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Stabilization of copper-contaminated sludge using the microwave sintering

Ching-Lung Chen [a], Shang-Lien Lo [a,*], Wen-Hui Kuan [b], Ching-Hong Hsieh [a]

[a] Research Center for Environmental Pollution Prevention and Control Technology, Graduate Institute of Environmental Engineering, National Taiwan University, No. 71 Chou-Shan Rd., Taipei 106, Taiwan, ROC

[b] Department of Safety Health and Environmental Engineering, MingChi University of Technology, No. 84, Gongjhuan Rd., Taishan Township, Taipei County 243, Taiwan, ROC

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ABSTRACT

A sintering with a microwave process was considered to stabilize copper-contaminated sludge and transform it into a sinter because microwave can provide uniform and quick heating. The parameters of addition of iron powder and ferric oxide, crucible modification, and air-forced leading were used in the microwave sintering. The results showed that reduced copper was present and some holes, caused by the high copper-contaminated synthetic sludge passing through the microwave sintering, were distributed throughout the sinters. However, when microwave sintering with the modification of parameters (improved microwave sintering) was used, the phenomena of copper reduction and hole formation were dispelled. Moreover, the improved microwave sintering of synthetic sludge with iron powder at 800 W at 30 min formed cuprospinel with peaks of 2θ degrees of 18.508 and 57.05 shifting to 18.9 and 56.55 and the leaching concentration from this sinter passed the limit of toxicity characteristic leaching procedure (TCLP) for copper.

1. Introduction

Previous studies show that using a microwave process with either iron powder or aluminum powder or an additive-inertia gas hybrid system to stabilize acid-extracted industrial sludge of low copper content [1–4] is fast and effective. In addition, the stabilized sludge can be used as an adsorbent for copper ions in industrial wastewater [5]. However, the stabilized sludge is in powdered form, which limits transportation and its possible reuse. Hence, methods to transform the stabilized sludge into block form are very important. High-temperature treatment processes have been used for powdered waste such as ash and sludge in numerous investigations [6–14], and all kinds of products like aggregate, glass ceramics, and adsorbents for heavy metals have been yielded. On the other side, using a microwave sintering for the formation of alloys, ceramics, and various materials is popular because the required temperature and time of formation by this method are less than those required by traditional sintering [15–17]. Moreover, the characteristics of some products made by microwave sintering are strengthened [18–20]. Hence, a combination of microwave sintering and a waste treatment process for copper-contaminated sludge was considered.

This study aims to establish a microwave sintering by which copper-contaminated sludge is stabilized and transformed into block form at the same time. The stabilization effect of a sinter was evaluated from the result of the toxicity characteristic leaching procedure (TCLP) test.

2. Experimental materials and methods

High copper-content synthetic sludge was prepared in this study, and its composition is shown in Table 1. Chlorides and sodium silicate were solved separately into DI water, and then the solutions were mixed. After the pH value of the mixed solution was adjusted to 7.0 ± 0.2, a 0.5 wt% of polymer was added to assist the sediment in settling completely, and then the sediment was washed and dehydrated several times. After that, the sediment was dried in an oven at 105 °C and crushed with a grinder. After crushing, the particle size of the sediment was between mesh nos. 100 and 400, hereafter referred to as synthetic sludge.

Two modified crucibles with volume 50 cm^3 were used in this study. The first modification (crucible I) included the following: (1) a piece of graphite was placed on the bottom of the crucible; (2) a mixture consisting of powdery active carbon (PAC) and gypsum (ratio 3/1), and a suitable amount of DI water was added as a lining on the crucible wall. The second crucible (crucible II) was modified as follows: (1) a piece of graphite, with a gypsum cake on top of it, was placed on the bottom of the crucible; (2) the crucible wall lining was composed of PAC and gypsum (ratio 2/1) and a suitable amount of water.

For crucible I, three samples, pure synthetic sludge, synthetic sludge with ferric oxide, and synthetic sludge with iron powder, were used. The ratio of synthetic sludge to ferric oxide was 7.0/1.43,

* Corresponding author. Tel.: +886 2 23625373; fax: +886 2 23928830.
E-mail address: sllo@ntu.edu.tw (S.-L. Lo).

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Table 1
The compounds for the preparation of high copper-content synthetic sludge.

