Sulfidation of zinc plating sludge with Na$_2$S for zinc resource recovery

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Abstract

A high amount of zinc disposed in the landfill sites as a mixed-metal plating sludge represents a valuable zinc source. To recover zinc from the plating sludge, a sulfidation treatment is proposed in this study, while it is assumed that ZnS formed could be separated by flotation. The sulfidation treatment was conducted by contacting simulated zinc plating sludge with Na$_2$S solution at S^{2-} to Zn^{2+} molar ratio of 1.5 for a period of 1–48 h, while changing the solid to liquid (S:L) ratio from 0.25:50 to 1.00:50. The conversion of zinc compounds to ZnS was determined based on the consumption of sulfide ions. The reaction products formed by the sulfidation of zinc were identified by X-ray diffraction (XRD).

As a result, it was found that the conversion of zinc compounds to ZnS increased with an increase in S:L ratio. A maximum conversion of 0.809 was obtained at an S:L ratio of 1.00:50 after 48 h. However, when the zinc sludge treated at S:L ratio of 1.00:50 for 48 h was subjected to XRD analyses, only ZnS was identified in the treated zinc sludge. The result suggested that the rest of zinc sludge remained unreacted inside the agglomerates of ZnS. The formation behavior of ZnS was predicted by Elovich equation, which was found to describe the system satisfactorily indicating the heterogeneous nature of the sludge.

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1. Introduction

The surface finishing treatment of metal products is characterized as an important part of their manufacturing process since it ensures their high surface resistance against corrosion, as well as improving their thermal and electrical properties, among others. Electroplating is most widely used technique for surface finishing of metals, ceramics and plastics, in which heavy metals such as zinc, copper, nickel, chromium and tin are commonly used. In particular, zinc accounts for more than 30% (6054 tonnes/year) of the total amount of metals used in Japan [1].

The heavy metals employed are mainly deposited on the surface of electroplating products, but a part of these metals is discharged in rinsing wastewater. The discharged wastewater contains soluble metallic salts such as ZnSO$_4$, CuSO$_4$ and NiSO$_4$ at high concentrations of 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 mg/L and 5 mg/L for Cu and Zn, respectively [2]. For comparison, the daily permissible limits allowed for common metal finishing facilities discharging more than 38,000 L of wastewater per day defined by the U.S. Environmental Protection Agency are 4.5 mg/L, 4.2 mg/L and 4.1 mg/L for Cu, Zn and Ni, respectively.

For the removal of heavy metal from wastewater, various techniques such as chemical precipitation [3–5], ion exchange [6], adsorption, chelation [7] or combination of chemical precipitation with reverse osmosis, ion exchange or electrodialysis [8] are available. Among the above techniques, chemical precipitation has been widely employed for the conversion of heavy metals to insoluble metal hydroxides, metal oxides, metal carbonates or metal sulfides [3]. In the majority of plating shops, the chemical precipitation with either NaOH or Ca(OH)$_2$ is commonly used to treat the rinsing wastewater and the precipitate formed by the chemical precipitation is called plating sludge [3,9]. The plating sludge containing various metal compounds is dehydrated [10], and then solidified with a stable binder in order to prevent the heavy metals from dissolving in the landfill sites [11]. As solidification binder, cement, lime, fly ash [12–14] or asphalt emulsion is usually employed [15].

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Nomenclature

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a	Elovich parameter [1/h]
b	Elovich parameter
n_{S_a}	initial amount of sulfide ions [mol]
n_{S_b}	amount of sulfide ions consumed during blank experiment [mol]
n_{S_c}	amount of residual sulfide ions [mol]
n_{Zn}	total amount of Zn involved in simulated Zn sludge [mol]
t	time [h]
t_o	Elovich time constant [h]
X	fractional conversion
X_{calc}	fractional conversion obtained from Elovich kinetic equation
X_{exp}	fractional conversion obtained from experiments

However, it is envisaged that the metal deposits of Zn, Cu and Ni may be depleted within 30, 36 and 50 years, respectively [16]. Therefore, from the viewpoint of environment protection as well as conservation of metal resource, a development of effective systems for recycle and reuse of the metals involved in industrial waste is required. McLay and Reinhard [17] reported that the number of companies interested in using metal-bearing sludges, such as smelters, has recently increased. However, the recovery of heavy metals from the mixed metal sludge by smelting was found to be difficult because of the sludge heterogeneity as well as the presence of inorganic salts [17]. Given this, it is considered to first convert heavy metals involved in plating sludges to a uniform chemical form such as sulfides, and then to selectively recover the heavy metal sulfides from mixed plating sludges by flotation, a widely used separation technique in processing the metal sulfides ores [18,19].

