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Copper Aluminate Spinel in the Stabilization and Detoxification of Simulated Copper-Laden Sludge

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Abstract
This study aims to evaluate the feasibility of stabilizing copper-laden sludge by the application of alumina-based ceramic products. The processing temperature, material leaching behaviour, and the effect of detoxification were investigated in detail. CuO was used to simulate the copper-laden sludge and X-ray Diffraction was performed to monitor the incorporation of copper into the copper aluminate spinel (CuAl$_2$O$_4$) phase in ceramic products. It was found that the development of CuAl$_2$O$_4$ increased with elevating temperatures up to and including 1000 °C in the 3 h short sintering scheme. When the sintering temperature went above 1000 °C, the CuAl$_2$O$_4$ phase began to decompose due to the high temperature transformation to CuAlO$_2$. The leachability and leaching behaviour of CuO and CuAl$_2$O$_4$ were compared by usage of a prolonged leaching test modified from U.S. EPA’s toxicity characteristic leaching procedure. The leaching results show that CuAl$_2$O$_4$ is superior to CuO for the purpose of copper immobilization over longer leaching periods. Furthermore, the detoxification effect of CuAl$_2$O$_4$ was tested through bacterial adhesion with *Escherichia coli* K12, and the comparison of bacterial adhesion on CuO and CuAl$_2$O$_4$ surfaces shows the beneficial detoxification effect in connection with the formation of the CuAl$_2$O$_4$ spinel. This study demonstrates the feasibility of transforming copper-laden sludge into the spinel phase by using readily available and inexpensive ceramic materials, and achieving a successful reduction of metal mobility and toxicity.

Keywords: Sludge; Spinel; Ceramic; Stabilization; Detoxification; Copper
1. Introduction

The discharge of hazardous metals into receiving waters is detrimental to human health and the environment. As a type of hazardous metal that is subject to potential bioaccumulation, copper may cause stomach and intestinal distress, liver and kidney damage, and anaemia in humans (Gardea-Torresdey et al., 1996). Copper is present in the wastewater generated from printed circuit board manufacturing, electroplating, wire drawing, copper polishing, paint production, wood preservatives and printing operations. Common strategies that are chosen to remove hazardous metals from wastewater include physicochemical processes such as precipitation, coagulation, reduction, ion exchange and membrane processes (Park et al., 2005). However, the treatments mentioned above always result in the production of large amounts of hazardous-metal bearing sludge which requires additional treatment.

At present, sludge with hazardous metal residues 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 highly toxic metal wastes, has made the development of effective and economical treatment technologies essential. Many investigators have attempted to immobilize toxic metals using sorbents or cements and then correlating the performance directly with metal leachability (Kapoor and Viraraghavan, 1996; Lin et al., 1998; Bailey et al., 1999). However, solidification/stabilization technologies via sorption or cementation mechanisms are not generally successful in the prevention of leaching in acidic environments, i.e. a pH value less than 4.0 (Bonen and Sarkar, 1995; Yousuf et al., 1995).
Based on phase transformation at high temperature, attempts to stabilize radioactive waste in vitrified glass or ceramic materials have been carried out through a variety of thermal treatments (Lewis et al., 1993; Lewis et al., 1994; Wronkiewicz et al., 1997; Wang et al., 2005; Shih and Leckie, 2007). However, the products are not reusable due to their radioactive nature. A similar thermal treatment process with relatively lower firing temperatures (900-1600 °C) compared to vitrification may be helpful in promoting the effective incorporation of waste materials into ceramic products, such as bricks, tiles, refractories, and aggregates (Teixeira da Silva et al., 1998; Shih and Leckie, 2007). Converting hazardous sludge to ceramic products via well-controlled thermal treatment can remove hazardous metals from the waste stream and enable them to become reusable. The leachability of hazardous metals can be reduced because of the change of mineral phase after thermal treatment. Shih et al. (2006a, 2006b) successfully stabilized simulated nickel sludge by sintering with alumina, hematite and kaolinite as the ceramic raw materials. They reported significant reduction of nickel leachability from the spinel phases of the products, compared to the phase of nickel oxide.

