

Stabilization and phase transformation of CuFe_2O_4 sintered from simulated copper-laden sludge

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ARTICLE INFO

Article history:

Received 12 November 2010

Received in revised form 20 February 2011

Accepted 24 March 2011

Available online 31 March 2011

Keywords:

Copper

Sludge

Spinel

CuFe_2O_4

Stabilization

ABSTRACT

The feasibility of stabilizing copper-laden sludge by high-temperature CuFe_2O_4 ferritization process is investigated with different sintering temperature, and the prolonged leaching test. The thermal behavior, structural morphology, phase composition, and phase transformation of the stabilized sludge were investigated by using thermal gravimetry-differential scanning calorimetry, scanning electron microscopy and X-ray diffraction. The leaching behavior of the stabilized sludge under acidic environment was evaluated by modified Toxicity Characteristic Leaching Procedure (TCLP). The results indicated that CuFe_2O_4 could be effectively formed at around 800 °C by the iron oxide precursor with a 3 h of short sintering. The transformation was discovered on crystallographic spinel structures: the low-temperature (800–900 °C) tetragonal phase (t- CuFe_2O_4) and the high-temperature (~1000 °C) cubic phase (c- CuFe_2O_4). At higher temperatures (~1100 °C), the formation of cuprous ferrite delafossite phase (CuFeO_2) from the dissociation of CuFe_2O_4 was also noticed. Both CuFe_2O_4 spinel and CuFeO_2 delafossite phase have a better intrinsic resistance to acidic environment when compared to that of CuO phase by the modified TCLP test. The sintering strategy designed for copper-laden sludge is proven to be beneficial in stabilizing copper.

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1. Introduction

Heavy metal sludge from metal surface treatments, anodizing, plating, and printed circuit board manufactures are regarded as hazardous solid waste [1]. According to Taiwan EPA's statistics, about 190,000 tons of heavy metal sludge is generated per year in Taiwan. Leaching concentration of the heavy metals from residual sludge through Toxic Characteristic Leaching Procedure (TCLP) is still above the legal limit for land disposal [2,3]. Hence, waste sludge needs to be stabilized or transformed into non-toxic materials.

Cement solidification/stabilization is the most prevalent treating method for heavy metal sludge. Unfortunately, solidification process increases the final disposal volume of sludge and reduces the capacity and lifetime of landfill sites [2–4]. Long-term leaching problem of heavy metal from the solidified sludge during acidic environment (pH < 4) is also concerned and regarded as the disadvantage of cementation stabilization. To investigate an economical and environmental-friendly method to deal with waste sludge becomes a critical issue.

Stabilization of heavy metal sludge by thermal treatment has the potential for converting hazardous metal sludge into mineral phase and reusable product, such as spinel ceramics [5–8]. Spinel pro-

vides advantages of no permeability for liquid and gas, low thermal conductivity, high chemical resistibility, and its Mohs Hardness is equal to 8 [9]. For the characteristics of spinel materials, they are widely used as refractory materials employed in the glass and steel industries [10–12], and as a potential candidate material for internal reforming solid oxide fuel cell anodes [13].

The formation of spinel materials by thermal process from the parent oxides was extensively studied [5–8,14,15]. Because of the similar precursors existed in heavy metal sludge, stabilizing heavy metal via thermal treatment has the potential to convert hazardous metal-laden sludge from the waste stream into reusable spinel products. Shih et al. successfully converted nickel into spinel species by sintering the precursors with alumina (Al_2O_3), hematite (Fe_2O_3) and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) [6–8]. The formation of nickel aluminate spinel and nickel ferrite spinel were found after sintering the simulated sludge at 1000 °C with alumina and 600 °C with hematite, respectively. The long-term nickel leachability declined considerably by transforming nickel oxide (NiO) into nickel aluminate spinel (NiAl_2O_4) and nickel ferrite spinel (NiFe_2O_4) phases. Transforming nickel-laden sludge into aluminate and ferrite spinel phases by high-temperature process and the successful reduction of metal mobility under acidic environment has been well demonstrated. Copper sludge was found to react with alumina at high temperature, and the strategy of transforming copper-laden sludge with aluminum-rich precursors into copper aluminate spinel (CuAl_2O_4) shows potential of stabilizing

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copper [14–16]. Stabilization of copper sludge by high temperature CuFe_2O_4 ferritization process from 600 to 1000 °C was also conducted successfully [5]. Nevertheless, the phase transformation and stabilization efficiency at the temperature higher than 1000 °C is still needed to discuss.

