Formation and leaching behavior of ferrite spinel for cadmium stabilization

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ABSTRACT

Highly mobile and toxic cadmium (Cd) is often found in waste incinerator residues. To investigate the effectiveness of immobilizing Cd-bearing residues, two iron oxide precursors, hematite (α-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$), were reacted with cadmium oxide (CdO) at 600–850 °C for 3 h. The XRD results showed that cadmium ferrite spinel (CdFe$_2$O$_4$) was the only Cd-hosting product phase in both systems. Both of the iron oxides were found to be efficient in incorporating Cd into the CdFe$_2$O$_4$ spinel structure, but Fe$_3$O$_4$ was more reactive in the Cd incorporated at low temperatures. The weight factions of the crystalline phases in the sintered products were quantified by the Rietveld refinement method, and the transformation ratio (TR) index was used to reveal the Cd incorporation efficiencies of the iron oxides. A TR of 100% was achieved at 850 °C, indicating the potential for efficient stabilization of Cd through thermal reactions with iron oxide precursors. The Cd stabilization effects were further assessed by leaching CdFe$_2$O$_4$ and CdO in constant pH (2.0, 3.0 and 4.0) leaching tests. The results revealed the incongruent dissolution of CdFe$_2$O$_4$. The amount of Cd leached from the CdFe$_2$O$_4$ was more than three orders of magnitude smaller than that from the CdO, signifying a highly promising and reliable strategy for Cd stabilization. To our knowledge, this study is the first work to systematically report the roles of different Fe-rich precursors in Cd stabilization mechanism, and indicates the significant reduction of Cd leachability via CdFe$_2$O$_4$ formation. These findings have provided further understanding on the stabilization of cadmium by sintering with low-cost and attainable Fe-rich precursors at relatively low temperatures.

1. Introduction

The increasing amount of municipal solid waste (MSW) is a well-known global worldwide environmental issue (Cheng et al., 2007; Lam et al., 2010; Li et al., 2007; Tian et al., 2012). Incineration, while an efficient and effective technique that is widely used to reduce the volume of waste (Lam et al., 2010; Li et al., 2007), inevitably produces large amounts of MSW incinerator (MSWI) residues such as bottom and fly ash (Ferreira et al., 2003; Li et al., 2007; Tian et al., 2012). The main environmental and health concern associated with these residues is the enrichment of toxic metals such as zinc (Zn), copper (Cu), chromium (Cr), lead (Pb) and cadmium (Cd) (Ferreira et al. 2003; Lee et al., 2005; Li et al., 2007; Tian et al., 2012). Cd concentrations in the flue gas of MSW incinerators range from 24 to 1500 µg/m^3, and most of the Cd eventually accumulates in fly ash (Lee et al., 2005), leading to its enrichment in MSWI residues. Thus, these hazardous MSWI residues need further immobilization and detoxification treatment prior to disposal (Ali and Gupta, 2007; Ferreira et al., 2003; Gupta et al., 2012; Jamode et al., 2004; Lam et al., 2010; Lewinsky, 2007).

Several matrices, including bauxite (Uberoi and Shadman, 1991), alumina (Kuo et al., 2009; Liu et al., 2005), kaolinite (Tran et al., 2004; Uberoi and Shadman, 1991; Yao and Naruse, 2005), silica and montmorillonite (Lee et al., 2005), calcium oxide (Uberoi and Shadman, 1991) and cement (Cartledge et al., 1990), have been used to physically and chemically sorb toxic metals in the stabilization and solidification processes. However, due to the weak binding to these matrices, the metal stabilization effects are often inefficient and unsatisfactory (Chen et al., 2009; Lee et al., 2005; Quina et al., 2008; Yan et al., 2002). The treated products contain hazardous metals such as Cd that are easily leached under an acidic environment (Chen et al., 2009; Quina et al., 2008; Yan et al., 2002), and thus the development of a reliable technique for stabilizing Cd is critical. Thermal treatment, which takes advantage of the existing industrial ceramic sintering process, has been proven to be an effective strategy for stabilizing certain hazardous metals (e.g., Ni, Cu, Pb and Zn) into crystal structures with commonly available aluminum or iron-rich precursors (Lu et al., 2013; Shih et al., 2006a; Tang et al., 2011a, 2011b). Such crystalline products possess desirable acid-resistant properties and can

