

## Stabilization of copper sludge by high-temperature $\text{CuFe}_2\text{O}_4$ synthesis process

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### Abstract

Copper sludge was stabilized by high-temperature  $\text{CuFe}_2\text{O}_4$  ferritization technique with different sintering temperature, isothermal time and  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio. Copper is stabilized by inserting the copper ion into the stable  $\text{CuFe}_2\text{O}_4$  structure by ferritization. The result indicates that sintering temperature above 800 °C would be proper temperature range for  $\text{CuFe}_2\text{O}_4$  synthesis. When the  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio of sludges are above the stoichiometric ratio of 2, copper ion in sludge would be stabilized and hence be kept from leaching out. From the result of relative XRD intensity ratio, the equilibrium of the ferritization reaction could be reached by prolonging the isothermal time to 10 h. Judging by the TCLP results, the optimum ferritization parameters are  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio equal to 3.5, sintering temperature at 800 °C and isothermal time above 10 h.

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### 1. Introduction

Ferrites, known as spinel ferrites, have the general formula  $\text{M}^{2+}\text{O}\cdot\text{Fe}_2^{3+}\text{O}_3$  where  $\text{M}^{2+}$  is divalent metallic ion, such as  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ . In the close-packed cubic crystal structure of ferrites, tetrahedral (T sites) and octahedral (O sites) oxygen sites have been provided for both the  $\text{M}^{2+}$  and  $\text{Fe}^{3+}$  ions [1]. In traditional wet chemical method for ferrite synthesis, divalent metallic ion could be fixed onto one-eighth of the T sites and one-half of the O sites by using aqueous metallic ions as starting reactants [2]. The process usually involves two steps. In the first step, aqueous divalent metallic ions co-precipitate with iron ions to form hydrous iron oxides by controlling the

pH and ORP of the solution. In the second step, the divalent metals are fixed onto the ferrite by dehydration process of the precipitates [3]. Environmental engineers bring the wet chemical ferrite process in the concepts for the treatments of aqueous heavy metals. In the wet process, serial delicate controls of pH, oxidation–reduction potential (ORP) and ferrous ion/divalent metals ( $\text{Fe}^{2+}/\text{M}^{2+}$ ) molar ratio are required for the formation of ferrite in waste water. Aqueous heavy metals are fixed onto the ferrites and hence heavy metal concentrations could be eliminated to meet the requirement for waste-water discharge [4–10].

In addition to waste-water treatment, several processes for heavy metal sludges stabilization have been developed in recent years, including microwave process, ferrite process, etc. Microwave process for heavy metal sludge stabilization has been attracting growing interest with advantageous characteristic of uniform and rapid heating. Heavy metal containing sludges like sediment sludge from print circuit board manufacturing wash water and acid-extracted industrial sludge are well

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stabilized by microwave process with controlling microwave power, reaction time, additive reagents, reaction atmosphere and cooling gas [11–13]. The existing ferrite process for the treatment/stabilization of divalent metallic ion in solid waste could be divided into three categories. In the first category, sludges have to be dissolved into aqueous form by acid digestion, and then the dissolved aqueous divalent metallic ions would be treated by the wet chemical method described above [14]. Although divalent metal oxide could be selectively recovered by additional procedure, the ferrite process is still inconvenient due to volumes of acid and alkaline would be consumed. In the second category, solid waste is stabilized by coating a thin film of  $\text{Fe}_3\text{O}_4$  on the surface [15]. Ferrous ion was added and adsorbed onto the surface of solid waste, then pH, temperature and air flow rate in reaction vessel should keep at a stable value with continually monitoring ORP for the formation of  $\text{Fe}_3\text{O}_4$  layer. The whole coating process would repeat many times to make sure that  $\text{Fe}_3\text{O}_4$  layer is thick enough and divalent metallic ions are stabilized inside the coating. In the last category, divalent metallic waste could be stabilized by high-temperature ferritization with suitable trivalent iron/divalent metals ( $\text{Fe}^{3+}/\text{M}^{2+}$ ) molar ratio and sintered at specific temperature [16]. The high-temperature ferritization is a direct procedure and also simplifies the operation in comparison to the other two methods. Therefore, high-temperature ferritization could be a potential solidification/stabilization (S/S) technique for metallic solid wastes treatment.