The objective of this study is to clarify the conditions of sulfidation of zinc compounds involved in simulated zinc plating sludge to zinc sulfide. The sulfidation treatment was conducted by contacting simulated zinc plating sludge with Na$_2$S solution, while keeping the molar ratio of S^{2-} to Zn^{2+} at 1.5 and varying the solid to liquid (S:L) ratio from 0.25:50 to 1.00:50. The conversion of zinc compounds to zinc sulfide was evaluated based on the determination of the amount of sulfide ions consumed by sulfidation reactions for a period ranging from 1 h to 48 h. In addition, an attempt was made to describe the sulfidation characteristics of zinc compounds involved in the sludge by using Elovich kinetic model [20–23].

2. Experimental

2.1. Preparation of simulated zinc plating sludge

Fig. 1(a) shows the flow chart used for the preparation of simulated zinc plating sludge. An amount of 14.5 g ZnSO$_4$·7H$_2$O was dissolved in a 400 mL distilled water, and then the pH value of the solution was increased to 9.40 ± 0.10 using 1 M NaOH aqueous solution making up the total volume to 500 mL. The pH value of 9.40 ± 0.10 was chosen with respect to neutralization conditions generally used in the treatment of mixed-metal wastewater streams to lower heavy metal solubilities below the permissible limits [3]. According to Eq. (1), zinc ions reacts with hydroxyl ions to form insoluble zinc hydroxide.

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2(s) \tag{1}$$
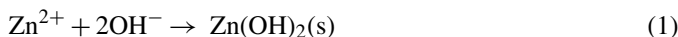
In our experiments, the precipitation was allowed to proceed for 30 min, and then the slurry/precipitate was filtered using a filter paper with pore size of 1 μm. After the filtration, the precipitate was rinsed in 500 mL distilled water for another 30 min at a constant pH value of 9.40 ± 0.10, in order to purify the zinc precipitate. Subsequently, the precipitate was filtered and
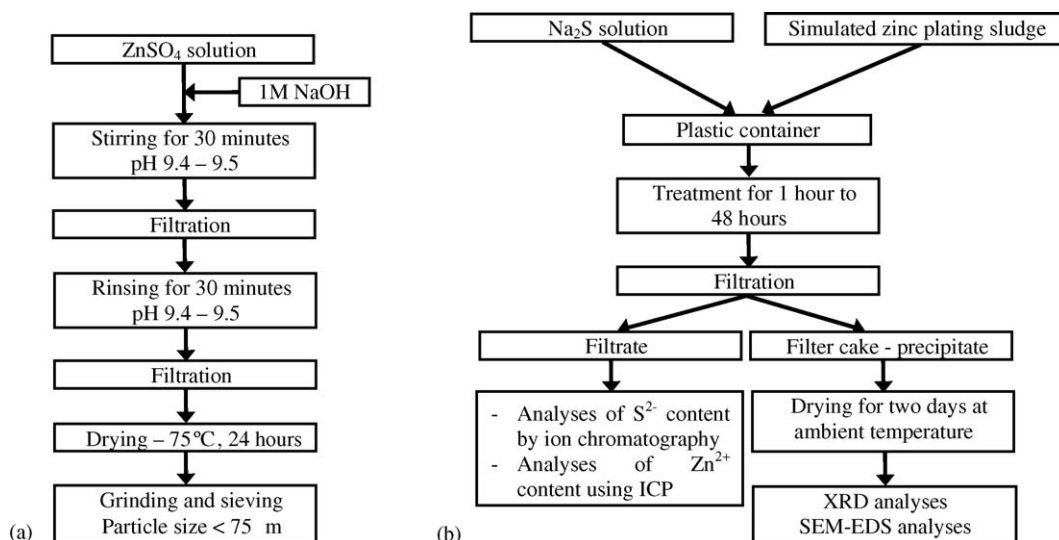

Fig. 1. Flow chart of: (a) preparation of simulated zinc plating sludge and (b) sulfidation treatment of zinc plating sludge.

dried in a muffle furnace at a temperature of 75 °C for 24 h. The dried precipitate was ground in an agate mortar and screened to particle size lower than 75 μm. The precipitate treated in such manner is hereafter referred as the simulated zinc plating sludge.

In order to determine the content of zinc in the simulated zinc plating sludge, an amount of 100 mg of the sludge was dissolved in hydrochloric acid and the solution was analyzed by inductively coupled plasma (ICP) equipment (Vista-MPX Simultaneous ICP-OES, Varian, Inc.). The average content of zinc in the simulated zinc sludge was found to be 0.6021 g Zn/g sludge and this value was used to calculate the amount of $Na_2S \cdot 9H_2O$ to adjust the molar ratio of S^{2-} to Zn^{2+} to 1.5 in solutions.

In order to determine the composition of simulated zinc plating sludge, thermogravimetric analysis of the simulated sludge was conducted using TG analyzer (TGA-50, Shimadzu) under N_2/O_2 atmosphere of N_2:80%/O_2:20%, at gas flow rate of 50 mL/min and heating rate of 2 °C/min. Further, the simulated sludge was subjected to X-ray powder diffraction (XRD) analysis with scanning mode of 2θ/θ, under the condition of 50 kV/100 mA (RINT-2500 TTR, Rigaku Model), and finally to scanning electron microscopy-energy dispersive spectrometric (SEM-EDS) analysis (JSM-6330F-JEOL, JED-2140-JEOL).

