

Copper Stabilization via Spinel Formation during the Sintering of Simulated Copper-Laden Sludge with Aluminum-Rich Ceramic Precursors

Yuanyuan Tang,[†] Stephen Sin-Yin Chui,^{*,†} Kaimin Shih,^{*,†} and Lingru Zhang[†]

[†]Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, China

^{*}Department of Chemistry and HKU-CAS Joint Laboratory on New Materials, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, China

 Supporting Information

ABSTRACT: The feasibility of incorporating copper-laden sludge into low-cost ceramic products, such as construction ceramics, was investigated by sintering simulated copper-laden sludge with four aluminum-rich ceramic precursors. The results indicated that all of these precursors (γ - Al_2O_3 , corundum, kaolinite, mullite) could crystallochemically stabilize the hazardous copper in the more durable copper aluminate spinel (CuAl_2O_4) structure. To simulate the process of copper transformation into a spinel structure, CuO was mixed with the four aluminum-rich precursors, and fired at 650–1150 °C for 3 h. The products were examined using powder X-ray diffraction (XRD) and scanning electron microscopic techniques. The efficiency of copper transformation among crystalline phases was quantitatively determined through Rietveld refinement analysis of the XRD data. The sintering experiment revealed that the optimal sintering temperature for CuAl_2O_4 formation was around 1000 °C and that the efficiency of copper incorporation into the crystalline CuAl_2O_4 structure after 3 h of sintering ranged from 40 to 95%, depending on the type of aluminum precursor used. Prolonged leaching tests were carried out by using acetic acid with an initial pH value of 2.9 to leach CuO and CuAl_2O_4 samples for 22 d. The sample leachability analysis revealed that the CuAl_2O_4 spinel structure was more superior to stabilize copper, and suggested a promising and reliable technique for incorporating copper-laden sludge or its incineration ash into usable ceramic products. Such results also demonstrated the potential of a waste-to-resource strategy by using waste materials as part of the raw materials with the attainable temperature range used in the production of ceramics.

INTRODUCTION

Copper, which is one of the hazardous metals that tend to bioaccumulate, is a major component of printed circuit board manufacturing, electroplating, wire drawing, copper polishing, paint production, wood preservatives, and printing operations.¹ At present, sludge with hazardous metal needs to be disposed of in controlled landfills. However, the high cost of this strategy, combined with the limited number of landfills capable of accepting toxic metal waste, has made the development of effective and economical treatment strategies essential. Many investigators have attempted to immobilize toxic metals using sorbents or cements, and correlated performance directly with metal leachability.^{2,3} However, the solidification/stabilization technologies via sorption or cementation mechanisms have not generally been successful in preventing leaching in acidic environments.⁴

On the basis of phase transformation at high temperatures, a variety of thermal treatments have been carried out to try to stabilize radioactive waste in vitrified glass or ceramic materials.⁵ However, the products are not considered to be reusable because of their radioactive nature. Similar to the vitrification process, thermal treatment with lower firing temperatures (900–1400 °C) may be a promising approach for the efficient incorporation of metal-containing waste materials into a variety of ceramic products, such as bricks, tiles, and refractory aggregates.^{6,7} Converting hazardous metal-containing waste sludge or its incineration ash into ceramic products enables the reduction of the environmental impact of

waste streams because of the significant reduction in metal leachability as a result of the irreversible phase change in mineral matter after thermal treatment.^{8,9} This strategy also explores the possibility of a waste-to-resource technology that uses waste materials as part of the raw materials in the production of new ceramics. It was previously reported that copper could be incorporated into the reaction products of minerals from heated soil, but the incorporation mechanisms and phase transformation pathways were not examined further.¹⁰ Although the publication of the equilibrium phase diagram for the Cu–Al oxide system has provided the opportunity to form copper aluminate spinel (CuAl_2O_4),¹¹ it is necessary to quantitatively evaluate whether this reaction plays an important role in stabilizing the hazardous metal by sintering the copper-laden sludge with common ceramic raw materials. Quantitative phase analysis using XRD data can be approached with a method named Rietveld refinement,^{12,13} which consists of fitting the complete experimental diffraction pattern with a calculated profile.¹⁴ Nowadays, this method has been widely used in characterizing natural or industrial materials, and has been proved to be a reliable, precise and very reproducible method to quantify the relative phase

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abundances,¹⁵ such as in the cement industry needed for accurate phase composition.