High-temperature ferritization noted above has been currently accepted and applied in the field of material science and engineering. Ristic et al. [17] prepared  $\text{CuFe}_2\text{O}_4$  utilizing solid state reaction by  $\text{CuO}$  and  $\text{Fe}_3\text{O}_4$  sintering at  $800^\circ\text{C}$  then  $1000^\circ\text{C}$  with an initial atomic ratio of  $\text{Fe}/\text{Cu} = 3.29$  or by  $\text{CuO}$  and  $\alpha\text{-Fe}_2\text{O}_3$  sintering at  $800^\circ\text{C}$  with an initial molar ratio of  $\text{Fe}_2\text{O}_3/\text{CuO} = 1$ . Selvan et al. [18] prepared  $\text{CuFe}_2\text{O}_4$  powder from cupric nitrate, ferric nitrate and urea by sintering at  $1000^\circ\text{C}$  with  $\text{Fe}^{3+}/\text{Cu}^{2+}$  molar ratio of 2. Cross et al. [19] prepared  $\text{CuFe}_2\text{O}_4$  at  $800^\circ\text{C}$  then  $1150^\circ\text{C}$  with  $\text{Fe}/\text{Fe}_2\text{O}_3/\text{CuO} = 2/1/2$  by self-propagating high-temperature synthesis (SHS) reaction. Rahman and Ahmed [20] prepared  $\text{NiZnCu}$  ferrite in a series of composition  $\text{Ni}_{(0.8-x)}\text{Zn}_{0.2}\text{Cu}_x\text{Fe}_2\text{O}_4$  ( $x = 0\text{--}0.55$ ) with  $600\text{--}1000^\circ\text{C}$  for 4 h. In summary, sintering temperature, isothermal time and  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio are the three important controlling parameters for high-temperature ferritization. Nevertheless, diverse parameter settings have been reported. For further application in metallic solid waste treatment, clarification in the parameter settings of high-temperature ferritization is needed.

In this study, copper sludge from surface finishing industry was sintered with different sintering temperature, isothermal time and  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio. The crystalline phases of resultant specimens in the process were studied using X-ray powder diffraction. Relative mass ratios of crystalline phases formed were evaluated based on the relative intensity ratio of crystalline phases. In the meanwhile, stability of sintered specimens was evaluated by toxicity characteristic leaching procedure (TCLP). Finally, the optimal sintering parameters of copper sludge ferritization were investigated by judging the relationship between

relative mass ratio of  $\text{CuFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$  and TCLP test in sintered specimens.

## 2. Experimental

### 2.1. Materials

Sludge was collected from a filter press of waste-water treatment process in a surface finishing plant. The sampled sludge was oven-dried at  $105^\circ\text{C}$  to remove the residual moisture. Then the dried sludge was crushed by a jaw crusher (Breitlander Eichprobenund Labormaterial GmbH HD60, Germany) and ground to pass a  $74\ \mu\text{m}$  sieve (ASTM 200 mesh) by a centrifugal ball mill (FRITSCH pulverisette 6, Germany) for further experiments.

Table 1 summarizes the major metal content and the TCLP results of the sludge. The major metals in the sampled sludge are iron, silicon and copper, while other heavy metals' concentrations are quite low ( $<50\ \text{mg}/\text{kg}$ ). Leaching concentration of copper in TCLP leachate is as high as  $1240\ \text{mg}/\text{L}$ . According to the Taiwan EPA TCLP regulatory standard (copper:  $15\ \text{mg}/\text{L}$ ), the sludge would be considered as a hazardous waste.

### 2.2. Procedures

To control the  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio of the sludge for ferrite synthesis, analytical grade iron oxide powders (Merck, Germany) was added for the adjustment. In which,  $\text{Fe}^{3+}$  means the moles of  $\text{Fe}^{3+}$  ion in unit weight of dried sludge, and  $\text{M}^{2+}$  means the total moles of divalent ions, including  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Cu}^{2+}$  calculated from Table 1. After adjustment, the mixture was consequently homogenized by ball mill at 200 rpm for 10 min. Then the mixture was pelletized into pellet with the weight of 10 g, 30-mm diameter, thickness of 6-mm and uniaxial compression at 27 MPa to improve the solid-state reaction during high-temperature ferritization. An electric furnace (Nabertherm HT08, Germany) was used for the sintering of sludge pellets.