Compound	Amount (g)
$Al_2Cl_3{\cdot}7H_2O$	9.31
$CaCl_2{\cdot}2H_2O$	42.18
$CuCl_2{\cdot}2H_2O$	8.62
$FeCl_3{\cdot}5H_2O$	13.57
Na_2SiO_3	26.31
Total	99.99

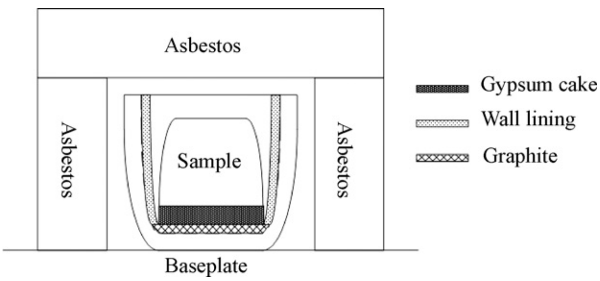

Fig. 1. The structure of crucible II on the microwave baseplate.

and that of synthetic sludge to iron powder was 7.0/1.0. A 7.0 g sample of each was stirred thoroughly with 8 mL DI water, and each mixture was kneaded to a pill by hand. For crucible II, the two mixed samples were prepared without any water. A sample of 7.0 g of each was pressed into a pellet with a diameter of 2 cm and height of about 3 cm with hand held equipment consisting of a stainless steel bar and ring.

After each sample was placed into its corresponding crucible, a piece of refractory material (asbestos) was set in position 0.5 cm away from the crucible opening (Fig. 1). For crucible I, microwave power was set at 200 W for 10 min and then at 800 W for 5, 10, 15, 20, 25, and 30 min. For crucible II, microwave power of 800 W alone was used for 5, 10, 15, 20, 25, and 30 min and air was led forcedly before the start of each microwave process. After each microwave process was completed, the crucible was cooled in the microwave oven until the shine that resulted from the high temperature disappeared, and then the crucible was moved to a ventilation system to cool down completely. The sinter was crushed with an agate mortar and sifted with a sieve of mesh no. 14 (diameter 1.0 mm). From the particles that passed through the sieve, 1.0 g was taken to undergo the TCLP test with extraction solution B (0.1 N acetic acid solution, pH 2.88 ± 0.05) of 20 mL and the filtrate was analyzed with an inductively coupled plasma-atomic emission spectrometry. The particles were ground further and sifted with a sieve of mesh no. 200. The powders made from this process were prepared for an X-ray diffraction (XRD) analysis.

3. Results and discussions

In studies of microwave sintering for ceramic materials, carbon silicide (SiC) is used popularly for the preheating of raw materials. However, the raw material in this study was waste and the sinter value was not high enough to assume the risk of the sintering of sludge with SiC. In fact, one crucible was discarded because it was sintered with the sinter. Hence, the PAC lining described above was placed in the crucible to preheat the pill or pellet before either of them started to absorb microwave energy and to protect the crucible from sintering by preventing direct contact with the sinter. In addition, the graphite set on the bottom of the crucible also played a protecting role.

Initially, the pill with water, crucible I and a microwave sintering of two steps were used. Microwave power of 200 W was used to remove the sample moisture before the sample underwent microwave sintering of 800 W. High power microwave heating assisted in drying the sample moisture quickly. However, the quick heating caused the vaporization of too large a quantity of water in the sample inner too fast to be vented. Hence, the vapor caused the sample to break, which resulted in an incomplete sludge sintering.

The sintering mechanism included four steps: (1) the PAC lining absorbed and transformed microwave energy into heat at room temperature; (2) heat from the PAC lining raised the temperature of the pill or pellet; (3) the temperature of the pill or pellet was high enough to let its matrix absorb and transform microwave energy into heat; (4) the temperature of the pill or pellet was high enough to sinter itself. Step 2 took the most heat and time, but both these decreased after that because the space of the crucible was small enough to finish the sintering in several minutes.

Fig. 2 shows the section of a sinter formed from synthetic sludge with iron powder by microwave sintering for 30 min. Reduced copper and some small holes were spread throughout the sinter; whether ferric oxide or iron powder was added or not, each sinter presented the problem of copper reduction and hole formation. The leaching concentrations of copper ions from the sinters after microwave sintering are shown in Fig. 3. The leaching of the sinters from synthetic sludge increased suddenly from 405 to 2658 mg/l at 5 min and decreased gradually to 1560 mg/l at 30 min. Those from synthetic sludge with ferric oxide had a similar tendency; the highest leaching concentration was 2587 mg/l and the

