

Thermal detoxification of hazardous metal sludge by applied electromagnetic energy

Ching-Hong Hsieh^a, Shang-Lien Lo^{a,*}, Ching-Yao Hu^b, Kaimin Shih^c,
Wen-Hui Kuan^d, Ching-Lung Chen^a

^a *Research Center for Environmental Pollution Prevention and Control Technology, Graduate Institute of Environmental Engineering, National Taiwan University, 71 Chou-Shan Road, Taipei 106, Taiwan, ROC*

^b *School of Public Health, Taipei Medical University, 250 Wu-Xin Street, Taipei 110, Taiwan, ROC*

^c *Rm. 5-26, Haking Wong Building, Department of Civil Engineering, University of Hong Kong, Pokfulam Road, Hong Kong*

^d *Department of Environmental and Safety Engineering, Ming-Chi University of Technology, No. 84 Gongjhuang Road, Taishan, Taipei Hsien 243, Taiwan, ROC*

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Abstract

Industrial wastewater sludge was treated by microwave processes to enhance the stabilization of laden copper. The effects of additives, processing time, microwave adsorbents, moisture content, reaction atmosphere, and cooling gas were investigated. The stabilization results were significantly enhanced by metal powder additives, prolonged microwave processing time, proper moisture content, the addition of carbonaceous materials, and a reaction environment with inert gas. It was also found that the moisture content would increase the homogeneity of applied microwave energy, and thus achieve a better overall efficiency between stabilizing agents and copper. The added metal powders may reduce Cu(II) to Cu(0) in the sludge or TCLP. The resulting thermal energy of microwave radiation, and microarcing process and the oxidation heat of Al powder may also assist the transformation of Cu(II) into CuO and CuAl₂O₄ phases. Part of the sludge was vitrified within inert gas environment when the processing time was longer than 18 min and active carbon dosage was more than 3 g. Reduction reactions also occurred in the hybrid microwave processes, leading to the reduction of sulfates and metal ions, and the formation of Cu₂S and FeS. Moreover, the microwave radiation can also enhance the feasibility of co-treating of inorganic and organic solid waste.

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1. Introduction

Industrial wastewater sludges resulting from the chemical precipitation in printed circuit board plants are often classified as hazardous materials. Metal ions, metal hydroxides, inorganic salts (CaSO₄, CaCO₃, NaCl, and NaHCO₃) and polymeric materials may exist in the sludges (Nemerow, 1978). In Taiwan, the copper in industrial wastewater sludge can mostly be recovered by sulfuric acid

extraction. However, the toxicity characteristics leaching procedure (TCLP, US EPA) test results of copper concentration in the residual sludges still exceed the legal limit for land disposal (<15 mg l⁻¹). The copper-bearing waste sludge has a great potential to pollute the groundwater and soil system, and endanger human and animal lives. Therefore, appropriate treatment of the residual sludge is required before landfill disposal.

The metal-bearing solid wastes are commonly treated by extracting metal ions from the wastes, or stabilizing the metals in solid forms. The strategies of metal-stabilization methods include concentrating metals in an area with an electrode, cementing metals with concrete or polymeric

* Corresponding author. Tel.: +886 223625373; fax: +886 223928830.
E-mail address: slo@ntu.edu.tw (S.-L. Lo).

materials, or transforming metals into high temperature phases via thermal reactions. All of them are capable of effectively reducing the mobility of metal ions. Among thermal treatments, microwave technique has the character of polar oscillation and the presence of dielectric materials offers the advantages of selective, uniform, and rapid heating. The phenomena of superheating and hot spot were also encountered in heterogeneous solid samples (Loupy, 2002). Microwave technique has been widely applied to the remediation of waste materials, such as pyrolysis of sewage sludges (Inguanzo et al., 2001; Menendez et al., 2002), assisted extraction and digestion (Lamble and Hill, 1998; Kuo et al., 2005), and stabilization of metal ions in soils or sludges (Sedhom et al., 1992; Tai and Jou, 1995; Gan, 2000; Chen et al., 2005; Jou, 2006). Results indicated that the microwave radiation enhanced the stabilization effect of metal ions and facilitated the subsequent disposal of these solid wastes. This study focuses on the following objects: (1) discussing the effects of additives, processing time, microwave adsorbents, moisture content, reaction atmosphere and cooling gas, (2) determining a feasible process for the treatment of industrial wastewater sludge, and (3) investigating the stabilization mechanism(s) of copper in sludge.

