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Cubic and Tetragonal Ferrite Crystal Structures for Copper Ion Immobilization in Iron-rich Ceramic Matrix

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Abstract

This study proposed a strategy by reusing the incineration ash of municipal wastewater sludge as ceramic materials to immobilize copper. After sintering the mixture of CuO and sludge ash, hematite (\(\alpha\)-Fe\(_2\)O\(_3\), one major component) incorporated copper into
cubic CuFe\(_2\)O\(_4\). To observe copper incorporation mechanisms, mixtures of CuO+\(\alpha\)-Fe\(_2\)O\(_3\) were sintered from 650 to 1050 °C, and different copper incorporation behavior was detected. A low temperature CuFe\(_2\)O\(_4\) phase with tetragonal structure was detected at 750 °C, and the cubic CuFe\(_2\)O\(_4\) developed at 1000 °C. The incorporation efficiencies were first quantitatively determined by Rietveld refinement analysis of the X-ray diffraction data. The maximum copper incorporation into tetragonal and cubic CuFe\(_2\)O\(_4\) reached around 80% and 73%, respectively. The leachability analysis pointed to superiority of both copper ferrites in stabilizing copper, suggesting a promising technique for incorporating copper into the iron-rich ceramic matrix. Both tetragonal and cubic CuFe\(_2\)O\(_4\) were observed with incongruent leaching behavior, but the lower copper concentrations and higher [Cu]/[Fe] ratio in tetragonal CuFe\(_2\)O\(_4\) leachates indicates its higher capacity for copper stabilization. With high transformation ratio into CuFe\(_2\)O\(_4\) phases and dramatic reduction in metal leachability, the beneficial use of sludge ash to immobilize hazardous metal contaminated soil may be potentially succeeded.

**Keywords**

Municipal wastewater sludge; Copper ferrite; Quantification; Ceramics; Leaching; Immobilization
1. Introduction

The release of metals from mine activities to the surrounded sites can pose severe soil contamination, and may last for a long time without remediation.\textsuperscript{1,2} Once in the soil, the metal pollutants may disperse mechanically and undergo weathering reactions, leading to metal ion distribution within the soil system in forms more mobile than the original ones.\textsuperscript{3} Remediation approaches such as soil flushing, vacuum extraction, electro reclamation, bioremediation, and soil washing\textsuperscript{4} are employed for metal-contaminated soil, but methods above are highly challenging and expensive for a large scale remediation.\textsuperscript{5,6} Other investigators have also attempted to immobilize hazardous metals in contaminated soil by adding amendments that are able to adsorb, complex, or (co)precipitate elements in the soil.\textsuperscript{7-9} The suggested copper immobilization mechanisms were reported to precipitate as copper carbonates and oxy-hydroxides, and formation of SO\textsubscript{4}\textsuperscript{2-} or PO\textsubscript{4}\textsuperscript{3-} complexes.\textsuperscript{8} However, the mobility of heavy metals such as copper in soil is strongly pH dependent, and usually reaches the lowest value at slightly alkaline.\textsuperscript{8} Once in acidic conditions, the immobilization effect of copper will be destroyed.\textsuperscript{8,10}

By adding aluminum-rich materials into hazardous metal waste, the metals can be stabilized through well-controlled thermal treatment schemes.\textsuperscript{11-14} By thermally reacting with alumina and kaolinite precursors, the nickel and copper in the spinel-type crystalline structure were found to have substantial reduction in their
leachability under acidic environments.