It was previously reported that copper could be incorporated into the products sintered from clay materials, but the incorporation mechanism and phase transformation pathway have not been discussed in detail (Wei et al., 2001). An equilibrium phase diagram for Cu$_2$O-Al$_2$O$_3$ system was published (Wartenberg and Reuch, 1935), and the formation of the copper spinel was obtained by calcining the co-precipitation mixture of copper and aluminium hydroxide (Gadalla and White, 1964). Jacob and Alcock (1975) investigated the thermodynamics of copper aluminate spinel (CuAl$_2$O$_4$) formation and delineated the equilibrium phase diagram of the
\( \text{Cu}_2\text{O}-\text{CuO}-\text{Al}_2\text{O}_3 \) system. The above equilibrium studies have provided a great opportunity to highlight the interaction between copper oxide and alumina at high temperatures. It is thus anticipated that the incorporation of copper-laden sludge into ceramic materials through thermal treatment may be a promising strategy for stabilizing hazardous copper wastes. However, the potential of initiating copper spinel formation in the industrial short-sintering scheme of ceramic products (i.e. tiles, insulators, refractories) will require further investigation.

As an environmentally benign product, the material’s surface should be capable of supporting microbial activities. The adhesion of bacteria is usually the key factor for developing biofilm on material surfaces, which later becomes the major support basis for other biological growth. Due to the strong aquatic toxicity, copper oxide has been used in paints for marine environments to reduce the formation of biofilm on material surfaces. Copper-based paint may work as a selective medium for organisms by creating a toxic boundary layer at the surface as the component biocides leach out (Evans, 1981; Douglas-Helders et al., 2003). The use of copper-based paints to prevent biofilm development and a biofouling effect has gained increasing attention due to its environmental impact of releasing toxic copper ions into aquatic ecosystems (Chamberlain et al., 1988; Katranitsas et al., 2003). It has been reported that concrete sewer pipes coated with copper oxide exhibit antimicrobial characteristics and can achieve 99% inhibition against the bacterium (Hewayde et al., 2007). Toxicities of compounds can be measured singly and in mixtures of various complexities, using acute toxicity bioassays (Fernández-Alba et al., 2001, 2002). Recently, Xu et al. (2005) conducted a bacterium attachment study to evaluate the effectiveness of antifouling. Therefore, the density of bacteria adhering to product’s surfaces may potentially be
used to evaluate the results of metal detoxification after the incorporation of hazardous copper waste into ceramics.

In this study, the effect of incorporating CuO, as the simulated copper-laden sludge, into γ-alumina (γ-Al₂O₃) ceramic precursors was observed under a short sintering process (3 h) with temperatures ranging 650-1150 °C. A prolonged leaching procedure similar to the toxicity characteristic leaching procedure (TCLP) was carried out to examine the stabilization effect of copper in the product phases. Whilst considering the toxic nature of CuO for microbial adhesion, the surfaces of CuO and the CuAl₂O₄ were compared through bacterial adhesion experiment to evaluate the detoxification effect of producing the copper aluminate spinel in ceramics.

2. Materials and Methods

When thermally treated, the metal components of sludge are usually first transformed into oxide forms and thus CuO (Sigma Aldrich) was used to simulate the thermal reaction of copper-laden sludge. Experiments were carried out by firing the mixture of CuO and γ-Al₂O₃ precursor. The γ-Al₂O₃ was prepared from HiQ-7223 alumina powder (Alcoa), which has a reported average particle size (d₅₀) of 54.8 nm. The HiQ-7223 alumina was confirmed by X-ray Diffraction (XRD) to be the boehmite phase (AlOOH; ICDD PDF # 74-1875), and after heat treatment at 650 °C for 3 h it was successfully converted to γ-Al₂O₃ with an XRD crystallite size of 2-5 nm (Zhou and Snyder, 1991; Wang et al., 2005). The γ-Al₂O₃ precursor and CuO were mixed to a total dry weight of 200 g at the Cu/Al molar ratio of 1:2, together
with 1 L of deionized water for ball milling of 18 h. The slurry samples were then
dried and homogenized by mortar grinding. The derived powder was pressed into 20
mm pellets at 650 MPa to ensure consistent compaction of the powder sample in
readiness for the sintering process. After sintering, the samples were air-quenched and
ground into powder for XRD analysis and the leaching test.