The study aims to evaluate the technical feasibility of transforming heavy metal sludge into high-value spinel ceramic materials by thermal processes, and to reduce the toxicity of the hazardous waste. By varying the sintering temperature from 600 to 1200 °C for 3 h, the study investigated the transformation behavior of the precursors (copper oxide and iron oxide). The change of CuFe_2O_4 crystalline phase at different temperature was also discussed in this study. A modified TCLP was carried out to evaluate the long-term stability of copper in the stabilized phases.

2. Materials and methods

2.1. Materials preparation

In general, the metal components of sludge are usually first transformed into oxide forms when thermally treated [14]. An analytical grade copper oxide was used to simulate the thermal reaction of copper-laden sludge in this study. Experiments were carried out by sintering the mixture of copper oxide and iron oxide powder. The iron oxide powder was identified as hematite (Fe_2O_3 ; ICDD PDF #24-0072). In order to investigate the incorporation mechanism between copper ion and iron oxide, the raw materials in this study were prepared with Cu/Fe mole ratios of 0.5. Copper and iron oxides were mixed by ball-milling in alcohol slurry at 200 rpm for 20 h and then dried for 1-day at 105 °C. Then, the dried solids were homogenized by mortar and pestle grinding to pass a 74 μm sieve (ASTM 200 mesh). Then the contact area between particles was increased by pelletizing into a small cylindrical disc with 30 mm diameter under the compression pressure of 1 t/cm². The pelletized samples were carried by a crucible and sintered at targeted temperature for 3 h at a heating rate of 10 °C/min in air atmosphere. After sintering, the pellets were air quenched at room temperature and ground into powders for product characteristic analysis.

2.2. Product analysis

The thermal behavior and weight loss of the precursor powders were characterized by means of thermal gravimetry–differential scanning calorimetry (TG–DSC, TA instruments SDT-2960) with variation of temperature from 23 °C up to 1000 °C with a heating rate of 20 °C/min in air atmosphere. The structural morphology of the sintered sludge was observed by scanning electron microscopy (SEM, Hitachi S-2400). The crystallographic study and phase composition of the sintered sludge were determined by X-ray diffraction (XRD, Rigaku RINT2000) with voltage 45 kV and current 40 mA. XRD was calibrated by silicon standard before measurement. The calibrated peaks are 28.443, 47.304, 56.123, and 106.711.

2.3. Long-term leaching tests

The leaching behavior of the stabilized sludge under acidic environment was evaluated by using the modified TCLP with a pH 2.9 acetic acid solution. Each triplicate testing vial was filled with 10 mL of extraction solution and 0.5 g of powder. The testing mixtures were rotated end-over-end at 60 rpm for extraction period of 0.25–7 days. After the leaching process, the leachates were filtered with 0.45 μm syringe filters with pH measured, and copper concentration was analyzed with an inductively coupled plasma–atomic emission spectroscopy (ICP–AES, Jobin Yvon, JY24).

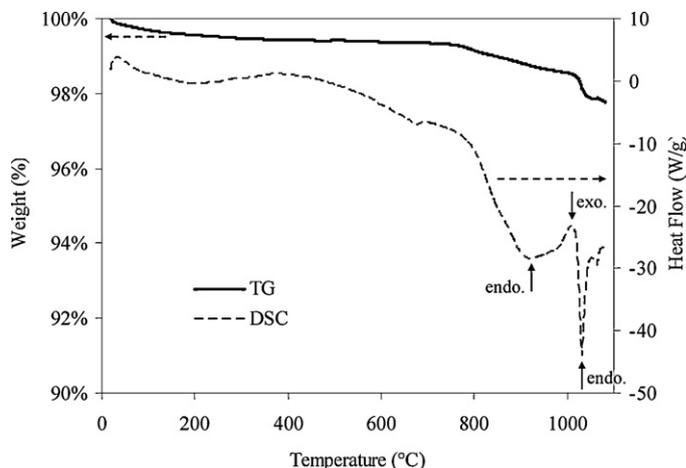
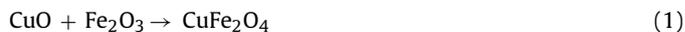


Fig. 1. TG–DSC curves of the precursor samples.