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be safely used in construction materials (Shih et al., 2006a, 2006b; Tang et al., 2011b). Equilibrium studies have indicated that a reaction mechanism for forming a Cd ferrite spinel structure may be available (Chinnasamy et al., 2001a, 2001b; Mahmoud et al., 2003), but whether this reaction can be efficiently achieved via solid-state reactions in a reasonable industrial processing timeframe is unknown. Therefore, it is necessary to determine whether a thermal treatment scheme with iron-rich precursors is feasible for stabilizing Cd.

Iron (Fe) exists in six oxidized forms (α-Fe_2O_3, Fe_3O_4, γ-Fe_2O_3, β-Fe_2O_3, ε-Fe_2O_3 and FeO) in the natural environment. Two of the most important forms are α-Fe_2O_3 (hematite) and Fe_3O_4 (magnetite) (Cornell and Schwertmann, 2003; Schwertmann and Cornell, 2000), which are commonly found in natural materials and industrial residues (Cablik, 2007; Liu et al., 2007; Pappu et al., 2007). For example, the Fe-containing minerals present in ash residues that commonly affect the incorporation of Cd are hematite and magnetite (Gieré et al., 2003; Giero and Stille, 2004). However, to date, studies on $CdFe_2O_4$ formation have not investigated the roles of different iron oxide precursors. Therefore, in this study, hematite and magnetite were chosen as the precursors to observe their influence on $CdFe_2O_4$ formation. Quantitative X-ray Diffraction (QXRD) analysis has been proven to be a reliable, precise and reproducible method to identify the compositions of crystalline phases in the samples (Tang et al., 2011a; Su et al., 2015). It has been widely employed to qualitatively and quantitatively analyze natural and industrial materials. The main goal of the study was to unambiguously identify the Cd incorporation mechanism during the sintering process, and quantitatively determine the incorporation efficiency by QXRD technique. As a fundamental understanding of the chemical properties of the stabilized product is crucial, the chemical durability of the products was examined by leaching experiments. The constant pH leaching test is a highly beneficial method for revealing the leachability and leaching behavior of materials and was thus used in this work to evaluate the stabilization of Cd in the product phase (Islam et al. 2004; Su et al., 2015; USEPA, 2004).

2. Experimental

2.1. Materials and sample preparation

Analytical reagents of cadmium oxide (CdO), hematite (α-Fe_2O_3) and magnetite (Fe_3O_4) were used as the starting materials, purchased from Fisher Scientific (USA), Sigma-Aldrich (USA) and Beijing HWRK Chem Co., LTD. (China), respectively. CdO is one of the predominant cadmium species in the waste incinerator residues (Kuo et al., 2009), in this study we thus used CdO as the cadmium source. Mineralogical identification of the starting materials was performed by X-ray diffraction (XRD). The results are presented in Fig. S1 in Supplementary Material. The mineral phases were identified as cubic CdO (space group (S.G.): $F3-3m$ (no. 225)), rhombohedral α-Fe_2O_3 (S.G.: R-$3c$ (no. 167)) and cubic Fe_3O_4 (S.G.: Fd-$3m$ (no. 227)). The specific surface areas (S_{BET}) of the CdO, α-Fe_2O_3 and Fe_3O_4 powder were determined by a Beckman Coulter SA3100 Surface Area and Pore Size Analyzer using the Brunauer-Emmett-Teller (BET) method with the nitrogen adsorption-desorption isotherms at liquid nitrogen temperature (77 K), yielding 2.63 ± 0.05, 4.30 ± 0.03 and 7.00 ± 0.06 m^2/g, respectively. To evaluate the feasibility of Cd incorporation, a mixture of CdO $+\alpha$-Fe_2O_3 with a total dry weight of 10 g (Cd/Fe molar ratio of 1/2) was wet-ground for 30 min. After drying at 105 °C for 24 h in a vacuum oven, the mixture was further homogenized by mortar grinding. Pressure of 250 MPa was applied to form the powder into Φ 20 mm pellets. The preparation procedure for the CdO+Fe_3O_4 sample was identical to that for the CdO+α-Fe_2O_3 sample. A well-controlled thermal treatment scheme with a dwelling time of 3 h was then applied to observe the Cd incorporation efficiency.

