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Stabilization of Cu in acid-extracted industrial sludge using a microwave process

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Abstract

The leaching concentration of copper ions from the industrial sludge that has been extracted using sulfuric acid may still exceed 15 mg/L, which is the leaching standard of the toxicity characteristic leaching procedure (TCLP) for hazardous waste in Taiwan. Therefore, the acid-extracted industrial sludge is still an important source of hazardous waste. Usually, hazardous waste in Taiwan must be solidified and passed through the TCLP test before it is disposed in a landfill. The aim of this study is to develop a microwave process to stabilize copper ions in the sludge to replace the use of traditional solidification. In this study, two parameters – the reaction time of the microwave process and the additive reagents – were considered. The efficiency of stabilization of the microwave process was evaluated from the result of the TCLP test. The results showed that the stabilization efficiency of copper ions obtained using a microwave process without any added reagent depends highly on the property of the original acid-extracted sludge. Under some conditions, the leaching concentrations were much lower than those of the raw sludge. In additive reagent systems, the results showed that iron powder promoted the stabilization of copper ions more than the other additives such as sodium carbonate and sodium silicate. The leaching concentration of copper ions decreased dramatically from 179.4 to 6.5 mg/L below in the iron additive system.
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1. Introduction

Industrial wastewater sludge is a hazardous waste because it has a high copper ion concentration. Most of the copper ions in sludge can be recovered by extraction using sulfuric acid. However, the concentration of copper ions in the residue of the acid-extraction process is high. The leaching concentration of copper ions from the residue after TCLP test may still exceed 15 mg/L so acid-extracted industrial sludge must be stabilized. The most commonly used method of the hazardous waste stabilization in Taiwan is solidification. Cement solidification fixes the heavy metal ions in the cement. However, cement solidification increases the volume of the sludge, and it reduces the useful lifetime of a landfill site.

Microwaves are widely used because they offer the advantage of uniform and rapid heating. Therefore, microwaves are used to assist in extraction [1,2], digestion [3–5], sample pretreatment [6] and synthesis [7,8]. Lidström et al. [8] showed that microwave heating is very convenient for use in organic synthesis. The heating is instantaneous, highly specific and involves no contact between the energy source and the reaction vessel. Microwave-assisted organic synthesis can be used to explore rapidly "chemistry space" and increase the diversity of the compounds produced. All of the previously conventionally heated reactions could be performed using this technique.

Microwaves can assist in sludge chemical conversion and pyrolysis [9,10]. The conversion effects of microwave

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treatment are better than those of treatment using a conventional electric furnace. During microwave-induced pyrolysis, the sludge temperature can be increased from 200 to 900 °C when some microwave receptors such as the carbonaceous residue (char) generated by the pyrolysis of the sewage sludge are present in the sewage sludge [9].

Microwave process not only dries the sludge from printed circuit board manufacturing wash water, but simultaneously decreases the leaching of heavy metal ions in the sludge [11]. Microwave technology can be applied to vitrify contaminated soil wastes and immobilize the heavy metal ions to this purpose to meet the leachate test standard [12]. Over 90% of the chromium-contaminated soil undergoes the glass/ceramic transformation and is vitrified after it is radiated in microwaves for 60 min.

Microwave process has been showed that it can affect the drying, pyrolysis and stabilizing of heavy metal ions within the sludge. However, many details such as the effects of the microwave power and the reaction time during microwave process have not yet been investigated.

This study aims to investigate the influences of two parameters – the reaction time of the microwave process and the additive reagents – on the stabilization of the copper ions in the acid-extracted industrial sludge. The stabilization efficiency of the microwave process was evaluated from the result of a TCLP test.

2. Materials and methods

The sample used in this study was the sludge cake which was the residue in the acid extraction process. TD-01, TD-02, TD-03 and TD-04 were denoted sludge obtained on different dates. The sludge cake was dried at 105 °C for three days, and was then grinded using a mortar before being stored in a 20 L bucket with a cover. When each experiment started, 40 g of dried sludge whose weight had already been recorded was placed in a container. A 40 mL volume of deionized water was added into the dried sludge, so the moisture of the sample was 50%.

The maximum power of the industrial microwave oven employed in this study was 1600 W. When the aforementioned sludge was prepared, the container was moved into the microwave oven. Then, the microwave power and reaction time were set as presented in the Table 1. After the microwave process had been completed, the container was cooled at room temperature, and the weight of the sludge was recorded.

