

HIGH STRENGTH PHOSPHATE CEMENT USING INDUSTRIAL BYPRODUCT ASHES

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ABSTRACT

During our effort to stabilize contaminated ashes in the U. S. Department of Energy's (DOE's) complex by a novel chemically bonded phosphate ceramic, we formulated a high strength concrete made of benign ashes (such as fly ash and coal bottom ash) that may be useful for specialized applications in construction industry. It is formed by a room temperature process in which MgO is reacted with a solution of one of the soluble hydrophosphates to form a dense matrix. Any ash or slag may be incorporated during the reaction. The slurry formed by mixing these components for 15-30 minutes is a pourable, low viscosity paste. Once it is left undisturbed, it sets into a hard mass in ≈ 45 minutes with a small amount of heat evolution. Its density ranges between 1.7 g/cc to 2.0 g/cc, open porosity is $< 5\%$. For a typical ash loading of 60 wt. %, it has a strength of $\approx 12,000$ psi. The micro structure of the concrete is glass-crystalline. This product is not very sensitive to the ash composition. Unlike in portland cement, it is unaffected by the unburnt carbon in the ash or to any Cl ions, and thus a wide variety of combustion products may be incorporated to develop this product. The material cost is generally 50% higher than portland cement, but processing advantages, such as faster setting, setting in cold environment, and self binding characteristics may off-set some of the costs, or improved properties may justify slightly higher costs for specialized product development.

INTRODUCTION

The ever increasing industrial activity in the western world and in developing countries is depleting the natural resources and at the same time, producing wastes that need disposal. Much of the volume of the solid waste that is produced is non hazardous. For example the 1986 statistics (1) reveals that nearly 40 tons of waste per person was generated in the United States that year. Most of it was non hazardous. Preferred methods of handling the solid waste is to reduce its volume by incineration if possible (such as incineration of municipal solid waste). The incineration products, such as ashes, are then disposed at a reduced cost.

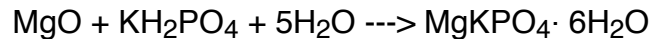
In addition to the incineration ash, a large amount of ash is also produced by the utility industries that use fossil fuels. Approximately one third of this ash is recycled in the cement based products as an additive. Typically, cement products can incorporate $\approx 15\text{-}20\%$ ash in them. Efforts are being made to improve this loading [2], but have not been successful because of several reasons. These include the following:

- 1) Cement chemistry is sensitive to the components of the ashes. Ashes, particularly those obtained from the incineration of municipal solid wastes, contain chlorides resulting from the destruction of polymers. Chlorides and other anions hinder setting of cement.
- 2) Carbon content of the ash is also a major factor. High carbon ashes are not suitable for cement setting. In particular, ashes produced by low- NO_x burners produce high carbon ashes [2] and it is likely that, to meet the clean air act requirements, future industries may opt for low- NO_x burners that will produce ashes unsuitable for incorporation in cement.
- 3) The ash loading in the cement products is generally low, and thus large scale utilization of ash in cement is not very economical.

We propose development of a novel chemically bonded phosphate cement that is formed at room temperature that addresses these issues. This cement was developed initially for stabilization of hazardous and radioactive wastes (3). While exploring stabilization of contaminated ashes, it was realized that ash itself participates in the setting reaction, producing a high strength cement that sets like conventional cement. The end product was a low-open-porosity, light weight structural material with high strength. This article describes the process of forming the ash and slag based cement, its physical and mechanical properties and micro structure. This novel structural material with its improved properties should be particularly useful in those applications where conventional cement products have limitations. These properties are elaborated in this article.

THE PHOSPHATE-CEMENT PROCESS

The phosphate-cement process is based on an acid-base reaction between magnesium oxide (MgO) and a solution of alkali phosphate salt such as sodium or potassium phosphate. Here we describe the process based on monopotassium dihydrogen phosphate (KH_2PO_4). The reaction product is magnesium potassium phosphate ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$) that is formed by dissolution of MgO in the solution of KH_2PO_4 and its eventual reaction to form the product according to the reaction,



This product (referred to as MKP here after) is a binder that can be used as the matrix material to host any inorganic waste material. Wastes such as ashes and slags are mixed with the binder powders and reaction is allowed to occur by mixing the components for 30 min. in a concrete mixer. The resulting slurry is a smooth paste that can be poured in the molds to form any desired shape. The exothermic reaction between the components starts heating the slurry. The slurry starts thickening and when the temperature reaches 55°C it sets into a hard mass. The exothermic reaction proceeds to heat the monolith. Typically the maximum temperatures of 60°C in small samples of 100 g and 82°C in 55 gal. size monoliths have been noted. In approximately 2 hours, the samples attain sufficient structural integrity and hence may be removed from the molds, but actual curing continues for several weeks.

