

Sulfidation treatment of copper-containing plating sludge towards copper resource recovery

D. Kuchar^a, T. Fukuta^b, M.S. Onyango^a, H. Matsuda^{a,*}

^a Department of Chemical Engineering, Nagoya University, Furo-cho, Chikusa-ku, 464-8603 Nagoya, Japan

^b Sanshin Mfg. Co., Ltd., 1-2 Kifuneura Haguro, Inuyama, Aichi 484-0894, Japan

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Abstract

The present study is concerned with the sulfidation treatment of copper-containing plating sludge towards copper resource recovery by flotation of copper sulfide from treated sludge. The sulfidation treatment was carried out by contacting simulated or real copper plating sludge with Na₂S solution for a period of 5 min to 24 h. The initial molar ratio of S²⁻ to Cu²⁺ (S²⁻ to Me²⁺ in the case of real sludge) was adjusted to 1.00, 1.25 or 1.50, while the solid to liquid ratio was set at 1:50.

As a result, it was found that copper compounds were converted to various copper sulfides within the first 5 min. In the case of simulated copper sludge, CuS was identified as the main sulfidation product at the molar ratio of S²⁻ to Cu²⁺ of 1.00, while Cu₇S₄ (Roxbyite) was mainly found at the molar ratios of S²⁻ to Cu²⁺ of 1.50 and 1.25. Based on the measurements of oxidation–reduction potential, the formation of either CuS or Cu₇S₄ at different S²⁻ to Cu²⁺ molar ratios was attributed to the changes in the oxidation–reduction potential. By contrast, in the case of sulfidation treatment of real copper sludge, CuS was predominantly formed, irrespective of S²⁻ to Me²⁺ molar ratio.

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1. Introduction

Heavy metals, such as copper, zinc, nickel, chromium and tin are commonly used in the electroplating industry to form a thin layer on the various products, and thus, to achieve a high surface resistance against the severity of the environment. Consequently, the durability of the products manufactured is significantly increased. The major part of heavy metals employed in the electroplating process is deposited on the surface of products being plated; however, a minor part of these heavy metals is discharged as rinsing wastewater. The rinsing wastewater contains soluble metallic salts such as CuSO₄, ZnSO₄, and NiSO₄ at high concentrations of about 100–300 mg/L. In Japan, the rinsing wastewater is treated to decrease the concentrations of the heavy metals to values below the permissible limits of 3 and 5 mg/L for Cu and Zn, respectively [1].

Presently, the heavy metals are removed from the rinsing wastewater by chemical precipitation, in which the dissolved heavy metals are converted to insoluble hydroxides, oxides, carbonates or sulfides [2]. In the majority of plating shops, the chemical precipitation is carried out using either NaOH or Ca(OH)₂, and the pH value is kept within the range of 9.20–9.50 for at least 15 min. As far as the pH value is kept in this range, the content of various heavy metals involved in mixed-metal wastewaters can be reduced below the permissible limits [2,3]. The precipitate/plating sludge containing various heavy metals is then subjected to the dewatering process to reduce the total sludge volume [4], followed by the final disposal of plating sludge. In order to prevent heavy metals from leaching into the environment, the plating sludge is stabilized/solidified with the binding materials such as cement, lime, fly ash or asphalt emulsion [5–9]. In Japan, the amount of plating sludge generated annually amounts to 65,000 t [10], posing a potential risk to the environment. Besides, the presently used sludge treatment methods focus rather on the immobilization of heavy metals than on the recovery of these metals from plating sludge, although the mineral deposits of Zn, Cu and Ni are envisaged to be depleted

* Corresponding author. Tel.: +81 52 789 3382; fax: +81 52 789 5619.
E-mail address: matsuda@nuce.nagoya-u.ac.jp (H. Matsuda).

Nomenclature

$a_{S^{2-}}$	activity of S^{2-} ions (mol/L)
$a_{S_2^{2-}}$	activity of S_2^{2-} ions (mol/L)
E	oxidation–reduction potential of the reacting system (V)
E_o	standard oxidation–reduction potential of S_2^{2-}/S^{2-} couple (V)
F	Faraday's constant (C/mol)
ΔG	Gibbs free energy (kJ/mol)
ΔG_f°	Gibbs free energy of formation (kJ/mol)
n	number of electrons transferred (–)
R	gas constant (J/(K mol))
$[S^{2-}]$	concentration of S^{2-} ions (mol/L)
$[S_2^{2-}]$	concentration of S_2^{2-} ions (mol/L)
T	temperature (K)

within 30, 36 and 50 years, respectively [11]. Therefore, a development of effective systems for recycle and reuse of the metals involved in plating sludges is required. According to McLay and Reinhard [12], the number of companies showing the interest in making use of metal-bearing sludges has recently increased, but the recovery of heavy metals from the mixed-metal sludge was found to be difficult because of the sludge heterogeneity as well as the presence of inorganic salts [12].

In this work, the sulfidation treatment of plating sludges was investigated in order to convert heavy metals to metallic sulfides and thus to overcome the difficulties resulting from the sludge heterogeneity. The sulfidation treatment is a method which has been used in the sulfidation treatment of various oxidized copper ores such as chrysocolla, brochantite [13], malachite [14,15] and copper oxide [16] in order to improve the metal recovery

from natural resources. After the sulfidation treatment, the heavy metal sulfides are separated by means of flotation which is a commonly used separation technique in the process of refining metal resource from sulfide ores [17,18]. In this work, the sulfidation experiments were conducted for simulated and real copper plating sludge by using Na_2S aqueous solution as a sulfidation agent. The initial molar ratio of S^{2-} to Cu^{2+} (S^{2-} to Me^{2+} in the case of real plating sludge) was adjusted to 1.00, 1.25 or 1.50, while the solid to liquid (S:L) ratio was fixed at 1.00:50 (1.00 g sludge to 50 mL Na_2S solution). The S:L ratio of 1:50 was chosen with respect to the results of our previous experiments [19], where the effect of S:L ratio on the conversion was investigated for copper hydroxide in the range of S:L ratio of 1:250 to 1:25 and it was found that, in this range, the conversion of copper hydroxide to copper sulfide was not affected by the S:L ratio. The amount of sulfide ions remaining after contacting the simulated or real copper plating sludge with Na_2S solution for a period of 5 min to 24 h was analyzed using an ion selective electrode. Further, the sulfidation products were identified by means of an XRD analysis of sulfidation products. Finally, the effect of particle size on the conversion was investigated.