Kaolin and alumina are inexpensive raw ceramic materials that are rich in aluminum. Kaolin, which consists chiefly of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), is a common clay type. Most ceramics contained high percentages (40–65%) of kaolinite.¹⁶ Calcined kaolin is a major byproduct generated by heating spray-dried kaolin particles to render them anhydrous through their transformation into mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and silica (SiO_2). Alumina has several forms, including corundum ($\alpha\text{-Al}_2\text{O}_3$), and several metastable phases (γ , δ , κ , etc.).^{17,18} Therefore, in this study, four aluminum-rich precursors ($\gamma\text{-Al}_2\text{O}_3$, corundum, kaolinite, mullite) were examined for their ability to incorporate copper. The reaction pathways and levels of efficiency of copper incorporation into the spinel structure were quantitatively evaluated through ceramic sintering, and a prolonged leaching procedure was carried out to examine the stabilization result of copper in spinel structure.

EXPERIMENTAL METHODS

The simulated copper-laden sludge can be prepared by using lime to precipitate metal from its nitrate and chloride solutions, or directly via using copper hydroxide. When thermally treated, these copper-bearing phases decompose to copper oxide before sintering reaction occurs. Therefore, the efficiency of copper incorporation was investigated by firing CuO with $\gamma\text{-Al}_2\text{O}_3$, corundum, kaolinite and mullite. A short-sintering scheme with 3 h dwelling time¹⁹ at the targeted temperature was used for temperatures ranged from 650 to 1150 °C. CuO powder was purchased from Sigma Aldrich and the average particle size (d_{50}) was 18.8 μm . $\gamma\text{-Al}_2\text{O}_3$ was prepared from HiQ-7223 alumina powder (Alcoa Corp.), which has a measured average particle size (d_{50}) of 53.1 μm . Qualitative phase identification of HiQ-7223 alumina was confirmed by powder X-ray diffraction (XRD) as boehmite (AlOOH), which converts to the $\gamma\text{-Al}_2\text{O}_3$ upon thermal treatment at 650 °C for 3 h.¹⁷ The corundum used as another copper stabilization precursor was obtained by further calcining the as-formed $\gamma\text{-Al}_2\text{O}_3$ at 1500 °C for 6 h and has a measured average particle size (d_{50}) of 55.3 μm . The XRD patterns of these three raw materials are confirmed and provided in Figure S1 of the Supporting Information. USP-grade acid-washed kaolinite powder was obtained from Fisher Scientific as the kaolinite precursor used in this work. The mullite precursor was prepared by calcining the kaolinite precursor at 1350 °C for 24 h. XRD data suggested that both mullite and cristobalite (SiO_2) coexisted in the sample (Figure S2 of the Supporting Information).

Samples for the incorporation experiments were prepared by mixing each precursor powder with CuO powder for a total dry weight of 60 g at a molar ratio of Cu:Al = 1:2. The mixing process was carried out by ball milling the powder in water slurry for 18 h to homogenize the particle sizes of different raw material mixtures into a similar size range at around 10 μm as shown in Figure S3 of the Supporting Information. The slurry samples were dried and homogenized by mortar grinding, and then pressed into 20 mm pellets at 650 MPa before fired in a top-hat furnace (LHT 02/16 LB, LBR, Nabertherm Inc.). After sintering, the pellets were quenched in air for scanning electron microscopy (SEM) and ground into randomly oriented powders for XRD analysis. All SEM investigations were performed on a Hitachi S-4800 SEM system equipped with a secondary electron

detector for morphological information and a backscattered electron detector for energy dispersive spectroscopy (EDS). Prior to SEM, all pellet samples were polished using submicrometer diamond lapping films and gold coated to mitigate the electron charging effect. The secondary electron images were used to observe the microstructure of samples, and the backscattered electron images were employed to identify compositionally distinct areas. Point- and line-mode EDS and mapping analyses were also carried out throughout this work.

Phase transformation during sintering was monitored by using the powder XRD technique. The step-scanned XRD pattern of each powder sample was recorded by Bruker D8 Advance X-ray powder diffractometer equipped with $\text{Cu K}\alpha_{1,2}$ X-ray radiation and a scintillation detector. The 2θ scanning range was 10–90°, and the step size was 0.02° with a scan speed of 1 s/step. Qualitative phase identification was executed by matching powder XRD patterns with those retrieved from the standard powder diffraction database of International Centre for Diffraction Data (ICDD PDF-2 Release 2004). Four copper-containing crystalline phases were found in the products, including CuO (PDF#89–2529), CuAl_2O_4 (PDF#78–1605), CuAlO_2 (PDF#75–2356), and Cu_2O (PDF#77–0199). They were all subjected to quantitative phase analysis together with aluminum- and silicon-containing phases: corundum (PDF#10–0173), mullite (PDF#79–1455), and cristobalite (PDF#76–0938) using GSAS/EXPGUI, a program that uses the Rietveld refinement method.²⁰ To assess the validity of the refinement procedure in quantifying the crystalline phases described in this study, solid mixtures containing authentic CuO, CuAl_2O_4 , and glass as the amorphous phase in known weight fractions of were tested with satisfactory results (Table S1 of the Supporting Information).