FABRICATION OF TEST SAMPLES

Using the process described above, we made several cylindrical test samples incorporating various amounts of ash loading. To demonstrate the versatility of the process, we made samples of several different ashes that included, utility class F and C fly ashes, high carbon ash, municipal solid waste (MSW) incinerator ash, steel industry slag, and simulated ash compositions that represented U. S. Department of Energy's contaminated ash inventory. In all the cases, the reaction slurry mixed and set the same way and the temperature rise was also similar. Some additional heating was observed wherever calcium content in the ash was higher. This must be due to additional exothermic reaction between calcium oxide and the phosphate. Other than this heating, no other variations were observed during formation of the samples, and in all cases equally good samples were formed. This indicates that the phosphate-cement process may produce a very versatile technology for manufacture of ash products.

We made test samples in cylindrical form of diameter 2cms and length of 4-5 cms. Each sample was made by pouring the slurry in a polyethylene syringe and allowing it to set for a week. It was then taken out of the syringe by cutting the narrow end of the syringe and then extruding the set sample out. Each sample was then cut on a diamond saw to the desired size, and the two end surfaces were polished to make them parallel to each other.

Though samples of various ashes were made and studied, we focus here on three ashes that were representative of most of the ashes. They were class F fly ash supplied by Monex Corp., and class C fly ash and a mixture of class F and C

fly ashes supplied by American Fly Ash Company. The elemental composition of these ashes is given in Table 1.

Cements of class F and class C ashes were made at different loadings (ash loading is defined as its weight % in the total powder mixture) and physical and mechanical properties were measured. Realizing that optimal strength in both cases is obtained at a loading of 60 wt%, only samples of 60 wt% loadings of class F + class C were made and the strength was studied.

Table 1: Elemental compositions (wt.%) of the ashes used in this trial

Element	Class F	Class C	Class F + Class C
Al	11.5	9.74	11.6
Ca	1.54	16.8	5.71
Fe	4.16	3.44	5.11
K	2.31	---	0.69
Si	21.8	16.5	21.9
C	8.78	0.08	5.56

To gain an insight into the micro structure of the cements, the one made with class F was investigated in detail using X-ray diffraction method, differential thermal analysis (DTA) and scanning electron microscopy (SEM).

PHYSICAL AND MECHANICAL PROPERTIES

We measured the density, open porosity and compressive strength in each case. The density was measured by weighing the samples and measuring their dimensions. The open porosity was estimated by water intrusion method. To do this, each sample was first dried at 70°C in an oven and weighed. It was then immersed in water and the water was heated and maintained at 70°C for 2 hours so that the air in the open pores expanded and left the samples. When cooled, these pores would be filled with water. The samples were taken out, wiped lightly using a paper towel and weighed. The difference in two weights provided the weight of water in the pores. That allowed us to calculate the open porosity.

The compressive strength was measured on an Instron machine in an uniaxial mode. We obtained an average of 5 samples for each reading. The results of these measurements are given in Table 2.

The density measurements show that the class C ash products are slightly heavier than class F products. This may be due to the fact that class F ash contains more carbon and hence may be slightly lighter. Since the ashes and the binder powder have nearly the same density, there is hardly any effects of the ash loading on the density. Overall the ash products are approximately 25% lighter than corresponding cement products.

The open porosity, that affects water absorption, also is comparatively less in this cement than in portland cement. The open porosity in cement products is approximately 20%. Comparatively, phosphate-cement products exhibit much lower open porosity.