Sewage sludge (municipal wastewater sludge) is generated with huge quantity in urban environments, resulting from the accumulation of solids through wastewater treatment. With complex and variable organic and inorganic substances, sewage sludge may contain viable pathogens and parasites as well as a variety of potentially toxic elements and compounds. The amount of sludge produced annually is keeping dramatic increase all over the world. In Europe, the production of dry sewage sludge is in average 90 g per person per day, and there will be an increase of 50% by year. While in Hong Kong, the amount of sludge will increase from the current quantity of about 800 tons per day to some 1,500 tons per day by 2014, and subsequently over 2,000 tons per day in 2020. The disposal of sewage sludge is one of the most difficult problems to be solved, and the need to achieve a sustainable sludge management strategy has become of global concern. Incineration has become an alternative to largely reduce the sludge volume, destruct pathogen agents, and remove organic pollutants for easier and safer handling and disposal. Sludge incineration technology, as one of the most attractive disposal methods in the world, was also chosen by Hong Kong government as the core treatment technology to resolve sludge problems. Nevertheless, approximately 30% of the solids remain as residues after sludge incineration. With further development of the incineration technology, the subsequent disposal of incineration residues is becoming a serious concern.
Since sewage sludge ash always contains aluminum, silicon, and iron as the main components, as a waste-to-resource technology, the use of sludge resulting from wastewater treatment processes has attracted much attention. More than 70% of the total amount of sewage sludge generated in Hong Kong is through the chemically enhanced primary treatment (CEPT). CEPT involves the use of chemical coagulants (such as alum, lime, ferric chloride, and polyaluminum chloride) to induce coagulation or flocculation of the suspended particles. Once the incineration technology was adopted, iron and/or aluminum might become the main components in the ash after sludge incineration process. Therefore, it is predicted that the sludge ash may be potentially used to stabilize metals in contaminated soils. In this study, the sewage sludge ash will be reused and its potential for effectively stabilizing hazardous copper during the sintering process will be evaluated. Furthermore, to quantify the reaction mechanisms and immobilization efficiencies, the simulated system will also be analyzed to assist in the exploration of metal incorporation processes. A prolonged leaching experiment will be carried out to examine the copper stabilization effect, and the leaching behavior of the sintered products will be further discussed.

2. Experimental

The collected CEPT sludge sample was first dried at 105 °C, and the weight loss of the sludge calcined at a temperature range of 200-1000 °C was illustrated in Figure S1.
The weight of the dried sludge significantly reduced from 200 to 500 °C, and kept stable afterwards. The ash from 900 °C and 30 min fired sludge was ground into powder for elemental composition analysis by X-ray fluorescence spectroscopy (XRF) (JEOL JSX-3201Z). Normalization into metal oxides (Figure S2) shows Si, Fe, Ca and Al to be the major constituents in the ash. The XRD pattern (Figure S3) further indicates predominant iron-containing crystalline phase as hematite (Fe₂O₃), while Si, Ca and Al are mainly contained in hauyne (Na₆Ca₂Al₆Si₆O₂₄(SO₄)₂), anhydrite (CaSO₄), and a type of zeolite (Na₆(AlSiO₄)₆). Works by others also reported the existence of aluminosilicate and anhydrite phases in the sewage sludge ash.

The 900 °C and 30 min fired sludge was used as soil amendment, and mixed with copper oxide (Sigma Aldrich) which was simulated as the predominant pollutant of the contaminated mining areas. Since both aluminum and iron will potentially react with copper in the system, samples were first prepared by mixing CuO and the sludge ash with the molar value of Al and Fe together as two times of Cu. The mixture was then sintered at 950 °C, and the XRD pattern (Figure S4) shows Fe₂O₃ as the only component reacting with copper and forming CuFe₂O₄ product phase. Therefore, the CuO was further mixed with the sludge ash at a Cu:Fe molar ratio of 1:2 to guarantee the maximum production of CuFe₂O₄ in the sludge ash system. To explore the detailed mechanisms of copper incorporation, the Fe₂O₃ was used as iron-rich material to react with CuO at a Cu:Fe molar ratio of 1:2. All mixing processes were 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, and then fired. A sintering scheme with a 3-h dwelling time at the targeted temperature in a high-temperature furnace (LHT 02/16 LB, LBR, Nabertherm Inc.) was used for temperatures ranging from 650 to 1050 °C with furnace-controlled cooling.

Phase transformation during sintering was monitored using the powder X-ray diffraction (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 Kα1,2 X-ray radiation source (40 kV 40 mA) and a LynxEye detector. The 2θ scanning range was 10 to 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 powder XRD patterns with those retrieved from the standard powder diffraction database of the International Centre for Diffraction Data (ICDD PDF-2, Release 2008). In hematite series, the crystalline phases in the products are all subjected to quantitative phase analysis using Topas 4-2, which employs the Rietveld refinement method. The refinement quality was monitored by the reliability values provided in Table S1.

