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DEVELOPMENT OF VALUE-ADDED PRODUCTS FROM ALUMINA INDUSTRY MINERAL WASTES USING LOW-TEMPERATURE-SETTING PHOSPHATE CERAMICS*

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ABSTRACT

We have developed a novel room-temperature process to stabilize mineral waste streams based on an acid-base reaction between magnesium oxide and phosphoric acid or an acid phosphate in solution; the resulting waste form sets into a hard ceramic in a few hours. Using this process, we have demonstrated that various alumina-industry wastes, such as red mud and treated potliner waste, can be solidified into hard and dense ceramics. These ceramics can be used as structural materials in waste management operations and the construction industry. Here, we present details on ceramic development from red mud as an example.

The red mud ceramics made by this process were low-porosity materials (≈2 vol.%) with a compression strength equal to that of portland cement concrete (4944 psi). The bonding mechanism responsible for this strength seems to be the result of reactions of boehmite, goethite, and bayerite with the acid solution, and also encapsulation of red mud particles in the Mg-phosphate matrix.

Our process is very attractive for fabricating construction components in regions where the conventional cement industry cannot satisfy the demand. In addition, the low porosity and durability of these materials in a range of acidic to basic environments suggest special applications in the mining industry, including liners for ponds and thickened-tailings disposal, dikes for waste ponds, and quick-setting grouts to stop leakage. Availability of waste in high volumes at the user site eliminates the high costs of transporting the clay normally used for these applications. Because the waste itself is a part of the engineered barrier system that confines the waste, the compatibility problems arising at the interface of the liner and the waste are avoided. Thus, meeting the needs of environmental management may be a very attractive proposition for alumina industry wastes.

KEY WORDS:
Red mud, phosphate ceramics, boehmite, goethite, Bayerite, pond liners

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1.0 INTRODUCTION

Chemically bonded phosphate ceramics were originally developed in our laboratory to stabilize low-level mixed waste streams. These room-temperature-setting materials can be produced by acid-base reactions between magnesium oxide and phosphoric acid or an acid phosphate in solution; the waste form sets into a hard ceramic in a few hours. The wastes in solid, liquid, or sludge form can be incorporated during fabrication. Because the process is based on acid-base reactions, both acidic and alkaline waste streams can be incorporated into the waste streams. Details of this process may be found in Ref. 1.

Our process may be used to stabilize and solidify various alumina industry wastes, including red mud, Bayer sand, and potliner residue. We studied red mud in detail and fabricated dense, hard, and durable ceramics. The study was then extended to potliner residue, and ceramics were also formed with this waste. We present the basic characteristics of red mud ceramics and, based on their properties, identify their applications in waste management areas as well as in the construction industry.

2.0 RED MUD CERAMIC DEVELOPMENT

2.1 Physical and Chemical Properties of Wastes

The red mud waste used in this study was produced in Jamaica from gibbsitic bauxite. It was dry mud collected from the outskirts of a red mud pond. Although the particles are extremely fine, when the red mud slurry is dried in the sun, they form hard, nonfriable agglomerates. Details on this material may be found in Ref. 2.

Figure 1 shows the particle-size distribution of crushed dry red mud. As one may see, it is a superfine material with more than 60 wt.% particles finer than 10 mm. Due to its low friability, crushing costs for any application can be high. For this reason, we did not crush it to its finest size but used the material passing through 1 mm size mesh. Even then, finer fractions dominated the powder.