Phase transformations during sintering were monitored by XRD. The diffraction
patterns were collected using a Bruker D8 diffractometer (Bruker Co. Ltd.) equipped
with Cu X-ray tube operated at 40 kV and 40 mA. Scans were collected from 10 to
90° 2θ-angle, with a step size of 0.02° and a counting time of 1 s step⁻¹. Phase
identification was executed by matching XRD patterns with the powder diffraction
files (PDF) database of the International Centre for Diffraction Data (ICDD). The
leachability of the pure phase was tested using a leaching experiment which is a
leaching procedure modified from the U.S. EPA SW-846 Method 1311 - 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 10 mL
of TCLP extraction fluid and 0.5 g of powder. The leaching vials were rotated end-
over-end at 60 rpm for agitation periods of 0.75 to 22 d. At the end of each agitation
period, the leachates were filtered with 0.2 μm syringe filters, the pH was measured
and the concentrations of all metals were derived from ICP-AES (Perkin-Elmer
Optima 3300 DV).

In this study, the bacterial adhesion experiment was carried out to first qualitatively
observe the toxicity of CuAl₂O₄ surface. The *Escherichia coli* K12 bacteria strain was
chosen for use in this adhesion evaluation on the surfaces of soda-lime glass (silica-
based), CuAl₂O₄ and CuO pellets. The culture solution was prepared with 10 g of peptone bacteriological (Beijing Chemical Works, 44075-2H, 250 g), 10 g of NaCl (Riedel-deHaen) and 5 g of yeast extract in 1 L of water. The glass material was taken from the microscope slides commonly designed for laboratory work, and it is an example of a non-toxic surface in the study of bacterial adhesion. The CuO powder was pressed into pellets and heated at 950 °C for 3 h. This was to effectively enhance the pellet strength and surface smoothness to facilitate the experimental needs, but also aimed to maintain the phase status (CuO) of the material. The mixture of CuO and γ-Al₂O₃ powder (Cu/Al molar ratio = 1:2) was also pressed into pellets and heated until CuAl₂O₄ was observed as the single phase in the product (990 °C for 20 d). Both CuO and CuAl₂O₄ pellets derived from the above processes were later polished by the diamond lapping films progressively down to a diamond grit size of 0.1 μm.

Measurement of the surface roughness of glass, CuO and CuAl₂O₄ samples was conducted using a JPK Instruments atomic force microscope (AFM) equipped by silicon-cantilevers with a force constant of 0.1 N m⁻¹ under the Cleveland method (Cleveland et al., 1993). Height images (40 × 40 μm²) were used to calculate the roughness measurement based on the arithmetic average. Bacteria adhered on the substrata were stained with SYTO9 and observed using a fluorescence microscope (Nikon Eclipse E600).

3. Results and Discussion

3.1 Copper Spinel Formation
By sintering the mixture of CuO and \(\gamma\)-Al\(_2\)O\(_3\), copper incorporation may proceed under a recrystallization reaction as follows:

\[
\text{CuO + } \gamma\text{-Al}_2\text{O}_3 \rightarrow \text{CuAl}_2\text{O}_4
\]  

(1)

