K molar ratio on both the true density of the formed cement and the bulk density of pressed specimens.

The corresponding value of porosity, as calculated from equation (2) is shown in Fig. 3.

Fig. 2 shows a simultaneous decrease in true and bulk densities as the Mg:K ratio increases. It can be seen that the difference between the values of both densities reaches a minimum value at about 1:1 ratio.

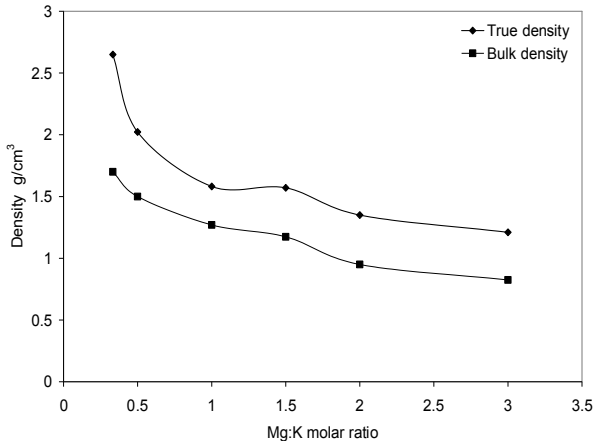


Fig.2: Effect of Mg:K ratio on density (%retardant = 10%, excess water = 50%)

This is best shown in Figure 3 which depicts the relation between the total porosity and the Mg / K ratio. It is clear that a minimum value of porosity of about 16% is reached at the aforementioned ratio of 1:1. That is why; this ratio was kept throughout the work.

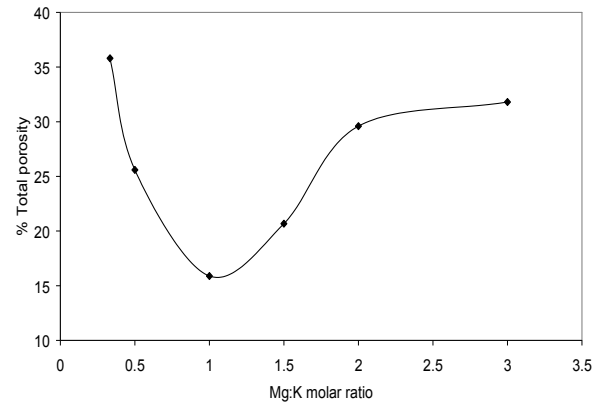


Fig.3: Effect of Mg:K ratio on total porosity (%retardant = 10%, excess water = 50%)

The compound formed under the aforementioned conditions (mixing speed = 100 rpm, mixing time = 20 min., Mg:K molar ratio = 1:1, percent excess water = 50%, percent boric acid = 10%) was characterized using XRD. Fig.4 shows the pattern obtained. All lines were identified as being those of the compound $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$.

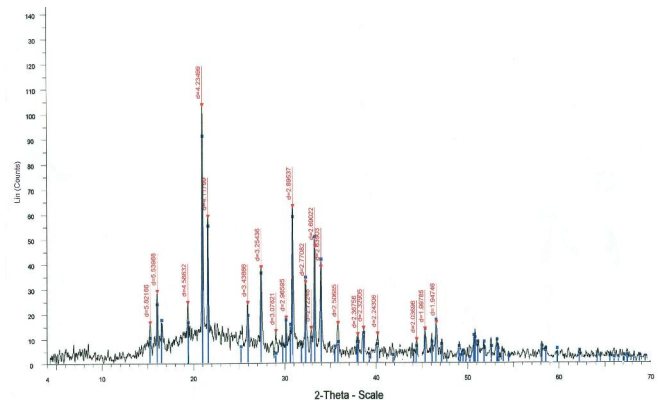


Fig.4: XRD pattern of the formed phosphate (% retardant = 10%, excess water = 50%, Mg/K = 1)

3.2. Porosity and permeability of pressed compacts

Fig. 5 shows the results obtained on studying the effect of both pressing duration and applied uniaxial pressure on the porosity of set cement. Two conclusions can be drawn from this figure: First, an increase in forming pressure will result in decreased porosity and second, increasing the duration of pressing up to 15 minute decreases porosity to reach an asymptotic level that doesn't practically depend on the applied pressure. This is related to the expected decrease in interparticle spacing on applying pressure. A longer duration of pressure application will give room for more air to be removed from the paste thus decreasing the porosity.