2. Materials and methods

2.1. Sample preparation and analysis

The raw industrial wastewater sludge used in this study was obtained from a heavy metal sludge treatment plant and had been treated by sulfuric acid extraction process for recovering most of the copper. The pH value of the raw sludge in TCLP was around 4.5 ± 0.2 . However, the “treated” sludge still contains hazardous copper and does not meet the criteria of TCLP regulated in Taiwan (15 mg l^{-1}). Prior to landfill or reuse, an appropriate stabilization strategy to render the residual sludge non-hazardous is necessary.

Pretreatments of the raw industrial wastewater sludge follows: (1) drying in an oven at 105°C for 12 h to reach a constant (within $\pm 1\%$ variation) weight value, (2) crushing the dried sludge with a grinder and sieved them to particle size ranging from 100 to 400 mesh (0.15–0.063 mm), (3) applying microwave radiation at 600 W for 12 min ($450\text{--}550^\circ\text{C}$) to remove the unknown organics and volatile compounds, and (4) storing the pretreated sludge in oven at 105°C before all the experiments. The term “DeS” in this study means the sludge after pretreatments. The stabilization efficiency of Cu in DeS by microwave radiation was investigated.

The chemical composition of raw industrial wastewater sludge was determined by a microwave digestion method modified from a previous study (Lamble and Hill, 1998). After the microwave-assisted digestion, the mixtures were cooled to room temperature, mixed with saturated H_3BO_4 solution, filtered, and the filtrate volume adjusted

to 50 mL before analysis. In the experiments, 40 g of DeS was put in a SiO_2 ceramic crucible (11 cm in diameter) and the sludge moisture content was adjusted to 0 or 50 wt.% with deionized water. The deionized water was added in the sludge by a pipet directly and mixed with the dry sludge by a stirring stick. The water sludge mixture was continuously mixed until the moisture was well distributed in the sludge.

An industrial microwave oven with microwave frequency of 2.45 GHz and a fixed power of 600 W was used in this study. The microwave radiation is emitted continuously from a microwave transmitter and reflected in the stainless steel oven. The microwave power and process time are controlled on a control panel. Solid samples were placed on a piece of asbestos in the oven and rotated horizontally. When the power was turned on, the microwave radiation would reflect in the oven and apply to the solid samples. Samples were leached using the TCLP and the metal concentrations (Cu, Al, and Fe) of leachates were analyzed by inductively coupled plasma-atomic emission spectrometry (Jobin Yvon, JY24). The concentration of Fe(II) in leachates was analyzed by colorimetry method, where samples were mixed with 1,10-phenanthroline monohydrate in $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ buffer solution and analyzed with a spectrophotometer (AWWA 7110C) at wavelength 510 nm (APHA, 1989). The species of solid samples were characterized by a multi X-ray diffraction system (XRD, X'Pert Pro, PANalytical) with voltage 45 kV and current 40 mA.

2.2. Effect of additives

To understand the effect of additives on the stabilization of copper in DeS, three types of additives, Al series, Fe series, and Zn series, were utilized. The experiments were performed with the same microwave power, processing time and reaction atmosphere/cooling gas as listed in Table 1. A similar experiment was also conducted with pure agents, $\text{Cu}(\text{OH})_2$ and Al powder, and microwave condition of 600 W for 15 min. The $\text{Cu}(\text{OH})_2$ was prepared from chemical precipitation process by CuSO_4 and NaOH, and was desalted and dried at 105°C for 3 d before used. The molar ratio between Al and Cu of this pure agent experiment was 2.

2.3. Microwave adsorbents

Microwave adsorbent would affect the heating efficiency by microwave radiation. In this section, the experiments were proceeded with two parts. In part I, Al powder and AC (a commercially available activated carbon) were added into the systems with moisture contents controlled at 0% or 50%. In part II, as Al powder was added, the AC used in part I was replaced by coal cinder (CC) for comparison. The CC was the product of coal-fired power plant and its major component is carbon. The effect of microwave processing time was also investigated in this