Table 1  
Elemental analysis and leaching characteristic of copper containing sludge

	Elemental analysis (%) (dry basis)	TCLP (mg/L)
Ca	1.72	–
Si	11.63	–
Al	0.15	–
Fe	32.35	–
Mg	0.21	–
Cu	17.50	1240 <sup>c</sup>
Pb	ND <sup>a</sup>	ND <sup>b</sup>
Cr	ND <sup>a</sup>	ND <sup>b</sup>
Cd	ND <sup>a</sup>	ND <sup>b</sup>
Molar ratio		
$\text{Fe}^{3+}/\text{M}^{2+}$	1.8	–
$\text{Fe}^{3+}/\text{Cu}^{2+}$	2.1	–

<sup>a</sup> ND: not detected ( $<50\ \text{mg}/\text{kg}$ ).

<sup>b</sup> ND: not detected ( $<0.1\ \text{ppm}$ ).

<sup>c</sup> Exceeding regulatory standard (copper:  $15\ \text{mg}/\text{L}$ ).

Sludge pellet made from raw sludge was sintered at different temperatures and isothermal time, and then quenched with deionized water to room temperature. The quenched specimens were crushed and ground to pass through ASTM 200 mesh for further analysis.

### 2.3. Analysis

Metal analyses of the raw sludge were completed by ICP with microwave-assisted digestion (Milestone MLS 1200, USA) with nitric acid, hydrochloric acid and fluoroboric acid. For evaluation of the heavy metal leaching behavior of raw sludge and sintered specimens, the leaching characteristics were tested according to TCLP (SW-846 Test Method 1311, USEPA). An inductively coupled plasma spectrometer (ICP, Perkin-Elmer Optima 2000) was used for the analysis of inorganic contents in the digests from microwave digestion and TCLP leachates. The crystalline phases of samples were studied by X-ray diffractometer (Bruker AXS D8 advance) using Cu K $\alpha$  radiation with scanning range 25–80° (2 $\theta$ ), and the XRD patterns were identified with International Center for Diffraction Data database (ICDD–JCPDS).

## 3. Results

### 3.1. Influence of sintering temperature on CuFe<sub>2</sub>O<sub>4</sub> synthesis

As noted previously, the raw sludge is considered as a hazardous waste due to the high-copper leaching characteristic. Ordinarily, this kind of sludge should be stabilized and solidified and then disposed in an isolated landfill site. Nevertheless, limited by the availability of landfill space in Taiwan, the traditional S/S techniques with cement-pozzolan-based as firming agents for heavy metals fixation [21] might cause possibility negative effects of volume expansion, which is opposite to the reduction strategy in the integrated solid waste management. However, the Fe<sup>3+</sup>/M<sup>2+</sup> molar ratio of raw sludge is around 1.8, which is nearby the stoichiometric molar ratio (2.0) for ferrite structure (CuFe<sub>2</sub>O<sub>4</sub>). It suggests that the copper sludge might have potential for ferritization.

Hence, the ferritization of raw sludge was conducted by sintering at 600, 800 and 1000 °C for 1 h. The crystalline phases of the sintered samples are shown in Fig. 1. No significant crystalline phases were found before sintering, but a minor CuFe<sub>2</sub>O<sub>4</sub> ferrite phases could be identified after sintering at 600 °C. As sintering temperature rises to 800 and 1000 °C, the CuFe<sub>2</sub>O<sub>4</sub> ferrite phases became much significant. This means that copper ions were incorporated into the ferrite structure by high-temperature synthesis process. The result is consistent with the results reported by Ristic et al. in which concluded that sintering temperature at 800 or 1000 °C and adjustment of Fe<sup>3+</sup>/Cu<sup>2+</sup> molar ratio at 2 or 3.29 with pure copper and iron compounds would present CuFe<sub>2</sub>O<sub>4</sub> crystalline [17]. The above results suggest that copper ferrite could be synthesized from the sampled sludge by sintering above 800 °C.