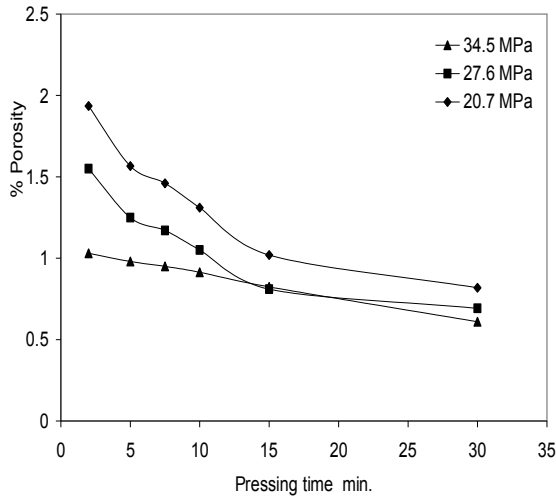


Fig.5: Effect of pressing time on percent porosity (Mg/K=1 & % retardant =10%)

To establish the relative effect of both variables on porosity, a correlation table was set that is shown in Table 2:

Table 2: Correlation table for porosity

	Time	Pressure	Porosity
Time	1		
Pressure	0	1	
Porosity	-0.717	-0.565	1

This table shows that both variables negatively affect porosity as evidenced by the negative sign of the correlation coefficient. On the other hand, it shows that porosity is more sensitive to pressure duration than forming pressure.

On the other hand, Fig.6 shows the effect of pressing conditions on the permeability of samples. The results are compatible with those of porosity, an asymptotic minimum value of permeability being obtained at a pressing time of 30 minutes and an applied pressure of 34.5 MPa. It is also clear that for practical purposes, one needs not apply pressure more than 10 minutes. That is why; in all forthcoming experiments the pressing duration was kept constant at 10 minutes.

The value of permeability achieved under such conditions is about 10^{-12} m^2 . This value is compatible with observed values for cured concretes ⁽¹⁵⁾.

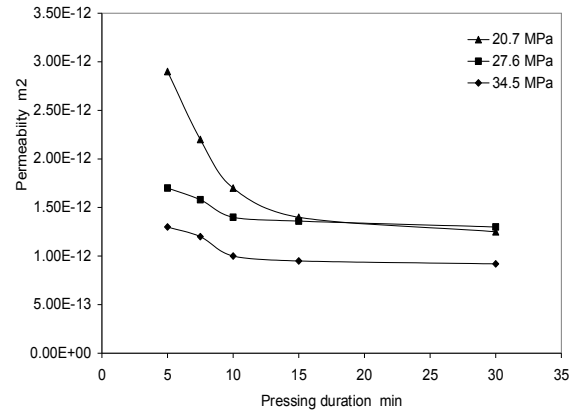


Fig 6: Effect of pressing time on permeability (Mg/K=1 & % retardant)=10%

3.3. Compressive strength of pressed compacts

As curing proceeds there is a steady increase in compressive strength of tested cement cubes having a molar Mg:K ratio of 1, with 10% retardant and 15 minutes pressure duration. Figure7 shows that the increase in strength is linear at all forming pressures for pressure duration of 10 minutes.

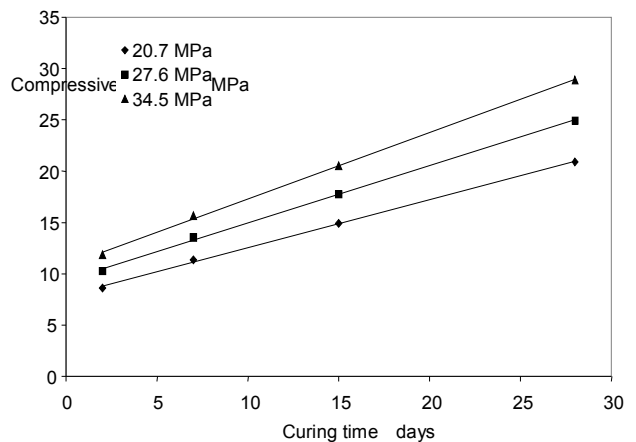


Fig.7: Strength development (Mg:K = 1, 10% retardant , pressing time = 10 min.)

On the other hand, Fig. 8 shows the effect of pressing time duration on the development of compressive strength for different forming pressures. It is clear that such strength increases with the increase in both factors. Also, the curves drawn at different forming pressures are almost parallel exhibiting a plateau after about 5 minutes pressing time followed by a slight increase in strength after 10 minutes.

This figure shows that when a pressure of 34.5 MPa for 10 minutes a reasonable compressive strength of 31 MPa is achieved.

