



# Alumina polymorphs affect the metal immobilization effect when beneficially using copper-bearing industrial sludge for ceramics



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## HIGHLIGHTS

- Spinel formation acts as the most crucial metal stabilization mechanism.
- Substantial improvement of metal leachability in spinel-containing products.
- Different copper incorporation behavior in two alumina polymorph systems.
- Provide preferred operational parameters for safe recycling metal bearing sludge.

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## ABSTRACT

The feasibility of recycling copper-bearing industrial sludge as a part of ceramic raw materials was evaluated through thermal interaction of sludge with aluminum-rich precursors. To observe copper incorporation mechanism, mixtures of copper-bearing sludge with alumina polymorphs ( $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\alpha$ - $\text{Al}_2\text{O}_3$ ) were fired between 750 and 1250 °C. Different copper-hosting phases were identified by X-ray diffraction, and  $\text{CuAl}_2\text{O}_4$  was found to be the predominant phase throughout the reactions. The experimental results indicate different  $\text{CuAl}_2\text{O}_4$  initiating temperatures for two alumina materials, and the optimal temperature for  $\text{CuAl}_2\text{O}_4$  formation is around 1100 °C. To monitor the stabilization effect, prolonged leaching tests were carried out to leach sintered products for up to 20 d. The results clearly demonstrate a substantial decrease in copper leachability for products with higher  $\text{CuAl}_2\text{O}_4$  content formed from both alumina precursors despite their different sintering behavior. Meanwhile, the leachability of aluminum was much lower than that of copper, and it decreased by more than fourfold through the formation of  $\text{CuAl}_2\text{O}_4$  spinel in  $\gamma$ - $\text{Al}_2\text{O}_3$  system. This study clearly indicates spinel formation as the most crucial metal stabilization mechanism when sintering multiphase copper-bearing industrial sludge with aluminum-rich ceramic raw materials, and suggests a promising and reliable technique for reusing industrial sludge.

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## 1. Introduction

The sludge generated from the industry's wastewater treatment processes often contains high levels of hazardous metals, which poses a serious environmental concern in many areas of the world (Li et al., 2010; Chen et al., 2011). For example, in China, electroplating sludge discarded every year contains more than 0.1 Mt of hazardous metals (Wang, 2006). The U.S. Environmental Protection Agency (EPA) estimates that about 1.3 Mt of wet electroplating sludge is generated each year in the U.S. which requires disposal in hazardous waste landfills (USEPA, 1998). Sludge generated from

the electroplating industry are highly complex due to the presence of metal ions and other inorganics, which pose serious problems for their disposal (Sophia and Swaminathan, 2005). It has been suggested that the extraction of copper, nickel and chromium metals from sludge might not always be an economical operation, due to the influence of different facility scales and metal levels (Naja and Volesky, 2009). Solidification/stabilization (S/S) is a widely accepted treatment process for hazardous metal immobilization, and this method achieves pollutant encapsulation through an interlocking framework of hydrated minerals (Sophia and Swaminathan, 2005; Zhou et al., 2006; Chen et al., 2009). Portland cement is the most commonly used media in S/S, but in practice cement-based S/S products are still subject to disposal in secure landfills (Malviya and Chaudhary, 2006; Chen et al., 2011). Even

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when solidified and encapsulated in cement-based materials, metal-laden sludge still possesses enough long-term metal leachability to be a discharge concern, since the main immobilization mechanism was simply the reduction of available leaching surface (Yousuf et al., 1995; Asavapisit et al., 1997). The limited number of landfills capable of accepting S/S substances, together with the environmental threat of industrial sludge (Malviya and Chaudhary, 2006), has made the development of effective and economical treatment technologies essential.

A promising strategy has been reported to effectively incorporate metal-containing waste materials into a variety of ceramic products (bricks, tiles and refractory aggregates) (Okuno et al., 2004; Shih and Leckie, 2007). The potential reaction mechanisms were identified when sintering the simulated metal-containing sludge with alumina, hematite and kaolinite precursors, and the metal leachability of product phases was found to be reduced remarkably due to the change of mineral phases (Shih et al., 2006a,b; Tang et al., 2010, 2011a,b; Shih and Tang, 2011). In this way, this strategy synergistically removes hazardous metals from the waste stream and reuses waste material as a new source for marketable ceramic products. Converting hazardous metal-containing waste sludge into ceramic products enables the reduction of the environmental impact of industrial activities such as electroplating with a significant reduction in metal leachability as a result of irreversible phase transformation.

Copper can be transformed into  $\text{CuAl}_2\text{O}_4$  spinel, which is the predominant phase detected in the sintering process of CuO with Al-rich precursors at temperatures lower than 1000 °C. A goal of this study was to determine metal stabilization mechanisms and how the Cu-hosting phases evolve in the reaction system when recycling the Cu-laden industrial sludge as the raw material for usable ceramic products. Comparing to previous work (Tang et al., 2010, 2011a) using CuO to simulate the Cu-laden sludge, this study used the Cu-laden sludge from the industrial waste stream to observe the copper stabilization mechanisms. Therefore, in this study, the reaction processes were observed through sintering the mixture of Cu-laden industrial sludge and Al-rich precursors ( $\gamma\text{-Al}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3$ ). To investigate the metal stabilization effect in ceramic products, a prolonged leaching experiment was carried out to examine the metal leachability and leaching behavior of products sintered at different temperatures.