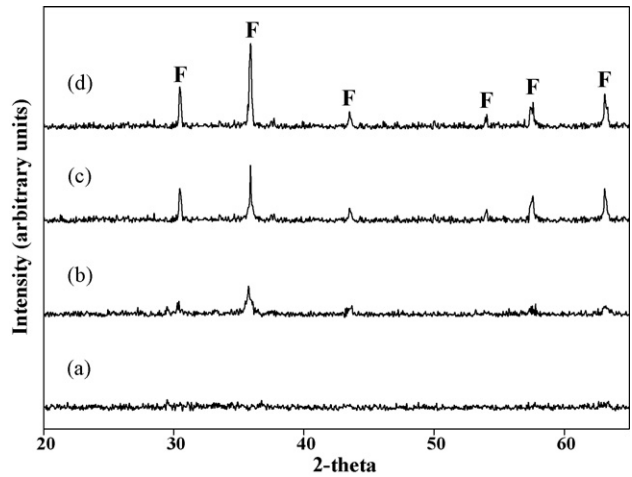


Fig. 1. X-ray powder diffraction patterns of copper sludge (a) in original form; (b) sintered at 600 °C; (c) sintered at 800 °C and (d) sintered at 1000 °C. F = Cuprospinel (ICDD #01-072-1174).

### 3.2. Influence of Fe<sup>3+</sup>/M<sup>2+</sup> molar ratio and isothermal time on CuFe<sub>2</sub>O<sub>4</sub> synthesis

The initial Fe<sup>3+</sup>/Cu<sup>2+</sup> molar ratio has also been concluded to have significant influence during high-temperature ferritization in literatures. Assuming copper is the major divalent metal in ferrite synthesis, the Fe<sup>3+</sup>/Cu<sup>2+</sup> molar ratio is 2.1 in sampled sludge, which is close to the stoichiometric value of copper ferrite. Nevertheless, the sludge also contains other divalent ions and it would cause the Fe<sup>3+</sup>/M<sup>2+</sup> molar ratio to be below the stoichiometric value for ferrite synthesis. To investigate the optimal molar ratio for copper stabilization, Fe<sup>3+</sup>/M<sup>2+</sup> molar ratio were set at 1.8, 3.5, 5.5 and 7.5, and specimens were sintered at designed temperature 800 °C for 1, 6, 10 and 15 h, respectively. Crystalline phases of the specimens sintered for 15 h with different Fe<sup>3+</sup>/M<sup>2+</sup> molar ratio are shown in Fig. 2. Significant copper ferrite phases were observed but no other kinds of

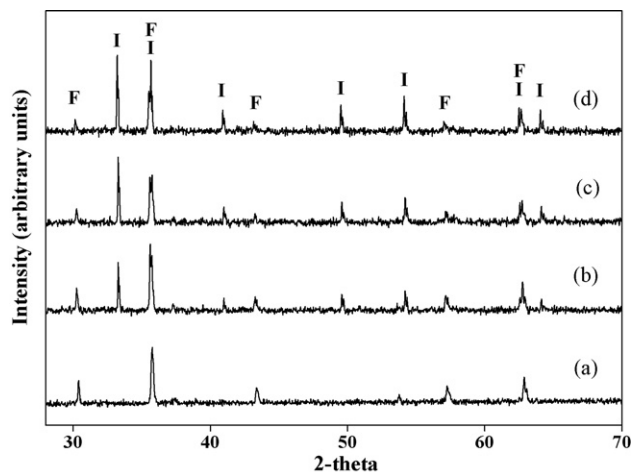


Fig. 2. X-ray powder diffraction patterns of sintered sludge with molar ratios adjusted to (a) Fe<sup>3+</sup>/M<sup>2+</sup> = 1.8; (b) Fe<sup>3+</sup>/M<sup>2+</sup> = 3.5; (c) Fe<sup>3+</sup>/M<sup>2+</sup> = 5.5 and (d) Fe<sup>3+</sup>/M<sup>2+</sup> = 7.5 (isothermal time: 15 h; sintering temperature: 800 °C) (F = Cuprospinel (ICDD #01-072-1174); I = iron oxide (ICDD #01-089-8103)).

copper crystalline phases were detected in all the sintered specimens, indicating that copper compounds in sludge might fully transform to copper ferrite by sintering process. For the sake of adjusting the  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio of raw sludge, tremendous amount of iron powder were added to raw sludge and the quantities of copper ferrite phases in sintered samples were diluted. The dilution effect leads to the decrease in the intensities of copper ferrite phases as indicated in Fig. 2. Besides that, when the  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio was set at 3.5 or above, crystalline phases of iron oxide could be observed and the intensities increase as the  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio rises. The results indicate that too much iron oxide had been added to the modified sludges for copper ferrite formation; hence an optimal  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio might exist. Judging by powder raw mixtures are less homogenous (copper and iron compounds in this case), suitable  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio for maximum degree of ferritization should be greater than the stoichiometric value (2) of  $\text{CuFe}_2\text{O}_4$ . Therefore, to estimate the optimal  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio, TCLP for sintered specimens was performed.

