Quantitative Mineral Phase Analysis for Reliable Waste Metal Stabilization and Recovery

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ABSTRACT

The ability of designing marketable products derived from waste to simultaneously prevent the environmental pollution and recover valuable material resources is a major technological challenge in the 21st century. Conventional inorganic product designs are often assisted by X-ray diffraction (XRD) technique to qualitatively identify the mineral phase types in the products. However, a further advancement in the quantitative capability of XRD technique is now available to further accurately control product quality. In this study, we will demonstrate the successful applications of the state-of-the-art quantitative X-ray diffraction (QXRD) on stabilizing the hazardous metals in ceramic products and on extracting metallic lead from waste electronics. The feasibility of stabilizing metal-laden waste sludge and ash materials by a wide variety of aluminum- and iron-rich ceramic precursors will be demonstrated by the high metal transformation efficiency and the significant reduction of intrinsic metal leachability. Our work of recovering metallic lead from waste cathode ray tube (CRT) glass will also reflect how the QXRD can assist the development of new resource recovery technologies. A method of reductively transforming the lead in CRT glass into its metallic form through the reactive sintering with zero-valent iron was invented and optimized by the QXRD technique. With the rapid progresses in materials science and characterization techniques, substantial new technological developments in the beneficial uses of waste materials are now spearheaded by the interdisciplinary environmental materials research.

Keywords: Hazardous Metals; Incineration Ash; E-Waste; Ceramic Materials; Thermal Treatment

INTRODUCTION

Heavy metals are toxic and their discharge into receiving waters is detrimental to human health and the environment. Many researchers have attempted to immobilize toxic metals via sorption, using natural or synthetic sorbents or cement, and then correlate their performance directly for metal leaching ability (Bolger & Szlag, 2002). In the immobilization processes, cementitious or pozzolanic materials have been received as an acceptable way to achieve solidification/stabilization with reduced environmental risks associated with their subsequent disposal (Viguri et al., 2001). The cementation method uses the binder to either chemically bind toxic waste matter into solid bulk or physically cut them off from the outside by forming a capsule. However, these solidification/stabilization technologies were not successful in preventing leaching in acidic environments, i.e., pH less than 4.0 (Yousuf et al., 1995).

Stabilizing hazardous sludge via thermal treatment has the potential to convert hazardous metal-laden sludge from the waste stream into reusable products, such as construction ceramics. After thermal treatment, the metal leachability of products via irreversible transformation of metal mineral phase can be significantly reduced (Hsieh et al., 2008). For examples, the simulated nickel sludge was sintered with alumina (Al_2O_3), hematite (Fe_2O_3) and kaolinite ($Al_2Si_2O_5(OH)_4$), and the formation of aluminate and ferrite spinels was found in the products (Shih et al., 2006a,b). The long-term nickel leachabilities were found to drop dramatically in its alumina and ferrite spinel phases, comparing to that in nickel oxide (Shih et al., 2007). Similarly, in the feasibility study of stabilizing simulated copper-laden sludge, copper aluminate spinel ($CuAl_2O_4$) was formed at a most efficient temperature of 1000 ^oC under 3-hour short sintering (Tang et al., 2010). The copper leachabilities of CuO and $CuAl_2O_4$ were evaluated by a pH 2.9 acetic acid solution, and $CuAl_2O_4$ was superior to CuO in metal immobilization over longer leaching periods. In a study attempting to observe the interaction of copper with the iron content in the chemically-enhanced primary treatment sludge, the $CuFe_2O_4$ was found. A low-temperature $CuFe_2O_4$ phase with tetragonal structure was detected at 750 ^oC, and the cubic $CuFe_2O_4$ developed at 1000 ^oC (Tang et al., 2016).

Management of electrical and electronic equipment waste (commonly known as e-waste) has been recognized as a great environmental challenge, and the obsolete cathode ray tubes (CRTs) is one of the main e-waste targets. A good strategy to dispose CRT glass is to extract lead content. In the literature, most of the lead extraction methods from glass matrix were found with very high energy consumption (Chen et al., 2009). In this study, metallic iron (Fe(0)) was used as the reducing agent to treat lead-containing glass to extract the metallic lead from the glass matrix at temperatures of 500-950 ^{o}C in the air.