2. Experimental part

2.1. Preparation of copper plating sludge

2.1.1. Simulated copper plating sludge

The simulated copper plating sludge was prepared according to flow chart shown in Fig. 1(a). An amount of 12.8 g $CuSO_4 \cdot 5H_2O$ of reagent grade (Wako Pure Chemical Industries, Ltd.) was dissolved in a 400 mL distilled water. Then, the pH value of the solution was increased from about 4.2 to 9.40 ± 0.1 using 1 M NaOH solution, under continuous stirring,

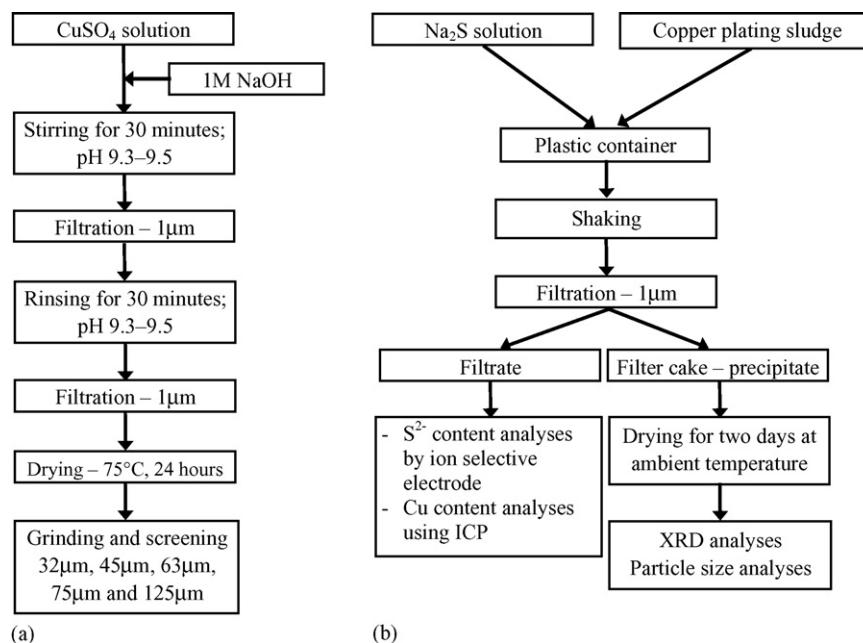


Fig. 1. Experimental flow chart of preparation of simulated copper plating sludge (a) and sulfidation treatment (b).

Table 1
Composition of real and simulated copper plating sludge

	Real sludge content (mg/g)	Simulated sludge content (mg/g)
Cu	257.1 ± 8.75	623.8 ± 11.9
Cd	1.020 ± 0.01	–
Cr	2.300 ± 0.01	–
Fe	3.600 ± 0.16	–
Ni	48.16 ± 1.12	–
Mn	0.390 ± 0.01	–
Pb	12.69 ± 0.15	–
Zn	19.46 ± 0.51	–
Na	28.56 ± 0.94	8.200 ± 0.29
Ca	46.83 ± 1.42	–
K	0.570 ± 0.04	–

to make up a total volume of about 500 mL. As a consequence of the increase in pH, copper ions were precipitated as insoluble copper hydroxide and copper hydroxide sulfates such as posnjakite and brochantite [20,21]. The precipitation was allowed to proceed for 30 min and then the slurry/precipitate formed was filtered using a filter paper with pore size of 1 µm. The precipitate was, then, rinsed in 500 mL distilled water for another 30 min, in order to purify the copper precipitate. During rinsing, the pH value was kept constant at the value of 9.40 ± 0.1 . In the subsequent step, the precipitate was again filtered using a filter paper with pore size of 1 µm. Finally, the precipitate was dried in a muffle furnace at a temperature of 75 °C for 24 h. The precipitate obtained in such a manner was denoted as simulated copper plating sludge. Before the sulfidation experiments, the simulated copper plating sludge was thoroughly ground and screened using sieves with mesh diameters of 32, 45, 63, 75 and 125 µm.

2.1.2. Real copper plating sludge

The sample of real copper plating sludge acquired from San-shin Mfg. Co., Ltd., Japan was used. In a similar way to that of simulated copper plating sludge, the real plating sludge was dried in a muffle furnace at a temperature of 75 °C for 24 h, and then thoroughly ground and screened using sieves with mesh diameters of 32, 45, 63, 75 and 125 µm.

2.2. Determination of plating sludge composition

The content of copper as well as other elements in the dried samples of the simulated and real copper plating sludge was determined in triplicate by dissolving 100 mg of each sample in aqua regia (a mixture of HCl and HNO₃ at a ratio of 3:1). Then, the solutions arising thereof were analyzed using inductively coupled plasma (ICP, Vista-MPX Simultaneous ICP-OES, Varian, Inc.). The composition of both plating sludges is given in Table 1. It can be seen that the copper content in the simulated plating sludge was more than twice higher than that of real plating sludge. In addition, other heavy metals such as nickel, zinc, lead, etc., as well as high amounts of sodium and calcium were found in the real copper plating sludge.

Furthermore, in order to analyze the crystallographic composition, the samples were subjected to X-ray powder diffraction

(XRD) analysis with scanning mode of $2\theta/\theta$, under the condition of 50 kV/100 mA (RINT-2500 TTR, Rigaku Model). Finally, in the case of simulated copper plating sludge, the amount of copper sulfate remaining in the sludge in copper hydroxide sulfates was determined by means of thermogravimetric analysis (TGA-50, Shimadzu Corporation, Japan) under N₂:O₂ atmosphere (ratio of N₂:O₂ of 4:1), at a gas flow rate of 50 mL/min and a heating rate of 2 °C/min.