Consequently, the leachability of CuO and phase-pure CuAl_2O_4 fabricated according to Figure S4 of the Supporting Information was tested in a leaching experiment modified from that described in U.S. EPA SW-846 Method 1311-TCLP, with a pH 2.9 acetic acid solution (extraction fluid #2) as the leaching fluid (USEPA, Method 1311). Each leaching vial was filled with 10 mL of TCLP extraction fluid and 0.5 g of powder sample. The leaching vials were then rotated end-overend at 60 rpm for agitation periods of 0.75 to 22 d. At the end of each agitation period, the leachates were filtered using 0.2 μm syringe filters, the pH values were measured and the concentrations of the Cu content were analytically derived using a flame type PerkinElmer model 3300 atomic absorption spectrometer (PerkinElmer Co. Ltd.) within the satisfactory calibration curve range (0.1–5 ppm, $R^2 = 0.9995$).

RESULTS AND DISCUSSION

The powder XRD data both qualitatively and quantitatively indicated that Cu could be successfully incorporated into CuAl_2O_4 structure by using the above-mentioned aluminum-rich precursors. Figure S5 of the Supporting Information shows the powder XRD patterns of products sintered at 1000 and 1150 °C with different precursors. The CuAl_2O_4 was predominantly observed in all four reactions at 1000 °C. At 1150 °C, CuAl_2O_4 decomposed to CuAlO_2 and corundum in the reaction using alumina ($\gamma\text{-Al}_2\text{O}_3$ or corundum) precursors. Under the same conditions, no CuAlO_2 was observed in the reaction with kaolinite or mullite precursor. Within the range of our sintering temperatures, both CuO and Cu_2O generated as the

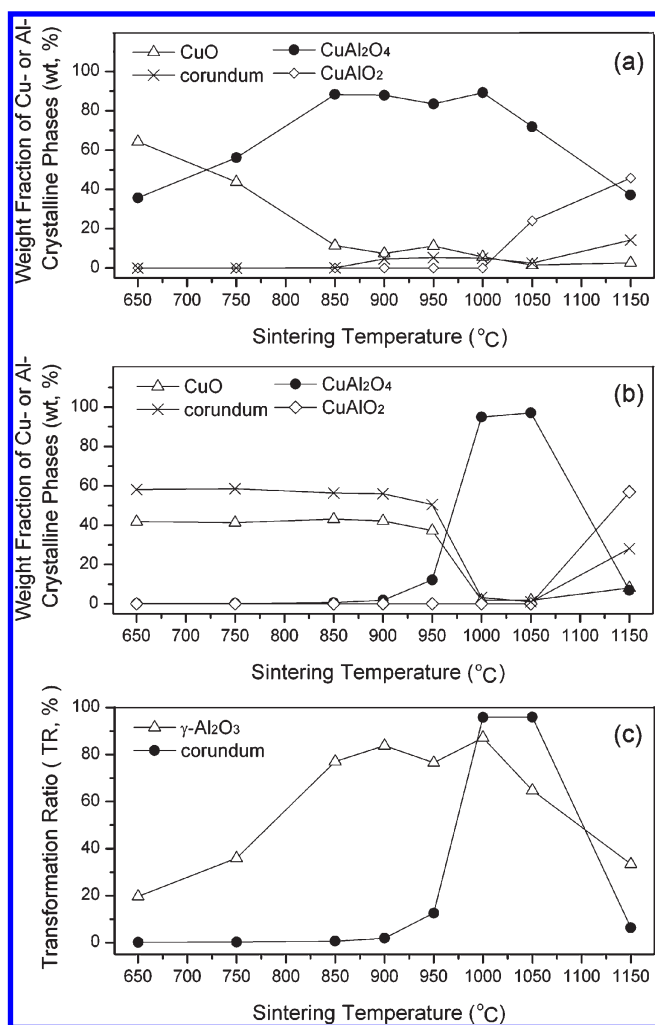


Figure 1. Variations of weight fractions of Cu- and Al-containing crystalline phases obtained from the CuO sintering reactions with (a) γ - Al_2O_3 and (b) corundum precursors, and (c) the transformation ratio (TR, %) of Cu into the CuAl_2O_4 spinel phase.

intermediate product and the reactants does not involve amorphization or evaporation as indicated in its phase equilibrium diagrams.¹¹ Furthermore, the observed weight losses of CuO heated at 950 °C and Cu_2O heated at 1150 °C for 3 h were $0.13 \pm 0.04\%$ and $0.98 \pm 0.03\%$, which suggested negligible copper evaporation within the sintering range of this study. In this work, a transformation ratio (TR) is used to determine the extent of copper incorporation efficiency among crystalline phases.

