Phase transformation and its role in stabilizing simulated lead-laden sludge in aluminum-rich ceramics

Xingwen Lu, Kaimin Shih*

Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, Hong Kong SAR, China

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ABSTRACT

This study investigated the mechanisms of stabilizing lead-laden sludge by blending it into the production process of aluminum-rich ceramics, and quantitatively evaluated the prolonged leachability of the product phases. Sintering experiments were performed using powder mixtures of lead oxide and γ-alumina with different Pb/Al molar ratios within the temperature range of 600–1000 °C. By mixing lead oxide with γ-alumina at a Pb/Al molar ratio of 0.5, the formation of PbAl2O4 is initiated at 700 °C, but an effective formation was observed when the temperature was above 750 °C for a 3-h sintering time. The formation and decomposition of the intermediate phase, Pb9Al8O21, was detected in this system within the temperature range of 800–900 °C. When the lead oxide and γ-alumina mixture was sintered with a Pb/Al molar ratio of 1:12, the PbAl12O19 phase was found at 950 °C and effectively formed at 1000 °C. In this system, an intermediate phase Pb3(CO3)2(OH)2 was observed at the temperature range of 700–950 °C. Over longer leaching periods, both PbAl2O4 and PbAl12O19 were superior to lead oxide in immobilizing lead. Comparing the leaching results of PbAl2O4 and PbAl12O19 demonstrated the higher intrinsic resistance of PbAl12O19 against acid attack. To reduce metal mobility, this study demonstrated a preferred mechanism of stabilizing lead in the aluminate structures by adding metal-bearing waste sludge to the ceramic processing of aluminum-rich products.

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1. Introduction

The contamination of ground and surface water with hazardous metals is a global problem and has become a growing threat to human health. The hazardous metals of particular concern include cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), vanadium (V) and zinc (Zn) (Gupta et al., 2009), which can enter the food chain through drinking water and crop irrigation (Al-Degs et al., 2001). In particular, lead is a widely found and non-biodegradable heavy metal that tends to accumulate in the cells of living organisms, which causes severe damage to the kidneys, liver, and the nervous and reproductive systems of humans (Gupta et al., 2011). Common sources of lead are the wastewater that comes from industries engaged in the manufacturing of lead batteries and oil-based paints, mining, plating, electronics and wood production (Jalali et al., 2002; Gupta et al., 2001; Conrad and Hansen, 2007). Current common techniques used to treat lead-containing wastewater include chemical precipitation, electrochemical reduction, ion exchange, coagulation, adsorption, and membrane processes (Husein et al., 1998; Lin and Navarro, 1999; Petruzelli et al., 1999; Saeed et al., 2005; Doyurum and Celik, 2006; Ali and Gupta, 2007). However, most of these methods produce enormous amounts of residual sludge that causes secondary pollution and additional operational cost (Gupta and Suhas, 2009).
Sludge containing hazardous metal residues should be disposed of in controlled landfills. However, the high cost of this strategy, combined with the limited number of landfills capable of accepting toxic metal waste, makes the development of effective and economical treatment technologies essential. Many researchers have attempted to immobilize toxic metals using sorbents or cements and then correlating the performance directly with metal leachability (Kapoor and Viraraghavan, 1996; Lin et al., 1998; Bailey et al., 1999). However, solidification/stabilization technologies via sorption or cementation mechanisms may not be successful in the prevention of metal leaching in acidic environments (Bonen and Sarkar, 1995; Yousuf et al., 1995).

Several processes of stabilizing radioactive waste in glass and ceramic materials through thermal reaction have been successfully demonstrated (Lewis et al., 1993; Wronkiewicz et al., 1997). However, the end products of these processes are radioactive and must be stored in geologic repositories. For non-radioactive hazardous metals, studies aiming to design a waste-to-resource strategy have shown the potential and mechanism of stabilizing them in ceramic products. For example, the reaction mechanism and incorporating efficiency for nickel- and copper-containing sludge with aluminum- or iron-rich precursors during the ceramic sintering processes were reported by Shih et al. (2006a, 2006b), Tang et al. (2010), and Hu et al. (2010). The intrinsic metal leachability of these sintered product phases was also investigated and the results clearly indicated the importance of initiating certain key phase transformations to significantly reduce leaching of the metal from the products.