As one objective of this study was to distinguish the leaching characteristics of different copper-hosting phases, single-phase samples were considered preferable in the leaching experiment. The leaching experiments for CuO and copper-containing product phase(s) were conducted by a method modified from the U.S. Environmental
Protection Agency’s SW-846 Method 1311: Toxicity Characteristic Leaching Procedure (TCLP), with an acetic acid solution (extraction fluid #2, pH 2.9) used as the leaching fluid. Each leaching vial was filled with 10 mL of leaching fluid and 0.5 g of the powder sample and rotated end-over-end at 60 rpm for 0.75 to 22 days. At the end of each agitation period, the leachates were filtered using 0.2-µm syringe filters, the pH was determined, and the concentrations of all metals were derived by inductively coupled plasma atomic emission (Perkin-Elmer Optima 3300 DV).

3. Results and discussion

3.1. Potential of reusing municipal wastewater sludge ash for copper stabilization

XRD patterns in Figure 1a demonstrate the phase transformation when the mixtures of sludge ash and CuO were sintered at temperatures ranging from 650 to 1050 °C for 3 h. The peaks of CuFe₂O₄ spinel were detected after the 3-h sintering process at 750 °C, even with very complicated compositions in the system. When the sintering temperature increased to 850 °C, the CuFe₂O₄ spinel phase developed substantially while peaks of CuO and Fe₂O₃ diminished accordingly. Further heating increased the crystallinity and production of the CuFe₂O₄ spinel phase. Besides the formation of CuFe₂O₄ spinel, other major components such as hauyne and zeolite kept continuously growing, while anhydrite and quartz eventually decreased with elevated temperatures. Although the decomposition temperature for anhydrite is usually higher
than 1000 °C, the disappearance of anhydrite at temperature ≤ 850 °C in this experiment may be due to the conversion of calcium into the growing phases: hauyne and zeolite. Apart from phases discussed above, anorthite (CaAl$_2$Si$_2$O$_8$) — a main crystalline phase in glass-ceramics kept relatively stable throughout the sintering mechanism.

From the standard diffraction pattern of CuFe$_2$O$_4$ spinel (PDF#77-0010), the highest peak is at 2\(\theta\) ~ 35.5° but was overlapped by peaks of other phases. Therefore, the second highest peak at 2\(\theta\) ~ 62.7° was selected for further observation of the CuFe$_2$O$_4$ spinel in the sintered products (Figure 1b). The peak intensity of the CuFe$_2$O$_4$ spinel kept increasing after its first appearance at 750 °C, and a significant growth was observed when the sintering temperature increased from 750 to 850 °C. With further heating (≥ 950 °C), the spinel phase kept stable throughout the sintering process. From the phase transformation during the sintering process of CuO + sewage sludge ash, iron was observed as the only component to incorporate copper, and the CuFe$_2$O$_4$ spinel was identified as the only copper-hosting product phase. It seems that other complicated compositions are not involved in the formation of CuFe$_2$O$_4$ spinel, and their existence might influence the efficiency of copper transformation. Therefore, the hematite (Fe$_2$O$_3$) without any other impurities was used as amendment to incorporate copper, and to further analyze the mechanisms of copper transformation in iron-rich systems.
3.2. The mechanisms of copper incorporation in simulated iron-rich systems