2.3. Treatment procedure

The sulfidation treatment of both sludges was carried out in a batch system, according to the diagram shown in Fig. 1(b). A volume of 50 mL aqueous Na₂S solution, prepared by dissolving Na₂S·9H₂O of reagent grade (Wako Pure Chemical Industries, Ltd.) in distilled water to adjust the initial molar ratio of S²⁻ to Me²⁺ to 1.00, 1.25 or 1.50, was poured into a plastic container. In the case of copper simulated sludge, Me²⁺ stands only for Cu²⁺, and thus the molar ratio of S²⁻ to Me²⁺ is referred to as S²⁻ to Cu²⁺ molar ratio. By contrast, in the case of real plating sludge, the initial molar ratio of S²⁻ to Me²⁺ of 1.50, 1.25 or 1.00 refers to the sum of all heavy metals present in the real sludge (Table 1).

In the next step, an appropriate amount of the sludge was charged into each plastic container adjusting a solid to liquid (S:L) ratio to 1.00:50 (sample weight concentration of about 20 g/L). Then, the plastic containers were shaken on a vertical shaker for a period of 5 min to 24 h. Finally, the slurry was filtered with a 1 µm pore size filter paper.

2.4. Analyses of filtrates and filter cakes

The filtrates were subjected to the determination of heavy metals using ICP. The concentration of sulfide ions remaining in the filtrates was measured by S²⁻ ion selective electrode (S-125, Ion meter IM-55G, DKK-TOA Corp.). In the measurements of residual concentrations of S²⁻ ions, the pH of the sample solution was kept at a value higher than 13.0, in accordance with the standard procedure for the measurement of S²⁻ ions, and then, the ionic strength of the sample solution was adjusted by L-ascorbic acid.

The filter cakes were dried at an ambient temperature of about 25 °C for 2 days, and then subjected to X-ray powder diffraction (XRD) analysis. In addition, the particle size distribution of sulfidation products was measured by means of a laser scattering particle size distribution analyzer (Horiba LA-920, Horiba Ltd., Tokyo, Japan).

2.5. Determination of oxidation–reduction potential

The oxidation–reduction potential (ORP) of the reacting system was measured using an ORP electrode (PST-5721C, DKK-TOA Corp.). The ORP electrode was immersed into the plastic container filled with Na₂S solution, which was placed on a magnetic stirrer, to obtain the initial ORP value. In the next step, a 1 g of the copper sludge was charged into the plastic container adjusting a solid to liquid (S:L) ratio to 1.00:50, and the change

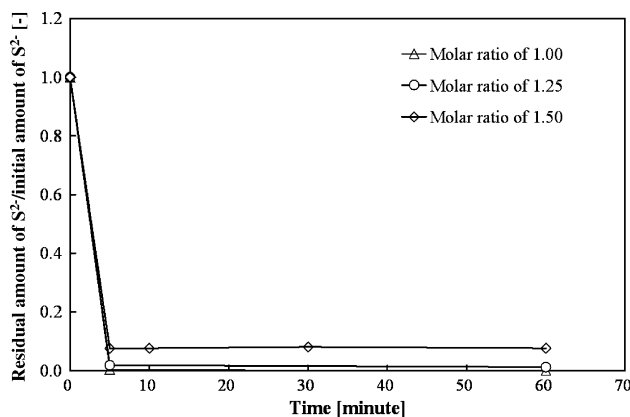


Fig. 2. Time change of residual concentration of S^{2-} ions for simulated copper plating sludge.

in the ORP value during sulfidation was recorded continuously. To avoid the consumption of sulfide ions in the sample solution by oxidation, the plastic container, with the ORP electrode immersed inside, was sealed with a wrap film.

3. Results and discussion

3.1. Sulfidation behavior of simulated copper plating sludge

3.1.1. Effect of S^{2-} to Cu^{2+} ratio on the composition of sulfidation products

The simulated plating sludge screened to a particle size lower than $32\ \mu\text{m}$ was contacted with Na_2S solution at the initial molar ratios of S^{2-} to Cu^{2+} of 1.00, 1.25 and 1.50, which corresponded to the pH value of the reacting system of 13.15, 13.25 and 13.30, respectively. In this work, no pH adjustment was performed and the pH value of the reacting system resulted from the amount of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ dissolved in distilled water to adjust an initial molar ratio of S^{2-} to Cu^{2+} . Fig. 2 shows the time change of the consumption of S^{2-} ions at different S^{2-} to Cu^{2+} molar ratios for the simulated copper plating sludge. It can be seen from the figure that S^{2-} ions were almost completely consumed within the first 5 min, which indicated a high reaction rate of sulfidation of copper compounds to copper sulfides. Similar to this study, the high sulfidation rate has been reported for the sulfidation of brochantite $[\text{Cu}_4(\text{OH})_6\text{SO}_4]$ and chrysocolla $[\text{CuO}\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O}]$ with ammonium sulfide [13], further for the sulfidation of chrysocolla and malachite $[\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2]$ with sodium sulfide [14], and for the sulfidation treatment of malachite with sodium sulfide and sodium tetrasulfide [15]. However, in the reported research works, the sulfidation rate of oxidized copper ores was found to be the highest at mildly acidic or neutral pH, and the sulfidation rate significantly decreased when the pH value was increased to a value of about 11.0. In particular, Raghavan et al. [13] reported that at the pH value of 7.4, the sulfide ions were consumed within the first 5 min of contacting brochantite with ammonium sulfide, while at a pH value of 10.5, a contacting time of 30 min was required. By contrast, a high sulfidation rate was obtained in this study at the pH value higher than 13.0 for the simulated