$$\text{TR}(\%) = \frac{\text{wt}\% \text{ of } \text{CuAl}_2\text{O}_4}{\text{MW of } \text{CuAl}_2\text{O}_4} \div \left(\frac{\text{wt}\% \text{ of } \text{CuAl}_2\text{O}_4}{\text{MW of } \text{CuAl}_2\text{O}_4} + \frac{\text{wt}\% \text{ of } \text{CuO}}{\text{MW of } \text{CuO}} + \frac{\text{wt}\% \text{ of } \text{Cu}_2\text{O}}{\text{MW of } \text{Cu}_2\text{O}} + \frac{\text{wt}\% \text{ of } \text{CuAlO}_2}{\text{MW of } \text{CuAlO}_2} \right)$$

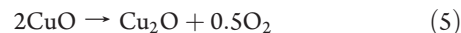
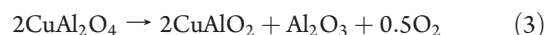
where MW = molecular weight and a TR value of 100% means complete transformation of copper into CuAl_2O_4 spinel.

Formation of CuAl_2O_4 Spinel from γ - Al_2O_3 and Corundum Precursors. The γ - Al_2O_3 is a low-temperature polymorph of Al_2O_3 and transformed to corundum at 1500 °C (Figure S1 of the Supporting Information). The chemical reactions for the formation of CuAl_2O_4 using γ - Al_2O_3 or corundum as

precursor are:



Upon sintering the mixture of CuO and γ - Al_2O_3 , the CuAl_2O_4 spinel was generally observed as the dominant product in this study (part a of Figure 1). At 650–850 °C, although the system was still dominated by the poorly crystalline γ - Al_2O_3 precursor, the growth of the crystalline CuAl_2O_4 was shown in the XRD result. When the mixture was sintered at 900 °C for 3 h, the development of corundum from the residual alumina content was observed in ~5% within the crystalline phases. This corundum formation temperature was approximately 100 °C lower than that of a previous study reported only with alumina.²¹ Our result highlights the role of CuO impurity in enhancing the extent of thermal transformation behavior of alumina. For the product sintered at 650 °C, the CuO and CuAl_2O_4 were refined with around 65 and 35%, respectively in the crystalline phases, which indicates that about 20% of copper was transformed from crystalline CuO into CuAl_2O_4 spinel (part c of Figure 1). The maximum TR of the $\text{CuO} + \gamma$ - Al_2O_3 samples reached 80% at temperatures between 850 and 1000 °C, and then declined at higher temperatures because of the CuAlO_2 formation as observed in part a of Figure 1. The potential reaction pathways are:¹¹



It is expected that in this experiment, eq 3 was the dominant mechanism, as cuprite (Cu_2O) was not observed in the system. In addition, the weight fraction of CuO dramatically decreased from 65 to 8%, indicating the successful stabilization of Cu within the temperature range of both CuAl_2O_4 and CuAlO_2 phase transformations.

For the reaction using corundum precursor, crystalline CuAl_2O_4 was found to increase within a relatively smaller temperature range of 900–1000 °C (part b of Figure 1). Unlike the reaction using γ - Al_2O_3 , no crystalline CuAl_2O_4 was observed below 900 °C. Nevertheless, a higher TR value (>90%) was achieved at 1000–1050 °C (part c of Figure 1). Similar to the reaction using γ - Al_2O_3 , no crystalline Cu_2O was observed in the samples sintered at above 1000 °C, and crystalline CuAlO_2 eventually dominated the system at the highest sintering temperature (1150 °C). The finding of different incorporation behavior using γ - Al_2O_3 and corundum precursors in the lower temperature range (<1000 °C) is similar to our previous study for sintering NiO with alumina precursors,⁸ in which we found that the reaction of NiO with γ - Al_2O_3 prevailed at low temperatures (<1150 °C), whereas the corundum precursor generally facilitated nickel incorporation at higher temperatures. The free energy of formation for γ - Al_2O_3 is higher than that for corundum.²¹ Thus, it may be concluded that the reaction between CuO and γ - Al_2O_3 is more energetically favored compared to the reaction between CuO and corundum, which explains the higher level of copper incorporation efficiency with