It has been reported that the incorporation ability of \(\gamma\)-Al\(_2\)O\(_3\) for nickel is affected by the sintering temperature (Shih et al., 2006a, 2006b). To investigate the effective temperature for alumina content to incorporate copper into the CuAl\(_2\)O\(_4\) in the practice of sintering construction ceramic products, a 3 h short sintering scheme at temperatures ranging from 650 to 1150 °C was conducted. According to the database of the CuAl\(_2\)O\(_4\) XRD pattern (ICDD PDF # 33-0448), its two major peaks are located at 2\(\theta\) = 36.868 and 31.294°, corresponding to the diffraction planes of (3 1 1) and (2 2 0) respectively. The result reveals that the sample sintered at 750 °C developed a distinguishable CuAl\(_2\)O\(_4\) crystalline phase as shown in Fig. 1a. Jacob and Alcock (1975) observed the formation of the CuAl\(_2\)O\(_4\) in their equilibrium thermal experiment (for 24 h) and reported the spinel formation temperature to start at 612 °C. However, when compared to the results observed in our short sintering experiment, it was discovered that an effective sintering period for industrial application to incorporate copper into CuAl\(_2\)O\(_4\) in ceramic products should be at least above 750 °C. Since the solid state reaction is usually affected by both thermodynamic conditions and the diffusion process, this comparison may further suggest that spinel formation at temperatures below 750 °C is largely limited by the prevailing slow diffusion although it is thermodynamically feasible at temperatures above 612 °C. Below 750 °C, the CuAl\(_2\)O\(_4\) phase formed by the short sintering scheme may only be limited at
the grain boundary of reactants, and the very small quantity of such phase in the system was not reflected in the XRD results.

Two 2θ ranges of the XRD pattern (2θ = 36.4-37.4° and 31.0-32.0°) were selected to further observe the peak intensity development to represent the CuAl₂O₄ spinel product generated from the system at elevated temperatures (Fig. 2). Figure 2a observes the crystallization of CuAl₂O₄ developed from the CuO + γ-Al₂O₃ precursor within the 2θ range of 36.4-37.4° at different sintering temperatures. Although there was a distinguishable CuAl₂O₄ phase in the 750 °C sintered sample, the substantial growth of CuAl₂O₄ in the system was observed to be at above 850 °C, which may indicate the energy needed to overcome the major diffusion barrier in the system. Below 1000 °C, the peak intensity of the CuAl₂O₄ phase increases as the temperature increases. However, at sintering temperatures higher than 1000 °C, the peak intensity of the CuAl₂O₄ phase was found to decrease with elevated temperatures.

The XRD patterns within the 2θ range of 31.0-32.0° (Fig. 2b) show that the decrease of CuAl₂O₄ at higher temperatures was due to the formation of another new Cu-Al oxide phase, cuprous aluminate delafossite (CuAlO₂; ICDD PDF # 75-2356). Figure 2b has further verified the optimal formation temperature of CuAl₂O₄ at 1000 °C, and the phase transformation to CuAlO₂ at higher temperatures was observed by the (0 0 6) diffraction plane signal of CuAlO₂ at 2θ around 31.63°. Since the decrease of CuAl₂O₄ at higher temperatures was accompanied with a corresponding increase of CuAlO₂ in the system, it is suggested that the formation of CuAlO₂ occurred immediately after the decomposition of CuAl₂O₄, or went through structural transformation by discharging the excessive aluminum and oxygen from the crystal
structure. Nevertheless, both phase transformation mechanisms indicate that the opportunity of immobilizing copper from the Al-O incorporated structures is small when this phase transformation process takes place at high temperatures. Together with the interaction between unreacted CuO and Al₂O₃ (Jacob and Alcock, 1975), the CuAlO₂ formation mechanisms at temperatures above 1000 °C can be organized in the following way:

\[
\begin{align*}
2\text{CuAl}_2\text{O}_4 & \rightarrow 2\text{CuAlO}_2 + \text{Al}_2\text{O}_3 + 0.5\text{O}_2 \\
2\text{CuO} & \rightarrow \text{Cu}_2\text{O} + 0.5\text{O}_2 \\
\text{Cu}_2\text{O} + \text{Al}_2\text{O}_3 & \rightarrow 2\text{CuAlO}_2
\end{align*}
\]

(2)

(3)

(4)