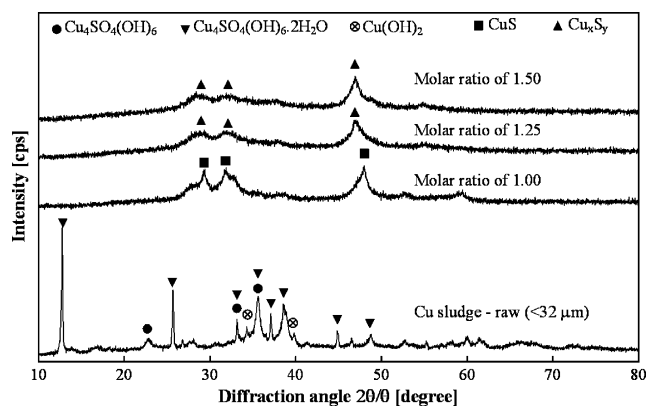
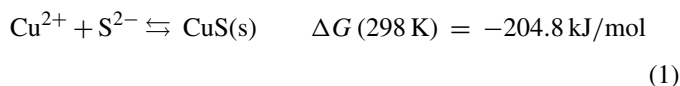


Fig. 3. XRD patterns of simulated copper plating sludge obtained after 5 min at different S^{2-} to Cu^{2+} molar ratios.

copper plating sludge containing a mixture of brochantite, posnjakite and copper hydroxide. It is considered that the difference in the sulfidation rate resulted from a significantly lower crystallinity of minerals involved in plating sludge compared to that of copper ores. Hence, the crystals of brochantite, posnjakite and copper hydroxide involved in simulated copper plating sludge were more susceptible to sulfidation treatment and therefore a high reaction rate was achieved resulting in the complete sulfidation within the first 5 min.

To identify the products of sulfidation reactions, the XRD analysis of sulfidation products was carried out and the results are shown in Fig. 3, together with XRD patterns of the raw simulated copper plating sludge. As shown in this figure, the presence of $\text{Cu}(\text{OH})_2$, posnjakite $[\text{Cu}_4\text{SO}_4(\text{OH})_6\cdot 2\text{H}_2\text{O}]$, and brochantite $[\text{Cu}_4\text{SO}_4(\text{OH})_6]$ was confirmed in the raw simulated copper plating sludge. The amount of copper sulfate remaining in the sludge in copper hydroxide sulfates was determined by means of TG analysis. At first, it was found that the crystalline water was evaporated in the temperature range of $140\text{--}380\ ^\circ\text{C}$ and then the remaining CuSO_4 of posnjakite and brochantite was decomposed to CuO in the temperature range of $580\text{--}710\ ^\circ\text{C}$. Based on the weight loss accompanying the decomposition of CuSO_4 to CuO , the amount of CuSO_4 remaining in copper hydroxide sulfates was estimated to be about 13.5 wt%.

Then, when the simulated copper plating sludge contacted with Na_2S at the S^{2-} to Cu^{2+} molar ratio of 1.00 was analyzed using XRD, the cupric (Cu^{2+}) sulfide was found as the main product of sulfidation, while no peaks of the raw sludge were observed. From this result, it was considered that cupric ions of copper hydroxide, brochantite and posnjakite reacted with S^{2-} ions to yield CuS at a molar ratio of S^{2-} to Cu^{2+} of 1.00, as expressed by Eq. (1).



By contrast, various cuprous (Cu^+) sulfides, such as Cu_2S , Cu_7S_4 , Cu_8S_5 and $\text{Cu}_{31}\text{S}_{16}$ with a molar ratio of copper to sulfur of about 2 to 1 were formed when the sulfidation experiments were conducted at S^{2-} to Cu^{2+} molar ratio of 1.25 and 1.50. This result suggests that the cupric ions were, at first, reduced

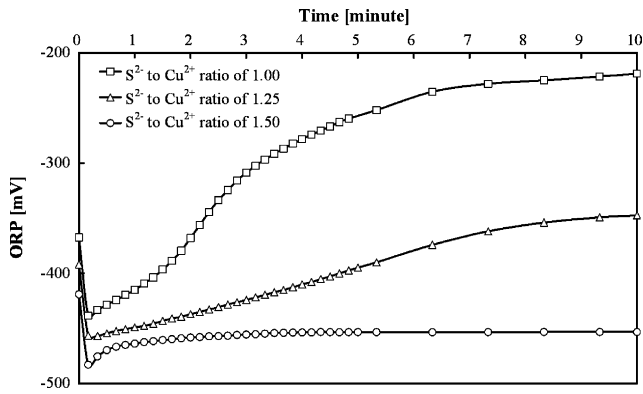
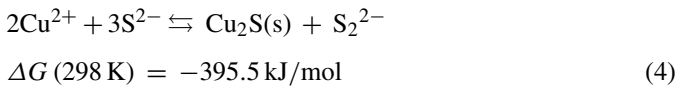
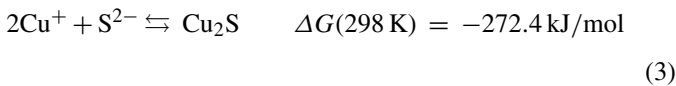
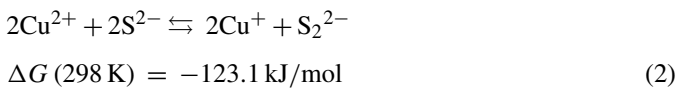


Fig. 4. Time change of oxidation–reduction potential for simulated copper plating sludge.

to cuprous ions and were subsequently precipitated to various cuprous (Cu^+) sulfides. Based on this result, it was considered that, at higher S^{2-} to Cu^{2+} molar ratios, the sulfidation of copper occurred according to the following reactions expressed by Eqs. (2) and (3).