Sodium carbonate (Na_2CO_3), sodium silicate (Na_2SiO_3) and iron powder were used to increase the effect of stabilization in additive reagent systems. The reagents were added and mixed before deionized water was added. Table 1 presented the dosage of each additive reagent.

The toxicity characteristic leaching procedure (TCLP) was used to evaluate the effect of sludge stabilization following the microwave process. The TCLP test was modified from the Toxicity Characteristic Leaching Procedure Standard (method 1311) published by USEPA. The most important difference was that the sample weight was reduced from 100 to 5 g. A 5.00 ± 0.01 g mass of sludge after microwave process was used and recorded. The dried sludge without any treatment was used to be the sample for a zero reaction time interval. In selecting the extractate, extraction fluid #2, 1.0 M acetic acid solution with a pH value of 2.88 ± 0.05, was used to provide a severe circumstance. After 18 ± 2 h, the leachate from the TCLP test was be filtered. The copper ions concentrations of the filtrate were instantly analyzed with ICP, Jobin Yvon JY24, following filtration to prevent the formation of colloid and sediment.

3. Results and discussion

3.1. Sludge moisture and weight reductions

Fig. 1 plots the reductions of the moisture and weight of all sludges. The results for all sludges were similar. The moisture began to decline after a reaction time of 3 min, and the moisture was almost zero when the reaction exceeded 6 min. When most of the moisture had been removed, the sludge weight began to decrease. The greatest loss of the weight by the sludge was approximately 40%.

The dipolar polarization mechanism and conduction mechanism are responsible for the rapidity of microwave heating [8]. The dipolar polarization mechanism is that the molecule which has a dipole moment in the microwave

Table 1
Operational parameters in the microwave process

Sludge	Reagent	Dosage (g/40 g-sludge)	Power (W)	Reaction time (min)
TD-01	–	–	600	5, 10, 15, 20, 25
	Na_2CO_3	2	600, 400	
TD-02	–	–	600	3, 6, 9, 12, 15
	Na_2CO_3	2, 1, 0.2		
	Na_2SiO_3	2, 1, 0.2		
	Fe	2		
TD-03	–	–	600	3, 6, 9, 12
	Fe	0.8, 0.4		
TD-04	–	–	600	3, 6, 9, 12
	Fe	0.8		

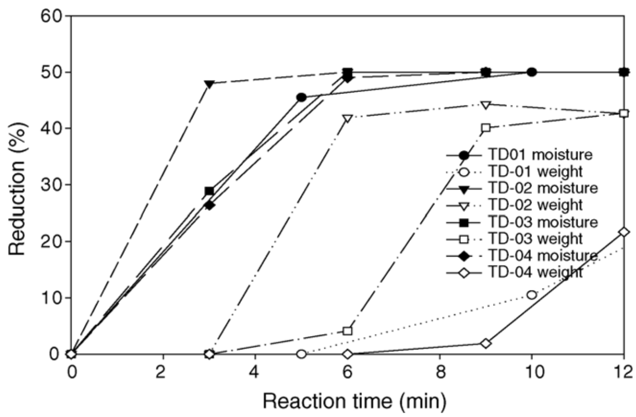

Fig. 1. Sludge moisture and weight change of all sludges with reaction time. The microwave power is 600 W and the amount of the dry sludge is 40 g.

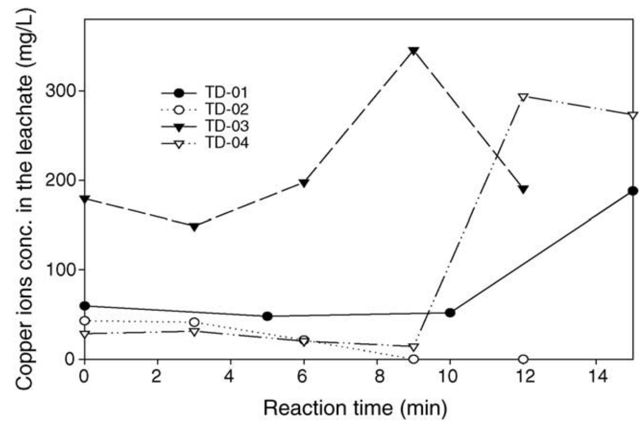

Fig. 2. Stabilization effects of copper ions in the three types of sludge with reaction time. The power is 600 W and the amount of the dry sludge is 40 g.

radiation region will rotate and align itself by turns, causing molecular friction and collision. Therefore, a substance with dipole structure, such as water, is heated rapidly. The conduction mechanism involves a solution that contains ions, or even a single isolated ion with a hydrogen bonded cluster. In the sample, the ions move through the solution due to the electric field, resulting in an expenditure of energy because an increase in collision rate, converting kinetic energy to heat.