XRD patterns in Figure 2 illustrate the phase changes in CuO + Fe₂O₃ systems when the mixture was sintered from 650 to 1050 °C for 3 h. After being sintered at 750 °C for 3 h, the observable peaks show that the CuFe₂O₄ with tetragonal structure (t-CuFe₂O₄) was first generated. Spinel-type ferrites usually display cubic symmetry but some show tetragonal distortion in which one of the lattice edges differs in length in relation to the other two.³⁵ Generally, in the normal AB₂O₄ spinel structure, B³⁺ ions occupy some of the octahedral sites and A²⁺ ions locate on tetrahedral sites.³⁶ But for an ideal inverse spinel, the Cu²⁺ ions occupy octahedral sites, whereas Fe³⁺ ions are found on octahedral and tetrahedral sites with approximately equal occupancy.³⁵,³⁷ The t-CuFe₂O₄ is a stable low temperature phase, and its crystal lattice exhibits a tetragonal distortion from the ideal inverse CuFe₂O₄ spinel.³⁵ From Figure 3, the t-CuFe₂O₄ phase kept developing with elevated sintering temperatures, while peaks of CuO and Fe₂O₃ diminished eventually. However, when the temperature reached 1000 °C, the CuFe₂O₄ phase mainly crystallized with cubic spinel structure with very strong peak intensities, and the peaks of t-CuFe₂O₄ reduced dramatically. In cubic CuFe₂O₄ (c-CuFe₂O₄) crystal structure, a few of the Cu²⁺ ions occupy tetrahedral sites.³⁷ When the sintering temperature kept increasing to 1050 °C, the orthorhombic compound CuFeO₂ was detected. The formation of CuFeO₂ under air atmosphere was also reported at a temperature range of 1000 to 1100 °C.³⁸,³⁹.
The copper-hosting crystalline phases together with the other iron-hosting phases were all subjected to quantitative analysis via Rietveld refinement, and the weight fractions were shown in Figure 3a. Sintering the sample at 750 °C for 3 h generated around 75% of the t-CuFe$_2$O$_4$ phase, and the weight fractions of CuO and Fe$_2$O$_3$ reduced to values lower than 15%. With elevated temperatures, the weight percentage of t-CuFe$_2$O$_4$ phase increased to about 90% and kept stable around this value until the temperature reaching 950 °C. Further heating at 1000 °C cause the significant reduction of t-CuFe$_2$O$_4$ phase and substantial formation (about 70%) of the c-CuFe$_2$O$_4$ phase as observed in Figure 2. At 1050 °C, the c-CuFe$_2$O$_4$ developed with the weight percentage of higher than 80%, and about 20% of the CuFeO$_2$ was generated as another copper-hosting product phase.

Therefore, reactions derived from both XRD and quantitative results are listed below:

$$\text{CuO} + \text{Fe}_2\text{O}_3 \xrightarrow{950 \degree \text{C}} \text{CuFe}_2\text{O}_4 \text{ (tetragonal)}$$ (1)

$$\text{CuO} + \text{Fe}_2\text{O}_3 \xrightarrow{1000 \degree \text{C}} \text{CuFe}_2\text{O}_4 \text{ (cubic)} + \text{CuFe}_2\text{O}_4 \text{ (tetragonal)}$$ (2)

$$\text{CuO} + \text{Fe}_2\text{O}_3 \xrightarrow{1050 \degree \text{C}} \text{CuFe}_2\text{O}_4 \text{ (cubic)} + \text{CuFeO}_2$$ (3)

To indicate copper transformation efficiencies into different product phases, the transformation ratio (TR) is used. Taking M$_n$ (n = 1, 2, 3,...) as copper-hosting product phases, the TR (n = 1, 2, 3,...) is calculated as follows:
where $MW$ = molecular weight; $a_n$ ($n=1, 2, 3, \ldots$) is the number of the target copper atom contained in the corresponding phase; and wt% is the weight fraction of its corresponding phase obtained through Rietveld refinement.

Therefore, the TR index for copper transforming into $t$-CuFe$_2$O$_4$ (TR$_t$), $c$-CuFe$_2$O$_4$ (TR$_c$) and CuFeO$_2$ (TR$_d$) can be calculated according to Eq (4). And the total transformation of copper (TR) into new crystal structures can be expressed as