3. Results and discussions

3.1. Thermal analysis

In order to assess the temperature which reactions occurred, the thermal stability, and the chemical composition of the powders, dry precursor powder was subjected to TG–DSC analysis. TG–DSC curves of dry precursors were determined and illustrated in Fig. 1. The DSC curve of precursor sample shows endothermic peaks around 790–920 and 1015–1030 °C, and exothermic peak around 920–1015 °C. The first endothermic peak at 790–920 °C may correspond to the solid-state interaction between CuO and Fe_2O_3 and formation of Cu–Fe–O compound [5,17,18]. Reaction at the temperature above 800 °C can be written as:



Therefore, an assumption that copper ions can incorporate into ferrite structure at the temperature above 800 °C was concluded. The weight loss peak located at around 1020 °C may correspond to the partial decomposition of the formed CuFe_2O_4 compound. These findings will be interpreted again by XRD measurements.

3.2. Temperature effect on formation of CuFe_2O_4

The product morphology of the samples sintered at the different temperature for 3 h is shown in Fig. 2. From the micrographs, the mixture sample melted together and become densely with the increasing of the temperature. The micrograph shown in Fig. 2a illustrates the heterogeneous texture related to an incompletely crystallization of CuO and Fe_2O_3 particles, and demonstrates that no reaction occurred at 600 °C. With the temperature increasing to 800 °C, parts of particles started to fuse and congregate with observed crystalline surface (Fig. 2b). As the sintered temperature increased to 1000 °C, the crystalline structure with clear facets was observed with homogeneous microstructure (Fig. 2c). As the sintered temperature rose to 1200 °C, the stereo structure was melted into the layer structure with low roughness and the high level of homogeneity (Fig. 2d). Therefore, the mixture oxide in the sample would gather together to become more dense from macroporous system to layer structure with the increasing of sintering temperature. The changes of microstructure at different temperatures may affect the leachability of copper ions in the following leaching test.

Fig. 3 shows the XRD patterns (within the 2θ range of 20–68°) of the samples sintered at the different temperatures (600–1200 °C). It was found that for the samples sintered at 600 °C and 700 °C, a considerable amount of the parent copper oxide and iron oxide was still