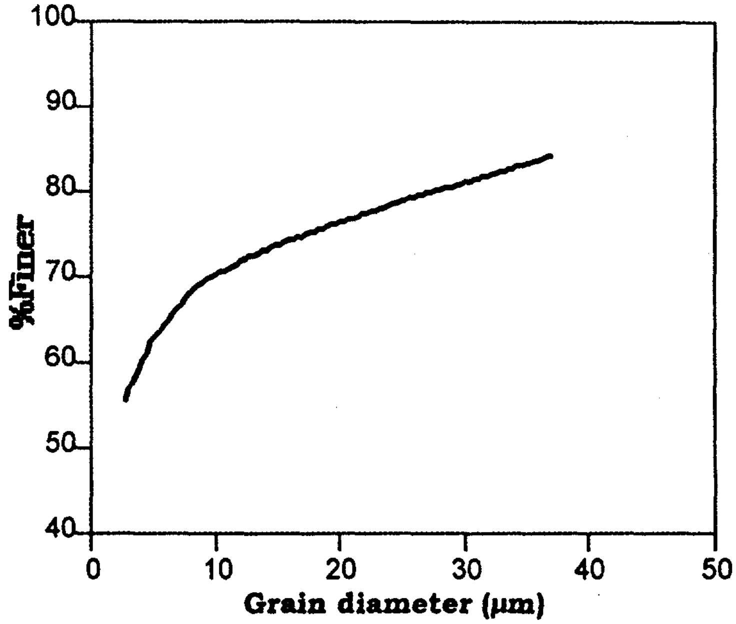

Fig. 1: Grain size distribution of red mud.

Expressed as oxides, its contents were ≈50 wt.% iron oxide (Fe_2O_3), 16.5 wt.% alumina (Al_2O_3), 3 wt.% silica (SiO_2), 5.7 wt.% calcium oxide (CaO), and 6.8 wt.% titania (TiO2). Thus, this is a low-silica red mud with a very high content of iron oxide. The alumina content of the red mud is significant, but calcium oxide is low. Loss on ignition is 13.4 wt.%, due to escape of CO_2 from carbonates and bound water.

X-ray diffraction output (Fig. 2) identifies haematite (α–Fe_2O_3), goethite (α–FeOOH), calcite ($CaCO_3$), boehmite (γ-AlOOH), anatase (TiO_2), and bayerite (β-AlOOH) as the major crystalline phases. Their occurrences were confirmed by differential thermal analysis (Fig. 3). Of these phases, boehmite, bayerite, and goethite are hydrated and, as we learned from our earlier studies, are very important for development of phosphate bonds in our process. We have developed ceramics of iron hydrophosphate and dense solidified plastic gel of aluminum hydrophosphate. Thus, we felt that the presence of these hydrated phases could provide the necessary bonds in developing the red mud ceramics.

As in any red mud, the pH of the as-received material was ≈11 because of the soda content of ≈1.4 wt.%. Leaching of this residual Na_2O is difficult and hence the mud was stabilized in our process without removal of the alkalinity.

A scanning electron photomicrograph of red mud showed needle-shaped goethite crystals embedded in the spherical pelletlike haematite crystals [3]. Considerable amorphous or microcrystalline material was also observed as coatings on the particles. Our earlier studies identified the amorphous material as alumina and silica [2], which plays a major role in the bonding mechanisms, and indicated that it may be responsible for the green strength of dried red mud. In fact, exploiting the presence of this amorphous content, we developed silicate-bonded red mud ceramics [3]. We believe that this amorphous material may also help in the setting reaction during formation of chemically bonded phosphate ceramics, because it will readily participate in the acid-base reaction.

