Journal of Environmental Management 187 (2017) 340–346

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Review

Stabilizing cadmium into aluminate and ferrite structures: Effectiveness and leaching behavior

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ARTICLE INFO

Article history:
Received 11 May 2016
Received in revised form
16 October 2016
Accepted 18 October 2016
Available online 8 November 2016

Keywords:
Sludge
Cadmium
Stabilization
Aluminate
Ferrite
Constant-pH leaching test (CPLT)

ABSTRACT

The inappropriate disposal of sludge, particularly for those enriched in heavy metals, is highly hazardous to the environment. Thermally converting sludge into useful products is a highly promising technique as heavy metals are immobilized and organic substances are mineralized. This work investigated the feasibility of stabilizing simulated cadmium-laden sludge by sintering with Al-and Fe-rich precursors. To simulate the process, cadmium oxide was alternatively mixed and sintered with γ-Al_2O_3 and α-Fe_2O_3. Cadmium was crystallographically incorporated into aluminate ($CdAl_4O_7$) monoclinic structure and ferrite ($CdFe_2O_4$) spinel, dependent on the type of precursor used. The $CdFe_2O_4$ formation was initialed at about 150–300 °C lower than that of $CdAl_4O_7$. With Rietveld refinement analysis of the collated XRD data, the weight percentages of crystalline phases in the fired samples were quantified. To evaluate the cadmium incorporation efficiency, a transformation ratio (TR) index was devised. The TR values revealed that, to effectively incorporate cadmium, 950 °C was favored by γ-Al_2O_3 and 850 °C was for α-Fe_2O_3 within a 3-h sintering treatment. Constant pH leaching test (CPLT) was used to assess the metal stabilization effects, revealing a remarkable reduction of cadmium by transformation into $CdAl_4O_7$ and $CdFe_2O_4$. Both $CdAl_4O_7$ and $CdFe_2O_4$ were incongruently dissolved in an acid solution. The overall finding indicated a potentially feasible technology in cadmium-laden sludge stabilization.

Contents

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http://dx.doi.org/10.1016/j.jenvman.2016.10.037
0301-4797/

1. Introduction

Heavy metals contamination from industrial activities is a well-recognized environmental issue, with cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), zinc (Zn) and mercury (Hg) frequently encountered (Ahmaruzzaman, 2011; Hua et al., 2012; Jabłońska and Siedlecka, 2015). Of these heavy metals, cadmium shows greater mobility because it is highly water soluble (Bhatnagar and Minocha, 2009). Since 1990s, cadmium and its compounds have been classified as a "Category-I" carcinogen by International Agency for Research (IAR) on Cancer, and categorized into a "Group-B1" carcinogen by US Environment Protection Agency (EPA), owning to their high toxicity and long retention time in organisms after bioaccumulation (Järup, 2003; NTP, 2014; USEPA, 1999). In 2015, 24,200 tons of cadmium were produced globally, with 2000 tons increased, in comparison to the amount in 2014 (USGS, 2016). Cadmium is widely used in manufacturing Ni–Cd batteries, pigments, coatings, alloys, solar cells and stabilizers, etc. (USGS, 2014). When manufacturing these products, a considerable amount of cadmium is often released into aqueous medium and finally accumulated in sludge mainly in the form of hydroxide by mean of precipitation (Hossain and Mukherjee, 2012). Without any treatment, such hazardous sludge would leach cadmium out, posing great threats to the environment. The development of an effective and reliable technique to environmental-friendly and safely treat cadmium-laden sludge to achieve metal stabilization as well as volume reduction, with technical feasibility and cost-effectiveness, is often challenging.

