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Copper stabilization in beneficial use of waterworks sludge and copper-laden electroplating sludge for ceramic materials

Yuanyuan Tang [a], Siu-Wai Chan [b], Kaimin Shih [a,*]

[a] *Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, Hong Kong Special Administrative Region*
[b] *Department of Applied Physics and Applied Mathematics, Henry Krumb School of Mines, Columbia University, New York, NY 10027, USA*

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ABSTRACT

A promising strategy for effectively incorporating metal-containing waste materials into a variety of ceramic products was devised in this study. Elemental analysis confirmed that copper was the predominant metal component in the collected electroplating sludge, and aluminum was the predominant constituent of waterworks sludge collected in Hong Kong. The use of waterworks sludge as an aluminum-rich precursor material to facilitate copper stabilization under thermal conditions provides a promising waste-to-resource strategy. When sintering the mixture of copper sludge and the 900 °C calcined waterworks sludge, the $CuAl_2O_4$ spinel phase was first detected at 650 °C and became the predominant product phase at temperatures higher than 850 °C. Quantification of the XRD pattern using the Rietveld refinement method revealed that the weight of the $CuAl_2O_4$ spinel phase reached over 50% at 850 °C. The strong signals of the $CuAl_2O_4$ phase continued until the temperature reached 1150 °C, and further sintering initiated the generation of the other copper-hosting phases ($CuAlO_2$, Cu_2O, and CuO). The copper stabilization effect was evaluated by the copper leachability of the $CuAl_2O_4$ and CuO via the prolonged leaching experiments at a pH value of 4.9. The leaching results showed that the $CuAl_2O_4$ phase was superior to the $CuAlO_2$ and CuO phases for immobilizing hazardous copper over longer leaching periods. The findings clearly indicate that spinel formation is the most crucial metal stabilization mechanism when sintering multiphase copper sludge with aluminum-rich waterworks sludge, and suggest a promising and reliable technique for reusing both types of sludge waste for ceramic materials.

1. Introduction

Pollution caused by hazardous metals has become an increasingly significant concern. Industrial processes such as electroplating produce solid sludge containing significant amounts of toxic metal-laden compounds (Peng and Tian, 2010). The electroplating sludge discarded each year in China contains more than 100,000 tons of hazardous metals (Wang, 2006), and about 1.3 million tons of wet electroplating sludge is generated each year in the United States, according to the US Environmental Protection Agency (US EPA, 1998). A widely accepted treatment process is the stabilization/solidification (S/S) method, which can convert hazardous wastes into chemically stable solids (Chen et al., 2011; Sophia and Swaminathan, 2005). The S/S method achieves pollutant encapsulation through an interlocking framework of hydrated minerals (Sophia and Swaminathan, 2005; Zhou et al., 2006). In addition to the severe environmental problems caused by industrial wastewater treatment, waterworks processes also generate treatment sludge containing the residues of treatment chemicals used as coagulants (usually aluminum based) (Vicenzi et al., 2005). The costs of handling the constantly generated waterworks sludge from drinking water treatment systems are significant and continually increasing as more stringent regulations are introduced (Babatunde and Zhao, 2007). The ceramic products may include a wide variety of interior and exterior tiles for walls and floors, decoration objects, partitioning materials, soundproofing and fire-resistant materials, which are with a continuous and increasing demand for built environment. In general, the products of solidification/stabilization (S/S) and waterworks sludge are disposed of in landfills (Babatunde and Zhao, 2007; Chen et al., 2011). However, the limited land available for waste disposal, and the adverse environmental impact (Malviya and Chaudhary, 2006), has made the development of effective and financially viable treatment technologies essential. Recent studies have evaluated the feasibility of using waterworks sludge as a raw material for ceramic production, and suggested that incorporating harmful metals into crystal structures can successfully reduce the risks to the environment (Lin and Weng, 2001; Vicenzi et al., 2005; Xu et al., 2008). In our previous studies (Tang et al., 2010, 2011), we found that simulated copper sludge reacted with the aluminum-rich precursors to form $CuAl_2O_4$ spinel phases after a 3-h sintering process. The

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* Corresponding author. Tel.: +852 2859 1973; fax: +852 2559 5337.
E-mail address: kshih@hku.hk (K. Shih).

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metal leachability after thermal treatment was also significantly reduced due to the formation of spinel phases (Tang et al., 2010, 2011).

As a waste-to-resource technology, the use of waste sludge resulting from water and wastewater treatment processes has attracted attention (Babatunde and Zhao, 2007). Recycling industrial and waterworks sludge for ceramic production can encourage a more sustainable use of natural resources and provide economic incentives. Moreover, if the application of waste waterworks sludge in ceramic systems can further benefit the stabilization of hazardous metals, it will simultaneously reduce the burden of waste management and environmental hazards. Therefore, in this study we evaluated the potential use of waterworks sludge and industrial metal sludge for ceramic materials, and explored the feasibility of metal immobilization during the sintering process. The work reported in this study is different from the previous studies (Tang et al., 2010, 2011), although similar copper reaction mechanisms were found to involve in the process. This study first used two real sludge samples derived from the waste streams (waterworks sludge and copper electroplating sludge) to observe the copper stabilization mechanisms under ceramic processing conditions.