Table 2: Physical and Mechanical Properties

Sample Description	Density (g/cm ³)	Open Porosity (vol%)	Compression Strength (psi)
Phosphate Binder	1.73	2.87	3337
Class F loading (wt%)			
30	1.67	5.22	5651
40	1.77	4.09	6207
50	1.80	2.31	7503
60	1.63	8.15	5020
70			2177
Class C loading (wt%)			
50	1.966	4.79	8809
60	2.069	3.4	11924
70	2.058	5.34	7608
80	1.918	8.025	4753
Class C+F loading (wt%)			

It should be noted that, though the open porosity in phosphate-cement is very low, it has a significant amount of closed or isolated pores. Calculations based on the densities of individual minerals formed in the final products show that the closed porosity is approximately 20 vol%. Coupled with this, a significant amount of bound water (typically 15 wt%) makes this material a lightweight composite.

The major advantage of the phosphate-cement as a structural material is in its compressive strength. As one may notice from Table 2, the compressive strength of the binder itself is only 3337 psi, but even a 30% wt% of class F fly ash enhances its strength to 5651 psi. As the loading is increased, the strength also increases. It is clear from the data that the strength is optimal between 50 and 60% ash loading. Assuming the strength of conventional cement products is approximately 4000 psi, the optimal strength obtained for class F ash products is nearly 75% higher, while the same for class C ash it is three fold. As one would expect, the mixture of class F and class C product exhibits a strength between the class F and class C products and this strength is at least twice that of conventional cement products.

It is interesting to see how the strength evolved during the setting period of the phosphate-cement products. We measured the strength of class C product at 60 wt% ash loading during curing time and thereafter. The results are shown in Fig. 1. One notices that the material attains a strength equal to that of conventional cement products within a day of curing. Subsequently, it more than doubles in 5 days and keeps increasing, though less rapidly. In 45 days, the strength is slightly less than 3 times that of conventional cement and then it tapers off. The long term curing has a significant effect on the strength though the product itself is ready for use after a day.

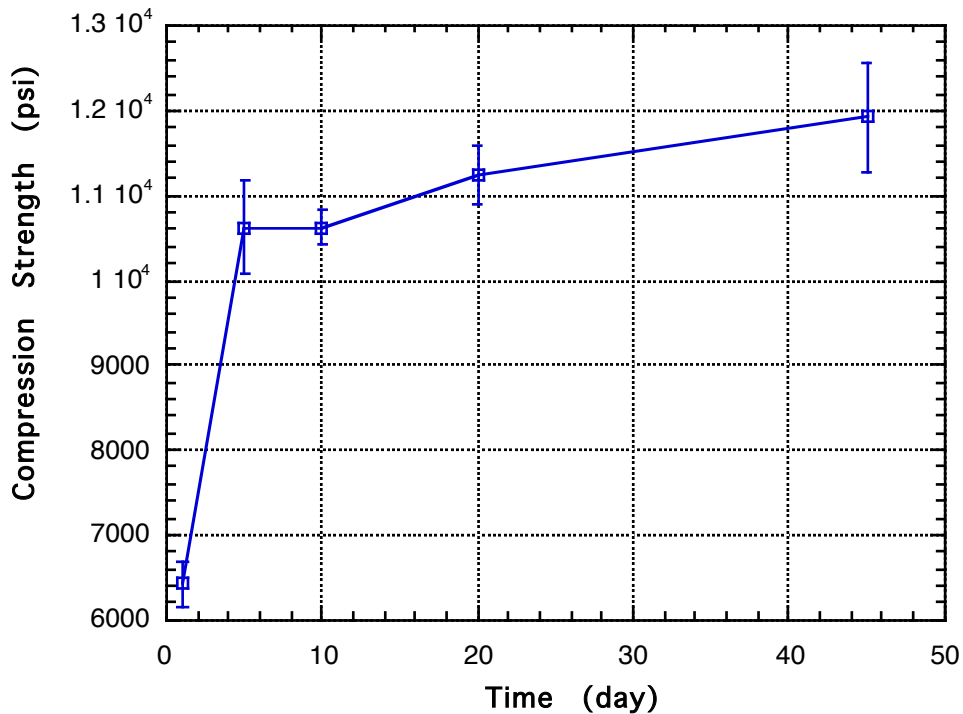


Fig. 1: Evolution of compressive strength with time during curing.

PHASE ANALYSES

To gain some insight into the mechanisms of the strength enhancements, we performed phase analyses of the ash products using X-ray diffraction technique, differential thermal and thermogravimetric analyses (DTA and TGA) and scanning electron microscopy.