Table 1
Experimental conditions

Experiment	Additives (g)	Water content (%)	Processing time (min)	Atmosphere and cooling gas
Effect of additives	Al powder (0–3.09), α -Al ₂ O ₃ (0–2), γ -Al ₂ O ₃ (0–2) Fe powder (0–2), FeSO ₄ · 7H ₂ O (0–3) Zn powder (0–2), Zn(NO ₃) ₂ · 6H ₂ O (0–3.72)	50	12	Air
Effect of microwave adsorbent I	Al powder (0–1.74), AC (0–1.5)	50 or 0	12	Air
Effect of microwave adsorbent II	Al powder (0.58), AC (1.5), CC (1.5)	50 or 0	3–15	Air
HMP I	Al powder (0.2 and 0.39)	50	3–12	Air or N ₂
HMP II	AC (1.5–10)	50	0–25	N ₂

section (see Table 1). The functional groups of AC and CC were analyzed by Fourier transform infrared spectroscopy (FT-IR).

2.4. Hybrid microwave process (HMP)

The experiments were performed under either air or nitrogen atmospheres. In part I, different dosages of Al powder (0.2 and 0.39 g) were added with moisture content of 50%. The procedure follows: (1) put the sample in the microwave oven and close the ventilation channel, (2) withdraw air from the oven with a vacuum pump, (3) fill the oven with the reaction gas (air or nitrogen) to a pressure of 101 kPa, (4) stop the pumping of reaction gas and apply microwave radiation to stabilize Cu, and (5) purge the system with cooling gas (air or nitrogen) for 15 min after the stabilizing process.

In part II, different amount of AC was added with moisture content of 50%. The experimental steps were similar to part I, and only step 4 and step 5 were replaced as: (4) open the ventilation channel and continuously purge nitrogen gas during the microwave stabilization process, and (5) purge nitrogen gas to cool the system for 15 min.

3. Results and discussion

3.1. Chemical composition and TCLP results

The chemical composition of raw wastewater sludge and TCLP results of DeS are listed in Table 2. The major metals in raw wastewater sludge were Si, Ca, Na, Fe, Cu, K, and Al in decreasing order. The existence of Ca, Fe, and Al in the sludge is mainly attributed to the use of chemical precipitants, such as lime, ferrous sulfate, and poly aluminum chloride, in wastewater treatment. The Cu and Si came from the manufacturing of printed circuit board. Comparing the chemical composition and TCLP results, Si was found to be in the form of insoluble particles. The TCLP results of DeS show the major leachable metals were Cu, Ca, Mg, Na, and Al, and the concentration of Cu (445 mg l⁻¹) is the only metal exceeding the TCLP criterion. Moreover, the TCLP concentration of Cu was still around 221 mg l⁻¹ even when the 0.58 g aluminum powder was added directly in 40 g DeS. From the XRD analysis of raw sludge (Fig. 1a), only CaSO₄ with different numbers of

Table 2
TCLP results of DeS and chemical composition of raw industrial wastewater sludge

Element	TCLP (mg l ⁻¹)	Chemical composition (mg g ⁻¹)
Ag	N.D. (5 ^a)	N.D.
Al	20.43	3.77
Ba	N.D.	2.06
Ca	270	66.91
Cd	N.D. (1 ^a)	N.D.
Co	N.D.	N.D.
Cr	N.D. (5 ^a)	N.D.
Cu	445 (15 ^a)	11.58
Fe	N.D.	13.68
Ga	N.D.	N.D.
K	16	6.01
Mg	59	1.68
Mn	1.83	0.05
Na	40	14.69
Ni	N.D.	N.D.
Pb	2.81 (5 ^a)	0.15
Si	N.D.	85.4
Zn	3.51	0.52

N.D.: not detected.

^a TCLP criteria.

crystalline water had better crystalline structure. Copper species were not detected by XRD which may be attributed to the minor content of copper species and the amorphous structure in the raw sludge. The instrument detection limit of the liquid extract was 0.1 mg l⁻¹, which translates into a detection limit of 0.05 mg g⁻¹ for the sludge. The “N.D.” in Table 2 means <0.05 mg g⁻¹. Further, the method detection limit of TCLP acetic acid leachate was also measured for Cu, Fe, and Al. The values were 0.3, 0.3, and 0.5 mg l⁻¹ for Cu, Fe, and Al, respectively.