Conventional material designs are often assisted by the X-ray diffraction (XRD) technique to identify the mineral phases in the products via matching the observed diffraction peak positions with those of standard mineral phases. In quantitative X-ray diffraction (QXRD) analysis using the Rietveld methods, relative weight fractions of crystalline phases in a multiphase sample can be calculated directly from scale factors of the respective calculated intensities. This technique is now available to further contribute to the accurate control of product quality.

In this study, the applications of QXRD on extracting metallic lead from waste electronics and on stabilizing the hazardous nickel and copper in ceramic products was investigated. The simulated metal-laden waste sludge and ash materials were thermally treated with a wide variety of alumina precursors. Our work of recovering metallic lead from waste CRT glass will also serve as a good example to reflect how the quantitative phase composition analysis can assist the development of new resource recovery technologies. A method of reductively transforming the lead in CRT glass into its metallic form through the reactive sintering with zero-valent iron was also invented and optimized by the QXRD technique.

METHODOLOGY

The hazardous metal (Zn and Cu) oxides were used as the simulated metal-laden waste sludge and ash materials to react with the aluminum oxide precursors. The γ-Al_2O_3 was derived from the fired boehmite (AlOOH) at 650 °C for 3 h. The hazardous metal (Me) oxide was mixed with aluminum oxide precursor at a Me:Al/Fe molar ratio of 1:2. The mixing process was carried out by ball milling the powder in water slurry for 18 h. The slurry samples were dried and homogenized by mortar grinding, pressed into 20 mm pellets at 650 MPa, and then fired from the temperature of 650 °C to 1450 °C. The leachability of single-phase samples was tested by means of a leaching experiment, with a pH 2.9 acetic acid solution as the leaching fluid. Each leaching vial was filled with 10 mL of TCLP extraction fluid and 0.5 g of powder, and rotated from 0.75 d to 22 d.

The CRTs glass was collected in Hong Kong and crushed into small pieces with the coating fully removed by the wet scrubbing method. The cleaned funnel glass particles were further dry ball milled and sieved to smaller than 45μm. The powder obtained was dried at 105°C for 24 h. The chemical composition of the glass powder was examined by X-ray fluorescence (XRF) with 21.5 wt. % of PbO. The waste funnel glass was mixed with metallic ion powder at different weight fractions. The mixtures were then homogenized by ball milling and pressed into pellets under a pressure of 650 MPa to ensure the consistent compaction of the samples. The pellets were then transferred to a muffle furnace preheated at the target temperatures (600-950 °C), and thermally treated with a dwell time ranging from 3 to 180 min in air.

All of the heat-treated samples were then quenched in the air and then ground into powder for X-ray diffraction scanning. Subsequently, the collected XRD patterns were conducted the qualitative XRD analysis by matching XRD patterns with the powder diffraction files (PDF) database of International Centre for Diffraction Data (ICDD) to investigate the phase composition of these samples. Furthermore, Rietveld refinement analysis was also conducted to quantitatively explore the weight percentages of the crystalline phases in the sintered products.

RESULTS AND DISCUSSION

The stabilization of copper and zinc through the formation of aluminate spinel

In order to investigate the reaction kinetics of the mixtures, the transformation ratio of Zn/Cu into spinel was defined as Equation 2. From Figure 1, about 20% of copper was transformed from CuO into $CuAl_2O_4$ when the mixture was sintered at 650 ^{o}C. The maximum TR of the CuO + γ-Al_2O_3 samples reached 80% at temperatures between 850 and 1000 ^{o}C, and then declined at higher temperatures because of the formation of $CuAlO_2$. Meanwhile, the TR values of zinc incorporated into $ZnAl_2O_4$ phase was strong and even reached over 60% transformation at 750 ^{o}C. The zinc transformation continued to increase with the elevation in sintering temperature and reached nearly full incorporation after sintering at 1450 ^{o}C.

$$TR = \frac{w_S/M_S}{w_S/M_S + w_{MeO}/M_{MeO}} \times 100\% \quad (2)$$

Where w_s presents for the weight percentage of spinel ($ZnAl_2O_4$ or $CuAl_2O_4$); M_s is the molar weight of spinel ($ZnAl_2O_4$ or $CuAl_2O_4$); w_{MeO} is the weight percentage of residual ZnO/CuO; and M_s presents for the molar weight of ZnO/CuO.