Studies have shown that the calcining of lead oxide (PbO) on $\gamma$-Al$_2$O$_3$ produces the various phases of magnetoplumbite-like structure (PbAl$_{12}$O$_{19}$) and lead aluminate (PbAl$_2$O$_4$), which can be used as catalysts for oxidative coupling with methane. However, the incorporation mechanism and phase transformation pathway have not been discussed in detail (Wendt et al., 1988; Park and Chang, 1993). Both PbAl$_{12}$O$_{19}$ and PbAl$_2$O$_4$ have been reported in the equilibrium phase diagram of the PbO–Al$_2$O$_3$ system (Kuxmann and Fischer, 1974), and the published PbO–Al$_2$O$_3$–SiO$_2$ equilibrium phase diagram also confirmed the presence of PbAl$_{12}$O$_{19}$ and PbAl$_2$O$_4$ (Chen et al., 2001). These equilibrium studies have provided the opportunity to observe the potential interaction between PbO and aluminum-rich precursors under industrial sintering processes. Therefore, incorporating lead-laden sludge into ceramic sintering may be able to initiate a beneficial phase-transformation process to further stabilize lead-containing waste.

The toxicity characteristic leaching procedure (TCLP), which was designed by the U.S. Environmental Protection Agency (EPA), is commonly used to assess the hazardous nature of metal-bearing waste (U.S. EPA, 1998; 1992). Using acetic acid (pH 2.88) as leaching fluid to simulate the presence of organic materials in municipal landfill leachate (Halim et al., 2004; U.S. EPA, 1998; MacKenzie et al., 2000), the TCLP simulates the worst possible scenario for co-disposing of wastes in landfill. However, due to the dependence of the TCLP on a single-point and short-term leaching result, its use in predicting leaching may result in misclassification of wastes, which consequently leads to the underestimation of long-term leachability or to unnecessary treatment cost (Kosson et al., 2002). As a result, extending this standardized leaching procedure will be a useful way to observe the leaching behavior of metal-bearing waste under prolonged leaching environment.

The objective of this work is to contribute a better understanding of the phase transformation to PbAl$_{12}$O$_{19}$ and PbAl$_2$O$_4$ during ceramic sintering, which may be the potential incorporation mechanisms of lead in aluminum-rich ceramics. The approach was to blend PbO with an alumina precursor for a short sintering process (3 h) with temperatures ranging from 600 to 1000 °C. Furthermore, a prolonged leaching procedure modified from the TCLP was carried out to evaluate the long-term stabilization effects of lead in the two product phases.

2. Materials and methods

PbO was purchased from Sigma–Aldrich. The phase composition of the PbO powder was identified by X-ray diffraction (XRD) method as a mixture of $\alpha$-PbO (litharge) and $\beta$-PbO (massicot) phases. PbO powder gave a measured surface area of 0.51 m$^2$/g after 300 °C heating and He-gas purging for 3 h degassing. The surface area was measured by a Beckman Coulter SA3100™ Surface Area and Pore Size Analyzer using the BET method. The $\gamma$-Al$_2$O$_3$ was prepared from PURAL SB powder fabricated by Sasol with an average particle size ~45 μm. The phase of PURAL SB powder was identified by XRD as boehmite (AlOOH; ICDD PDF # 74-1875), and it was successfully converted to the $\gamma$-Al$_2$O$_3$ phase after heat treatment at 650 °C for 3 h (Zhou and Snyder, 1991; Wang et al., 2005).

Lead incorporation experiments were conducted using PbO to simulate the high temperature phase of lead in sludge under sintering condition. The $\gamma$-alumina precursor and PbO were mixed by ball milling in water slurry at Pb/Al molar ratios of 1:2 and 1:12 for 18 h. The slurry samples were then dried and homogenized by mortar grinding. The derived powder was pressed into 20-mm pellets at 650 MPa to ensure consistent compaction of the powder sample for the sintering process. The pellets were sintered at targeted temperatures from 600 to 1000 °C for 3 h (Sun et al., 2001) and then quenched in air to room temperature. The total mass loss after sintering was less than 1 wt.%. After sintering, the samples were ground in an agate mortar and pestle to a particle size of no more than 10 μm for XRD analysis and leaching test.

Phase transformation during sintering was determined by using the X-ray powder diffraction technique. The X-ray powder diffraction data of the samples were collected on a Bruker D8 Advance X-ray powder diffractometer equipped with a Cu Ka radiation and a LynxEye detector. The diffractometer was operated at 40 kV and 40 mA, and the 2θ scan range was from 10° to 80°, with a step size of 0.02° and a scan speed of 0.3 s/step. Qualitative phase identification was done using Eva XRD Pattern Processing software (Bruker Co. Ltd.) by matching powder XRD patterns with those retrieved from the standard powder diffraction database of the International Centre for Diffraction Data (ICDD PDF-2 Release, 2008).