The amount of polymeric materials in the raw wastewater sludge was usually around 25% by weight if the composition and molecular structure of the polymeric materials were unknown. In addition, the ability of processing polymeric materials with microwave radiation is depending on the dipole structure, frequency of processing, temperature, and additives or filters that have been included with the polymer (Thostenson and Chou, 1999). During pretreatment steps, the polymeric materials were removed by microwave radiation to prevent the effect of polymeric materials on stabilization of the wastewater sludge. However, the removal of polymeric materials increased the

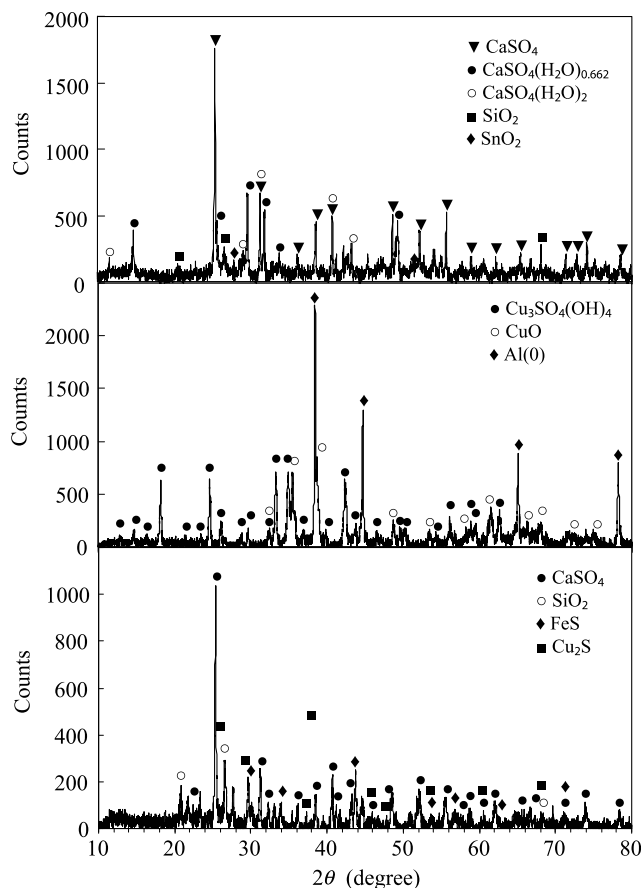


Fig. 1. XRD results of (a) raw heavy metal sludge, (b) pure agents experiment, and (c) sludge through hybrid microwave process.

leachable copper and made the TCLP concentration of Cu in DeS (445 mg l^{-1}) much higher than that in the raw wastewater sludge (132 mg l^{-1}). Also, the pH value of the DeS leachate during TCLP was around 4.2 ± 0.2 .

3.2. Effect of additive

The relationship between additive dosage and stabilization ratio (SR) of Cu in DeS is illustrated in Fig. 2

$$\text{SR} = \frac{\text{Total leachable Cu} - \text{TCLP Cu}}{\text{Total leachable Cu}} \quad (1)$$

The SR in Fig. 2 increased rapidly (over 90%) upon the addition of Al, Fe, and Zn powders to the dosage of 0.7 g, but maintained the same stabilization effect even with more additives dosage. With the same dosage, Zn powder yielded a lower SR. When the additive dosage unit was in mole, the stabilization efficiencies of Fe, Zn, and Al powder were in decreasing sequence. This phenomenon may be attributed to the oxidation tendency of metal powders under microwave radiation and the presence of oxygen which decreased the reduction tendency of Cu(II) in the sludge. In the cases of $\alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ additives, no significant increases of SR were observed, although $\gamma\text{-Al}_2\text{O}_3$ is a better microwave adsorbent than

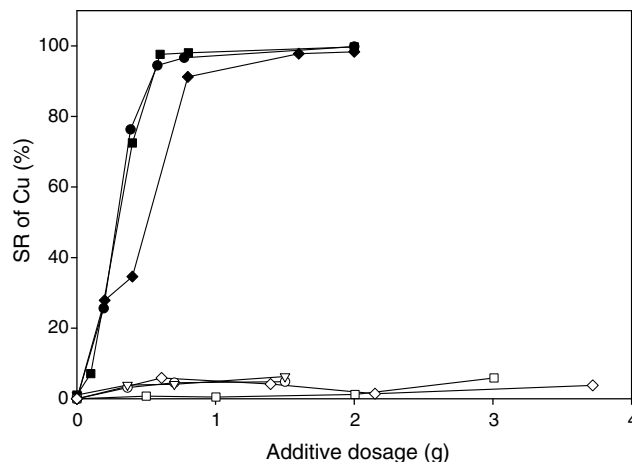
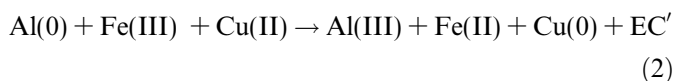