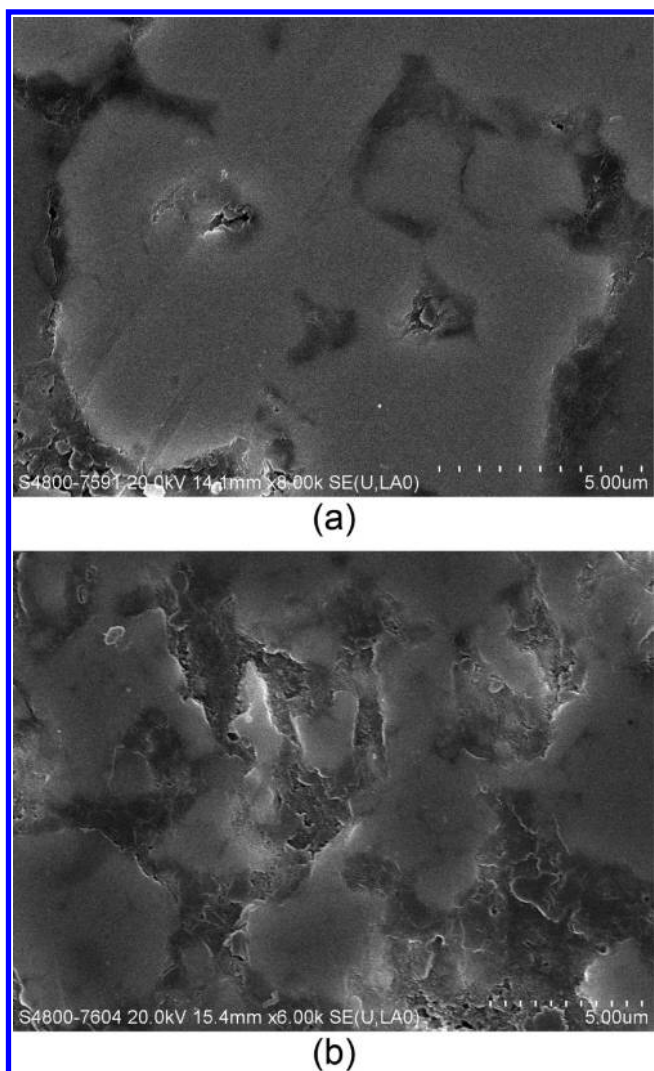


Figure 2. Secondary electron images of the polished surfaces of the products sintered from (a) the CuO + γ -Al₂O₃ mixture at 1000 °C for 3 h and (b) the CuO + corundum mixture under the same conditions. Both products show a high degree of spinel formation, but the product microstructure sintered from (b) the corundum precursor has a much more porous texture even after extensive polishing.

γ -Al₂O₃ at lower temperatures. When the $\gamma \rightarrow \alpha$ -Al₂O₃ transformation rate exceeds that of spinel crystallization using γ -Al₂O₃, the mechanism for CuAl₂O₄ formation is predominantly due to the reaction between corundum and CuO (eq 2). Therefore, at high temperatures (i.e., >1000 °C), the chemical reactions for these two alumina precursors might associate with in situ generated corundum that react with the surrounding CuO.

Figure 2 shows the microstructures of surface-polished samples sintered at 1000 °C for 3 h. Although EDS was used to confirm the chemical composition (Cu:Al atomic ratio \approx 1:2) of the CuAl₂O₄ grains produced in both the γ -Al₂O₃ and corundum precursor series, the products sintered from these two series demonstrated distinctively different microstructures in the scanning secondary electron micrographs. The product sintered from γ -Al₂O₃ precursor consisted of closely packed crystalline grains of CuAl₂O₄, whereas that from the corundum precursor had a very porous texture even subjected to intensive surface polishing. The fully dense microstructure sintered from the γ -Al₂O₃ precursor indicates the greater