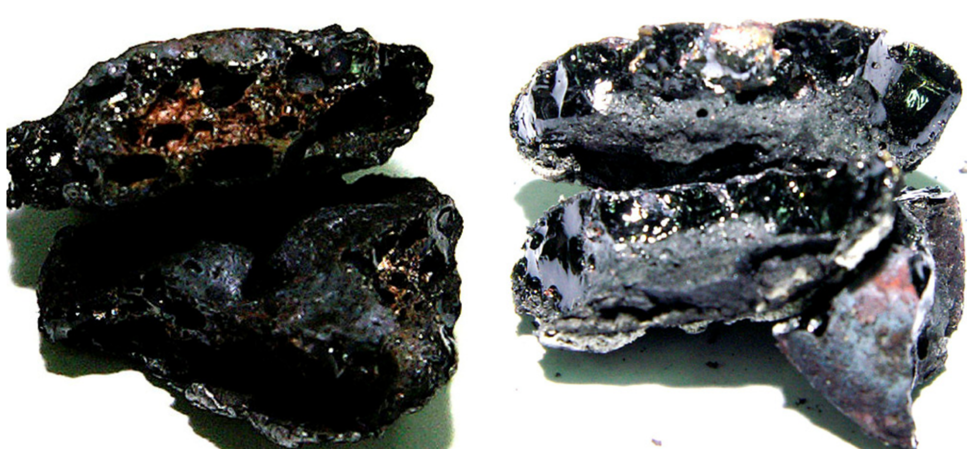

Fig. 2. The sections of the sinters made from synthetic sludge with iron powder by microwave sintering (left) and by improved microwave sintering (right) at 800 W for 30 min.

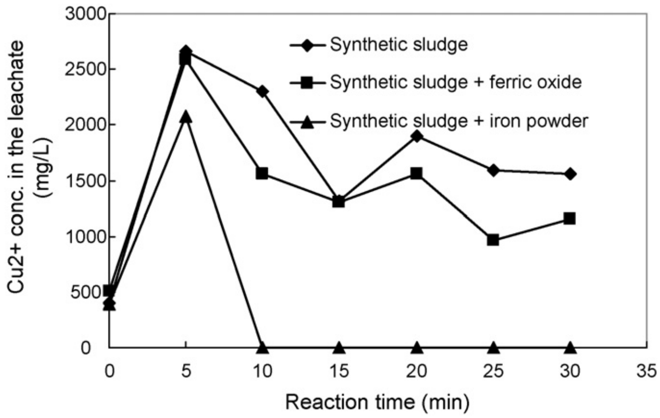

Fig. 3. The leaching of the parts of the sinters by microwave sintering at 800 W without reduced copper after a TCLP test.

final one 1153 mg/l. The leaching of the sinters made from synthetic sludge with iron powder also showed a sudden increase but then decreased quickly. The maximum leaching concentration was 2082 mg/l at 5 min and then decreased to lower than 15 mg/l. In addition, the pH values of the filtrates from the TCLP test for the samples before and after the microwave sintering were different: those before sintering were just over 5.2, and those after sintering were just under 4.9.

From the TCLP results, it was found that all leaching concentrations from the sinters, except for those made from synthetic sludge with iron powder at more than 5 min, were higher than the leaching concentrations from the samples before the microwave sintering. If only the formation of $Cu(OH)_2$, of which Ksp was 4.8×10^{-20}, was considered, the maximum amount of copper ions in a solution at pH value of 5.2 was 766 mg/l and that at pH value of 4.9 was 4835 mg/l this means that the leaching concentration from each sample before the microwave sintering was inhibited by the final pH of the extraction solution after a TCLP test. Besides, the elemental analysis result displayed in Table 2 shows the copper ion content in synthetic sludge was 73.4 mg/g; this means that the concentration of copper ions leached completely from synthetic sludge by a TCLP test would be 3670 mg/l when the final pH of the extraction solution was 4.9. From all the foregoing conditions, it could be concluded that the sudden increase in each leaching result was because of the difference of the pH values in filtrates. The results at more than 5 min showed decreased tendencies, which seems to show that some copper ions in those sinters were stabilized in their matrixes. However, as mentioned above, copper reduction occurred in all sinters; this reduced copper was ground into copper tinsel and then got caught in the sieve when the sinters underwent crushing and sifting. Hence, it was hard to confirm whether copper reduction or the sintering effect was the reason for the decrease in the leaching concentration of copper ions. Because of the presence of reduced copper in the sinters, broken sinters and acidic conditions could lead to environmental pollution. Moreover, the small holes in the sinter might result in its compressive strength not being enough to be used as an aggregate.