Nüchter et al. [13] indicated that the ratio of the temperature change and the time change of microwave heating is proportional to the square of the value of the electrical field strength. In other words, when the electrical field strength is fixed, increasing the time change of microwave heating will raise the temperature change of a polar substance. In this study the microwave power, the amounts of the water and dry sludge were fixed respectively at 600 W, 40 mL and 40 g. Therefore, the temperature changes of sludge, the reductions of the sludge moisture and weight depended on the change of the reaction time. The times which those happenings started at would not change substantially because of the fixing of those physical factors.

Water had a suitable dielectric loss factor and was a solution, so water was easier to absorb and transform microwave energy to heat than the solid port of the sludge. Hence, the solid part began to absorb microwave radiation when water had been almost removed by microwave heating. In this study the time difference between moisture began decline and sludge began to decrease was 3 min. The result of TD-02 was more intense and that of TD-04 was milder. It seemed that the property of sludge might make slight differences to the reductions of the sludge moisture and weight.

3.2. Sludge stabilization

Table 2 shows the elemental composition of all sludges. About 0.1 g of dried sludge was recorded and passed through the microwave-assisted digestion. Then the ions concentrations of the digestion solution were analyzed with ICP. Fig. 2 presents the stabilization effects of them and the results are quite different. The leaching concentrations of copper ions of TD-01, TD-03 and TD-04 declined initially and then increased. The result for TD-02 showed an immediate fall to below 15 mg/L. This difference might arise from the their characteristics. However, it is hard to find the relationship between the leaching situation and the element composition. Gan [11] indicated that microwave radiation has shown a remarkable effect on immobilization of the heavy metal ions within the sediment solid structure though the underlying

Table 2
The element compositions of the three sludges

Element	Concentration (mg/g)				Element	Concentration (mg/g)			
	TD-01	TD-02	TD-03	TD-04		TD-01	TD-02	TD-03	TD-04
Ag	4.18	1.99	2.20	–	K	0.28	–	–	0.32
Al	8.43	7.58	6.93	10.37	Li	–	–	–	–
Ba	1.45	1.74	1.58	1.38	Mg	3.64	0.42	–	3.71
Ca	93.6	79.9	61.4	78.54	Mn	4.67	–	–	–
Cd	–[a]	–	–	–	Na	–	5.78	3.26	3.65
Co	–	–	–	–	Ni	2.43	–	–	–
Cr	1.36	–	–	–	Pb	5.67	11.6	12.3	–
Cu	13.4	13.2	21.4	20.86	Si[b]	–	61.9	24.4	74.41
Fe	97.0	22.2	23.6	30.71	Zn	–	–	–	–

[a] The concentration was lower than 0.05 mg/g.
[b] Silicon in TD01 was not analyzed.

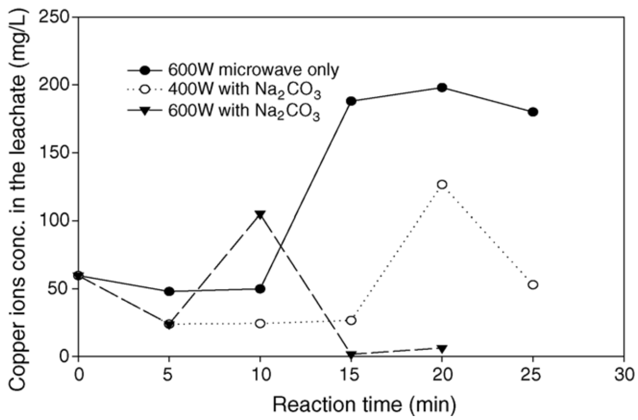

Fig. 3. Stabilization effects of copper ions in TD-01 with Na_2CO_3. The microwave powers are 400 and 600 W. The amount of the dry sludge is 40 g.

mechanism is unclear. The ion immobilization may be a resultant effect of a much higher drying temperature combined with the effect of electromagnetic waves which may facilitate a strong interaction and binding between residual free metal ions and dipolar polymeric molecules in the hydroxide sediments.

3.3. The effects of additive reagents on stabilization

The additive reagent was be added to promote the effect of sludge stabilization. Fig. 3 shows the stabilization results of TD-01 which was blended Na_2CO_3 with the various reaction times and microwave powers. It seemed that blending Na_2CO_3 into TD-01 could reduce the concentration of copper ions. An appropriate microwave power and reaction time reduced the copper ions concentration below 15 mg/L.