Fig. 2. Effect of additive dosage on the stabilization of wastewater sludge (DeS). (■) Ferrous powder, (●) aluminum powder, (◆) zinc powder, (○) $\alpha\text{-Al}_2\text{O}_3$, (▽) $\gamma\text{-Al}_2\text{O}_3$, (□) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and (◇) $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

$\alpha\text{-Al}_2\text{O}_3$. These results indicate that the valence charges of the additives may be the dominant factor of assisting the stabilization of heavy metal sludge. This experiment shows the metal powder can effectively increase the SR of copper in the sludge under microwave radiation. Similar studies also indicated that under microwave radiation, Fe powder and Fe wire could efficiently decrease the leachability of metal ions from solid wastes (Tai and Jou, 1995; Chen et al., 2005; Jou, 2006). Although silicon is essentially unaffected by microwave radiation, a large amount of silicon may still slightly reduce the metal stabilization effect due to the adsorption of small amount of microwave energy by silicon (Haque, 1999). The existence of silicon in the sludge may also increase the distance between stabilizing agents and copper ions, and thus reduce the efficiency of stabilization reaction.

Fig. 3 shows the variation of leaching concentrations of metal ions at different processing time with the addition of 0.58 g Al powder. The decreasing of copper ions during the first 3 min may attribute to the reducing ability of Al powder. The dissolved copper species may be reduced to Cu(0) in the sludge and during TCLP test, which was not oxidized or leached out during the TCLP test. As the copper ions was stabilized, the concentration of Al and Fe increased with time. Also, the trend of Fe(II) concentration was coincident with that of totally dissolved Fe. The reaction mechanisms may be proposed as: (1) Al(0) reduces Fe(III) to form Al(III) and Fe(II) or Fe(0), and subsequently Fe(II) or Fe(0) reduces Cu(II) to form Cu(0) and Fe(II), contributing to the stabilization of Cu and the leaching of Fe. (2) Al(0) reduces Fe(III) and Cu(II) simultaneously to form Fe(II) and Cu(0). The reaction equation follows:



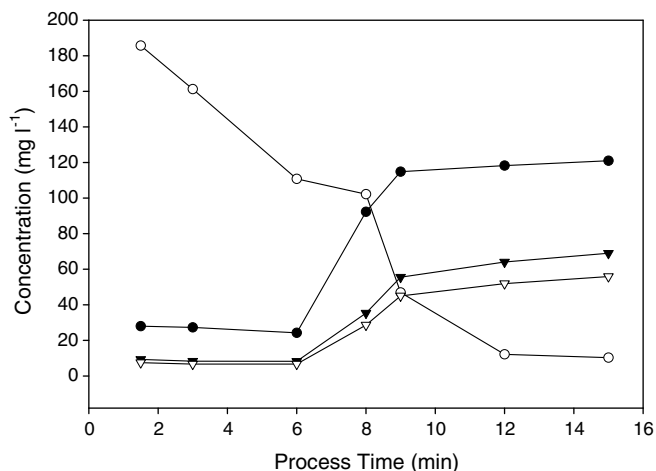
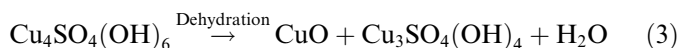


Fig. 3. TCLP concentrations of stabilized heavy metal sludge at different processing time. (○) Cu, (●) Al, (▼) Fe, and (▽) Fe(II).

where EC' is the energy consumption. However, the addition of polymeric materials during wastewater treatment and the insufficient aging were responsible for the poor crystalline nature of copper species in industrial wastewater sludge. The poor crystalline character hinders the phase identification by XRD.