2.2. Product characterization and quantification

After sintering, the pellets were air-quenched and their diameters were measured with a Vernier caliper. To observe the product microstructures, the cross-sections of the sintered pellets were polished with UltraPrep Diamond Lapping Films (Buehler, USA) with different grain sizes from 0.1 to 30 μm, and then monitored on a Hitachi S-4800 SEM system. The fired pellets were also ground into a powder for the XRD analysis. The XRD pattern of each powder sample was obtained using a Bruker D8 Advance X-ray powder diffractometer equipped with Cu K$\alpha_{1,2}$ X-ray radiation and a LynxEye detector. The 2θ ranged from 10 to 90º, and a step size of 0.02° with a rate of 0.5 s per step was used to obtain quality diffraction data.

Phase identification was executed by matching the XRD patterns of the collected powder with those retrieved from the standard powder diffraction database published by the International Centre for Diffraction Data (ICDD PDF-2 Release 2008). The crystalline phases were used to quantify the Cd incorporation efficiency into a crystalline structure. The refinement of the crystal structure and quantification of the phase compositions were performed by the Rietveld refinement method using the TOPAS V4.2 program (Bruker AXS, Karlsruhe). The quality of each refinement analysis was assessed by the weighted pattern factor (R_{wp}), pattern factor (R_p) and goodness of fit (GOF) indicators, as shown in Table S1. The GOF values from the refinement analyses ranged from 1.1 to 1.5 and were within the reported range for satisfactory conditions (Fansuri et al. 2004; Tang et al. 2011a).

2.3. Stabilization effect evaluation

The leachabilities of the Cd product phase and CdO were examined by the constant-pH leaching test (CPLT) (Su et al., 2015). The initial leachants were nitric acid (HNO_3) aqueous solutions with pH values of 2.0, 3.0 and 4.0. HNO_3 was used due to its weak affinity for further complexing heavy metals (Benjamin and Leckie, 1982; Galvín et al., 2012). The solution pH values were monitored and maintained with a 0.1 unit fluctuation through the addition of 1 M HNO_3 aqueous solution (an estimated 10 μL for each adjustment, if needed). Prior to the CPLT, the S_{BET} and particle size distributions (PSD) of the solid samples were determined. The PSD test was conducted on an LS 13320 Laser Diffraction Particle Size Analyzer (Beckman Coulter, Inc.). The CPLT was performed in a jar filled with 500 mL of leachant and 0.5 g of tested powders. The leaching system was strongly agitated by mechanically stirring at 200 rpm. As the CPLT proceeded, 5 mL of leachate was extracted together with the suspended solids at 10-min intervals. The leachates were filtered with 0.2 μm syringe filters and then stored in sealed vials for further analysis. The leached Cd and Fe contents in the leachates were determined by ICP-OES 800 (Perkin Elmer).

3. Results and discussion

3.1. Formation of cadmium ferrite

The XRD patterns of the CdO+α-Fe_2O_3 and CdO+Fe_3O_4 samples treated with a Cd/Fe molar ratio of 1/2 at 600–850 °C for 3 h are given in Fig. 1. The XRD results revealed that Cd was crystallographically incorporated into the cadmium ferrite ($CdFe_2O_4$) structure using either an α-Fe_2O_3 or Fe_3O_4 precursor. The $CdFe_2O_4$ in the products crystallized into a cubic space group Fd-$3m$ (no. 227) "spinel" structure. The diffraction signals corresponding to the residual Fe_3O_4 completely disappeared in the CdO+Fe_3O_4 sample after sintering at 600 °C for 3 h (Fig. 1b), which corresponds with the phase transformation temperature of Fe_3O_4 (Fig. S2). At 600 and 650 °C, the diffraction peak intensities of the $CdFe_2O_4$ with Fe_3O_4 as the precursor were significantly higher than those with α-Fe_2O_3 as the precursor. This suggests that Fe_3O_4 was more reactive than α-Fe_2O_3 in incorporating the Cd at low sintering temperatures. The formation of $CdFe_2O_4$