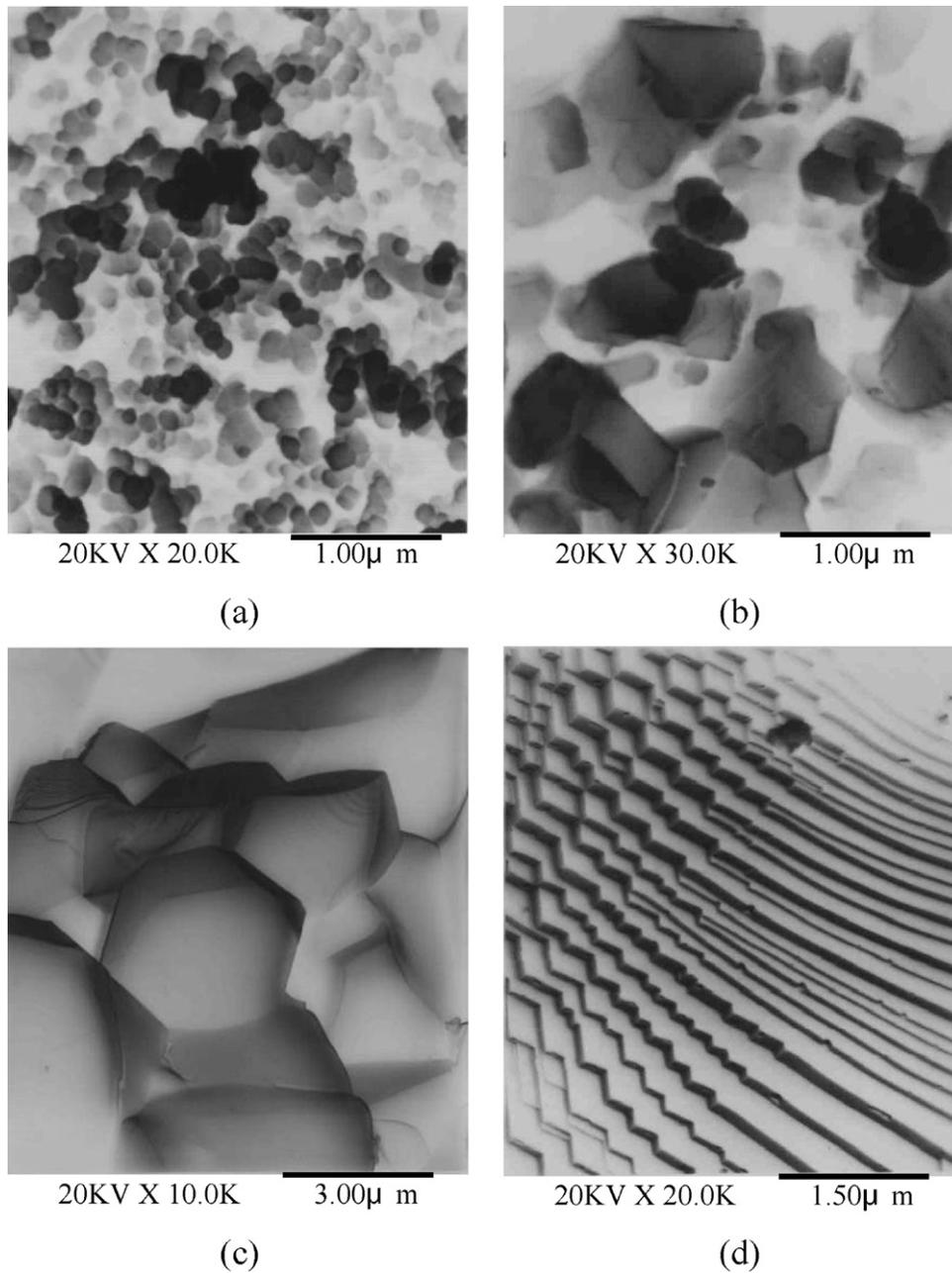


Fig. 2. SEM micrographs of samples sintered at different temperatures: (a) 600, (b) 800, (c) 1000, and (d) 1200 °C.

detected in the sample, which indicated that the external energy was not sufficient to trigger the diffusion of CuO and Fe_2O_3 , and the formation of ferrite spinel. Fig. 4 shows the XRD pattern details within the 2θ range of $30\text{--}42^\circ$ for the samples sintered at a temperature range of $600\text{--}1200^\circ\text{C}$. Within this 2θ range, several major diffraction peaks of the species can be used to observe the phase transformation process more obviously. As the sintered temperature rose to 800°C , copper ferrites with body-centered tetragonal crystal structure phase were formed. The results are also consistent with the past studies in which CuFe_2O_4 crystalline would present as sintering temperature at 800°C with pure copper oxide and iron oxide [5]. The reaction of forming CuFe_2O_4 spinel can be expressed as reaction (1). The formation of tetragonal CuFe_2O_4 is an endothermic reaction which also be confirmed by Fig. 1 around $790\text{--}920^\circ\text{C}$. In addition, the peaks characterized for both copper oxide and iron oxide almost disappeared and only copper ferrite peaks with tetragonal structure were present at 800°C . On further increasing

the sintering temperature to 1000°C , an important change in the crystal structure of the formed copper ferrites from body-centered tetragonal to cubic crystal structure was observed. The peak intensity of tetragonal CuFe_2O_4 phase decreased with the increasing intensity of cubic CuFe_2O_4 phase at the temperature from 800 to 1000°C . The result indicates that copper ferrite has two crystallographic spinel structures: the low-temperature tetragonal phase spinel (t- CuFe_2O_4) and the high-temperature cubic phase spinel (c- CuFe_2O_4) [19,20]. And the transformation of CuFe_2O_4 spinel from tetragonal to cubic phase is an exothermic behavior around $920\text{--}1015^\circ\text{C}$ which also be confirmed by Fig. 1. However, the XRD results suggest that copper ferrite could be synthesized from the simulated sludge by sintering above 800°C .