$$TR (%) = TR_t (%) + TR_c (%) + TR_d (%) \quad (5)$$

The copper incorporation into $t$-CuFe$_2$O$_4$ reached around 70% at 750 °C and increased to about 80% at the temperature range of 850-950 °C. The copper transformation into $c$-CuFe$_2$O$_4$ increased significantly to around 60% after being sintered at 1000 °C for 3 h. At the highest temperature (1050 °C) of this sintering mechanism, about 73% of copper distributed in $c$-CuFe$_2$O$_4$ with 27% in CuFeO$_2$. The total TR value kept stable around 80% at temperature ≤ 1000 °C, and reached 100% at 1050 °C, indicating the complete transformation of copper into product phases.
When the transformation behavior of copper in Fe$_2$O$_3$ and sewage sludge system is compared, it can be found that the tetragonal CuFe$_2$O$_4$ never appeared in sewage sludge system. Since a small amount of dopant ions can change structural properties of ferrites, and the site preference of dopant ions might lead to transfer Fe$^{3+}$ from A-sites to B-sites and cause a crystallographic transformation from tetragonal to cubic structure. Therefore, the structure of the as formed CuFe$_2$O$_4$ in sewage sludge system will predominantly crystallize as cubic structure due to the existence and influence of Al, Si or other minor compositions.

3.3. Leaching behavior of product phases

Because t-CuFe$_2$O$_4$ and c-CuFe$_2$O$_4$ are the potential and predominant copper-hosting phases in the sintered products, their capacity in metal stabilization must be taken into account and compared with the initial copper-containing phase (CuO). Thus, this study prepared single-phase samples to determine their intrinsic leachability and leaching behavior in a prolonged (22-d) leaching experiment. The as-received CuO powder was used as the single-phase sample after phase confirmation by XRD. The single-phase t-CuFe$_2$O$_4$ and c-CuFe$_2$O$_4$ sample were obtained by sintering the CuO + Fe$_2$O$_3$ mixture at 950 °C for 60 h and at 1000 °C for 72 h, respectively. The purpose of such prolonged sintering processes is to ensure the complete reaction at grain boundaries/surface. The XRD patterns of single-phase products are provided in Figure S5.
The pH value of the CuO leachate (Figure S6) underwent a significant increase in the first few days and then held steady at around pH 4.8. For c-CuFe$_2$O$_4$ and t-CuFe$_2$O$_4$ leachates, in contrast, were very close to the initial pH value of the leaching fluid throughout the leaching period. As an increase in leachate pH may be accompanied by the destruction of the sample crystal structure, the increase in the CuO leachate’s pH may indicate that the CuO phase is more vulnerable to proton-mediated dissolution than the copper ferrite phases. Since the compositions of different metal-hosting phases will affect the contact between solid and solution, the total metal content should be normalized for comparison of the leachability. The normalized copper concentrations in both the CuO and copper ferrites leachates are presented in Figure 4a, which shows that the leached copper from the CuO sample is two orders greater than those from the CuFe$_2$O$_4$ samples. When the metal leachability of both ferrites is compared, the c-CuFe$_2$O$_4$ phase performed both higher copper and iron leaching than the lower temperature phase (t-CuFe$_2$O$_4$) as demonstrated in Figure 4a & b. At the end of the leaching period, a four-time higher copper concentration in c-CuFe$_2$O$_4$ leachate than that in t-CuFe$_2$O$_4$ leachate indicates the tetragonal CuFe$_2$O$_4$ phase as a more promising structure for copper stabilization. Moreover, the iron concentrations in t-CuFe$_2$O$_4$ leachate are lower than those in c-CuFe$_2$O$_4$ leachate, which confirms the higher resistance to acidic attack of the tetragonal structure.

With the proceeding of leaching process, the congruent dissolutions of these
crystalline phases in an acidic solution may be expressed as follows:

\[ \text{CuO}_\text{(s)} + 2\text{H}^+ \text{(aq)} \rightarrow \text{Cu}^{2+} \text{(aq)} + \text{H}_2\text{O} \]  
(6)

\[ \text{CuFe}_2\text{O}_4\text{(s)} + 8\text{H}^+ \text{(aq)} \rightarrow \text{Cu}^{2+} \text{(aq)} + 2\text{Fe}^{3+} \text{(aq)} + 4\text{H}_2\text{O} \]  
(7)

The concentrations of both \([\text{Cu}^{2+}]\) and \([\text{Fe}^{3+}]\) may also be limited by the potential precipitation/dissolution of the \(\text{Cu(OH)}_2\) and \(\text{Fe(OH)}_3\) solid, respectively\textsuperscript{,44,45} as listed in followings:

\[ \text{Cu(OH)}_2 \leftrightarrow \text{Cu}^{2+} + 2\text{OH}^- \]  
\(K_{spCu} = 10^{-19.3}\)  
(8)

\[ \text{Fe(OH)}_3 \leftrightarrow \text{Fe}^{3+} + 3\text{OH}^- \]  
\(K_{spFe} = 10^{-37.4}\)  
(9)