## 2. Experimental section

Copper-bearing industrial sludge was collected from an industrial sludge treatment facility in Guangdong Province in China, and the collected sludge was dried at 105 °C for further sintering experiments in this study. The sludge elemental composition detected via X-ray fluorescence (XRF) was normalized by their oxide forms (Fig. SM-1a in Supplementary material (SM)) and showed copper as the predominant constituent. The X-ray diffraction (XRD) pattern of the 105 °C dried sludge in Fig. SM-1b shows that the predominant crystalline Cu-bearing phase was posnjakite ( $\text{Cu}_4(\text{SO}_4)(\text{OH})_6(\text{H}_2\text{O})$ , PDF #83-1410). Other Cu-bearing phases were malachite industrial ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ , PDF #76-0660) and copper oxide (CuO, PDF #80-1916). Precursors of  $\gamma\text{-Al}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3$  were used to mix with the industrial sludge for ceramic sintering. The alumina precursors were fabricated from alumina powder purchased from Pural SB (Sasol), which was identified as boehmite ( $\text{AlOOH}$ ) by XRD and could be transformed into  $\gamma\text{-Al}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3$  under different thermal conditions (Zhou and Snyder, 1991). The boehmite powder was converted to the  $\gamma\text{-Al}_2\text{O}_3$  phase with a thermal treatment at 650 °C for 3 h, and the  $\alpha\text{-Al}_2\text{O}_3$  phase was obtained by calcining the boehmite powder at 1500 °C for 6 h.

Samples for sintering experiments were prepared by mixing each precursor with the dried industrial sludge for a total dry

weight of 60 g at a Cu:Al molar ratio of approximately 1:2.5 (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, pressed into 20-mm pellets at 480 MPa to ensure consistent compaction of the powder samples for the sintering process. A sintering scheme with a 3-h dwelling time at the targeted temperature was used for temperatures ranging from 750 to 1250 °C. After sintering, the samples were air-quenched and ground into powders for XRD analysis and the leaching test. Phase transformation 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 (Bruker MA) equipped with  $\text{Cu K}\alpha_{1,2}$  X-ray radiation source (40 kV 40 mA) and a LynxEye detector. The  $2\theta$  scanning range was 10–90°, and the step size was 0.02° with a scan speed of 0.8 s  $\text{step}^{-1}$ . Qualitative phase identification was executed by matching 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 leachability of each sintered sample was tested by a leaching procedure modified from the U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP), with a pH 2.9 acetic acid solution (extraction fluid #2) as the leaching fluid. Each leaching vial was filled with 5 mL of TCLP extraction fluid and 0.25 g of powder, and the vials were rotated end-over-end at 30 rpm for agitation periods of 18 h to 20 d. At the end of each agitation period, the leachates were filtered with 0.2- $\mu\text{m}$  syringe filters, the pH was measured, and the concentrations of the predominant metals were derived from ICP-AES (Perkin-Elmer Optima 3300 DV).

## 3. Results and discussion

### 3.1. Incorporation of copper during the sintering process

XRD patterns in Fig. 1 show the phase transformation when the Cu-laden sludge was sintered for 3 h with alumina precursors at temperatures ranging from 750 to 1250 °C. In Fig. 1a, peaks of the  $\text{CuAl}_2\text{O}_4$  phase were clearly observed, along with the disappearance of Cu-bearing phases (posnjakite, malachite and CuO) from the starting material when the mixture of sludge +  $\gamma\text{-Al}_2\text{O}_3$  was sintered at 750 °C for 3 h. Another Cu-bearing phase,  $\text{CaCu}_2\text{O}_3$  (PDF #34-0284), in the sintered products was also identified but generally with very low peak intensities. When the temperature was higher than 1100 °C, CuO reappeared with the generation of another Cu–Al–O compound ( $\text{CuAlO}_2$ ). When using  $\alpha\text{-Al}_2\text{O}_3$  as the precursor (Fig. 1b), the  $\text{CuAl}_2\text{O}_4$  spinel phase was detected at sintering temperatures above 850 °C, and CuO was observed as the main Cu-bearing component in the  $\alpha\text{-Al}_2\text{O}_3$  system at lower temperatures. The  $\alpha\text{-Al}_2\text{O}_3$  system behaved similarly to the  $\gamma\text{-Al}_2\text{O}_3$  system, in that the  $\text{CaCu}_2\text{O}_3$  phase also existed as a minor Cu-bearing component and the formation of  $\text{CuAlO}_2$  and the reappearance of CuO was observed at temperatures higher than 1100 °C. The XRD patterns of samples of sludge +  $\gamma\text{-Al}_2\text{O}_3$  sintered at 1000 °C for 3 h identified crystalline phases of  $\text{CuAl}_2\text{O}_4$ ,  $\alpha\text{-Al}_2\text{O}_3$ , quartz and  $\text{CaCu}_2\text{O}_3$ . Peak intensities of the  $\text{CuAl}_2\text{O}_4$  spinel phase were significantly higher than those derived from the other phases. Similarly, in the sludge +  $\alpha\text{-Al}_2\text{O}_3$  system sintered at 1000 °C, the  $\text{CuAl}_2\text{O}_4$  spinel also had higher peak intensity than other phases. The generation of the predominant  $\text{CuAl}_2\text{O}_4$  phase in both systems after ceramic sintering suggests that copper in the industrial sludge, despite its complicated phase composition, could be incorporated into the spinel structure. According to the standard  $\text{CuAl}_2\text{O}_4$  XRD pattern (PDF #33-0448), the strongest peak is located at  $2\theta = 36.87^\circ$ , corresponding to the diffraction plane of (3 1 1), and it is not overlapped by the major peaks of other phases in the system. Therefore, the  $2\theta$  range

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