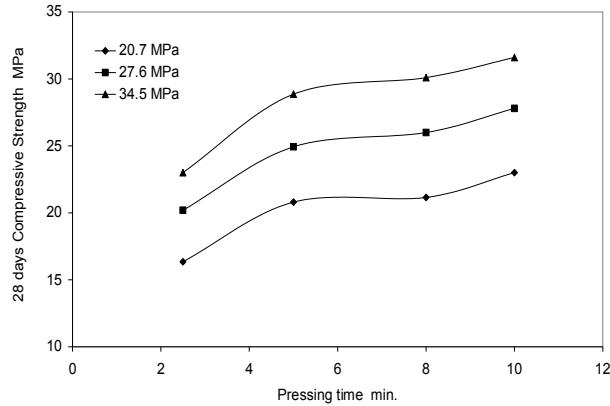


Fig.8: Effect of pressing time on 28 days strength (Mg:K = 1 & 10% retardant)

The effect of pressing time duration was however much more pronounced than that of forming pressure as can be seen in the following correlation table.

Table 3: Correlation table for strength

	Time	Pressure	Strength
Time	1		
Pressure	0	1	
Strength	0.922906	0.364354	1

Finally, it was possible to correlate the 28 days strength to porosity and permeability as it is expected that increased porosity will yield decreased strength. This relation is shown in Fig. 9. The correlation obtained takes the form:

$$\sigma_c = 29.12 \times p^{-0.83} \quad (4)$$

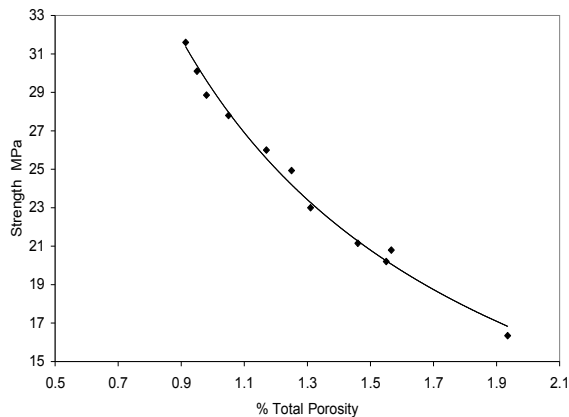


Fig.9: Effect of porosity on 28 days strength (Mg:K = 1, 10% retardant)

Whereas the corresponding relation for permeability, depicted in Fig.10 is:

$$\sigma_c = 1.88 \times 10^{-5} \times \pi^{-0.52} \quad (5)$$

Where π is the permeability in m^2

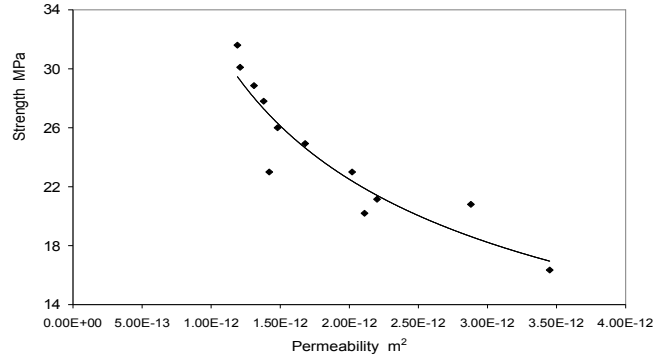


Fig.10: Effect of permeability on 28 days compressive strength (Mg:K = 1, 10% retardant)

Conclusions

A chemically bonded phosphate ceramic material has been prepared for the sake of encapsulating lead battery waste starting from magnesium hydroxide and potassium hydrogen phosphate. To this mixture was added water and mixing performed followed by poring the paste into molds and pressing under pressures ranging from 4.5 to 34.5 MPa.

The effect of the following parameters on density, porosity and permeability were followed up: speed and time of mixing, magnesium to potassium molar ratio and excess water added. The optimum conditions were found to be:

Mixing speed = 100 rpm for 20 minutes with 50% excess water and 10% boric acid added as setting retardant. The optimum Mg:K ratio that gives minimum porosity and permeability was found to be 1:1

The compressive strength of compacts was found to increase linearly with curing time up to 28 days. Also, the pressing duration was found to have a much more pronounced effect on the 28 – day strength than the magnitude of applied pressure. Application of a pressure of 34.5 MPa for 10 minutes was found to yield compacts of both reasonable compressive strength (31 MPa) and permeability ($10^{-12} m^2$).

Corresponding author

M. F. Abadir
 Chemical Engineering Department, Faculty of Engineering, Cairo University
magdi.abadir@yahoo.com

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