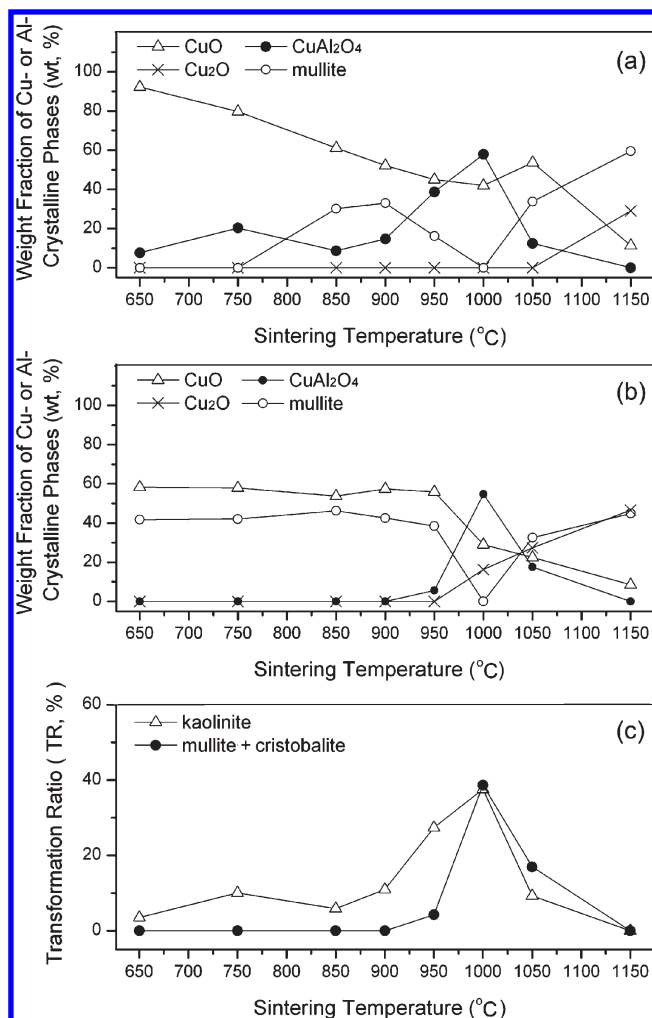


Figure 3. Variations of weight fractions of Cu- and Al-containing crystalline phases obtained from the CuO sintering reactions with (a) kaolinite, and (b) mullite precursors, and (c) the transformation ratio (TR, %) of Cu into the CuAl₂O₄ spinel phase.

diffusion barrier for continuous formation of CuAl₂O₄ from the remaining reactants. However, the porous microstructure sintered from the corundum precursor may provide greater contact opportunity for the remaining reactants through surface diffusion. This is also likely supported by the slightly higher TR value observed in the reaction with corundum precursor (Figure 1).

Formation of CuAl₂O₄ from Kaolinite and Mullite Precursors. The phase transformation of kaolinite through treatment has been extensively studied, and the reaction sequence is known to lead to the kaolinite-to-mullite series.^{22,23} Without impurity interference, the chemically bound water of kaolinite is removed at 550 °C, which is followed by the formation of amorphous metakaolin. At 1000 °C, mullite started to develop with excess amount of cristobalite converted from amorphous silica at around 1300 °C, even though cristobalite crystallization at a lower temperature was observed when the system was doped with nickel oxide.^{8,9} Both kaolinite and calcined kaolinite (mullite + cristobalite) are readily available ceramic raw materials. The feasibility of using them to stabilize copper in simulated laden sludge was also quantitatively evaluated using the same reaction condition as that for the two alumina precursors.

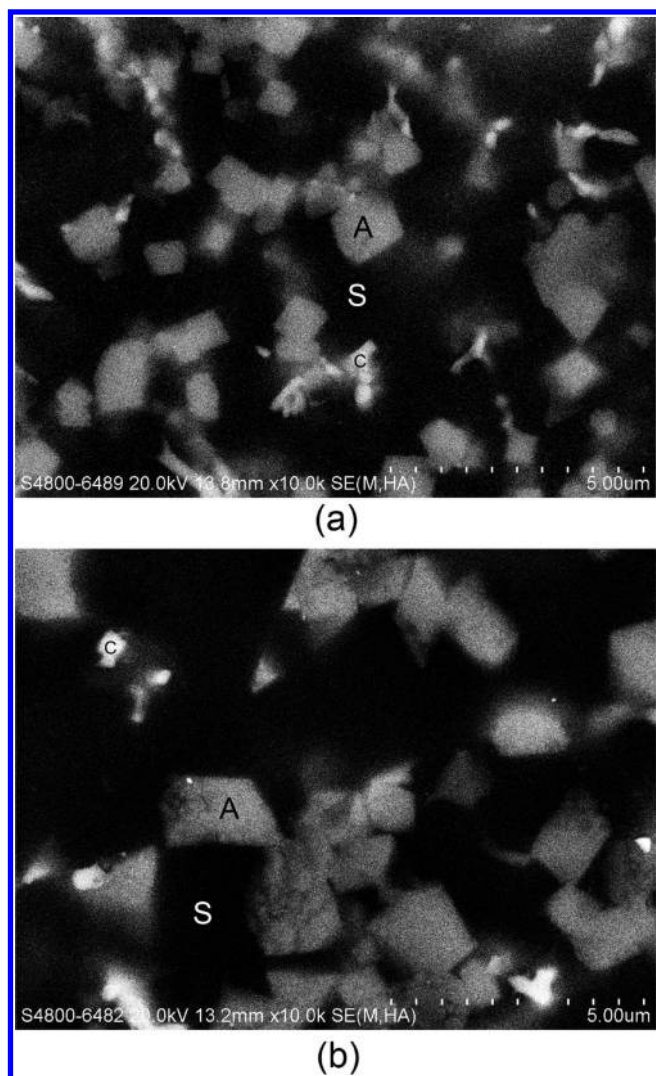
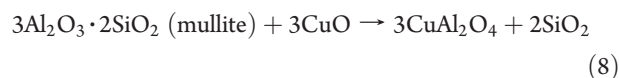


Figure 4. Backscattered electron images of the polished surfaces of the products obtained from reaction using (a) kaolinite and (b) mullite sintered at 1000 °C for 3 h. The grains marked “C” are the residual CuO reactants and the light-color grains marked “A” show the enrichment of both Cu and Al (CuAl₂O₄ spinel). The dark-color matrix (marked “S”) is strongly dominant by Si (cristobalite).