Throughout the 22-d leaching experiment, the copper and zinc concentrations of MeO and $MeAl_2O_4$ leachates were shown in Figure 2a & b, respectively. Within the first 18 h, both copper and zinc ions increased substantially in leachates of metal oxides, and then they remained at approximately this value throughout the rest of the leaching period. When the leaching of $MeAl_2O_4$ was considered, the concentration of Cu^{2+} and Zn^{2+} kept slow increasing from the first 18 h to the end of this leaching procedure. However, even at the end of the leaching procedure, the concentration of Me^{2+} leached out from $MeAl_2O_4$ phase is much lower than that from MeO phase. The amount of leached copper and zinc in MeO leachate was about 3 orders of magnitude greater than that in the leachates of $MeAl_2O_4$. In comparison to metal oxides, the spinel demonstrated much higher inherent resistance to acidic attack, and thus the spinel incorporation strategy proved to be beneficial in stabilizing copper and zinc.

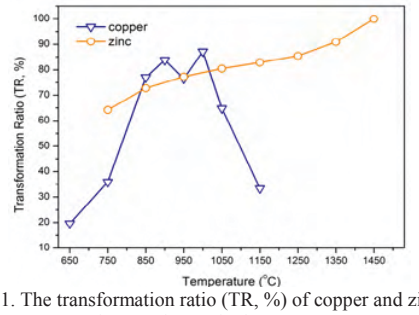

Figure 1. The transformation ratio (TR, %) of copper and zinc into the $MeAl_2O_4$ spinel structure.

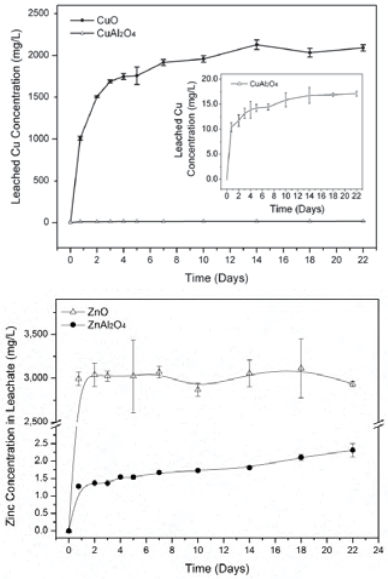

Figure 2. Variation of the (a) copper and (b) zinc concentrations of the leachates from MO and the as-prepared MAl_2O_4 powders.

The extraction of metallic lead from cathode ray tube (CRT) funnel glass

To further study the extraction efficiency of the Pb, the weight percentage of Pb related crystalline phases was refined by XRD quantitative method and then further converted into Pb Extraction Ratio as defined by Equation 1.

$$ER = \frac{m_T \times (w_{Pb} + w_{PbO} \times \frac{M_{Pb}}{M_{PbO}})}{m_O \times w'_{Pb}} \times 100\% \quad (1)$$

Where m_O is the original mass of Fe + glass before thermal treatment; m_T is the mass of Fe+glass after thermal treatment; w_{Pb} and w_{PbO} are the weight percentage of metallic Pb and PbO; M_{Pb} and M_{PbO} are the molecular weight of metallic Pb and PbO; and w'_{Pb} is the weight percentage of Pb element in the mixture of Fe + glass before thermal treatment.