Eq. (2) shows the oxidation–reduction reaction of Cu^{2+} (reduced to Cu^+) with S^{2-} (oxidized to S_2^{2-}) followed by the precipitation of Cu_2S as expressed by Eq. (3). Eq. (4) summarizes the overall reaction mechanism and Gibbs free energy of this reaction (calculated using HSC Chemistry Ver.3.02) was found to be -395.5 kJ/mol , which was almost twice greater than the Gibbs free energy of the reaction given by Eq. (1). Thus, from thermodynamic point of view, it was considered that the sulfidation of copper should proceed via Eqs. (2) and (3) rather than Eq. (1).

3.1.2. Effect of ORP on sulfidation of copper

In order to clarify the mechanism of sulfidation of copper, the ORP measurements were carried out and the results expressed in terms of ORP against standard hydrogen electrode are shown in Fig. 4. In this figure, it can be seen that the ORP value steeply decreased when the sludge was added to the plastic container filled with Na_2S solution, irrespective of S^{2-} to Cu^{2+} molar ratio. The decrease in the ORP value was caused by the oxidation half reaction (Eq. (5)), which coexisted with the reduction half reaction of Cu^{2+} to Cu^+ given by Eq. (6):

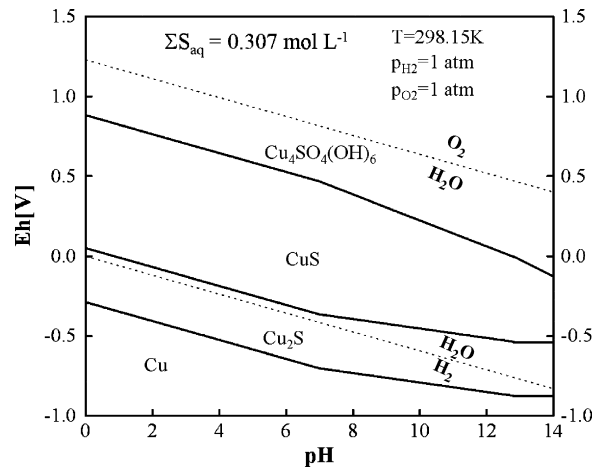


Fig. 5. Eh–pH diagram of Cu–S–H₂O system at 298 K.

By using the Nernst equation for half reaction given by Eq. (5), the ORP can be determined using Eq. (7).

$$E = E_o - \frac{RT}{nF} \ln \frac{a_{\text{S}_2^{2-}}}{a_{\text{S}^{2-}}}, \quad (7)$$

where E (V) is the oxidation–reduction potential (ORP) of the reacting system, E_o the standard oxidation–reduction potential of $\text{S}_2^{2-}/\text{S}^{2-}$ couple (V), R the gas constant ($\text{J}/(\text{K mol})$), T the temperature (K), n the number of electrons transferred ($-$), F the Faraday's constant (C/mol), $a_{\text{S}^{2-}}$ the activity of S^{2-} ions (mol/L) and $a_{\text{S}_2^{2-}}$ is the activity of S_2^{2-} ions (mol/L). Inserting the value of E_o for $\text{S}_2^{2-}/\text{S}^{2-}$ couple and n to Eq. (7), and further assuming that the activity coefficients of S_2^{2-} and S^{2-} are equal to one, gives Eq. (8)

$$E = -0.478 - \frac{RT}{2F} \ln \frac{[\text{S}^{2-}]^2}{[\text{S}_2^{2-}]}, \quad (8)$$

where $[\text{S}^{2-}]$ is the concentration of S^{2-} ions and $[\text{S}_2^{2-}]$ is the concentration of S_2^{2-} ions.

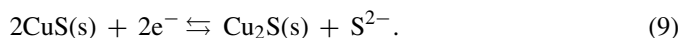
At the beginning of the sulfidation, the conversion is negligible, and thus, the concentration of S_2^{2-} ions is assumed to be almost zero. Hence, the initial ORP value calculated by Eq. (8) becomes almost negative infinite, which explained the steep decrease in ORP value shown in Fig. 3. Subsequently, the concentration of S_2^{2-} increased with the progress of sulfidation reactions resulting in an increase in oxidation–reduction potential, as also shown in Fig. 3.

Further, the stability as well as the formation of copper sulfides of Cu_2S and CuS strongly depends on the pH and potential values of the reacting system. Therefore, an Eh–pH diagram of Cu–S–H₂O system was constructed based on the assumption that only copper compounds of Cu, CuS , Cu_2S and $\text{Cu}_4\text{SO}_4(\text{OH})_6$ are present in the reacting system [13]. Fig. 5 shows the Eh–pH diagram constructed for S^{2-} to Cu^{2+} molar ratio of 1.50 and a temperature of 298 K by using the thermodynamic data given in Table 2. In this diagram, the potential boundary between Cu_2S and CuS at the pH range of 12.9–14.0

Table 2
Thermodynamic data for Eh–pH diagram

Species (state)	ΔG_f° (kJ/mol)	Reference
H ₂ O (liq)	–237.19	[22]
H ₂ S (aq)	–27.82	[22]
HS [–] (aq)	12.09	[22]
S ^{2–} (aq)	85.81	[22]
Cu (c)	0.00	[22]
Cu ₂ S (c)	–53.60	[22]
CuS (c)	–86.19	[22]
Cu ₄ SO ₄ (OH) ₆	–1818.45	[23]

was determined based on Eq. (9)