Fig. 2 shows the X-ray diffraction output of the ash, binder, and its corresponding class F ash product for 60 wt% ash loading. As one may notice, all the peaks that are found in the binder and the ash are also present in the ash product. There are no new peaks in the product itself. However one also notices a broad hump in the middle of the output of the product. This hump corresponds to the amorphous or non crystalline phases. Unfortunately, these amorphous phases cannot be identified by the X-ray diffraction technique.

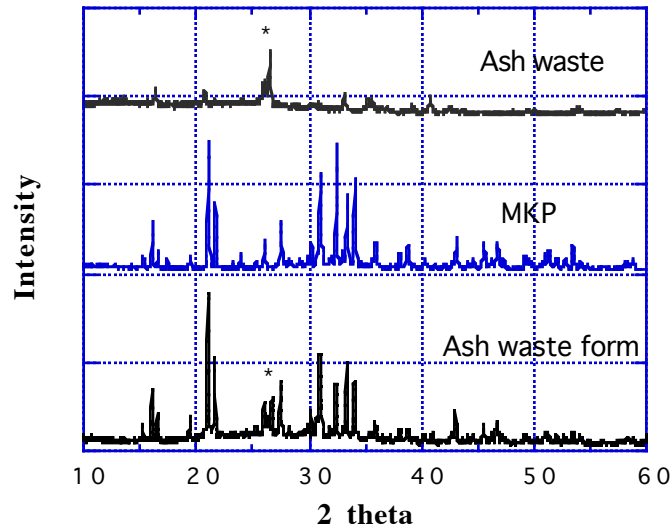


Fig. 2: X-ray diffraction output of the binder and class F ash product

Some insight into these phases may be gained from the DTA and TGA curves. Fig. 3 shows DTA outputs of the class F fly ash, the binder, and the ash product. The endotherm of the binder at 120°C is due to the escape of the bound water from the matrix. This was confirmed by TGA analysis (Fig.4) which showed the loss in weight was the same as stoichiometric amount of the bound water. This was the only endotherm found in matrix. This suggests that there may not be any other phases in the amorphous form other than those found by the crystalline phases by the X-ray diffraction technique; or if new amorphous phases are formed, they are thermally stable and hence do not produce any endotherms at the temperature studied. This second hypothesis is more likely, since a limited nuclear magnetic resonance (NMR) studies done on the ash product and the binder showed possibility of new phases.

The SEM micrographs of the ash product in Fig. 5 reveals these new amorphous phases. One notices a continuous glassy phase coating all the particles of ash including the cenospheres. This product may be responsible for the low porosity and also high strength in the ash product. Unfortunately, our analytical studies cannot reveal its composition, but earlier work (4) has revealed possibility of silico-phosphate bonds that are very strong. Ashes are known to contain amorphous silica. It is likely that this silica may participate in the setting reaction and form these bonds that contribute to the strength.