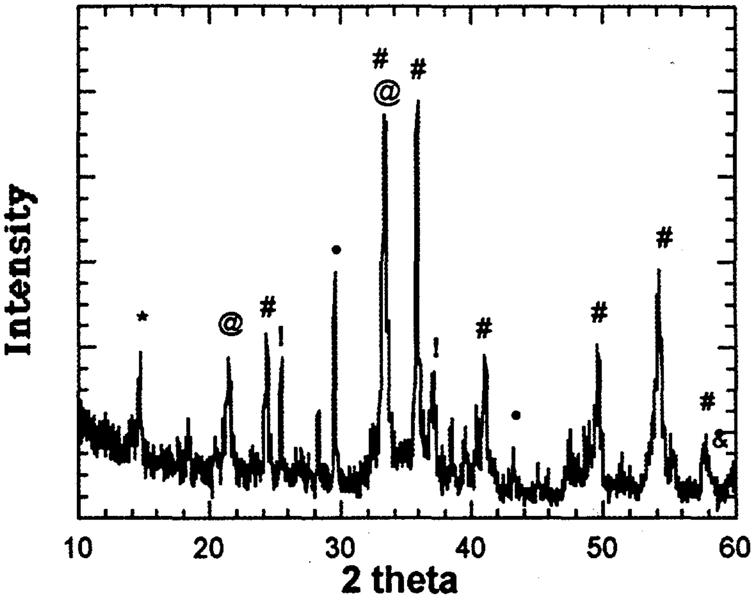

Fig. 2: X-ray diffraction output of Jamaican red mud. Symbols are * boehmite, @ goethite, # haematite, • calcite, & bayerite, and ! anatase.

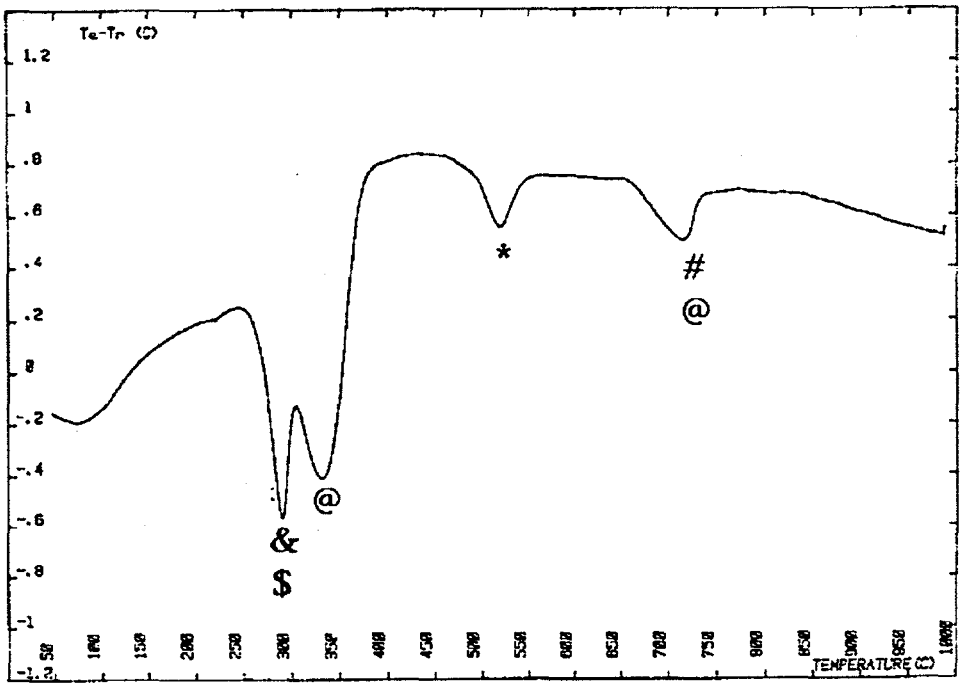

Fig. 3: Differential thermal analysis of Jamaican red mud. Symbols are * boehmite, @ goethite, # haematite, and & bayerite.

2.2 Fabrication of Samples

MgO, when reacted with phosphoric acid or an acid phosphate solution, forms magnesium phosphate precipitate in an exothermic reaction, which can be controlled by use of calcining MgO and adjusting the feed rate of the powder to the solution. The waste can be incorporated in powder form in the MgO powder by thorough mixing. In this study, red mud was mixed with calcined MgO powder; the red mud to MgO weight proportion was different for each set of samples. Details are given in Table 1. The mixture was then slowly reacted with the solution by constant stirring until all of the powder had been added to the solution. The mixture formed a low-viscosity paste that thickened as the reaction proceeded. It was then poured into syringes used as molds to form cylindrical specimens of 1.9 cm diameter. The paste set rapidly and formed dense ceramics within ≈15 min. Complete hardening occurred in one day, and the samples, when removed from the molds, were hard and dense. We cured the samples further for three weeks at room temperature to ensure that they gained their full strength. The ends of each sample were cut with a diamond saw to obtain cylindrical specimens of ≈5 cm length.