As the sintering temperature increasing to 1100°C , the significant changes on the characteristic peaks were noticed by the formation of cuprous ferrite delafossite phase (CuFeO_2). The formation mechanism of CuFeO_2 at the temperature over 1100°C can

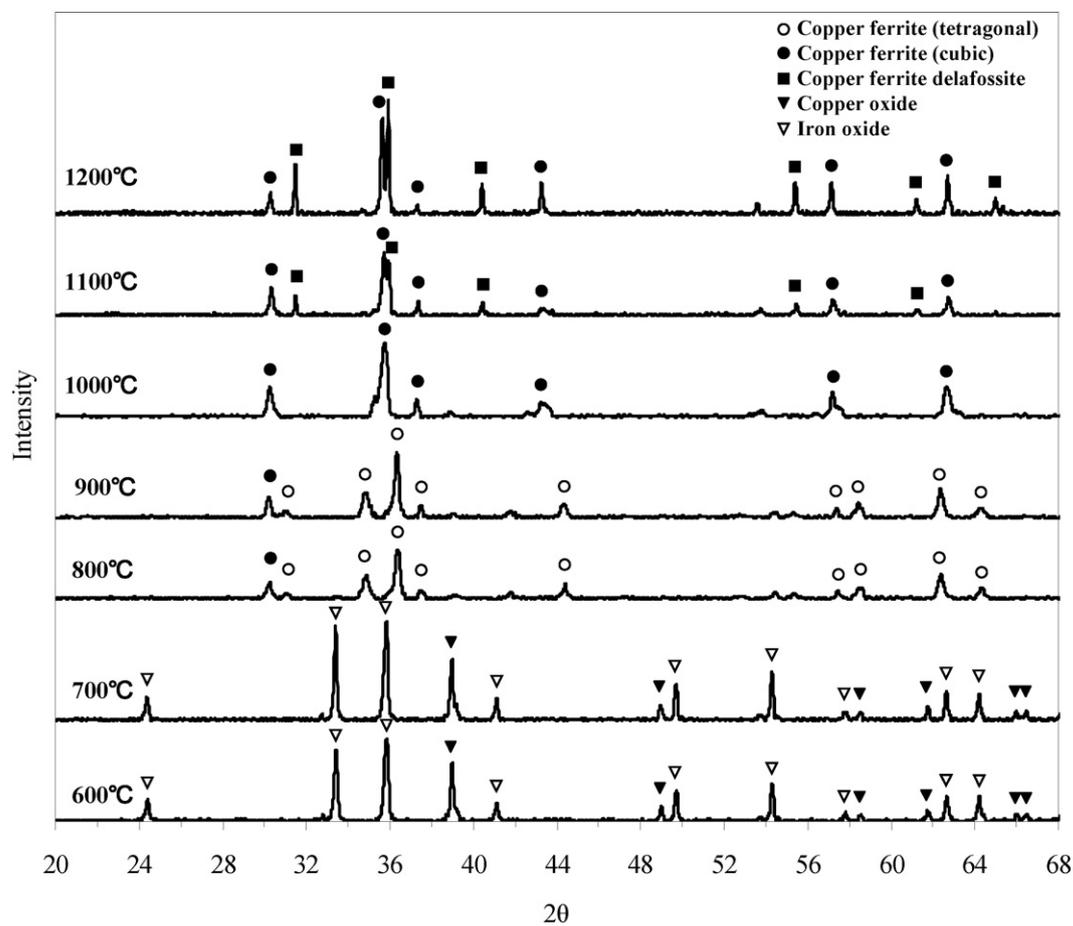
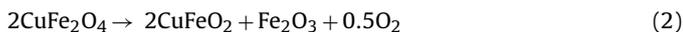


Fig. 3. XRD patterns of samples sintered at different temperatures.

be expressed as the following chemical reaction [14,15,20–22]:



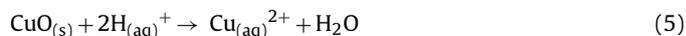
Reaction (2) shows that copper ferrite was dissociated into CuFeO_2 and Fe_2O_3 at higher temperature. Further excess of CuO was reduced to Cu_2O as described by reaction (3), and then reacted with iron oxide dissociated from CuFe_2O_4 as described by reaction (4). Although the mole ratio of Cu to Fe was equal to 0.5 in this experiment, CuFeO_2 could also form because the rates of CuFe_2O_4 and CuFeO_2 formation depended on the crystallographic orientation of the surface of iron oxide, especially if the system was not in thermodynamic equilibrium [15]. The observation from XRD results also verifies that CuFe_2O_4 and CuFeO_2 could coexist at the temperature over 1173°C with the Cu to Fe ratio of 0.5 [20]. In addition, the TG–DSC result also proves that the dissociation of CuFe_2O_4 occurred around 1015°C is an endothermic behavior.