To optimize the Pb recovery process, the reaction between Fe and Pb-glass was investigated under various thermal treatment temperatures, time periods, and Fe/Pb-glass ratios. The Pb extraction ratio (ER) values of Fe+Pb-glass under different recovery conditions were shown in Figure 3. Figure 3 (a) summarizes the observed ER index values over the temperature range of 600-950 °C for the samples with Fe/ Pb-glass mass ratios of 1/1 and 0.75/1. At temperatures of 600-700 °C, substantial increases in the Pb extraction efficiency were observed for both mass ratios, and the lead extraction ratios increased significantly to 33% (Fe/Pb-glass of 1/1) and 54% (Fe/Pb-glass of 0.75/1). However, the curves also

reflect a dramatic decrease in the lead extraction efficacy at higher temperatures (750-950 °C) for both the 1/1 system (a decrease from 33% to 0%) and the 0.75/1 system (a decrease from 56% to 12%). This finding demonstrates a particular condition for initiating the phase transformation of lead, and the results of the quantitative X-ray diffraction reveal 700 °C to be the most effective temperature for extracting the lead from the glassy network. In Figure 3 (b), the ER increases with the ratio increasing up to 1, and then maintains the ratio of 1.5/1. Therefore, the use of a Fe/Pb-glass mass ratio of close to 1/1 results in a more effective and economical extraction operation. In Figure 3 (c), the ratio of metallic lead extraction was enhanced by the use of prolonged heating time (180 min) to 37% at 600 °C. At 700 °C, the lead extraction efficiency first exhibited a significant increase to 56% after 30 min of heating, but then gradually decreased with prolonged heating time, dropping to 39% after 180 min of treatment. In contrast, a negative relationship between the lead extraction efficiency and thermal treatment time was found at 950 °C. The lead extraction ratio quickly reached 24% after 3 min of heating at 950 °C, but the extraction efficiency decreased continuously with prolonged heating. Therefore, the recovered Pb can be re-oxidized and over 30 min at 700 °C or over 3 min at 950 °C.

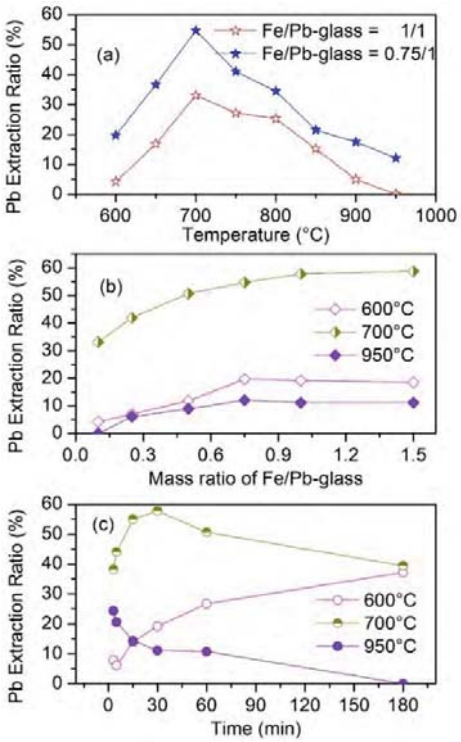

Figure 3. Extraction ratio (ER) values of Fe+Pb-glass (a) with the mass ratios of Fe/Pb-glass at 1/1 and 0.75/1 thermally treated at 600-950 °C for 30 min; (b) with different Fe/glass mass ratios treated at 600, 700, and 950 °C for 30 min; (c) with the mass ratio of Fe/Pb-glass at 1/1 treated at 600, 700, and 950 °C for 3-180 min.

CONCLUSIONS

The Pb in the Pb glass could be successfully recovered into metallic Pb by the oxidation of metallic ion. The reaction temperature, time, and the mass ratio of Fe/Pb-glass are significant to the Pb extraction efficiency. An optimal reaction condition is to sinter the Fe+Pb-glass with a mass ratio of 1/1 at 700 °C for 3 h, under which condition, about 56% of Pb could be recovered. The simulated hazardous metal (Zn or Cu) sludge and ash materials can be immobilized into spinel by Al_2O_3. Through the phase identification and quantification function of the XRD technique, copper and zinc were observed to be stabilized in the aluminate spinel ($MeAl_2O_4$).

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