The X-ray diffraction (XRD) technique is a basic material characterization method that has been successfully used for many decades to provide accurate information about the structure of materials (Pecharsky and Zavalij, 2009). The technique is often used as a qualitative technique to monitor and identify toxic metal phase(s) contained in samples (Dermatas and Meng, 2003; Malliou et al., 2007). However, when combined with the Rietveld refinement method, XRD can also be used to quantify the phase compositions of natural or industrial materials. It has been proven to be a reliable, precise, and very reproducible technique for quantifying the relative phase abundances (Walenta and Füllmann, 2004; Young, 1995), such as in the cement industry, where it is needed for accurate phase compositions. Therefore, the qualitative and quantitative functions of the XRD technique were adopted in this study to examine potential copper-hosting phases and to explore copper incorporation through ceramic sintering. A prolonged leaching procedure was also carried out under a pH value (4.9) which was much closer to the environmental condition to examine the stabilization result of copper in the sintered ceramic products.

2. Experimental methods

2.1. Sample preparation

The copper-containing electroplating sludge was collected from an industrial sludge treatment facility in Guangdong province in China, and then dried at 105 °C for use in the sintering experiments in this study. The sludge elemental compositions detected via X-ray fluorescence spectroscopy (XRF) (JEOL JSX-3201Z) were normalized by their oxide forms (Table 1), and showed that copper was the predominant constituent. A waterworks sludge sample collected in Hong Kong was heated for use as an aluminum-rich ceramic precursor. The sludge was fired at 900 °C for 30 min with a heating rate of 10 °C min^{-1} (Vulcan 3-550 PD) in the air and then cooled down to room temperature with a controlled cooling rate of 10 °C min^{-1}. The heated sludge was then ground into a powder for elemental composition analysis by XRF. Normalization into metal oxides (Table 2) showed aluminum to be the predominant constituent. Samples for the sintering experiments were prepared by mixing 900 °C calcined waterworks sludge with the dried electroplating sludge with a total dry weight of 60 g and a cation ratio of Cu:Al around 1:2.8 (with excess alumina available for copper incorporation). 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, then pressed into 20-mm pellets at 480 MPa to ensure consistent compaction of the powder samples for the sintering process. The overall sample preparation process can be organized in a schematic flow chart (Fig. 1).

2.2. Phase identification and quantification

To identify the potential phases responsible for the metal incorporation mechanisms in a 3-h sintering scheme, the pelletized powder mixture samples were fired in a high-temperature furnace (LHT 02/16 LB, LBR, Nabertherm Inc.) with a heating rate of 10 °C min^{-1} in the air for a 3-h dwelling time at targeted sintering temperatures, ranging from 650 to 1250 °C. After sintering, the samples were cooled down in the furnace to room temperature with a controlled cooling rate of 10 °C min^{-1} and ground into powders for XRD analysis. Phase formation during sintering was monitored using the powder XRD technique. The step-scanned XRD pattern of each powder sample was recorded by a Bruker D8 Advance X-ray powder diffractometer equipped with Cu $K\alpha_{1,2}$ X-ray radiation source (40 kV 40 mA) and a LynxEye detector. The 2θ scanning range was 10–90°, and the step size was 0.02° with a scan speed of 0.8 s step^{-1}. Qualitative phase identification was executed 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 quantitative analysis was carried out using TOPAS 4-2 (Coelho, 2003), which uses the Rietveld refinement method.

2.3. Leaching procedure

A prolonged leaching test was used to further examine the long-term leachability and leaching behavior of the sintered products. As the aim of this test was to distinguish the leaching characteristics of different copper-hosting phases, single-phase samples were considered preferable in the leaching experiment. Therefore, after identifying the potential copper-hosting phase(s) in the sintered products, single-phase copper samples were fabricated by extending the sintering time. In the modified leaching procedure, 10 mL of pH 4.9 acetic acid solution was used as the leaching fluid for 0.5 g of sample powder in each leaching vial. The acid solution was prepared according to fluid solution #1 listed in US EPA Method 1311 Toxicity Characteristic Leaching Procedure (US EPA, 1992). The leaching vials were rotated end-over-end at 60 rpm for agitation periods of 0.75–22 d. At the end of each agitation period, the leachates were filtered with 0.2 μm syringe filters. The pH values were tested with a pH meter (Thermo Scientific) and metal concentrations were measured with an ICP–AES (Perkin–Elmer Optima 3300 DV). The sample surface areas were determined from the nitrogen adsorption–desorption isotherms at liquid nitrogen temperature (77 K) on a Beckman Coulter SA3100 surface area and pore size analyzer by Brunauer–Emmett–Teller (BET) method.

3. Results and discussion

3.1. Characterization of the raw materials

According to the XRD pattern of the 105 °C dried copper-containing electroplating sludge in Fig. 2a, the predominant crystalline copper-hosting phase was detected to be posnjakite ($Cu_4(SO_4)(OH)_6(H_2O)$, PDF#83-1410). Other copper-hosting crystalline phases were identified as copper aluminum carbonate hydroxide hydrate ($Cu_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$, PDF#37-0630), malachite ($Cu_2(OH)_2CO_3$, PDF#76-0660) and copper oxide (CuO, PDF#80-1268). For waterworks sludge, the XRD pattern in Fig. 2b indicated that