3.3. Leaching mechanisms of CuFe_2O_4

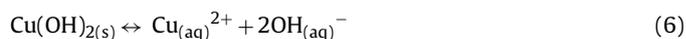
To investigate the immobilization of copper after the incorporation by the spinel structure, the modified TCLP tests were performed to compare the leachability of samples sintered at different temperatures. The solution pH of the 0.25–7 days leaching tests is plotted in Fig. 5. Both pure CuO and $\text{CuO} + \text{Fe}_2\text{O}_3$ precursor showed a significant increase of pH in the extraction solution for 0.25 days leaching test, as the pH value of sintered samples leachate decreased with the increase of the temperature. The increase of

leachate pH resulted from the dissolution of crystal cations through ion exchange with protons in the solution. This phenomenon was accompanied with the destruction of crystals at the solid surface by the acidic solution. The significant increase in leachate pH indicates that CuO is more vulnerable to proton-mediated dissolution. On the other hand, the formation of CuFe_2O_4 may show higher intrinsic resistance to such acidic environment.

When the pH of the CuO leachate reached 4.74 on the 7th day, the leaching concentration of copper was about 2200 mg/L ($\sim 10^{-1.46}\text{ M}$) in the leachate. As a general assumption of cation–proton exchange mechanism, the dissolution of CuO by the acidic attack of the solution can be expressed as:



However, the concentration of copper ions in the solution is also limited by the potential dissolution/precipitation reactions, such as in respect to $\text{Cu}(\text{OH})_{2(s)}$:



where the solubility constant (K_{sp}) of $\text{Cu}(\text{OH})_{2(s)}$ is $10^{-19.25}$ [23]. At pH 4.74, the product of $[\text{Cu}_{(aq)}^{2+}] \times [\text{OH}_{(aq)}^-]^2$ was found to be $10^{-19.98}$, which indicates that the system was close to the saturation of $\text{Cu}(\text{OH})_{2(s)}$, and the leaching behavior of copper ion may reach the equilibrium on about a week.

The long-term copper leaching concentration of sintered simulated sludge at different sintering time was presented in Fig. 6. The leaching tendencies of copper ions rose with the increasing of leaching time and declined with the increasing of temperature as expected. The copper ion in the CuO and precursor sample