3.2 The Leaching Mechanisms

To investigate the effect of copper immobilization after the incorporation by the spinel structure, the preferred method was to first compare the leachability of single phase samples under the same leaching environment. Therefore, this study prepared a leaching experiment sample with CuAl₂O₄ as the only phase appearing in the sample. From the incorporation efficiency experiment, it was observed that 1000 °C as the sintering temperature could attain the highest yield of CuAl₂O₄ phase without initiating the formation of the CuAlO₂ phase, although small amounts of reactants (Al₂O₃ and CuO) were still observed in the system. To ensure the complete transformation of reactants to the product phase (CuAl₂O₄), a longer sintering time (20 d) was used to facilitate reaction equilibrium. Moreover, the sintering temperature of 990 °C, which is slightly less than 1000 °C, was chosen to further prevent the generation of the CuAlO₂ phase during the prolonged sintering process. The XRD
pattern in Fig. 1b shows the success achieved by preparing the CuAl$_2$O$_4$ sample, where no peak of CuO or Al$_2$O$_3$ reactant phase was found in the pattern.

Samples used in the leaching test were ground into powder and measured to ascertain the BET surface area to yield values of 1.35 m$^2$ g$^{-1}$ for CuAl$_2$O$_4$ and 0.17 m$^2$ g$^{-1}$ for CuO. The pH values are shown in Fig. 3a, which reveals the greater pH increase of CuO leachate. Within the first few days, the pH of CuO leachate experienced a significant increase which was then maintained at around 4.7-4.9 throughout the rest of the leaching period. In contrast, the pH of the CuAl$_2$O$_4$ leachate was maintained at the beginning value of its leaching fluid throughout the entire leaching period. The increase of leachate pH may arise due to the dissolution of cations through ion exchange with protons in the solution. This is accompanied by the destruction of crystals at the solid surface by the acidic leaching fluid. The increase in leachate pH may indicate that CuO is more vulnerable to proton-mediated dissolution. On the other hand, CuAl$_2$O$_4$ (sintered from $\gamma$-Al$_2$O$_3$ + CuO) may show higher intrinsic resistance to such acidic attack, even with higher surface areas.

As the leaching for solid is likely dominated by surface reactions, it is expected to be proportional to sample surface area. In addition, since the same weight of sample (0.5 g) was always used, the total copper content in the sample, subject to the different copper phases, should also be normalized for comparison. Figure 4 summarizes the amounts of leached copper from samples normalized with respect to the surface areas of tested solids. The copper in the CuO leachate was over 400 times higher than that in the CuAl$_2$O$_4$ leachate near the end of the leaching period. This confirms that the CuAl$_2$O$_4$ spinel phase has a higher intrinsic resistance to such acidic attack compared
to the CuO phase and the sintering strategy designed for copper-laden sludge is proven to be beneficial in stabilizing copper. The curve in the small diagram of Fig. 4 further provides the details of copper concentrations in the CuAl₂O₄ leachate.

When the pH of the CuO leachate reached ~ 4.9, the leaching of CuO stabilized at a copper concentration of ~ 2500 mg L⁻¹ (~ 10⁻¹.4 M) in the leachate. As a general assumption of cation-proton exchange mechanism, the destruction of copper oxide by the acidic attack of the solution can be expressed as:

\[ \text{CuO}(s) + 2\text{H}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{H}_2\text{O} \]  \hspace{1cm} (5)

However, the concentration of copper ions in the solution [Cu²⁺(aq)] is also limited by the potential precipitation/dissolution reactions, such as in respect to Cu(OH)₂(s):

\[ \text{Cu(OH)}_2(s) \leftrightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \]  \hspace{1cm} (6)

where the solubility constant \((K_{sp})\) of Eq. 6 is \(10^{-19.25}\) (Stumm and Morgan, 1996). At pH 4.9, the product of \([\text{Cu}^{2+}(\text{aq})] \times [\text{OH}^-(\text{aq})]^2\) was found to be \(10^{-19.6}\), which is very close to the \(K_{sp}\) of Cu(OH)₂(s). This result indicates that the system was very close to the saturation of Cu(OH)₂(s) and the stabilization of copper concentration in the CuO leachate was likely controlled through the equilibrium with the Cu(OH)₂(s) phase.