After BET surface area measurement of the powder samples, the leachabilities of the single-phase samples were
tested using a leaching procedure modified from the U.S. EPA SW-846 Method 1311—TCLP with a pH 2.9 acetic acid solution (extraction fluid # 2) as the leaching fluid. Each leaching vial was filled with 10 ml of TCLP extraction fluid and 0.5 g of powder. The leaching vials were rotated end-over-end at 60 rpm for 0.75—23 days. At the end of each agitation period, the leachates were filtered with 0.2 µm syringe filters, the pH values were measured, and the concentrations of lead was analytically determined using a flame-type Perkin Elmer model 3300 atomic absorption spectrometer (Perkin Elmer Co. Ltd.).

3. Results and discussion

3.1. Formation of PbAl2O4

The two polymorphs of lead(II) oxide (the tetragonal form α–PbO and the orthorhombic form β–PbO) could transform into one another at certain temperature or under certain pressure. The transition of low-temperature-phase α–PbO to β–PbO may occur when the temperature reaches 540 °C (Wriedt, 1988). Moreover, the polymorphic transformation of β–PbO to α–PbO after ball-milling has been observed by Senna and Kuno (1971). As the sludge used for ceramic sintering preparation may experience both mechanical and thermal processes, the as-received and mixed-phase PbO was directly used as the raw material for sintering with γ-Al2O3. To explore the phases that may appear in the high-lead concentration sintering, Fig. 1 demonstrated the XRD patterns of the products from the Pb/Al = 1:2 mixture of PbO + γ-Al2O3 powder sintered at 600—1000 °C for 3 h. The result showed that when sintered at 700 °C, the formation of crystalline PbAl2O4 phase described by Eq. (1) was first observed.

\[ \text{PbO} + \gamma - Al_2O_3 \rightarrow PbAl_2O_4 \]  

Geller and Bunting (1943) reported the formation of PbAl2O4 at temperature 600 °C, but their experiment involved 1—2 months of dwelling time. Therefore, this difference may suggest that the formation of PbAl2O4 at temperatures below 700 °C is largely limited by the prevailing slow diffusion, although it is thermodynamically feasible at temperatures above 600 °C. The solid—state reaction is affected by both thermodynamic constraint and kinetic process. Below 700 °C, the PbAl2O4 phase formed by the short sintering scheme might only be limited at the grain boundary of reactants, and this small quantity in the sample was not reflected in the XRD results. As the intensity of the PbAl2O4 phase increased when the sintering temperature increases, a significantly higher intensity of PbAl2O4 signal was achieved at 750 °C, and no Bragg reflection of α–PbO or β–PbO phase was observed when the temperature was above 800 °C. An intermediate product of PbAl2O21 (ICDD PDF # 73-1875) was found when the sintering temperature was around 750 °C, but its Bragg diffraction peaks disappeared in the sample sintered at 900 °C. Above 950 °C, PbAl2O4 became the only product phase in the samples of this raw material system.

The powder diffraction database shows that the strongest diffraction peak (2θ = 29.12°) of the PbAl2O4 phase overlapped with the strongest of β-PbO (2θ = 29.08°) in the XRD patterns. As the second strongest peak of PbAl2O4 phase was located at 2θ = 19.96° and a major peak reflected from the (4 1 0) plane of PbAl2O4 was located at 2θ = 27.72°, the 2θ range of 18.8—22.2° and 27.4—28.0° demonstrated the details in the phase transformation processes to PbAl2O4 and Pb9Al8O21 (Fig. 2). Within the 2θ range of 18.8—22.2°, a few diffraction peaks of the PbAl2O4 phase could be observed to represent the formation of PbAl2O4 phase, and they are reflected by the (0 2 0), (1 2 0) crystal planes of PbAl2O4 structure, which correspond to 2θ of 19.21°, 19.96°, 20.99°, and 21.91°, respectively. A higher sintering temperature resulted in an increase in peak intensity, which indicates a continuing growth of the PbAl2O4 phase from 700 to 1000 °C sintering. The Fig. 2(b) illustrates that the peak intensity reflected by the (4 1 0) planes of Pb9Al8O21 increased with an increase in sintering temperature before reaching its maximum at 800 °C; this was followed by a decrease in intensity when the sintering temperature further increased.