In the given pH range, sulfide ions are present in the solution in the S^{2–} form, and therefore, the Cu₂S/CuS potential boundary is not affected by the pH value of the reacting system. The value of oxidation–reduction potential for Cu₂S/CuS potential boundary is then determined using the Nernst equation expressed by Eq. (10)

$$E = -0.554 - \frac{RT}{2F} \ln[\text{S}^{2-}], \quad (10)$$

where the value of –0.554 V represents the value of standard oxidation–reduction potential of Cu₂S/CuS couple (V), calculated using the thermodynamic data given in Table 2. It can be seen that at a constant temperature, the value of Cu₂S/CuS potential boundary depends only on the concentration of S^{2–} ions. Subsequently, the potential boundary between Cu₂S and CuS was calculated to be –0.538 V at the S^{2–} to Cu²⁺ of 1.50 (pH value of 13.30), and the value just slightly increased to –0.536 V at the molar ratio of S^{2–} to Cu²⁺ of 1.25 (pH value of 13.25). Based on the ORP results obtained for the molar ratios of S^{2–} to Cu²⁺ of 1.25 and 1.50 (Fig. 4), it was considered that the potential, at first, dropped below the Cu₂S/CuS boundary leading to the formation of Cu₂S rather than CuS. Then, as a consequence of a higher conversion, the ORP of the reacting system increased to a value of about –0.460 V at the molar ratio of S^{2–} to Cu²⁺ of 1.50, which brought about a shift in the ORP value from the stability region of Cu₂S to the stability region of CuS. As a result of the shift in the ORP value of the reacting system, a gradual conversion of Cu₂S to CuS was supposed to occur. Therefore, to support this conclusion, the contacting period of the simulated copper plating sludge with Na₂S was further extended up to 24 h at the molar ratio of S^{2–} to Cu²⁺ of 1.50. Fig. 6 shows the XRD patterns of sulfidation products obtained and it is shown that Cu_xS_y was partially converted to CuS after 24 h, which supported the above given conclusion.

In the case of S^{2–} to Cu²⁺ molar ratio of 1.00 (Fig. 4), the initial decrease in the ORP value was lower compared to those of S^{2–} to Cu²⁺ molar ratios of 1.25 and 1.50. Hence, it is assumed that the ORP value at the beginning of the sulfidation did not drop below the potential boundary of Cu₂S/CuS, which was calculated to be –0.533 V for this S^{2–} to Cu²⁺ molar ratio. Consequently, the copper compounds in the plating sludge were rather converted to CuS than to Cu₂S.

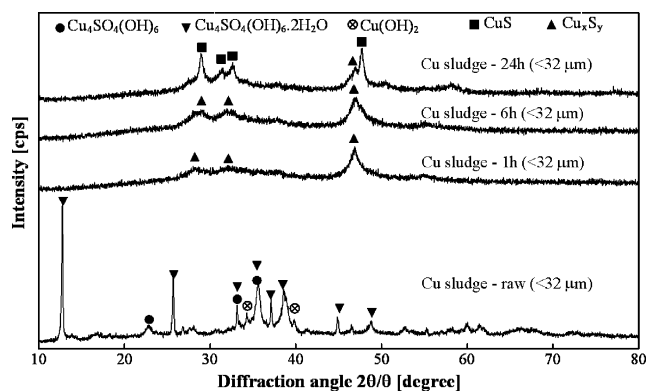


Fig. 6. XRD patterns of simulated copper plating sludge obtained at S^{2–} to Cu²⁺ molar ratio of 1.50 after different time.

3.2. Sulfidation behavior of real copper plating sludge

3.2.1. Effect of S^{2–} to Me²⁺ ratio on the composition of sulfidation products

The sulfidation treatment of real plating sludge was conducted in the same way as that of simulated sludge. The molar ratio of S^{2–} to Me²⁺ was adjusted to 1.00, 1.25 or 1.50, where Me²⁺ stands for the sum of all metals involved in the sludge (Table 1). The pH values of the reacting systems were 12.91, 13.01 and 13.10 for S^{2–} to Me²⁺ molar ratios of 1.00, 1.25 and 1.50, respectively. Fig. 7 shows the time change of the residual concentration of S^{2–} ions for different molar ratios of S^{2–} to Me²⁺. It can be seen from Fig. 7 that S^{2–} ions were almost completely consumed within a short period of 5 min indicating a high sulfidation rate of copper compounds, which was similar to the results obtained for simulated plating sludge (Fig. 2), except that the residual concentrations of S^{2–} ions were kept higher. This difference in the residual concentration of S^{2–} ions between the simulated plating sludge and the real plating sludge was attributed to lower sulfidation rates of heavy metals such as nickel and zinc contained in the real plating sludge, as reported in our previous works [19,24]. Further, the concentrations of the heavy metals in the filtrates were determined by ICP and it was found that the concentrations of copper and nickel were kept below 2 mg/L, while the concentrations of zinc, iron, lead,

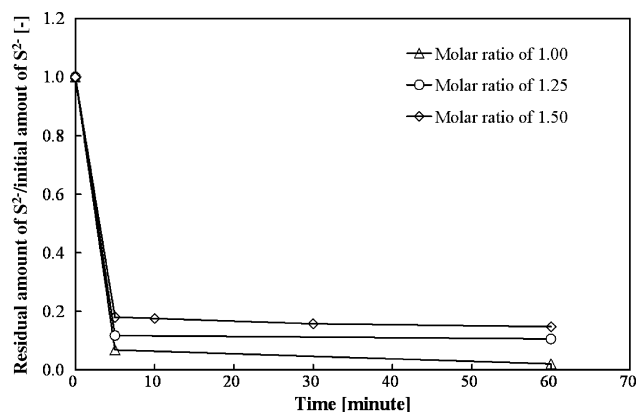


Fig. 7. Time change of residual concentration of S^{2–} ions for real copper plating sludge.

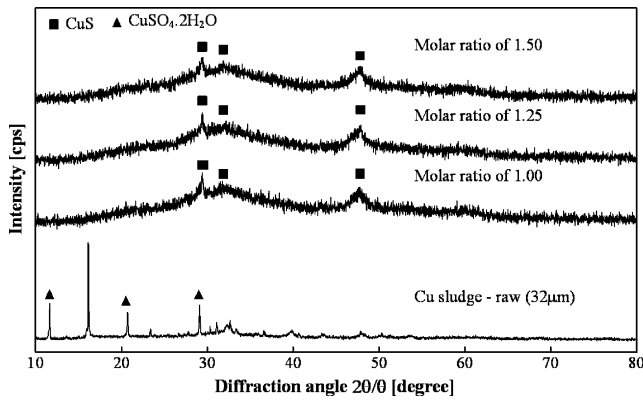


Fig. 8. XRD patterns of real copper plating sludge obtained after 5 min at different S^{2-} to Me^{2+} molar ratios.

etc., were kept below 0.1 mg/L (the lowest standard used in ICP analyses).