During 3–9 min period, the moisture content decreased gradually from 20–25% to 0%, so the average temperature reached about 100 °C at 9 min. From 9 to 15 min, the moisture content was maintained at 0%, and the average temperature detected by a thermal couple was up to 250–300 °C. In this period, the reactions between Al powder and copper species are solid state reactions. The actual temperature around Al powder should be much higher than the average temperature of the system owing to the local reflection of microwave radiation by Al particles and the heat released by its oxidation. Also, the “microarcing” phenomenon of Al fine particles under microwave radiation (Grant, 1992) could lead to the locally high temperature. The locally higher temperature may be responsible for the dehydration reaction of Cu(II) to form CuO, which is less soluble in TCLP. A pure reagent experiment was performed to figure out the stabilization mechanism of Cu(II) by dehydration reaction. The artificial Cu(OH)₂ was in the form of Cu₄SO₄(OH)₆ which was regarded as a more similar species to the copper in the raw sludge than Cu(OH)₂. The XRD result of this better crystal system (Fig. 1b) showed the formation of CuO and Cu₃SO₄(OH)₄ from dehydration reaction of Cu₄SO₄(OH)₆ during the microwave process. The reaction equation follows:



Furthermore, the pH values of the TCLP leachates of these stabilized sludge were slight decreased to around 4.0 ± 0.2 in spite of the process time. The small reduce of pH values compared with that of raw sludge or DeS may be attributed to the formation of Al(OH)₃ which may also

decrease the concentration of Cu(II) in TCLP. The Al(OH)₃ was mainly formed by the existence of Al(III) generated from reduction reaction.

3.3. Effect of microwave adsorbents

Water is an excellent microwave adsorbent. As shown in Fig. 4a, the case of moisture content 50% with Al additives has the best stabilization results. Water in the DeS does not only adsorb the microwave energy efficiently but can also transfer the energy to heat to facilitate the stabilization reaction of the system. In addition, the water also helps to distribute the Al power more homogeneously in the DeS. Organic carbon is another suitable microwave adsorbent and was applied efficiently to solid waste treatments in previous studies (Menendez et al., 2002). In this study, AC could adsorb microwave energy efficiently, and the local hot spot may form without adding water into the DeS. However, only the hot spot sites were of better stabilization results but not the whole samples. The SR of AC addition with moisture content 50% was better than that with moisture content 0%, even though the average temperature was almost the same in these two cases. The homogeneous dispersion of microwave energy and reactants is very important in the stabilization experiments.

The combined effect of additive and microwave adsorbent was studied (Fig. 4b). The CC used in this experiment is a solid waste generated from coal-fired power plant, and is a good microwave adsorbent. When stabilizing additive, Al powder, was added, the SR increased with processing time in all cases. The cases of adding CC yielded higher SR when comparing with the cases of adding AC. The average temperatures in the cases of adding CC were higher than those of adding AC at the same water content. From the characterizing results of FT-IR in Fig. 5, the functional groups of AC were defined as aromatic C–H stretching, symmetric COO⁻ stretching, and C–O stretching. For CC, the functional groups on the surface were aromatic C–H stretching, asymmetric COO⁻ stretching, C–OH stretching, and C–Cl stretching. Since the wavelength of microwave radiation applied in this study is about 12.2 cm which is far from the range of IR, the function group structures would not “adsorbed” microwave energy directly and resonated with the microwave radiation. However, the microwave radiation may induce the formation and rotation of dipole moment of these function groups. The dipole moment is related to the polarity of molecule and with the manner of C=O > C–O > C–Cl > C–H. The rotation of dipole moment induced by microwave radiation could cause the friction between molecules and influence the rising of temperature.

The SR was higher at higher temperature or longer processing time in the cases of adding Al powder. However, the differences among cases were minor at the processing time of 15 min. The results of this experiment indicated the feasibility of co-treatment of organic and inorganic