It has been reported that silica does not react with copper,²⁴ and for the sake of clarity, the quantitative distributions of the copper- and aluminum-containing crystalline phases from the kaolinite and mullite precursor systems were normalized in Figure 3 to allow the comparison of the results with those from the alumina precursor systems. With the kaolinite precursor, a smaller CuAl₂O₄ signal was detected at temperatures between 750 and 900 °C, showing that the formation of CuAl₂O₄ reaction could be initiated by metakaolin (eq 7). However, the small amount of spinel formation indicates that the solid-state reaction was confined to a limited extent, probably near the grain boundaries between the reactants, and that the majority of the packed particles still did not interact with each other. In contrast, there was neither spinel formation nor CuO reduction in the mullite precursor system before heating to 950 °C (part b of Figure 3).

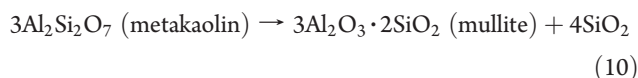
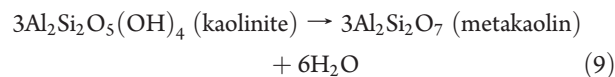
This observation clearly demonstrated the different reactivity in incorporating copper into the CuAl₂O₄ between the amorphous substance (metakaolin) and mullite, both derived from the

same kaolinite material. Similar to the cases for the alumina precursors, the formation of spinel was consistently optimized at 1000 °C for the reactions using kaolinite and mullite precursors. In the higher temperature range (>1000 °C), the quantity of spinel phases produced from the kaolinite and mullite precursors was very similar, which indicates that the copper incorporation behavior of these two precursors is essentially the same (eq 8) and reflects the prompt metakaolin–mullite transition:



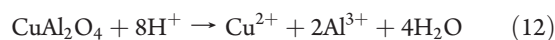
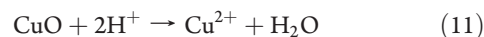
The crystalline copper TR for both precursors was found to be around 40% at its maximum temperature (1000 °C), and kaolinite generally showed a 10% TR at temperatures between 750 and 900 °C (part c of Figure 3).

Nevertheless, the microscopic textures of the copper-incorporated products reveal that substantially different mass transfer scenarios were initiated by the kaolinite and mullite precursors, even with similar crystalline copper TR. Figure 4 depicts the back-scattered electron micrographs of the 1000 °C and 3-h sintered samples, which shows the much larger CuAl₂O₄ grains derived from the mullite precursor. The CuAl₂O₄ grains sintered from the mullite precursor usually reached more than 1 μm in size (part b of Figure 4), in contrast to the case (in a submicrometer regime) obtained from kaolinite precursor (part a of Figure 4). Such a difference in microstructure is likely due to the enrichment of Al³⁺ ions in the mullite precursor, as the mullite was derived from the same kaolinite material by separating the excess amount of in situ generated SiO₂ (eqs 9 and 10):



In contrast, the homogeneously distributed Al³⁺ ions in kaolinite (or metakaolin) structure act as small nucleation sites for the crystallization of CuAl₂O₄. This resulted in large amount of small-sized CuAl₂O₄ microcrystals as depicted in part a of Figure 4. In the kaolinite and mullite precursor systems, the separated SiO₂ content served as a flux facilitating the frequency of contact between CuO and aluminum-containing reactants.

Leachability of CuO and CuAl₂O₄. The copper leachability of the CuAl₂O₄ sintered from the CuO and γ-Al₂O₃ mixture was compared with that of CuO. To ensure the complete transformation into the CuAl₂O₄ without residual reactants, the Cu/Al molar ratio = 1:2 mixture pellets were sintered at 990 °C for 20 d and ball milled into powder form. In leaching CuO and CuAl₂O₄ samples in an acidic environment, the reaction processes can be described as:



Therefore, a greater increase in leachate pH value, due to the more intensive consumption of protons, may indicate that the corresponding is more vulnerable to acidic attack and prone to