One widely adopted approach of eliminating the hazards of heavy metals bearing wastes is by thermally converting them into non-hazardous products. An effective thermal stabilization process, inspired by ceramic manufacturing, utilizing various ceramic matrices to permanently stabilize heavy metals at attainable temperatures has been documented recently (Shih et al., 2006; Tang et al., 2010). The metals in wastes were successfully conversed into extremely stable crystalline products thus could virtually eliminate the leaching of metals under acid surrounding. The stabilized products may be beneficially used for different applications, such as construction materials. Therefore, the strength and effectiveness of such thermal stabilization technique has also been verified with tough leaching tests, including Toxicity Characteristic Leaching Procedure (TCLP) (Shih et al., 2006) and Constant-pH Leaching Test CPLT (Su et al., 2015). When thermally treated the sludge, most of cadmium become oxide and it is known to be very soluble in acid environment. Therefore, a search for more acid-resistant cadmium hosting phases is of paramount importance. Both γ-Al_2O_3 and α-Fe_2O_3 are two common industrial materials for manufacturing industries of ceramics and other construction products, and they are abundant in natural environment and locally available (Cornell and Schwertmann, 2003; Wefers and Misra, 1987). Certain equilibrium diagrams have reported that CdO could thermally react with γ-Al_2O_3 and α-Fe_2O_3 via solid state reaction, forming aluminate (Colin, 1968; Su et al., 2015) and ferrite (Chinnasamy et al., 2001a, 2001b; Mahmoud et al., 2003; Su et al., 2017), respectively. However, to promote a reaction mechanism into a feasible treatment technique, the processing parameters for fast and highly efficient incorporation of cadmium into crystalline products by alumina and iron oxide are must be intensely investigated. Furthermore, the robustness of the product(s) to acids should be examined with leaching tests to verify the metal stabilization effects (Su et al., 2015). It has been demonstrated that constant-pH leaching test (CPLT) is a useful tool to assess the leachability of products, because CPLT could maintain the pH in a steady level while most of other leaching tests (*e.g.*, TCLP and column leaching test, etc.) failed (Al-Abed et al., 2007; Islam et al., 2004; Jackson et al., 1984). CPLT is often considered to be proficient in comparing the leaching behavior of different solids (Islam et al., 2004; Su et al., 2015). During the CPLT, no buffer solution was input, avoiding any possible complexation of heavy metals that causes abnormally high leached metal concentrations (Cappuyns and Swennen, 2008).

In this research, an environmentally-friendly and safe strategy is developed to detoxify and stabilize simulated cadmium-laden sludge. We quantitatively described the cadmium incorporation efficiency over a range of relevant processing conditions, resulting in various crystalized cadmium-hosting product phases with desired acid-resistant capability. The leaching behavior of products was compared and discussed with constant-pH leaching test (CPLT) to better assess the benefits of adopting this strategy.

2. Materials and methods

2.1. Materials and sample preparation

All the chemicals used in this study were of reagent grade, and most of chemicals were purchased from Sigma-Aldrich, except for the alumina powder and nitric acid which were obtained from Sasol and BDH Chemicals, respectively. Cadmium oxide powder, a cubic CdO phase (ICDD PDF no. 75-0594), used as the cadmium source, representing its major form in the thermally treated cadmium-laden sludge. γ-Al_2O_3 was prepared by sintering the as-received PURAL SB alumina powder at 650 °C for 3 h (Fig. S1). The as-received PURAL SB alumina powder is boehmite (AlOOH, ICDD PDF no. 74-1895), as confirmed by XRD (Fig. S1). Anhydrous iron (III) oxide powder (α-Fe_2O_3; ICDD PDF no. 87-1166) (Fig. S1) was used as iron-rich precursor. The BET specific surface area (S_{BET}) of CdO, γ-Al_2O_3 and α-Fe_2O_3 yielded 2.63 ± 0.05 m^2/g, 180.88 ± 1.24 m^2/g and 4.30 ± 0.03 m^2/g, respectively. The BET measurement was conducted on a Beckman Coulter SA3100 Surface Area and Pore Size Analyzer using nitrogen adsorption at liquid nitrogen temperature. Prior to the BET tests, sample degassing was undergone at 150 °C for 3 h. To immobilize Cd, CdO was alternatively mixed with γ-Al_2O_3 and α-Fe_2O_3 at Cd/Al and Cd/Fe molar ratios of 0.25 and 0.50, respectively. The mixtures were well mixed through wet-milling, and then dried in a vacuum oven at 105 °C for 24 h. Next, mortar grinding was conducted to further homogenize the mixtures. Finally, the homogenized mixtures were pressed into Φ 20 mm pellets at 250 MPa, followed by a thermal treatment scheme at temperature range of 600–1000 °C with a retention time of 3 h.

2.2. Microstructures characterization and XRD analysis

The fired pellets were air-cooled to room temperature. Some of the fired pellets were surface polished for microstructure observation on a Hitachi S-4800 SEM system equipped with a secondary