Table 2
The element compositions of high copper-content synthetic sludge.

Element	Concentration (mg/g)
Al	27.0
Ca	62.3
Cu	73.4
Fe	64.7
Si[a]	

[a] Silicon was not analyzed.

The reasons for copper reduction might include the following: first, the PAC in the wall lining burned incompletely and was transformed to carbon monoxide (CO), and then CO passed through the pores because of the removal of moisture. After that CO came in contact with copper oxide (CuO) and the latter was reduced to copper. Second, when part of a sample was being sintered, electrons from the graphite might have been transported to the sintering parts, which would also result in copper reduction. Besides, with the sample consisting of synthetic sludge and iron powder, iron powder would reduce CuO into copper during the sintering period. The small holes in the sinter thus resulted from copper formation. The fusion point of copper far exceeded the temperature provided by microwave sintering. Once copper was reduced, it would not react with the remainder of the sample to become supports, so the remainder could not sinter properly during the sintering period. After that, small scattered holes formed in the sinter.

The XRD results of sinters that passed through the sieve after microwave sintering at 800 W for 30 min are shown in Fig. 4. The results indicate that copper chloride ($CuCl_2 \cdot H_2O$), cupreous oxide (Cu_2O), and copper element were present in the parts without reduced copper. Because the results of the TCLP test of those parts of the sinters without reduced copper showed decreasing tendencies, and the XRD results showed the presence of copper substances extracted by the extraction solution, it could be deduced that fractions of the substances were wrapped in the sinter matrix; this means that the sinter effect was a certain reason for the decrease in leaching concentration of copper ions. As the reaction time increased, the sinter matrix became denser, which would decrease the leaching opportunity of the copper substances wrapped in

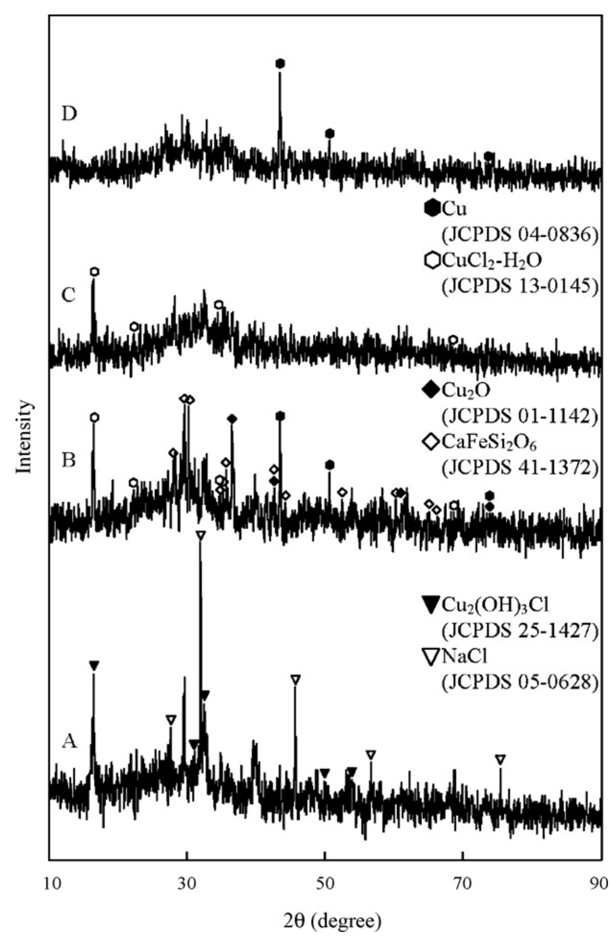

Fig. 4. The XRD results of the sinters made from synthetic sludge with/without ferric oxide or iron powder by microwave sintering at 800 W for 30 min.

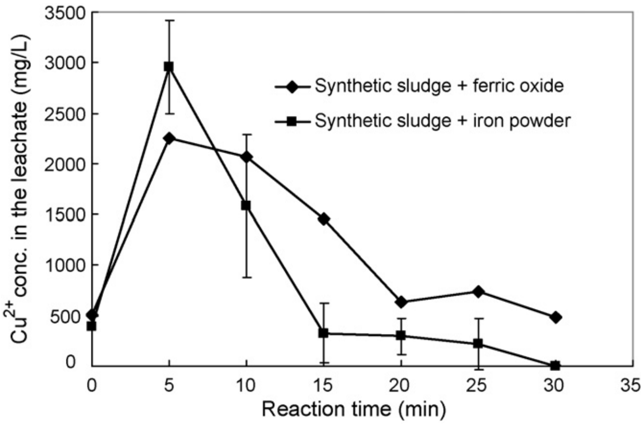

Fig. 5. The leaching of sinters by improved microwave sintering at 800 W without reduced copper after a TCLP test.