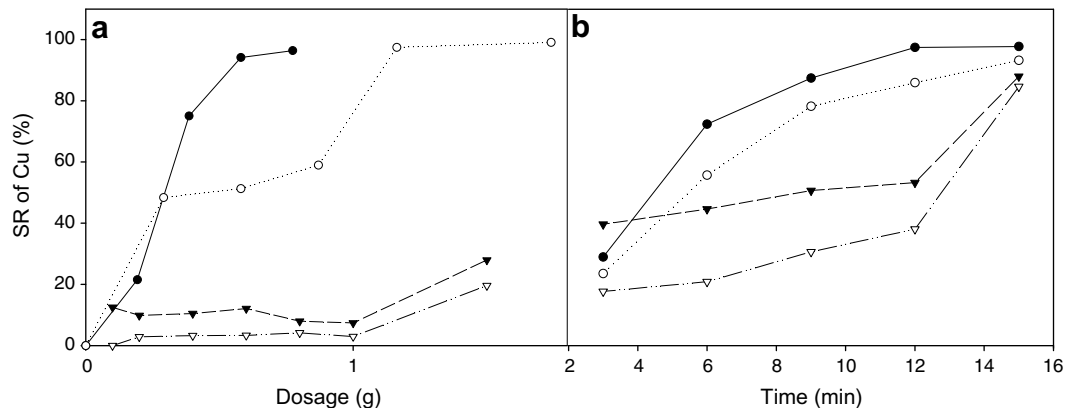


Fig. 4. Effects of microwave adsorbents and additive dosage. Case (a): (●) Al powder addition at moisture content 50%, (○) Al powder addition at moisture content 0%, (▼) AC addition at moisture content 50%, and (▽) AC addition at moisture content 0%. Case (b): (●) Al powder and CC addition at moisture content 50%, (○) Al powder and CC addition at moisture content 0%, (▼) Al powder and AC addition at moisture content 50%, and (▽) Al powder and AC addition at moisture content 0%.

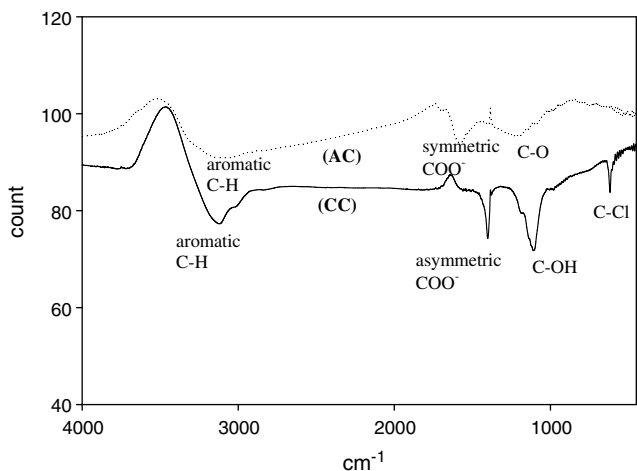


Fig. 5. Functional groups of AC and CC by FT-IR.

solid wastes with the addition of appropriate stabilizing agent under microwave radiation.

3.4. Hybrid microwave process

HMP I was conducted to understand the effect of reaction atmosphere and cooling gas on stabilization effect (Fig. 6a). The best result was derived by using N₂ as the reaction atmosphere and cooling gas. It can be attributed to the decrease of oxidation of Al powder to Al₂O₃ under inert atmosphere and cooling gas. The microwave radiation may also have increased the energy and reactivity of the aluminum powder. Both effects prevented the Al powder from being consumed and improved the stabilization efficiency. The lower temperature in the cases of N₂ reaction atmosphere was also observed in this study. The final temperatures of case air/air, N₂/air, and N₂/N₂ after the microwave radiation 600 W for 12 min were about 200, 150, 50 °C, respectively. In addition, in the case of N₂/air, the cooling air may have suddenly enhanced the oxidation of Al powder at higher temperature to release a large amount of oxidation heat and converted Cu(OH)₂ to CuO.