Figs. 4 and 5 plot the results of TD-02 with Na_2CO_3 and Na_2SiO_3 and the results were not regular and ideal. The carbonate anion of Na_2CO_3 has less ability to bond with copper ion than a strong anion such as sulfide anion. Na_2CO_3 which has the dielectric property was expected that it could be promoted to react with copper ion and form a stabile compound under the microwave radiation. In fact, the expected result did not appear and the copper ion concentration reached the peak at six minutes for systems with 1.0 and 2.0 g Na_2CO_3. Menéndez et al. [10] show that the temperature of sewage sludge with a suitable microwave absorber such as the char produced in the pyrolysis itself under microwave radiation can be up from 200 to 900 °C. In this study Na_2CO_3 might play the same role, so the sludge around Na_2CO_3 got more heat and that resulted in the extraction of copper ions. Then, the sludge TD-02 displayed its characteristic and made the fixation of the extracted copper ions. The same situation did not happen when the dosage was 0.2 g/100 g-sludge. It might be that the amount of the extracted copper ions under the dosage condition was not enough to compete with the capacity of the characteristic of TD-02.

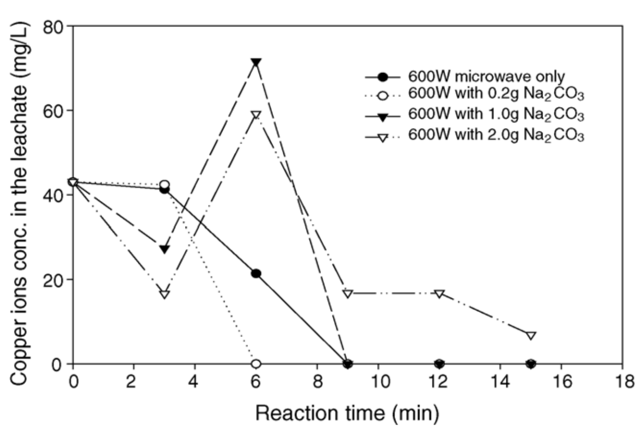

Fig. 4. Stabilization effects of copper ions in TD-02 with Na_2CO_3. The microwave power is 600 W and the amount of the dry sludge is 40 g.

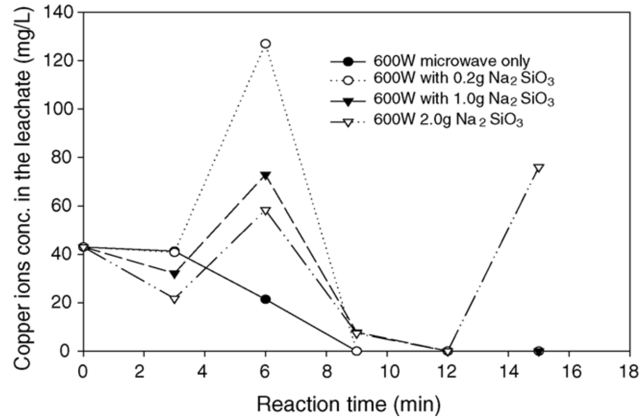

Fig. 5. Stabilization effects of copper ions in TD-02 with Na_2SiO_3. The microwave power is 600 W and the amount of the dry sludge is 40 g.

Na_2SiO_3 was selected because it is one of common additives in cement solidification. When it was blended into the sludge, the similar results which were increasing and then decreasing curves were presented. It might be that Na_2SiO_3 also caused the partial sludge to get more heat. The copper ions were extracted by heat and combined with Na_2SiO_3 at the same time. Hence, the peak at six minutes reduced with increasing dosage of Na_2SiO_3. The reason of following decrease was the same as the above-mentioned statement. When the reaction time was more than 12 min, the sludge might continuously smolder during the period of cooling after the microwave process. This situation could persistently reduce the organic compounds in sludge but might cause a chemical change to the stable compounds. It might be the reason why the concentration of copper ions for the sludge with 2.0 g Na_2SiO_3 increased when the reaction time was 15 min.