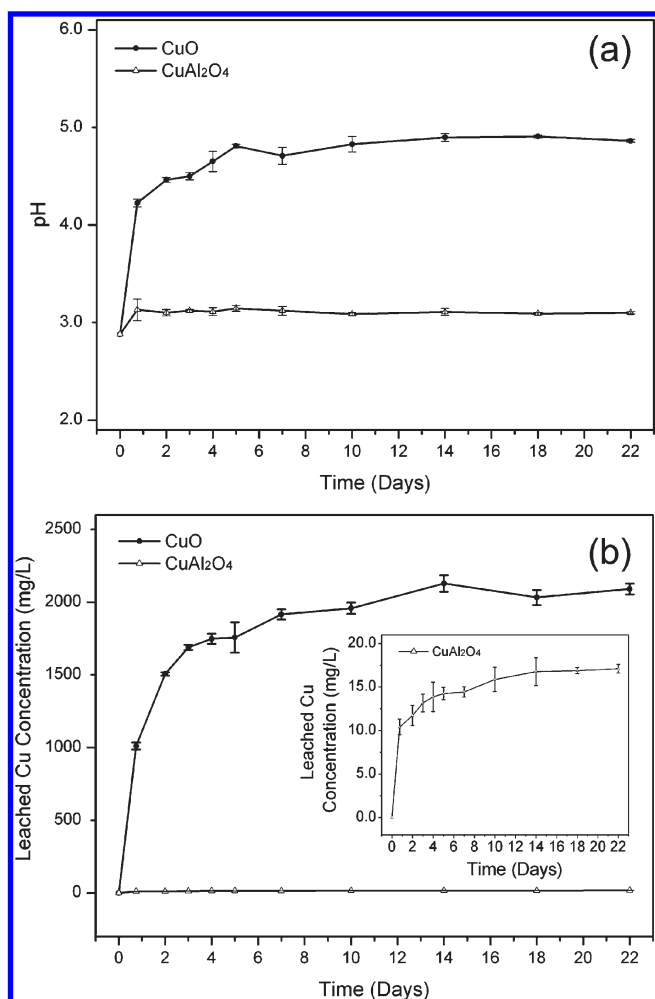


Figure 5. Variation of the (a) pH value and (b) copper concentrations of the leachates from CuO and the as-prepared CuAl₂O₄ powders. The CuAl₂O₄ powder was prepared by sintering the reaction mixture of CuO and γ -Al₂O₃ at 990 °C for 20 d. The leaching solutions were TCLP extraction fluid #2 (acetic acid solution) at pH 2.9. Each leaching vial was filled with 10 mL of extraction fluid and 0.5 g of powder, and then tumbled end-overend from 0.75 to 22 d.

destabilization when serving as a host for copper. Part a of Figure 5 shows that the pH value of the CuAl₂O₄ leachate was generally very stable throughout the leaching process (comparing to its starting value, pH 2.9). However, the pH value of the CuO leachate was found to increase significantly to ~pH 4.8 after 4–5 d of leaching. This result clearly indicates greater cation dissolution from CuO sample, which was accompanied by the severe destruction of crystals. Hence, it is demonstrated that the CuO sample is more vulnerable to proton-mediated dissolution compared to the CuAl₂O₄ one.

The copper concentrations in both the CuO and CuAl₂O₄ leachates are presented in part b of Figure 5, which shows that the leached copper from the CuO sample is 2 orders of magnitude greater than that from the CuAl₂O₄ sample. When the pH value of CuO leachate reached above 4.5, the level of copper leachability was greatly reduced and stabilized at ~2 g/L. However, although the CuAl₂O₄ leachate remained at a pH value of around 3.0 throughout the whole leaching process, the concentration of the leached copper was still significantly lower than that of the

CuO leachate at the end of leaching experiment. The result of prolonged leaching test favorably confirmed the good stabilization achieved through incorporating copper into a CuAl₂O₄ structure. Generally, a continuous-flow leaching reactor may better simulate the natural leaching environment. However, judging from the low leachability of stabilized product, the modified TCLP batch leaching test used in this study, which further extended the leaching time to 22 d, will be more effective in reflecting the leachability of such type of samples. As the four aluminum-rich precursors (γ -Al₂O₃, corundum, kaolinite, mullite) investigated in the study were all able to initiate the crystallization of the CuAl₂O₄ at an attainable sintering temperature (~1000 °C), the incorporation of copper-laden sludge into the fabrication process of some common ceramic products, such as those used for construction purposes, may be an effective and economical strategy to reduce the environmental hazard of copper-laden sludge.

■ ASSOCIATED CONTENT

S Supporting Information. One table and nine figures demonstrating the powder XRD patterns of the precursors used, selected sintered samples and examples of Rietveld refinement procedure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kshih@hku.hk (K.S.); chuissy@hkucc.hku.hk (S.S.-Y.C.).

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