2.3 Physical Properties of Red Mud Ceramics

The samples had a terra cotta color due to the red mud and appeared dense and hard with a slight glossy surface. Density was measured by weighing the samples and measuring the dimensions and hence the volume. Open porosity was determined by water immersion, in which the preweighed samples were immersed in water at 70°C for 2 h, cooled and removed from the water, and then, after wiping all excess water from the sample surfaces, samples weighed again to determine the amount of water that filled the open pores. This gave us the volume of the open pores, and hence allowed calculation of the open porosity.

Table 1
Physical Properties of Red Mud Ceramics and Matrix Material

Waste loading (wt.%)	Maximum particle size (mm)	Density $(g/cm)^3$	Open porosity (%)	Compression strength (psi)
40	5	2.19	0.82	4944
40	1	2.1	1.09	4294
50	5	2.26	2.98	2698
55	5	2.29	1.94	2310

Compression strength was measured with an Instron machine used in compression mode, and the crushing strength was determined. The results are given in Table 1.

The waste loadings attempted in this study were 40, 50, and 55 wt.% at two different particle sizes. Densities of samples with red mud are slightly higher than that of the matrix material, which was 1.73 g/cm^3. This is due to the higher density of the red mud (≈3.3 g/cm^3).

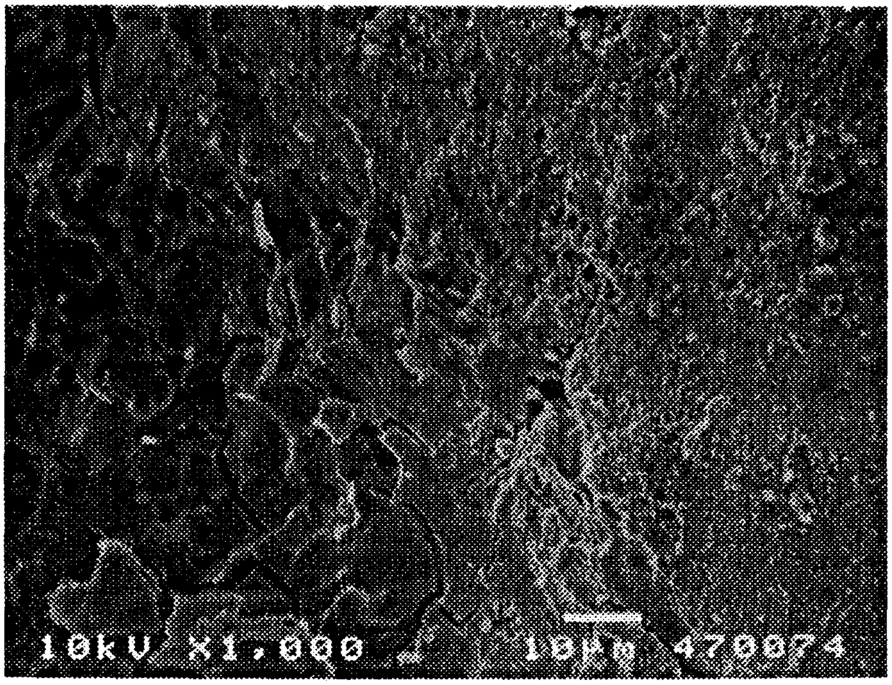

Fig. 4: SEM photomicrograph of red mud ceramic.

Open porosity of the red-mud-loaded samples is quite low. The compression strength of the samples with 40 wt.% loading is slightly higher than that of portland cement concrete, which is ≈4000 psi. This means that the red mud ceramic can be used as a structural material. As the loading is increased, the strength is reduced.