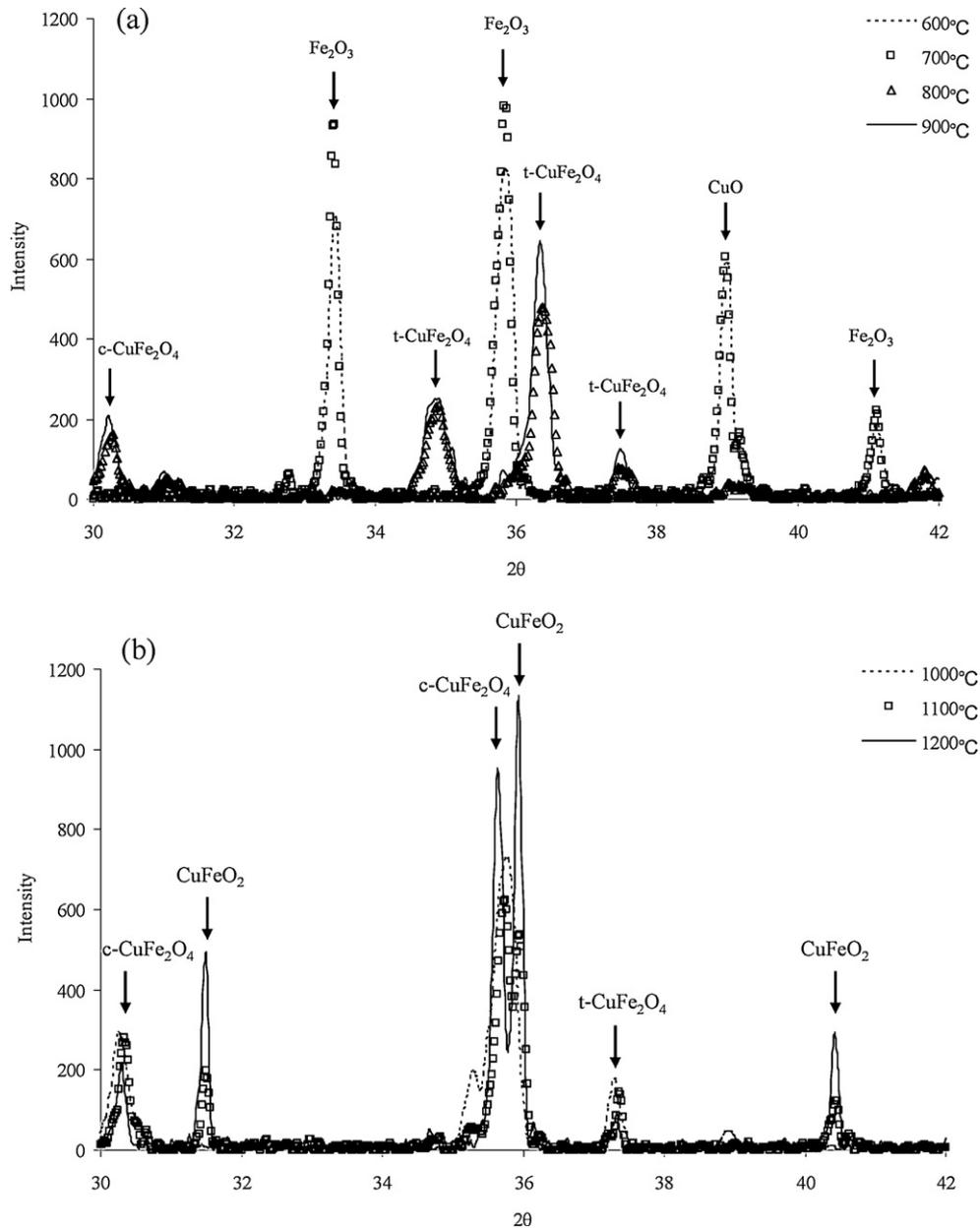


Fig. 4. XRD pattern details within the 2θ range of 32–40° for samples sintered at a temperature range of (a) 600–900, and (b) 1000–1200 °C.

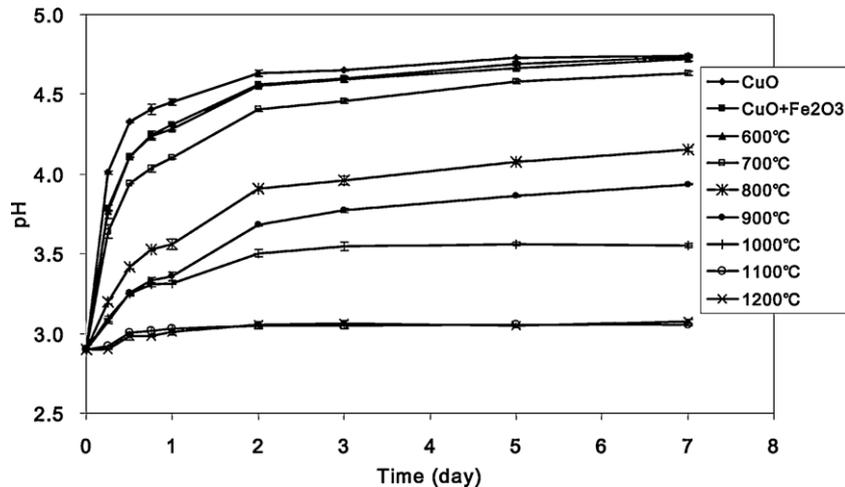


Fig. 5. The pH values of the sampled leachate of CuO, CuO + Fe₂O₃, and sample sintered at different temperatures.