the sinter matrix. Hence, the leaching concentration of copper ions from that part of a crushed sinter without reduced copper decreased with an increase in reaction time. The XRD results also indicated that copper element existed in part of the sinter made from synthetic sludge with iron powder, but the leaching concentrations of the parts sintered for more than 10 min passed the TCLP test. This might be because copper element was wrapped perfectly in the sinters made from synthetic sludge with iron powder.

The problem of copper reduction seriously influenced the usability of the above-mentioned microwave sintering. The solution was to remove the factors of copper reduction that occurred in the microwave sintering. In order to eliminate the possibility of electron transport, a gypsum cake was put on the graphite at the bottom of the crucible. For the prevention of copper reduction by CO, the sample preparation was changed by omitting DI water in the blend and instead of kneading the mixture, pressing it into a pellet to decrease the influence of the pores that would result from the removal of the moisture. In addition, the amount of PAC in the wall lining was decreased. Wall linings of PAC and gypsum of several ratios, such as 3/1, 2.5/1, 2/1, 1.5/1, and 1/1, were used for the sinter made from synthetic sludge with ferric oxide. When the ratio of PAC to gypsum was more than 2/1, slight copper reduction occurred in the sinter. However, the sample could not be sintered completely when the ratio was lower than 1.5/1. Hence, the wall lining of PAC and gypsum of the ratio of 2/1 was used and air was forcedly led into the microwave oven to help CO to burn completely, which resulted in no reduced copper being found in the sinter after the microwave process. This procedure, including the use of a gypsum cake insulator, the changes in sample preparation and ratio of gypsum and PAC in the wall lining, and the forced air leading, is referred to as the improved microwave sintering.

Fig. 5 shows the results of the sinters made from synthetic sludge with ferric oxide or iron powder by the improved microwave sintering after the TCLP test. The leaching of the sinters made from synthetic sludge with ferric oxide by the improved microwave sintering increased suddenly from 508 to 2253 mg/l at 5 min and decreased gradually to 491 mg/l at 30 min. The average leaching of those sinters made from synthetic sludge with iron powder increased to 2959 mg/l at 5 min and then decreased to 329 mg/l at 15 min. Finally, it decreased to 4.21 mg/l at 30 min. Because copper reduction did not occur in the sinters made from synthetic sludge with ferric oxide by the improved microwave sintering and slight reduction occurred from those with iron powder under 25 min, all crushed sinters passed through the sieve and no reduced copper was caught.

Fig. 6 shows the XRD result of the sinter made from synthetic sludge with ferric oxide or iron powder by the improved microwave sintering at 800 W for 30 min. It was found that there was no obvious copper substance in the sinter made from synthetic sludge with ferric oxide by the improved microwave sintering, which was totally different from the XRD result of that by the unimproved microwave sintering. The crystals that appeared in the sinter made from synthetic sludge with ferric oxide by the improved microwave sintering might be ferric oxide, cuprospinel or both. Because the peaks of ferric oxide and cuprospinel are similar, and the intensity of the peaks was not strong enough to confirm whether it was cuprospinel or not, it could not be proved that cuprospinel formed in the sinter, even if the sinter could be magnetized. However, the TCLP results of the sinters made from synthetic sludge with ferric oxide by the improved microwave sintering showed a decreasing tendency and the XRD result showed no recognizable copper compound in the sinter made by the improved microwave sintering at 30 min. Hence, it could be considered that cuprospinel indeed formed in the sinter, but the crystals were not fine enough and the content too little to distinguish it from ferric oxide. In addition, the low amount of cuprospinel might be the reason that the leaching concentrations of copper ions from the sinters made from synthetic sludge with ferric oxide by the improved microwave sintering, though much higher than 15 mg/l, were lower than those from the unimproved microwave sintering.

In Fig. 5, the error bars in the TCLP results of the sinters made from synthetic sludge with iron powder by the improved microwave sintering indicate the variables of leaching concentrations of the replicates at the same reaction time. Although the sample of synthetic sludge with iron powder was mixed as thoroughly as possible, iron powder might still not have been distributed uniformly through the sample, which sometimes resulted in reduced copper being formed in the areas containing high amounts of iron powder, and this situation is reflected in the error bars. However, the scale of the error bars decreased with the increase in the reaction time, and all leaching concentrations of the replicates at 30 min were lower than 15 mg/l of the TCLP limit. This situation means that the slight copper reduction in the sinter made by synthetic sludge with iron powder that resulted from uneven distribution of iron powder in samples could be eliminated when the reaction time was long.