In Fig. 3, the relationship between the amount of copper leached by TCLP test and  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratios of sintered specimens under different isothermal time was presented. Compared to that of the untreated sludges, the leach of copper was reduced by the ferrite process. Also, the lowest leach of copper can be found at the  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio of 3.5 for various isothermal times. That seems to be the optimal  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio in this case. The results coincided with the ferritization parameters concluded in previous study by Ristis et al. [17], in which utilized analytical grade copper oxide and iron oxide to formulate pure  $\text{CuFe}_2\text{O}_4$ .

On the other hand, extending isothermal time would effectively stabilize the sludges. Fig. 3 also shows that as the isothermal time increased from 10 to 15 h, the leach of copper was reduced from 0.14 to 0.06% (molar ratio = 3.5). It indicates that as the isothermal time prolongs to certain extent, the marginal effect would decrease. Fig. 4 shows XRD patterns of sintered specimens with modified sludges (molar ratio = 3.5) at different isothermal time that noted above. Significant copper

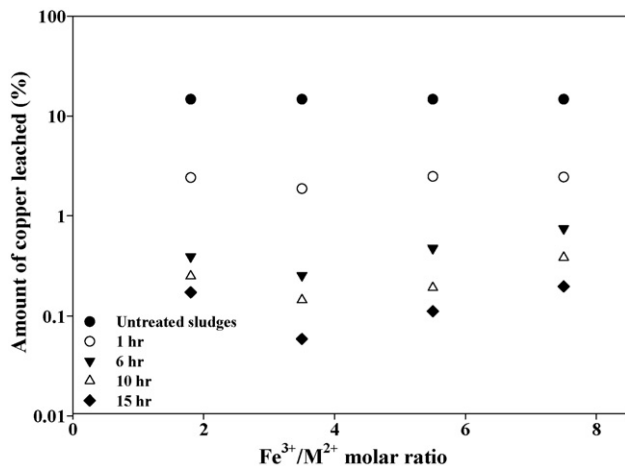


Fig. 3. Relationship between the amount of copper leached by TCLP test and  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratios of sintered specimens under different isothermal time.

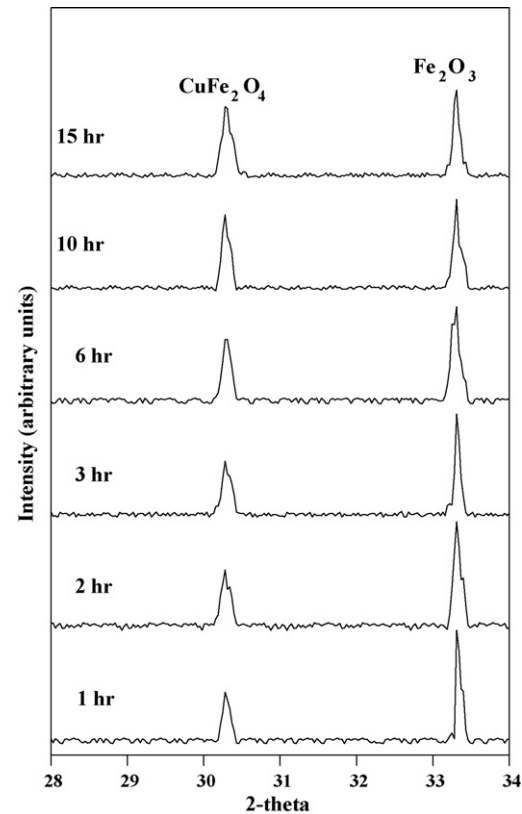


Fig. 4. X-ray powder diffraction patterns of modified sludge at different isothermal time ( $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio: 3.5).

ferrite phases ( $\text{CuFe}_2\text{O}_4$ ) and hematite phases ( $\text{Fe}_2\text{O}_3$ ) could be identified in modified sludges with various isothermal time. Nevertheless, lengthen the isothermal time during the high-temperature ferritization will lead to increase the intensity of  $\text{CuFe}_2\text{O}_4$  patterns, and in the meantime hematite crystalline phases reduce. Extension of isothermal time would be beneficial to the reaction of copper and iron compounds transforming into copper ferrite by high-temperature ferritization.