The pH value of the leachate at the end of the leaching process was measured as 4.9. According to Eq (8), the permitted \([\text{Cu}^{2+}]\) value was calculated to be \(10^{-1.1}\) M, which is higher than the measured total copper concentration of \(\sim 2090\) mg L\(^{-1}\) (\(\sim 10^{-1.5}\) M). Thus, copper ions might not be precipitated during the leaching process. Since the pH value of copper ferrite leachates kept stable at pH around 2.9, the system was maintained in a more acidic environment and the copper concentration was much lower than that of the \(\text{CuO}\) leachate. The copper concentrations in the leachates of c-\(\text{CuFe}_2\text{O}_4\) and t-\(\text{CuFe}_2\text{O}_4\) were all considerably under-saturated regarding to the
Cu(OH)$_2$ phase. At pH 2.9, the permitted concentration of total Fe$^{3+}$ ions is calculated as $10^{-4.1}$ M (4.45 mg L$^{-1}$) according to Eq (9). From Figure 4b, the iron ion concentrations were observed as 2.3 and 0.7 mg L$^{-1}$ for c-CuFe$_2$O$_4$ and t-CuFe$_2$O$_4$, respectively. The lower iron concentrations in both leachates than the permitted maximum value shows that iron ions were also not subject to reprecipitation from the leachates. Theoretically, if the c-CuFe$_2$O$_4$ and t-CuFe$_2$O$_4$ solid displayed a congruent dissolution, the [Cu]/[Fe] molar ratios would be at 1:2 which is coincident with the stoichiometry of Cu and Fe ions in their original phase. However, the observed [Cu]/[Fe] molar ratios (> 1:2) in Figure 4c illustrate that both c-CuFe$_2$O$_4$ and t-CuFe$_2$O$_4$ leachates are incongruent solutions, where the majority of the Fe-O bonds still remained on copper ferrite surfaces.

Although c-CuFe$_2$O$_4$ and t-CuFe$_2$O$_4$ displayed incongruent leaching, the behavior in both leachates is different from each other. Firstly, the [Cu]/[Fe] molar ratio decreased from about 18.0 to around 8.0 and kept stable around 8.0 in t-CuFe$_2$O$_4$ leachates, whilst the ratio in c-CuFe$_2$O$_4$ leachates kept stable from 4.3 to 5.0. Since both the leaching of copper and iron increased with the prolong leaching time, the decrease of [Cu]/[Fe] ratio might indicate the moderate leaching of copper from the tetragonal structure. Secondly, although the [Cu]/[Fe] molar ratio kept decreasing within the first 10 days in t-CuFe$_2$O$_4$ leachates, the value of this ratio is still much higher than that in c-CuFe$_2$O$_4$ leachates throughout the whole leaching process. The higher ratio means that there might be more Fe-O bonds remained on the solid surface, which may inhibit
further leaching of copper from the product phase. Therefore, it might explain much lower copper leachability observed in t-CuFe$_2$O$_4$ leachates.

Even though with different treatment methods and leaching conditions, the effect of copper immobilization in this study was further compared with what have been reported in other studies. Kumpiene et al.\textsuperscript{46} used coal fly ash and natural organic matter (peat) as the amendments to stabilize the metal contaminated soil, and reached a 98.2% decrease in the amount of leached copper. Solpuker et al.\textsuperscript{47} investigated the potential of using pervious concrete to immobilize copper, and detected the degree of copper immobilization (the ratio of leached copper to initial copper amount) to be around 0.19. Furthermore, a recent study\textsuperscript{48} reported that the combination treatment of calcined oyster shells (COS) and steel slag (SS) was sufficient enough to significantly decrease copper leachability (96% reduction). While in our study, a 99.7% and 99.4% decrease of the amount of leached copper was monitored for t-CuFe$_2$O$_4$ and c-CuFe$_2$O$_4$ phases compared to CuO, even with very fine milled powders and after a 22-d leaching period.