To identify the chemical composition of sulfidation products, the XRD analysis of the sulfidation products of the real plating sludge, was carried out. Fig. 8 shows the XRD patterns obtained and it was found that CuS was formed as the main sulfidation product within 5 min, irrespective of S^{2-} to Me^{2+} molar ratio. While, no characteristic XRD peaks of copper compounds were observed for the raw sample of real plating sludge indicating a low crystallinity of the copper compounds.

3.2.2. Effect of ORP on sulfidation of copper

Fig. 9 shows the time change of ORP of the reacting system of real plating sludge during sulfidation treatment. In the case of simulated plating sludge (Fig. 3), the potential steeply dropped to a value of about -0.490 V and then increased to a value of about -0.460 V, at S^{2-} to Cu^{2+} molar ratio of 1.50. To the contrary, somewhat different behavior was obtained for real plating sludge at S^{2-} to Me^{2+} molar ratio of 1.50, as shown in Fig. 9. It can be seen that the potential decreased more slowly, compared to that of simulated plating sludge, basically to attain a value of about -0.455 V at the S^{2-} to Me^{2+} molar ratio of 1.50. It was considered that the difference in ORP behavior observed between the simulated plating sludge and the real plating sludge resulted from the presence of other ions in the reacting system. Given the difference in the ORP behavior, it was assumed that

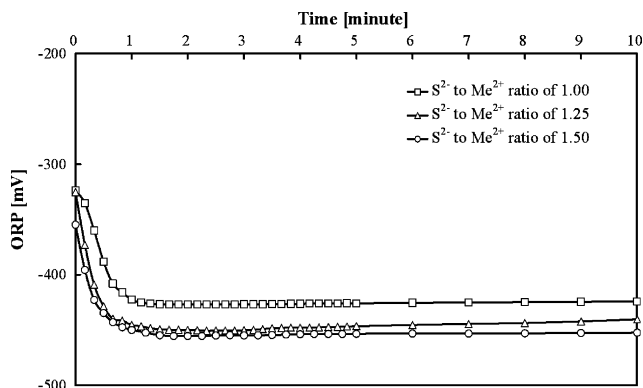


Fig. 9. Time change of oxidation–reduction potential for real copper plating sludge.

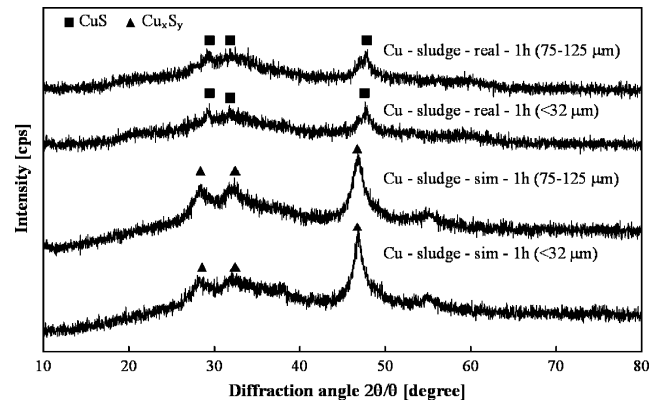


Fig. 10. XRD patterns of simulated and real copper plating sludge obtained for different particle size of initial sludge.

the potential value of the reacting system was kept above the Cu_2S/CuS potential boundary, which led to the formation CuS rather than Cu_2S . The Cu_2S/CuS potential boundary was determined to be -0.531 V, in the case of S^{2-} to Me^{2+} molar ratio of 1.50 and the corresponding pH value of 13.10.

3.3. Effect of particle size on sulfidation of copper sludges

In order to study the effect of particle size on the sulfidation of copper compounds to copper sulfides, the experiments were conducted for the simulated and real plating sludge screened to the particle size ranges of 0–32, 45–63 and 75–125 μm . The molar ratio of S^{2-} to Cu^{2+} (S^{2-} to Me^{2+} for the real plating sludge) was fixed at 1.50 and the treatment time was set at 1 h. Fig. 10 presents the XRD patterns of the sulfidation products obtained for the simulated plating sludge and the real plating sludge. As can be seen in the figure, no significant difference in the XRD patterns of simulated and real plating sludge was observed when the particle size was increased from a smaller particle size of 0 to 32 μm to a larger particle size of 75 to 125 μm . Thus, it was concluded that the conversion of copper compounds to copper sulfides, in the particle size range used, was not dependant on the particle size. Lower intensities of XRD peaks of copper sulfides in the case of the real plating sludge compared to those of simulated plating sludge were attributed to a lower crystallinity of the copper sulfides formed.

3.4. Particle size analysis of sulfidation products of copper sludges

Fig. 11 shows the particle size distribution of the sulfidation products formed at the molar ratio of S^{2-} to Cu^{2+} of 1.50 (S^{2-} to Me^{2+} for the real plating sludge) and the treatment time of 1 h. As can be seen in the figure, the particle size of sulfidation products was remarkably affected by the initial particle size of the raw sludge. In the case of particle size of raw sludges of 0–32 μm , the average particle sizes of the sulfidation products were 8.81 and 7.52 μm for simulated and real copper plating sludge, respectively. By contrast, the average particle sizes of sulfidation products of 25.25 μm for simulated copper plating sludge and 43.21 μm for real copper plating sludge