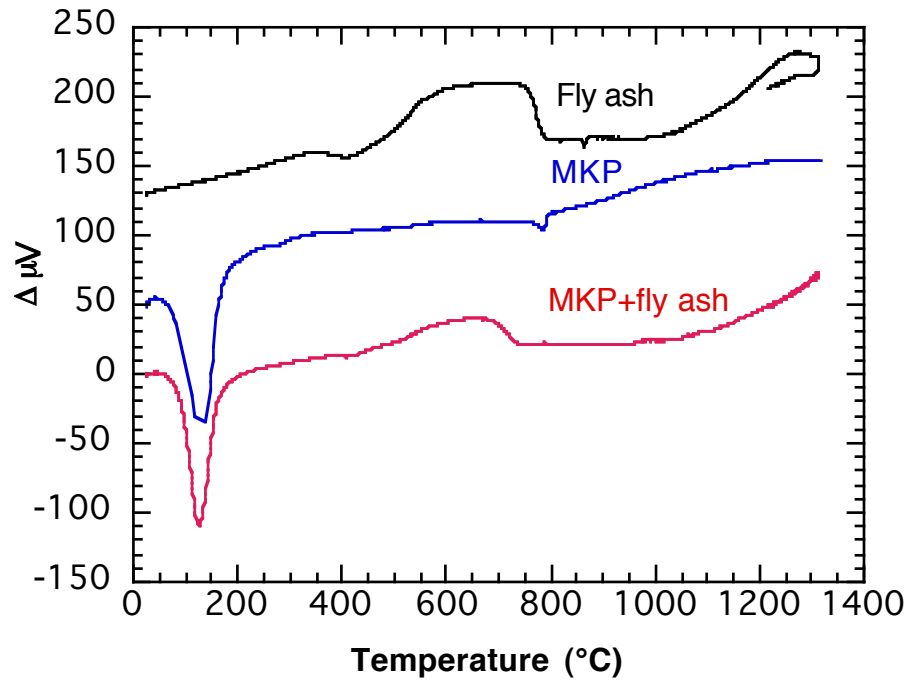


Fig. 3: Differential thermal outputs of the class F fly ash, the binder, the ash product with 60 wt.% ash.

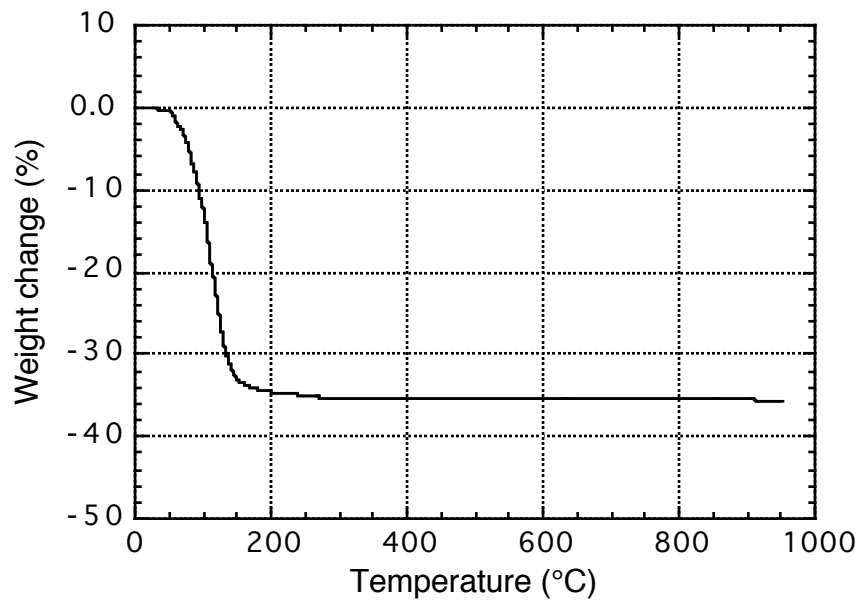


Fig.4: Thermogravimetric analyses output of the binder

Fig. 5: SEM micrographs of the binder and the ash product.

DISCUSSION

We have developed a high strength cement from chemically bonded phosphate ceramic and ash that is made like cement. This product has a strength approximately 3 times that of conventional portland cement products. It incorporates a high amount of ash. A comparison of the product formed by class F and class C fly ashes shows that class C fly ash that has higher level of calcium and low level of carbon gives the best strength.

The material cost is generally 50% higher than portland cement, but processing advantages, such as faster setting, setting in cold environment, and self binding characteristics may off-set some of the costs, or improved properties may justify slightly higher costs for specialized product development.

It is known from the conventional cement studies that carbon inhibits cement setting. In the phosphate cements discussed here, it does not hinder the reaction, but probably affects the strength. Therefore low carbon class C fly ash

exhibits high strength as compared to the class F fly ash that has high level of carbon.

The role of calcium is unknown at this stage of study. Generally, calcium that exists as oxide, participates in the setting reaction exactly in the same manner as MgO forms the phosphate bonds. Its reaction was detected by the higher rate of heat evolution during setting. It may be that this additional setting mechanism contributes to the strength by forming calcium phosphate cements.

Finally, the role of amorphous silica seems to be very significant. In both the fly ashes, the strength in the ash products is much higher than the binder. This gain in strength is most likely due to the silico-phosphate bonds. Such bonds are the basis of some dental cements (5). Unfortunately, since these phases exist in amorphous forms, a detailed identification of their role is difficult. More studies are underway to reveal their exact mineral form. Knowledge of these mineral forms is very important for further optimizing the strength in the ash products using the phosphate-cements discussed here.

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