2.4 Microstructure

Microstructure provides clues to the bulk properties of the material and also sheds light on the binding mechanisms. For this reason, we performed scanning electron microscopy (SEM) coupled with energy-dispersive X-ray (EDX) analyses to identify the phases at the microstructure level. A typical photomicrograph of a fractured surface is shown in Fig. 4. Two distinct regions are seen, a glassy phase on the left of the picture and a granular phase on the right. Both of these phases are well-bonded. The glassy phase is cracked everywhere, while the granular phase displays only those cracks propagating from the glassy phase.

To identify the two phases, EDX analysis was used; Table 2 gives the general composition of each. The values are averages of those measured in three different locations in each phase.

Table 2
Elemental distributions (%) of the two phases seen in Fig. 4

Phase	Fe	Al	Mg	P	Other
Glassy	5.78	4.7	23.53	34.23	31.76
Granular	23.66	18.6	5.3	16.2	36.2

The granular phase is rich in red mud elements such as Fe and Al, while the glassy phase is rich in Mg phosphate elements such as Mg and P. It is most likely that the granular phase is red mud and the glassy phase is mostly the phosphate matrix. The red mud region also contains significant amount of P and some Mg, which indicates that phosphate bonding has occurred in this phase. This is likely due to formation of phosphates of Fe and Al, because of reactions of goethite, boehmite, and bayerite, as predicted by our earlier studies (see discussion following X-ray diffraction output). Very small amounts of Fe and Al are observed in the matrix, due to very fine particles of red mud encapsulated in the matrix.

The glassy phase is heavily cracked because of its glassy nature. On the other hand, the red mud ceramic phase does not show such cracks. except for those that appear to originate in the glassy phase. This means that the strength of the ceramic is due to the red mud phase. To improve the strength of the ceramic, it is necessary to either reduce the glassy phase or reinforce the glassy phase with particulates. This may be done by using finer red mud in the starter powder, which will then distribute more evenly and provide better particle reinforcement. Such improvements are now being undertaken.

3.0 POSSIBLE APPLICATIONS

This study is the first attempt to develop red mud ceramics with the chemically bonded phosphate ceramic process. The low porosity and the strength equivalent to that of portland cement concrete suggest several applications for this product.

Disposal of red mud requires either containment ponds [4] or, in an improved method for thickened tailing disposal, red mud stacks [5]. In both methods, the pond bottoms or disposal slopes must be lined with an impermeable barrier, typically artificial polymer fabric or a clay. Each is expensive and requires a secure bonding between the liner and the stored red mud or the substrate below the liner. If bonding is inadequate, erosion of red mud or the liner clay material can occur in rains. Chemically bonded red mud ceramic may provide a cheap alternative with good bonding properties. If the reaction slurry loaded with red mud is poured as the barrier layer, it not only forms bonds with the substrate, but also quickly hardens to form a nonporous ceramic liner in short time. The subsequent red mud dispersed also will bind and hence provide a nonerodable stack. Because ≈40 wt.% red mud can be used in these liner, some red mud will be consumed and thus alumina production need not wait until the layers are in place. Total cost will be much lower than that for transporting clay or placing a fabric liner.

In other applications, one may consider building containment dikes, approach roads, and other structural barriers needed in the disposal area. Red mud waste forms will provide the necessary strength and physical properties for such applications.

In island economies, and also in many industrialized countries, storage of red mud is expensive due to high population density and limited land. At the same time, construction materials are not cheap. Red mud ceramics can fulfill some of the material needs of the local construction industry, while some of the land formerly used for storage of red mud can be released for other uses. These applications are very much site-specific, however, but considering that the process used for fabrication of red mud phosphate ceramics is applicable to all red muds, we believe that this work will be important for several Bayer process plants.

4.0 DISCUSSION

The process employed here is not limited to red mud wastes, but is also applicable to a wide range of alumina industry wastes. In this paper, we have presented red mud ceramics as only one such example. Potliner residue, Bayer sands, ashes generated at plant sites, and any other mining refuse can be stabilized by this process. Once the intellectual property rights are acquired by the Laboratory, details of the process and its applications in both recycling of wastes as value-added products and in stabilizing hazardous waste streams in the alumina industry will be reported.

ACKNOWLEDGMENTS

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