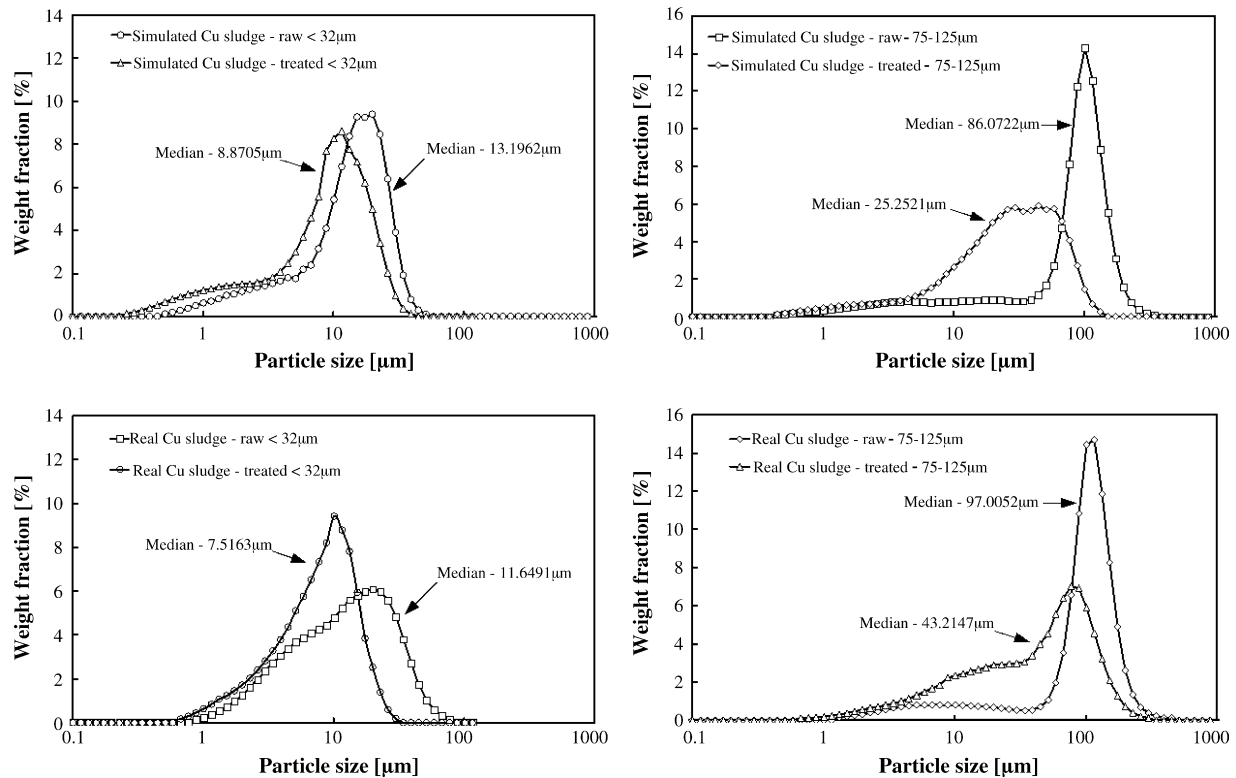


Fig. 11. Particle size distribution analyses of sulfidation products of simulated and real copper plating sludge.

were obtained when the particle size of the raw sludge in the range of 75–125 μm was chosen. From these findings, it is concluded that the conversion of Cu compounds to copper sulfides rather started with the formation of copper sulfides on the surface of the original sludge particles than with the precipitation of new particles of copper sulfides in the solution. This result is in agreement with the findings reported for malachite, where the copper sulfides were found to quickly form a primary layer on the malachite specimen and subsequently a secondary layer enclosing unreacted malachite inside [15]. Similarly, Castro et al. [16] reported that in the sulfidation treatment of CuO, the sulfide ions were at first adsorbed on the surface of CuO particles followed by the reaction of sulfide ions with CuO. However, in this study, an amount of unreacted sample enclosed under the sulfide layer is assumed to be negligible, since no XRD peaks of raw sample were found when the simulated copper sludge contacted with Na_2S was subjected to XRD analysis.

Finally, the reduction in the particle size during sulfidation treatment was attributed to the disintegration of the original sludge present in the form of agglomerates of particles as fine as 1 μm .

4. Conclusions

The sulfidation treatment of simulated and real copper plating sludge was carried out at S^{2-} to Cu^{2+} (S^{2-} to Me^{2+}) molar ratios of 1.00, 1.25 and 1.50, for a period of 5 min to 24 h. Some concluding findings obtained in this study are summarized as follows.

- The copper compounds involved in simulated and real plating sludge were easily converted to copper sulfides within the first 5 min of contacting the sludges with Na_2S .
- The XRD analyses of sulfidation products of simulated copper plating sludge obtained after sulfidation treatment for 5 min showed that the formation of copper sulfides is strongly affected by S:L molar ratio used. In the case of S^{2-} to Cu^{2+} molar ratio of 1.00, cupric sulfide of CuS was identified as the main sulfidation product, while various cuprous sulfides such as Cu_2S , Cu_7S_4 , Cu_8S_5 , $\text{Cu}_{31}\text{S}_{16}$ were formed at S^{2-} to Cu^{2+} molar ratio of 1.25 and 1.50. The formation of various copper sulfides was attributed to the changes in ORP of the reacting system at different S^{2-} to Cu^{2+} molar ratios.
- In the sulfidation treatment of real plating sludge, cupric sulfide of CuS was found as the main sulfidation product irrespective of S^{2-} to Me^{2+} molar ratio, which was attributed to a different behavior of ORP compared that of simulated copper plating sludge.
- The effect of particle size of the initial sludge was investigated in the range of 0–125 μm , at the S^{2-} to Cu^{2+} (S^{2-} to Me^{2+} for the real plating sludge) molar ratio of 1.50. It was found that the conversion was independent of the particle size of the initial sludge used.
- The particle size distribution analysis of sulfidation products contacted with Na_2S for 1 h at the molar ratio of S^{2-} to Cu^{2+} (S^{2-} to Me^{2+} for the real plating sludge) of 1.50 showed that particle size distribution of sulfidation products strongly depended on the initial particle size of the raw sludges.

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