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Formation of lead-aluminate ceramics: Reaction mechanisms in immobilizing the simulated lead sludge

Xingwen Lu, Kaimin Shih *

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

HIGHLIGHTS

- Formation of $PbAl_2O_4$ and $PbAl_{12}O_{19}$ for stabilizing Pb in different Pb/Al systems.
- $Pb_9Al_8O_{21}$ and $Pb_3(CO_3)_2(OH)_2$ were detected as intermediate phases during sintering.
- Pb incorporation efficiency into $PbAl_2O_4$ and $PbAl_{12}O_{19}$ was quantitatively evaluated.
- Incorporating Pb into $PbAl_{12}O_{19}$ crystal is a preferred stabilization mechanism.

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ABSTRACT

We investigated a strategy of blending lead-laden sludge and an aluminum-rich precursor to reduce the release of hazardous lead from the stabilized end products. To quantify lead transformation and determine its incorporation behavior, PbO was used to simulate the lead-laden sludge fired with γ-Al_2O_3 by Pb/Al molar ratios of 1/2 and 1/12 at 600–1000 °C for 0.25–10 h. The sintered products were identified and quantified using Rietveld refinement analysis of X-ray diffraction data from the products generated under different conditions. The results indicated that the different crystallochemical incorporations of hazardous lead occurred through the formation of $PbAl_2O_4$ and $PbAl_{12}O_{19}$ in systems with Pb/Al ratios of 1/2 and 1/12, respectively. $PbAl_2O_4$ was observed as the only product phase at temperature of 950 °C for 3 h heating in Pb/Al of 1/2 system. For Pb/Al of 1/12 system, significant growth of the $PbAl_{12}O_{19}$ phase clearly occurred at 1000 °C for 3 h sintering. Different product microstructures were found in the sintered products between the systems with the Pb/Al ratios 1/2 and 1/12. The leaching performances of the PbO, $Pb_9Al_8O_{21}$, $PbAl_2O_4$ and $PbAl_{12}O_{19}$ phases were compared using a constant pH 4.9 leaching test over 92 h. The leachability data indicated that the incorporation of lead into $PbAl_{12}O_{19}$ crystal is a preferred stabilization mechanism in aluminate-ceramics.

1. Introduction

Lead (Pb) is a type of heavy metal widely used in industry due to its versatile physical and chemical characteristics. The International Lead and Zinc Study Group estimated that global annual lead consumption approached 9 million tons in 2010. Serious environmental concerns have been raised about the release of lead into the environment from industries such as the production of lead batteries, oil-based paints, pigments, paper, pulp, and electrochemical electrodes, as well as mining, plating, hot dip galvanizing, and petroleum refining (Jalali et al., 2002; Gupta et al., 2001; Conrad and Bruun Hansen, 2007). Lead is a highly toxic and non-biodegradable metal that tends to accumulate in the cells of living organisms, causing severe damage to the kidneys, liver, and nervous and reproductive systems in humans (Gupta et al., 2011). The remediation of hazardous lead sludge has become a pressing challenge in recent years due to more stringent environmental regulations.

Ceramic technology is a technique to create ceramic products from inorganic, non-metallic materials by the action of heat and subsequent cooling (Vincenzini, 1991). Ceramics are either formed from a molten mass that solidifies on cooling, formed and matured by the action of heat, or chemically synthesized at low temperatures using, for example, hydrothermal or sol–gel synthesis (Richerson, 1982). Ceramic technology is considered useful for rendering hazardous metal sludge inert because they can destroy organic matters and immobilize hazardous metals in a stable matrix to reduce metal leachability (Xu et al., 2008, 2009). As ceramic technology involved in the crystallization and/or vitrification

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* Corresponding author.
E-mail address: kshih@hku.hk (K. Shih).

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of ceramic materials (Rawlings et al., 2006), this technology functions by binding hazardous metal ions into the framework of glass or the crystallization phases of ceramic products (Cheng, 2004; Tian et al., 2011). Previous studies have described mechanisms for stabilizing nickel and copper into aluminum-rich ceramic matrices and achieving reduced metal leachability through the intrinsic properties of spinel structures (Shih et al., 2006a,b; Tang et al., 2010; Hu et al., 2010).

Several studies have reported the potential formation of lead aluminate ($PbAl_2O_4$) and a magnetoplumbite-like structure ($PbAl_{12}O_{19}$) using γ-Al_2O_3 as an inexpensive ceramic precursor to treat PbO (Wendt et al., 1988; Park and Chang, 1993). Although the recently published $PbO–Al_2O_3–SiO_2$ equilibrium phase diagram confirmed the presence of $PbAl_{12}O_{19}$ and $PbAl_2O_4$ (Chen et al., 2001), the reaction sequences involved in the incorporation of lead at different temperatures and times are still unclear. As the dwelling time of the ceramic sintering process can vary from a few minutes to several hours (Völtzke and Abicht, 2001; Aksel et al., 2005), the dominant mechanism(s) for hosting lead in crystal structures under different thermal conditions needs to be unambiguously identified, if not also quantitatively evaluated.