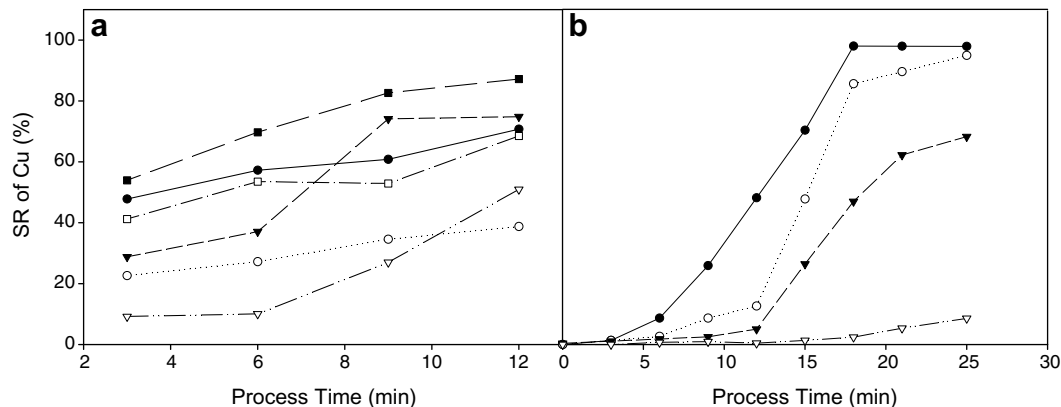


Fig. 6. Stabilization results by hybrid microwave process. (a) Adding 0.39 g Al powder with (■) N₂/N₂, (▼) N₂/air, and (●) air/air. Adding 0.2 g Al powder with (□) N₂/N₂, (▽) N₂/air, and (○) air/air. (b) Addition of AC of (▽) 1.5 g, (▼) 3 g, (○) 6 g, and (●) 10 g.

In the case of air/air, the gradual release of oxidation heat of Al powder led to a moderate increase of SR.

The effect of AC dosage and processing time under inert condition was studied (Fig. 6b). In a closed microwave system, steam would be generated and continuously adsorb the microwave energy to decrease the efficiency of the microwave stabilization. A preliminary experiment of adding 3 g of AC without the ventilation (step 4) in HMP II was performed. The result showed no stabilization effect, and thus implies the significant effect of steam on microwave strategy.

In the step (4) of HMP II, the ventilation channel was opened to eliminate the accumulation of steam in the system by pumping in N_2 . Results indicated that the SR increased with the increase of AC dosage and processing time. The AC added in the DeS adsorbed microwave energy and increased the temperature of DeS to enhance the formation of CuO. Owing to the minor amount of aluminum hydroxide or alumina in the DeS, the copper species may also be transformed into $CuAl_2O_4$ at higher temperature (Jacob and Alcock, 1975; Shaheen, 2002; Wei et al., 2004). When the processing time was longer than 18 min and the AC dosage was more than 3 g, a minor portion of the DeS went through the vitrifying process (glass/ceramic transformation) into a mineral phase with very low leachability of copper. Furthermore, in the case of adding 10 g of AC, the reduction reaction occurred at the inert and high temperature condition with processing time >21 min. The sulfates in the DeS was reduced to H_2S or S which may also reduce the leaching concentration of Cu. Metal burnish marks were also observed on the surface of the DeS which may be attributed to the reduction of metal oxide or metal hydroxide by burning carbon at high temperature. The XRD result of reduction reaction was shown in Fig. 1c, and anhydrate $CaSO_4$ was still the major species in the sludge. The Fe and Cu species were in the form of FeS and Cu_2S respectively which can interpret the occurrence of reduction reaction and the stabilization of copper. These results imply that the AC is a good dielectric material with the advantage of controlling temperature in the absence of oxygen. Similar results due to the effect of organic carbon can be found in the pyrolysis of sewage sludge (Menendez et al., 2002).

4. Conclusions

In this study, microwave-assisted stabilization of Cu in industrial wastewater sludge was investigated. The major metals in industrial wastewater sludge are Si, Ca, Na, Fe, Cu, K, and Al in decreasing order, and Cu is the only one exceeding the TCLP criterion. Leachable copper may be reduced to Cu(0) by redox reaction of metal powders in the sludge and during the TCLP, but the stabilization efficiencies by metal powders under microwave radiation were in the inverse order of metal reactivity. The majority of Fe in the sludge was also reduced to Fe(II) during the process. Formation of $Al(OH)_3$ could also decrease the

Cu concentration in the TCLP. With microwave radiation, the Cu(II) may also be transformed to CuO through dehydration reaction carried out by the reflection, oxidation heat and microarcing process of Al powder. Further, appropriate amounts of water in the solid samples would increase the homogeneity of microwave energy to increase the reactions between stabilizing agents and copper. Removing steam from the microwave oven, not in the sample, could increase the stabilizing efficiency. The inert atmosphere and cooling gas gave better performance in stabilizing copper as well. In hybrid microwave process, when processing time was longer than 18 min and AC dosage was more than 3 g, a minor portion of the DeS was vitrified and leading to low copper leachability. Adding carbonaceous materials in the samples would enhance the transformation of copper into $CuAl_2O_4$ due to the additional burning heat. Also, in this process, the reduction reaction may be also attributed to the formation of Cu_2S leading to the stabilization of Cu(II). Moreover, microwave radiations may be feasible for co-treating organic and inorganic solid wastes with appropriate blending.

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