When leaching the CuAl₂O₄ phase, a “congruent dissolution” through the cation-proton exchange reaction can be written as:
CuAl\(_2\)O\(_4\) (s) + 8H\(^+\) (aq) → Cu\(^{2+}\) (aq) + 2Al\(^{3+}\) (aq) + 4H\(_2\)O \hspace{1cm} (7)

Such congruent dissolution would result in a theoretical [Al\(^{3+}\) (aq)]/[Cu\(^{2+}\) (aq)] molar ratio of 2.0 in the leachates. However, this ratio was observed at 0.75-0.80 in the leachate of CuAl\(_2\)O\(_4\) as shown in Fig. 3b. Since the system was maintained in a more acidic environment (~ pH 3.2) and the copper concentration was much lower than that of the CuO leachate, the copper concentrations in the leachates of CuAl\(_2\)O\(_4\) were all considerably under-saturated regarding to the Cu(OH)\(_2\) (s) phase. The aluminium concentrations measured in the CuAl\(_2\)O\(_4\) leachates were ~ 9.5 mg L\(^{-1}\) (~ 10\(^{-3.45}\) M).

The reaction of amorphous aluminium hydroxide precipitation/dissolution is:

am\bullet Al(OH)\(_3\) (s) ⇌ Al\(^{3+}\) (aq) + 3OH\(^-\) (aq) \hspace{1cm} (8)

where the solubility constant (K\(_{sp}\)) of Eq. 8 is 10\(^{-32.7}\) (Stumm and Morgan, 1996). The product of [Al\(^{3+}\) (aq)] \times [OH\(^-\) (aq)]\(^3\) was found to be 10\(^{-35.9}\) and it did not reach the saturation ([Al\(^{3+}\) (aq)] \times [OH\(^-\) (aq)]\(^3\) = 10\(^{-32.7}\)) of amorphous Al(OH)\(_3\) (s) either. Therefore, this suggests that the leaching behaviour of CuAl\(_2\)O\(_4\) in this experiment is likely to be an incongruent dissolution, where the majority of the Al-O bonds still remained on the CuAl\(_2\)O\(_4\) spinel surface. Although some previous studies (Cailleteau et al., 2008; Ohlin et al., 2010) have further suggested the reorganization of remaining molecules in incongruent dissolution scenarios, the overall result indicates the existence of an Al-rich layer on the leached CuAl\(_2\)O\(_4\) surface, which is beneficial for preventing the further leaching of Cu and may increase product durability.

3.3 Adhesion of E. coli
Since the density of bacteria adhering to the product surface may potentially be used to evaluate the results of metal detoxification, this study first conducted a qualitative comparison of bacterial adhesion on the substrata of the CuAl$_2$O$_4$ spinel, CuO and soda-lime (silica-based) glass. Experimental studies have suggested the importance of the physicochemical and thermodynamic properties of both the substrata and the bacterial cell surface during the process of bacterial adhesion (Van Loosdrecht et al., 1989; Sjollema et al., 1990; Vadillo-Rodriguez and Logan, 2006).

In this study, a type of testing bacteria, *E. coli* K12, was cultivated in a solution with a pH of ~ 6.5 and all the substratum samples were collectively placed in the same solution for better comparison. Since surface roughness may impact bacterial adhesion (Brant and Childress, 2002), the tested surfaces of samples were polished using diamond lapping films and the roughness values were measured by AFM to be 2.3±1.7, 491±192 and 369±90 nm for glass, CuAl$_2$O$_4$ and CuO, respectively.