#### 4. Discussion

For further clarify the influence of ferritization process on copper sludge stabilization, crystalline quantification technique by X-ray powder diffraction is utilized to estimate the relative mass ratio of crystalline phases on copper ferrites and corresponding materials [22]. Assume the peak intensity of a specific crystalline phase  $m$  is in a mixture composed of  $N$  crystalline phases. The relationship between the peak intensity  $I_m$  with the mass fraction  $X_m$  could be written as (Eq. (1)).

$$I_m = K_m \frac{x_m / \rho_m}{\sum_{j=1}^N x_j \mu_j^*} = \frac{K_m x_m}{\rho_m \bar{\mu}^*} \quad (1)$$

$K_m$  is a coefficient that depends on the nature of the crystalline phase  $m$  (structure parameters of crystalline phase) and on equipment working condition;  $\rho_m$  the density of crystalline phase  $m$  and  $\bar{\mu}^*$  represents the average mass absorption coefficient that depends on the mixture crystalline phases. In multiple crystalline



phases of specimen, the specific peak intensities of two different (subscripted by m, n) phases could be presented based on (Eq. (2)),

$$I_m = \frac{K_m x_m}{\rho_m \mu^*} \quad (2a)$$

$$I_n = \frac{K_n x_n}{\rho_n \mu^*} \quad (2b)$$

And the relative mass ratio  $x_m/x_n$  of crystalline phase m and phase n could be calculated by dividing these two equations,

$$\frac{x_m}{x_n} = \frac{I_m}{I_n} \times \frac{K_n \rho_m}{K_m \rho_n} = K^* \left( \frac{I_m}{I_n} \right) \quad (3)$$

$K^*$  depends on the density, the crystalline parameters of these two phases and the working condition of the apparatus. Assuming differences between chemical compositions and densities of specimens are negligible, and the samples are analyzed under the same equipment and working condition,  $K^*$  between specimens would be the same and the variation on relative mass ratio  $x_m/x_n$  of crystalline phases could be simply calculated by the measured intensities of specific XRD patterns,

$$\frac{x_{m1}}{x_{n1}} : \frac{x_{m2}}{x_{n2}} = K^* \frac{I_{m1}}{I_{n1}} : K^* \frac{I_{m2}}{I_{n2}} = \frac{I_{m1}}{I_{n1}} : \frac{I_{m2}}{I_{n2}} \quad (4)$$

In this study, the  $d$ -spaces selected for  $\text{CuFe}_2\text{O}_4$  ( $2\theta$ :  $30.17^\circ$ ) and  $\text{Fe}_2\text{O}_3$  ( $2\theta$ :  $33.15^\circ$ ) were 2.96 and 2.70 Å, respectively.  $I_m$  and  $I_n$  means the selected peak intensity of  $\text{CuFe}_2\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  with different isothermal time. Comparing the peak intensity ratio ( $I_m/I_n$ ) with sintered specimens individually, and then a description of variation on relative crystalline mass ratio is obtained.

Fig. 5 shows the relative XRD intensity ratios of  $\text{CuFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$  with different isothermal time in modified sintered specimens, which showed a bendy trend toward the higher isothermal time-end. The trend indicates that the mass ratio of  $\text{CuFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$  reach a constant, hence the relative amount of  $\text{CuFe}_2\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  stops changing as the isothermal time increase. By observing the XRD patterns, a simple assump-

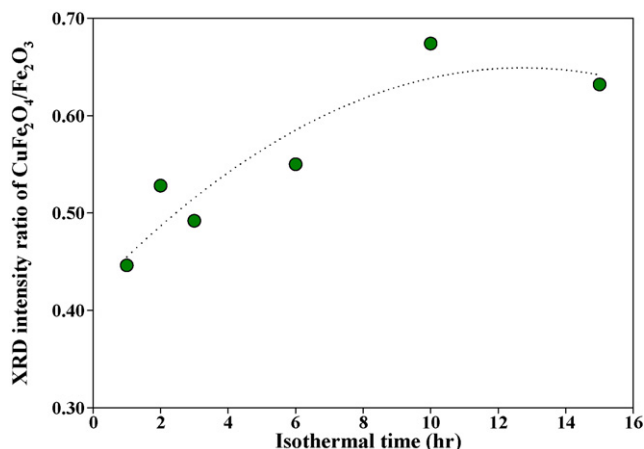


Fig. 5. Relative XRD intensity ratio of  $\text{CuFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$  to different isothermal time ( $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio: 3.5).