Fig. 6 shows that iron powder was a very effective additive reagent for TD-02. The concentration of copper ions began to be fall below 15 mg/L when the reaction time was 3 min. It is clear that iron powder shortened the stabilization time from 9 to 3 min. However, the TD-02 had the characteristic of stabilization after microwave process, so the more amount of iron powder was considered to prevent that the characteristic covered the positive or negative influence of iron powder

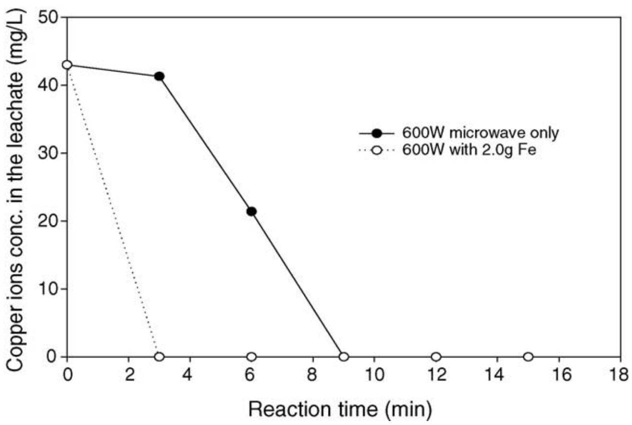

Fig. 6. Stabilization effects of copper ions in TD-02 with iron powder. The microwave power is 600 W and the amount of the dry sludge is 40 g.

on stabilization. Hence, the experiment of different dosage of iron powder was not performed. The result is effective and it let the experiments of iron powder system keep on performance.

Fig. 7 presents the results for TD-03 and TD-04 with iron powder. Iron powder was also an effective additive reagent for them. The results for TD-03 and TD-04 with 0.8 g of iron powder showed an amazing effect for the sludge stabilization using microwave process. The leaching concentrations of copper ions reduced quickly when the reaction time was 3 min. The result of half dosage of iron powder was not so charming. The result for TD-03 with 0.4 g of iron powder for 9 min exhibited a sudden increase and the duplicate yielded the same result. From the results of two additive dosages, it was guessed that the stabilization process in the iron powder system may include two steps. First, iron reacts with the organic compounds and copper ions in the sludge or promotes them to become a stable compound. When the moisture has been removed, the temperature of the sludge increases rapidly. Then the organic part of the stable compound is destroyed and the copper ions are released. Second, iron reacts with the remaining matrix and copper ions in the sludge and another stable compound is formed. The 0.4 g of iron powder for TD-03 may be not enough to rapidly promote the occurrence of the second step. Thus, the peak of TD-03 with 0.4 g of iron powder for 9 min appeared. A 2% dry sludge weight (0.8 g-Fe/40 g-sludge) dose was recommend. The dosage could assist microwave process in the stabilization of copper ions in sludge from 179.4 to 6.5 mg/L below.

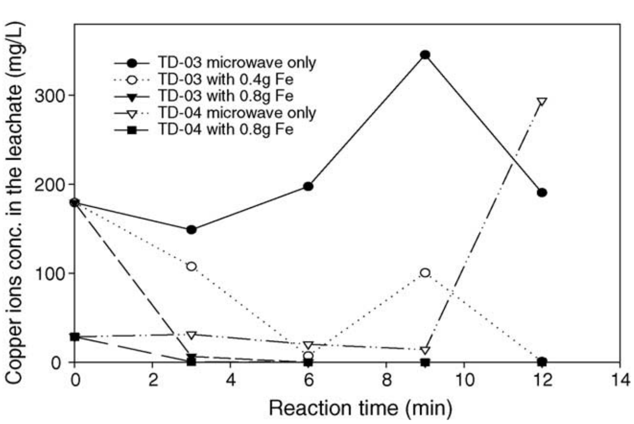

Fig. 7. Stabilization effects of copper ions in TD-03 and TD-04 with iron powder. The microwave power is 600 W and the amount of the dry sludge is 40 g.

4. Conclusions

The microwave process was shown to have the advantages of removing the moisture from, and reducing the weight of sludge. The results in this study indicated that the effect of microwave process without any additive reagent on the sludge stabilization depended strongly on the property of the original acid-extracted sludge. Under some conditions, the leaching concentrations were much lower than those of the raw sludge. In additive reagent systems, Na_2CO_3 and Na_2SiO_3 were not suitable additives because they did not provide a regular and effective assistance in sludge stabilization using microwave process. The result of the sludge with iron powder was amazing. The leaching concentration of copper ions fell greatly from 179.4 to 6.5 mg/L below in iron additive system. From the results, a dosage of 2% dry sludge weight of iron powder was recommended for the leaching concentration of 180 mg/L below of the copper ions. The mechanism of stabilization of copper ions in sludge under the microwave radiation remains unclear. It will be investigated in the future experiments.

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