The formation of Pb9Al8O21 during the sintering process was probably initiated by the reaction between PbO and γ-Al2O3 in a non-equilibrium system and due to the insufficient sintering time at the lower temperature range. The efficiency of a homogeneous reaction generally depends on the
encountering rate between reactant molecules (Kukukova et al., 2009). The short sintering time and low temperature were not able to provide sufficient contact, and hence the formation of PbAl$_2$O$_4$ is incomplete and an intermediate compound appeared in the product. At higher temperatures, more intensive interaction between reactants was achieved and Pb$_9$Al$_8$O$_{21}$ was not observed in the sintered samples. Therefore, to more effectively achieve the formation of PbAl$_2$O$_4$, the temperature of a short sintering scheme should be higher than 950°C.

3.2. Formation of PbAl$_{12}$O$_{19}$

When the PbO molar content in the PbO–Al$_2$O$_3$ system was lower than 50%, lead dodecaaluminate (PbAl$_{12}$O$_{19}$; ICDD PDF # 80-1174) was the only product phase reported in equilibrium experiments (Kuxmann and Fischer, 1974; Chen et al., 2001). Therefore, a potential thermal reaction of incorporating lead by γ-Al$_2$O$_3$ precursor at lower lead level is described by Eq. (2):

$$\text{PbO} + 6\gamma - \text{Al}_2\text{O}_3 \rightarrow \text{PbAl}_{12}\text{O}_{19}$$

Fig. 3(a) presents the XRD patterns of the 600–1000°C sintered PbO + γ-Al$_2$O$_3$ mixtures with a Pb/Al molar ratio of 1:12, and shows that the peaks of the PbAl$_{12}$O$_{19}$ phase appeared when the sintering temperature exceeded 950°C. The lowest temperature at which PbAl$_{12}$O$_{19}$ was observed after a short sintering scheme was about 200°C higher than that derived from the equilibrium experiment carried out by Kuxmann and Fischer (1974). Similarly, this discrepancy can be explained by the shorter sintering time and the potential diffusion barrier created by the newly formed PbAl$_{12}$O$_{19}$ layer between the PbO and γ-Al$_2$O$_3$ grains. At 1000°C, substantial growth of PbAl$_{12}$O$_{19}$ phase was found and PbAl$_{12}$O$_{19}$ was the only lead-containing phase in the product. However, an intermediate phase, hydrocerussite (Pb$_3$(CO$_3$)$_2$(OH)$_2$; ICDD PDF # 73-4362), formed in the products sintered at temperatures between 700°C and 950°C. The formation of poor crystalline Pb$_3$(CO$_3$)$_2$(OH)$_2$ phase was probably due to the instability of product phase(s) sintered at 700–950°C, which might be vulnerable to the attack of CO$_2$ and moisture in the air during sample quenching. Nevertheless, when sintered at 1000°C, the significant conversion to the PbAl$_{12}$O$_{19}$ phase completely eliminated the formation of hydrocerussite in the product, and this result may also indicate superior stability of the PbAl$_{12}$O$_{19}$ phase in the sintered product.

Further growth details of the PbAl$_{12}$O$_{19}$ phase can be carried out by observing its two major peaks located at $2\theta = 18.81^\circ$ and $2\theta = 36.10^\circ$, which correspond to the (1 0 1) and (1 1 1) planes of the PbAl$_{12}$O$_{19}$ structure (Fig. 3(b)). Starting from 950°C, the initiation of poor crystalline PbAl$_{12}$O$_{19}$ phase from sintering the PbO + γ-Al$_2$O$_3$ mixture could be observed. Significant growth of the PbAl$_{12}$O$_{19}$ phase clearly occurred within the temperature range of 950–1000°C. This result confirms the potential of forming PbAl$_{12}$O$_{19}$ to incorporate lead into the aluminum-rich ceramics for systems with lower Pb/Al ratios. Therefore, because PbAl$_{2}$O$_{4}$ and PbAl$_{12}$O$_{19}$ were identified as the potential hosting phases for lead in the ceramic products, both of them were later analyzed by the prolonged toxicity characteristic leaching procedure to observe their leachabilities and leaching behavior.

3.3. Leachabilities of product phases

To compare the effects of lead stabilization in different hosting forms, the use of single-phase samples in leaching experiments can further facilitate the interpretation of leachate data. In this study, both PbAl$_{2}$O$_{4}$ and PbAl$_{12}$O$_{19}$ single-phase samples were prepared from sintering the raw materials with Pb/Al molar ratios of 1:2 and 1:12 at 950 and 1000°C, respectively. The sintered products were then ground
into powder and confirmed by XRD to be the single-phase samples without observable reactant residues. In addition, the property of PbO powder used in sintering the raw material was also examined by the leaching experiment to compare it with those of aluminate phases. As the leaching process of solids is likely to be a surface reaction between solid and leachate, the observed lead concentrations in leachate are potentially proportional to the surface areas of samples. The BET surface areas of the powder samples before leaching were measured and yielded the values of 0.51 m²/g for PbO, 0.63 m²/g for PbAl₂O₄, and 3.76 m²/g for PbAl₁₂O₁₉.