The XRD result in Fig. 6 indicates that there were gamma-calcium sulfate and a crystal similar to cuprospinel (hereafter called "the crystal") in the sinter. Compared with the XRD datum of cuprospinel, the XRD result of the crystal showed that the two

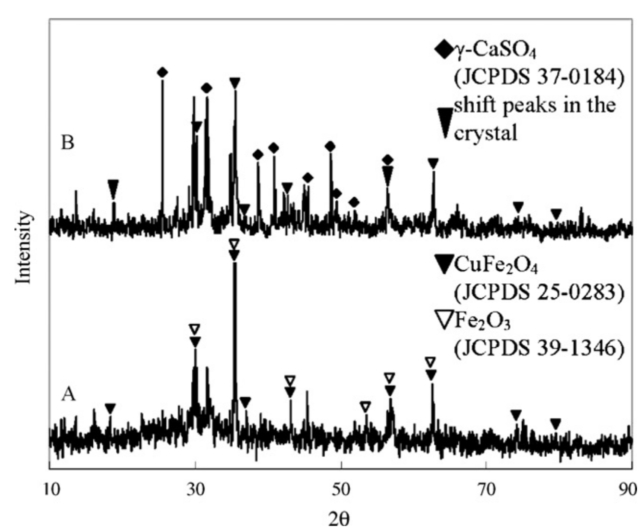

Fig. 6. The XRD results of sinters made from synthetic sludge with ferric oxide or iron powder by improved microwave sintering at 800 W for 30 min.

peaks of 2θ degrees of 18.9 and 56.55 were different from those in cuprospinel (18.508 and 57.05). However, there were no peaks in the XRD data of the possible compounds, matters, and elements from synthetic sludge with iron powder near the peaks of the crystal of 2θ degrees of 18.9 and 56.55. Furthermore, the relative intensity of peaks in the crystal and those in the XRD datum of cuprospinel were alike. Hence, it was concluded that the crystal was indeed cuprospinel and that the shift of the two peaks in the crystal might have resulted from the presence of other bivalent ions such as Ca^{2+} and Fe^{2+}. Besides, the formation reaction of cuprospinel in the sinter made from synthetic sludge with iron powder by the improved microwave sintering should be a kind of self-propagating high-temperature synthesis [21]. Because air was forcedly led in the improved microwave sintering, the oxygen provider was air, and a possible modified equation is as follows:

$$4CuO + 4Fe + 2Fe_2O_3 + 3O_2 \rightarrow 4CuFe_2O_4$$

The peaks of gamma-calcium sulfate occurred because a part of the gypsum cake fused with the sinter after the improved microwave sintering.

Fig. 2 shows a section of the sinter made from synthetic sludge with iron powder by the improved microwave sintering at 800 W for 30 min. When the section of the sinter made from synthetic sludge with iron powder by the unimproved microwave sintering was compared with that made by the improved microwave sintering, the latter showed no formation of copper metal or small holes. From the TCLP test result, the XRD result, and the section of the sinter made from synthetic sludge with iron powder, it seems that the improved microwave sintering at 800 W for 30 min could indeed achieve the goals of stabilization of synthetic sludge of high copper content and block formation of sludge at the same time.

Because the copper content in acid-extracted industrial sludge is lower than that of synthetic sludge, ferric oxide used as an additive should be suitable to stabilize industrial sludge. The use of by-products and waste such as coal ash and gypsum from thermal power plants and ferric oxide from industries for the recycling of copper ions by iron cementation processes to achieve the goal of waste reuse, sludge stabilization, and formation of block material at the same time should be considered.

4. Conclusions

It was confirmed that high copper-content synthetic sludge with a suitable amount of iron powder can be stabilized under the conditions of a crucible with wall lining of PAC and gypsum of the ratio 2/1 and a base consisting of a piece of graphite and a gypsum cake with forced air leading and microwave sintering at 800 W for 30 min. At the same time it was transformed into a hard sinter, and cuprospinel of peak shift was formed in the sinter. Besides, when iron powder or ferric oxide was used for cuprospinel synthesis by the improved microwave sintering, the former was more effective than the latter.

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