4. Conclusions

Copper ferrites were generated with two different crystal structures (cubic and tetragonal) when α-Fe$_2$O$_3$ was used as the ceramic precursor to incorporate copper, while the cubic CuFe$_2$O$_4$ was found as the only copper-containing product phase in
iron-rich municipal wastewater ash systems. The incorporation mechanisms of hazardous copper were explicated with the combination of quantitative and qualitative XRD technique. About 90% of the tetragonal CuFe₂O₄ phase was generated when samples of CuO+α-Fe₂O₃ were sintered at 850 °C for 3 h, while the weight percentage of cubic CuFe₂O₄ phase increased to 70% with a significant decrease of tetragonal CuFe₂O₄ when the samples were further heated at 1000 °C. Both copper ferrites exhibited good performance in copper ion immobilization, and the low-temperature tetragonal CuFe₂O₄ phase was further confirmed as a more promising structure for copper stabilization when copper concentrations in both cubic and tetragonal CuFe₂O₄ leachates were compared. Although with different metal leachability, both cubic and tetragonal CuFe₂O₄ displayed incongruent leaching behavior. In conclusion, through reliably reusing iron-rich materials (the municipal wastewater sludge ash and iron oxide), this study does not only show the potential to thermally stabilize the simulated copper-polluted soils, but also realize the feasibility of achieving “waste-to-resource” for a more sustainable environment.

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Supporting Information

One table and eight figures demonstrating the characterization of municipal wastewater sludge, powder XRD patterns of raw materials and pure phase products for leaching experiments, and two examples of Rietveld refinement results are available free of charge via the Internet at http://pubs.acs.org.
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Figure 1. (a) XRD patterns of the sludge ash + CuO system, and (b) the comparison of XRD peak intensities (between $2\theta = 61.5$ and $64.5^\circ$) for sludge ash + CuO samples sintered at 650-1050 °C for 3 h. The crystalline phases are identified as: CuO (PDF#80-1268), Fe$_2$O$_3$ (PDF#85-0599), CuFe$_2$O$_4$ (PDF#77-0010), anhydrite (CaSO$_4$, PDF#37-1496), quartz (PDF#79-1910), hauyne (Na$_6$CaAl$_2$Si$_6$O$_{24}$(SO$_4$)$_2$, PDF#73-1920), unnamed zeolite (Na$_6$(AlSiO)$_6$, PDF#42-0217), anorthite (Ca(Al$_2$Si$_2$O$_8$), PDF#89-1473), calcium magnesium phosphate (Ca$_7$Mg$_2$P$_6$O$_{24}$, PDF#20-0348), calcium aluminum oxide (Ca$_5$Al$_6$O$_{14}$, PDF#11-0357), andalusite (Al$_2$(SiO$_4$)O, PDF#39-0376).
Figure 2. XRD patterns of 650-1050 °C and 3 h sintered Fe$_2$O$_3$ + CuO samples. The standard patterns include CuO (PDF#80-1268), tetragonal CuFe$_2$O$_4$ (PDF#34-0425), cubic CuFe$_2$O$_4$ (PDF#77-0010), CuFeO$_2$ (PDF#75-2146), and hematite (α-Fe$_2$O$_3$, PDF#85-2599).
Figure 3. (a) Variations of weight fractions of Cu- and Fe-containing crystalline phases obtained from the CuO sintering reactions with Fe$_2$O$_3$ precursor, and (b) the transformation ratios (TR$_t$, TR$_c$, TR$_d$, and total TR, %) of Cu into the product phases.
Figure 4. (a) Normalized copper concentrations of the CuO, tetragonal CuFe₂O₄, and cubic CuFe₂O₄ leachates, (b) normalized iron concentrations and (c) [Cu]/[Fe] molar ratios of tetragonal CuFe₂O₄ and cubic CuFe₂O₄ leachates. 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.
Iron-Rich Sludge Ash

Copper-Polluted Systems

Copper Incorporated in Ferrites

Thermally Treated

Copper Ions
Copper Ferrites

150x84mm (300 x 300 DPI)