Since solution pH is usually responsible for the lead leachability (Kim et al., 2011; Pereira et al., 2001), the leachate pH after the prolonged leaching tests was measured and shown in Fig. 4. Although both PbO and PbAl₂O₄ showed increases in leachate pH in the first couple of days, the PbAl₂O₄ leachates stabilized at pH ~6.5 whereas the pH values of the PbO leachates increased to pH ~9.3. In contrast, the pH values of the PbAl₁₂O₁₉ leachates were kept close to the initial pH value of its leaching fluid throughout the entire leaching period. The increase of leachate pH is likely to be due to the dissolution of crystal cations through ion exchange with protons in the solution. This is usually accompanied by the destruction of the crystal structure by the acidic leaching fluid. Hence, the most significant increase in PbO leachate pH indicates that PbO is very vulnerable to proton-mediated dissolution. Similarly, the very limited change of PbAl₁₂O₁₉ leachate pH may also indicate its strong resistance to acid attack.

The leaching process of metals from a solid sample is probably dominated by surface reactions and also influenced by the available amount of metals in the sample. In this study, we demonstrated the leachability of lead from the samples by normalizing the concentrations of lead in the leachates with respect to its weight percentage in the solid sample and the surface areas of the powder samples (Fig. 5). The normalized leached lead per surface area of sample (NLPbSA; m⁻²) was calculated as follows,

$$NLP_{b, SA} = 10^{-6} \times \frac{n \cdot C_{PB} \cdot AW_{PB}}{S_{W} \cdot S_{A} \cdot MW_{Phase}}$$  \hspace{1cm} (3)$$

where n is the number of Pb atoms in each molecule; k is the ratio of sample weight (g) to extraction fluid volume (mL); C_{PB} is lead concentration in leachate (mg/L); AW_{PB} represents the atomic weight of lead; SW is sample weight (g); SA is the solid sample surface area (m²/g) and MW_{Phase} represents the molecular weight of tested phase.

The lead concentration observed in PbO leachate was ~21 g/L at the end of 23-day leaching process. After
normalization, it was nearly three times higher than that from the PbAl2O4 samples (~10 g/L before normalization) and over three orders of magnitude higher than that from the PbAl12O19 samples (~80 mg/L before normalization) at the end of the leaching period. At leachate pH less than 10, the leachability of lead was reported to increase at lower pH values (Dubey and Townsend, 2004; Pereira et al., 2001). Comparing with the pH value of PbO leachate at ~9.3, PbAl2O4 and PbAl12O19 leachate remained at a lower pH value of around 6.5 and 3.5 throughout the whole leaching process, but the concentrations of the leached lead in PbAl2O4 and PbAl12O19 leachate were still much lower than that of the PbO leachate at the end of leaching experiment. As shown in Fig. 5, the significant difference points out that both PbAl2O4 and PbAl12O19 have much higher intrinsic resistances to acid attack compared to the PbO phase. This result was also consistent with the observation in the changes of leachate pH. The inset of Fig. 5 further provides the details of normalized lead concentrations in the PbAl12O19 leachates.

4. Conclusions

The results of this study indicate that the formation of lead aluminates, PbAl2O4 and PbAl12O19 phases, may be initiated by sintering the simulated lead-bearing sludge and aluminum-rich ceramic precursors at temperatures above 750 and 950 °C. The findings of the prolonged TCLP leachability test show the superiority of both PbAl2O4 and PbAl12O19 over PbO in resisting proton-mediated dissolution. This result provides a promising strategy to further stabilize lead by incorporating it into its aluminate structures. However, the sintering experiment revealed that a higher lead content phase, Pb4Al2O7, may occur as an intermediate between 800 and 900 °C and when the Pb/Al molar ratio in the raw materials is around 1:2. In addition, when the raw materials have a lower Pb/Al molar ratio (1:12), another intermediate phase, Pb2(Al12O19)(OH)2, was observed at the temperature range of 700–950 °C. The approach we outline here provides an effective way of incorporating lead-laden sludge into aluminum-rich ceramic precursors by the formation of PbAl2O4 and PbAl12O19 in an optimal temperature range of 950–1000 °C.

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