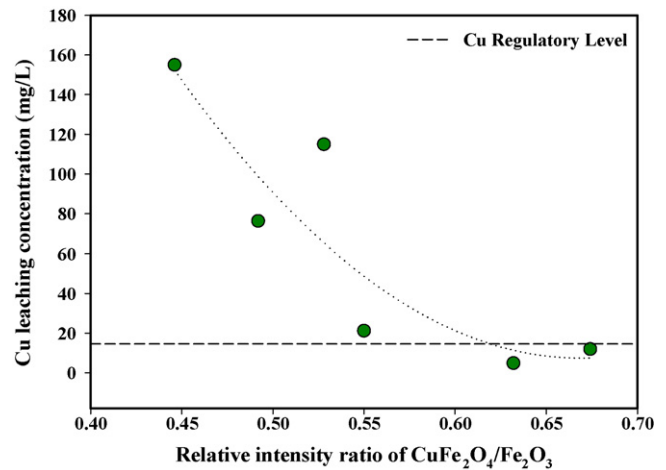
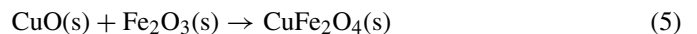


Fig. 6. Copper concentrations of sintered modified sludge ( $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio: 3.5) in TCLP leachate to relative XRD intensity ratio of  $\text{CuFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$ .

tion that copper ions incorporate into ferrite structure during high-temperature ferritization was proposed:



Nevertheless, the equation suggests a stoichiometric  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio of 2. The  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio in modified sludges, however, are 3.5;  $\text{Fe}_2\text{O}_3$  are over dosed. Therefore, copper compounds as  $\text{CuO}$  would be a limiting reactant, and the quantities of  $\text{CuFe}_2\text{O}_4$  in product side might rises to the constant value during the reaction. That means lengthen the isothermal time would contribute to increase the quantities of  $\text{CuFe}_2\text{O}_4$  close to the stable value which coincides with Fig. 5.

As mentioned above, during ferritization of copper sludge, divalent metals would be inserted into ferrite structure and exhibit the performance of high chemical stability. Fig. 6 shows copper concentrations of sintered modified sludge ( $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio: 3.5) in TCLP leachate to relative XRD intensity ratio of  $\text{CuFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$ . Copper concentrations in TCLP leachate are closely connected to relative XRD intensity ratio of  $\text{CuFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$ . Increasing the relative mass ratio of  $\text{CuFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$  in sintered specimens would improve the chemical stability. When the relative intensity ratio reaches 0.63, the concentration of copper in TCLP leachate drops below the regulatory level (Cu: 15 mg/L). Concluded from the result, the optimal sintering parameters in this study might be sintering temperature at  $800^\circ\text{C}$ ,  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio set at 3.5 and isothermal time set above 10 h. Comparing high-temperature ferritization with traditional S/S techniques for copper sludge treatment, metal stabilizers is unnecessary and hence the reduction tactic is easier to achieve. Therefore, the stabilization of copper sludge by high-temperature ferritization is proved to be applicable.

## 5. Conclusion

Stabilization of copper sludge by high-temperature  $\text{CuFe}_2\text{O}_4$  ferritization is conducted in this study. Copper is stabilized by inserting the copper ion into the stable  $\text{CuFe}_2\text{O}_4$  structure by

ferrite process and hence keeping copper from leaching out. The result indicates that sintering temperature above 800 °C would be proper temperature range for synthesis. By adjusting the  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio above the stoichiometric ratio (2), copper would be securely stabilized into the structure. With the relative XRD intensity technique, an increase of  $\text{CuFe}_2\text{O}_4$  crystalline quantity with respect to isothermal time could be observed in the beginning stage of sintering. As the isothermal time prolongs, the ferritization reaction reaches equilibrium. Judging by the TCLP results, the optimum ferritization parameters are  $\text{Fe}^{3+}/\text{M}^{2+}$  molar ratio equal to 3.5, sintering temperature at 800 °C and isothermal time above 10 h. The high-temperature  $\text{CuFe}_2\text{O}_4$  synthesis technique for future metallic waste stabilization is applicable.

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