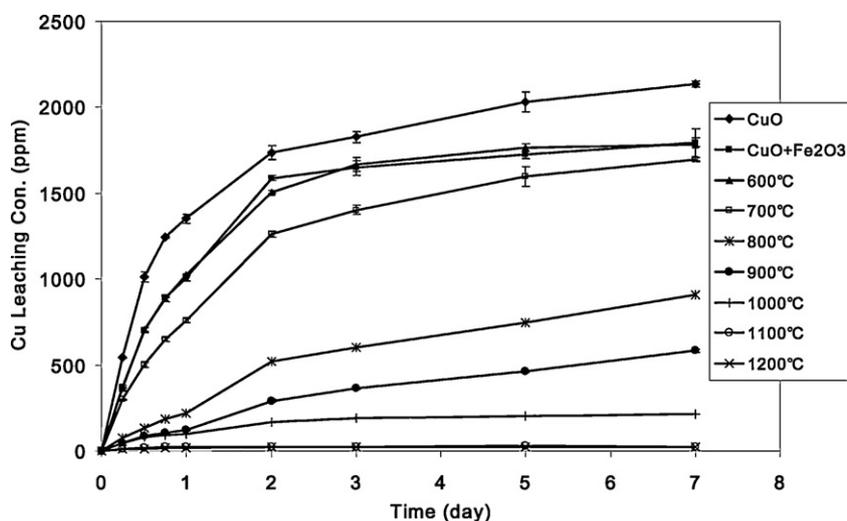


Fig. 6. Copper leaching concentrations of CuO, CuO + Fe₂O₃, and samples sintered at different temperatures.

(CuO + Fe₂O₃) leachate was much higher than that of sintered samples which was consistent with the pH change in the extraction solutions of CuO and precursor sample. However, the copper leachability of the sample sintered at 600 °C was similar to the leaching trend of precursor sample. As the temperature rose to 700 °C, the leaching concentration of copper is slightly lower than that at 600 °C. But while the temperature rose from 800 °C to 1200 °C, the leaching concentration of copper decreased significantly because of the formation of CuFe₂O₄. This means that copper ions could incorporate into the ferrite structure by high-temperature ferritization process and reach the objective of copper stabilization, and also coincides with the result of XRD patterns. In addition, the results of leaching test indicate that the copper stability would be constant even with the dissociation of CuFe₂O₄ and the formation of CuFeO₂ at higher temperature. Both CuFe₂O₄ spinel and CuFeO₂ delafossite phase have a higher intrinsic resistance to such acidic attack compared to that of CuO phase. The leachability of sintered samples may also be relative to the dense structure of the sintered sample observed from SEM micrographs at higher temperature. The sintering strategy designed for copper-laden sludge is proven to be beneficial in stabilizing copper.

4. Conclusion

Copper ferrite spinel (CuFe₂O₄) was obtained from a mixture of simulated copper-laden sludge and iron oxide via thermal treatment. From the investigation, the above results can be concluded:

- (1) The copper ferrite spinel (CuFe₂O₄), which is the less leachable copper phase during thermal treatment of simulated copper-laden sludge and iron oxide precursor, can be effectively formed at ~800 °C.
- (2) The mixture reactant showed in SEM micrographs would gather together to become more dense from particle phase to layer structure with the increasing of sintering temperature. The XRD result showed that copper ferrite has two crystallographic spinel structures: the low-temperature (800–900 °C) tetragonal phase spinel (t-CuFe₂O₄) and the high-temperature (~1000 °C) cubic phase spinel (c-CuFe₂O₄). As the sintering temperature higher than 1100 °C, the significant changes on characteristic peaks were noticed by the formation of cuprous ferrite delafossite phase (CuFeO₂).
- (3) About TCLP results, both pure CuO and CuO + Fe₂O₃ precursor samples showed a significant increase on pH in the extraction

solution for 0.25 days leaching test, as the pH value of sintered samples leachate was decreased with the increase of the temperature. The copper ion in the CuO and precursor sample (CuO + Fe₂O₃) leachate was much higher than those from sintered samples.

- (4) While the temperature rose from 800 °C to 1200 °C, the leaching concentration of copper decreased significantly because of the formation of CuFe₂O₄. Copper ions could incorporate into the ferrite structure by high-temperature ferritization process and reach the objective of copper stabilization.
- (5) Both CuFe₂O₄ spinel and CuFeO₂ delafossite phase have a higher intrinsic resistance to such acidic attack compared to that of CuO phase. The sintering strategy designed for copper-laden sludge is proven to be beneficial in stabilizing copper.

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