The objective of this work was to contribute a better understanding of the phase transformations to $PbAl_{12}O_{19}$ and $PbAl_2O_4$ during ceramic sintering, which potentially play a role in lead incorporation mechanisms in aluminum-rich ceramics. The dominant reaction mechanisms at different sintering periods were determined quantitatively, together with the influence of the sintering temperature and time. Furthermore, the stabilization effects of potential lead phases in the products were evaluated via leaching tests at a constant pH value. The obtained leachability of each phase was further normalized using the sample surface area and lead content to reflect the intrinsic lead leachability and suggest a more reliable mechanism to host the hazardous lead.

2. Materials and methods

PbO powder was purchased from Sigma–Aldrich. The phase composition of the PbO was identified using X-ray diffraction (XRD) for a mixture of α-PbO (litharge) and β-PbO (massicot) phases. The γ-Al_2O_3 was prepared from PURAL SB powder with an average particle size of $\sim$45 μm fabricated by Sasol. The phase of the PURAL SB powder was identified using XRD for boehmite (AlOOH; ICDD PDF # 74-1875) and it was successfully converted to the γ-Al_2O_3 phase after heat treatment at 650 °C for 3 h (Zhou and Snyder, 1991; Wang et al., 2005). The phase confirmation for the two materials was demonstrated by their XRD patterns, which are provided in Fig. S1 (Supporting Information).

As lead usually exist as lead(II) in wastewater (Acharya et al., 2009; Deng et al., 2007; Singh et al., 2008), the treatment of lead-containing wastewater by current common techniques (i.e. chemical precipitation, ion exchange, coagulation, adsorption, and membrane processes) produce enormous amounts of lead-containing sludge that mainly composed of some insoluble lead(II) compounds (i.e. lead(II) carbonate, lead(II) oxide, lead(II) hydroxide and lead(II) sulfate) (Mao et al., 2014; Volpe et al., 2009; Yao and Naruse, 2009). However, the major portion of lead may converted into lead oxide at the high sintering temperatures. For this reason, the lead incorporation experiments were conducted using PbO to simulate the lead in sludge under sintering condition (Yao and Naruse, 2005). The γ-Al_2O_3 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 specified temperatures from 600 to 1000 °C for 0.25–10 h, and then quenched in air to room temperature. The total mass loss after sintering was less than 1 wt.%.

After thermal treatment, the pellets were weighed and ground into powder with a particle size of less than 10 μm for XRD analysis. Some of the pellets were reserved for scanning electron microscopic (SEM) characterization and were polished using a submicrometer diamond lapping film and gold coated to mitigate the electron charging effect. All of the SEM investigations were performed using a Hitachi S-4800 SEM system equipped with a secondary electron detector to obtain morphological information and a backscattered electron detector for energy dispersive spectroscopy (EDS).

The X-ray powder diffraction data of the samples were collected using a Bruker D8 Advance X-ray powder diffractometer equipped with a Cu Kα radiation detector 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 performed using Eva XRD Pattern Processing software (Bruker Co. Ltd.) by matching the powder XRD patterns with those retrieved from the standard powder diffraction database of the International Centre for Diffraction Data (ICDD PDF-2 Release 2008).

The Rietveld refinements for quantitative analysis of the phase compositions were processed using the TOPAS (version 4.0) crystallographic program. Figs. S2–S6 (Supporting Information) present the Rietveld refinement plots for the products sintered from the PbO/γ-Al_2O_3 system. The derived reliability values for the refinement quality of this analytic scheme are provided in Tables S1–S3 (Supporting Information). For systems potentially containing amorphous or poorly crystalline phases, a refinement method using CaF_2 as the internal standard (De La Torre et al., 2001; Magallanes-Perdomo et al., 2009; Rendtorff et al., 2010) was used to quantify the amorphous content in the samples. Quantitative analysis data were collected from 10° to 120° 2θ-angle, with a step width of $2\theta = 0.02°$ and a sampling time of 0.5 s per step.

Before performing the leaching test, the surface areas of the single-phase powders were measured by a Beckman Coulter SA3100 Surface Area and Pore Size Analyzer using the BET method after degassing by heating at 300 °C for 3 h with He-gas purging. To distinguish the role and characteristic of each lead stabilization mechanism, the potential lead-bearing product phases were compared using the leaching test. The powder (<45 μm) samples of the target phases were subjected to batch leaching in amorphous silica vessels at a liquid/solid ratio of 50 ml/g (4 g powder sample with 200 ml of pH 4.9 acetic acid solution) for a total testing time of 92 h. Three duplicate experiments were conducted to ensure the reproducibility of the leaching test. Acid (1 N HNO_3) was added into each suspension to maintain a constant pH of 4.9 using a pH-stat system. Continuous stirring was conducted to keep the mixture homogeneous and the leaching vessel was held at room temperature (23 ± 0.5 °C). At different times, the suspensions were allowed to settle for 5 min and aliquots of 5 ml of the upper liquid were taken and centrifuged. Another 5 ml of pH 4.9 acetic acid solution, together with the filtered solids, was added to the vessels. At the end of each agitation period, the leachates were filtrated using 0.2 μm syringe filters and the concentrations of lead in the leachates were analytically determined using ICP-AES (Perkin–Elmer Optima 8300 DV).

3. Results and discussion

3.1. Lead incorporation into $PbAl_2O_4$ structure in Pb/Al 1/2 system

By adding 25 wt.% CaF_2 as an internal standard, the quantities of crystalline and amorphous phases in the PbO/γ-Al_2O_3 mixtures