Figure 5 shows the results from the comparison of *E. coli* bacterial adhesion on the surface of glass, CuAl$_2$O$_4$ and CuO after 18 h of bacterial cultivation. The amount of *E. coli* adhering to the glass surface visibly surpassed the amount on the surfaces of both the CuAl$_2$O$_4$ and CuO samples (Fig. 5a). However, due to the toxicity effect, no bacterial adhesion was found on the surface of the CuO substratum as shown in the Fig. 5c. With much lower copper leachability as compared to CuO, the CuAl$_2$O$_4$ spinel clearly developed bacterial adhesion on the surface which showed its capacity to support microbial activities, although the level was lower than that of the glass substratum (Fig. 5b).
As the inhibition effect of copper oxide on biofouling has already been indicated (Evans, 1981; Balls, 1987; Chamberlain et al., 1988; Hodson and Burke, 1994; Douglas-Helders et al., 2003; Katranitsas et al., 2003; Hewayde et al., 2007), the comparison result of glass and CuO in this study is consistent with previous findings. Moreover, some studies suggested that the increase of nano-scale roughness of a surface increases bacterial adhesion (Shellenberger and Logan, 2002); other studies have demonstrated no significant relationship between surface roughness and bacterial adhesion (Li and Logan, 2004). In our work, the highest level of bacteria adhered to the glass surface, even with much lower roughness, thus indicating the dominant effect of substrata material. The growth of bacteria on the surface of the CuAl$_2$O$_4$ substratum suggests the successful detoxification of copper through the stabilization strategy of incorporating CuO into the aluminate spinel phase. Since the formation of a biofilm covering on a surface begins with the adhesion of a small number of bacteria, the results shown here provide direct evidence of the environmental friendliness of waste-incorporated ceramic products. Such information on the intrinsic properties of material is also important and beneficial when aiming to minimize the environmental impact even after the end of a product’s life.

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References


Fig. 1. The XRD pattern of the CuO + γ-Al₂O₃ system shows the formation of the copper aluminate spinel when sintering at (a) 750 °C for 3 h, and (b) 990 °C for 20 d. The “C” represents copper oxide (CuO, ICDD PDF # 48-1548) and the “S” is for the copper aluminate spinel (CuAl₂O₄, ICDD PDF # 33-0448). The XRD pattern in (b) shows that CuAl₂O₄ was the only phase in the sample and it was later used to test the CuAl₂O₄ leachability.
Fig. 2. The comparison of XRD patterns between (a) \(2\theta = 36.4^\circ\) and \(37.4^\circ\) (b) \(2\theta = 31.0^\circ\) and \(32.0^\circ\) for CuO + \(\gamma\)-Al\(_2\)O\(_3\) samples (with a molar ratio for Cu:Al of 1:2) sintered at 650 - 1150 °C for 3 h. The formation of CuAl\(_2\)O\(_4\) was found to reach its maximum at 1000 °C, and the curves at the top-right corners of (a) and (b) illustrate the relative intensities of the spinel peaks at \(2\theta = 36.868^\circ\) and \(2\theta = 31.294^\circ\), respectively. The phase transformation to CuAlO\(_2\) at higher temperatures was observed by the peak at \(2\theta\) around 31.63°.
Fig. 3. The (a) pH values and (b) [Al]/[Cu] molar ratios of the leachates of the CuO and CuAl$_2$O$_4$ phases. The leaching solution was TCLP extraction fluid no. 2 (acetic acid solution) with a pH of 2.9. Each leaching vial was filled with 10 ml of extraction fluid and 0.5 g of powder sample, and then rotated end-over-end between 0.75 and 22 d.
Fig. 4. Normalized copper concentrations in the leachates of CuO and CuAl$_2$O$_4$. The surface area of CuO powder is 0.17 m$^2$ g$^{-1}$ and the surface area of CuAl$_2$O$_4$ is 1.35 m$^2$ g$^{-1}$. The leaching solution was TCLP extraction fluid no. 2 (acetic acid solution) with a pH of 2.9. Each leaching vial was filled with 10 ml of extraction fluid and 0.5 g of powder samples, and then rotated end-over-end between 0.75 and 22 d. The curve in the small diagram further provides the details concerning the copper concentrations in the CuAl$_2$O$_4$ leachate.

Fig. 5. The *Escherichia coli* K12 bacterial adhesion on the surface of (a) glass, (b) CuAl$_2$O$_4$ and (c) CuO. All three materials were used as substrate and cultured for 18 h in the same solution containing *E. coli* K12 bacteria.