2.2. Sulfidation of simulated zinc plating sludge

The sulfidation of the simulated zinc plating sludge was conducted in a batch system according to the procedure shown in Fig. 1(b), and all experiments were carried out in triplicates. First, 50 mL of each Na_2S aqueous solution in which the molar ratio of S^{2-} to Zn^{2+} was kept at 1.5, was poured into the plastic containers. The molar ratio of S^{2-} to Zn^{2+} of 1.5 was chosen in order to keep the S^{2-} ion in excess throughout the whole sulfidation period. Second, the simulated zinc sludge was charged into each plastic container in appropriate amounts to maintain the S:L of 0.25:50 (weight concentration of about 5 g/L), 0.50:50 (weight concentration of about 10 g/L) or 1.00:50 (weight concentration of about 20 g/L). Then, the plastic containers were shaken on a vertical shaker for 1–48 h. Finally, at the end of the experiment, the slurry was filtered with a filter paper of 1 μm pore size.

2.3. Analyses of filtrate and filter cake

The concentration of the residual sulfides in the filtrate was analyzed using an ion chromatography (Shimadzu, electroconductivity detector type: CDD-10Avp) equipped with a column-Tosoh, TSK gel IC-Anion-PW 6837, 50 mm × 4.6 mm i.d. The conversion of zinc compounds to zinc sulfide was calculated according to Eq. (2):

$$X = \frac{n_{S_a} - n_{S_b} - n_{S_c}}{n_{Zn}} \qquad (2)$$

where X is the fractional conversion, n_{S_a} the initial amount of sulfide ions [mol], n_{S_b} the amount of sulfide ions consumed during blank experiment [mol], n_{S_c} the amount of residual sulfide ions [mol] and n_{Zn} is the total amount of Zn involved in simu-

lated Zn sludge [mol]. The amount of the sulfide ions, n_{S_b} [mol] consumed by the oxidation of S^{2-} ions to SO_4^{2-} with oxygen present in water (blank experiment) was determined as the difference between the initial amount of sulfide ions (n_{S_a}) and the residual amount of sulfide ions after performing the blank experiment. In this work, the blank experiment was carried out by shaking only the aqueous Na_2S solution in a plastic container for a period of 1–48 h. The amount of $Na_2S \cdot 9H_2O$ dissolved in water to perform the blank experiments was exactly the same as in the case of experiments performed with simulated zinc plating sludge.

The filtrates were subjected to ICP measurement to determine the content of zinc. The filter cakes were dried for 2 days at ambient temperature, and were subjected to XRD and SEM-EDS analyses to confirm the presence of zinc sulfide formed.

3. Results and discussion

3.1. Characterization of simulated zinc plating sludge

From the results obtained by XRD and TGA, it was found that $Zn(OH)_2$ was not the main precipitation product formed during the preparation of simulated zinc plating sludge. Instead, the precipitate was mostly composed of various zinc sulfate hydroxide hydrates which are, in our work, denoted by general formula of $[Zn_x(OH)_y \cdot (SO_4) \cdot nH_2O]$. The TGA results showed that crystalline water in the sludge was evaporated in the temperature range of 165–300 °C and the remaining $ZnSO_4$ was decomposed to ZnO in the temperature range of 670–780 °C. Based on the weight loss resulting from the decomposition of $ZnSO_4$ to ZnO, the amount of $ZnSO_4$ involved in zinc sulfate hydroxide hydrate was estimated to be about 17 wt%.

The SEM images of the simulated zinc plating sludge taken at different magnifications are shown in Fig. 2. It can be seen from the figure that the particle of zinc plating sludge is an agglomerate of fine floccules of zinc compounds with a diameter of about 1 μm. It is considered that the particles agglomerated during filtration and drying process.

3.2. Effect of solid to liquid (S:L) ratio on fractional conversion

To investigate the effect of S:L ratio on the sulfidation of zinc compounds in the sludge, the experiments were performed at three different S:L ratios. The fractional conversion of Zn compounds to ZnS calculated by Eq. (2), is plotted against time in Fig. 3. In this figure, the fractional conversion increased rapidly within the first 6 h for all S:L ratios followed by a slower progress in conversion for the rest of the experimental period. Moreover, the progress in the fractional conversion seems to stop after 12 h for the S:L ratio of 1.00:50, and the maximum fractional conversion obtained after 48 h was 0.809.

The increase in the S:L ratio brought about an increase in the pH value of the reacting system owing to a higher amount of $Na_2S \cdot 9H_2O$ dissolved in water to establish the molar ratio of S^{2-} to Zn^{2+} of 1.5. Hence, higher values of the fractional conversion at higher S:L ratios were partially attributed to a higher pH value
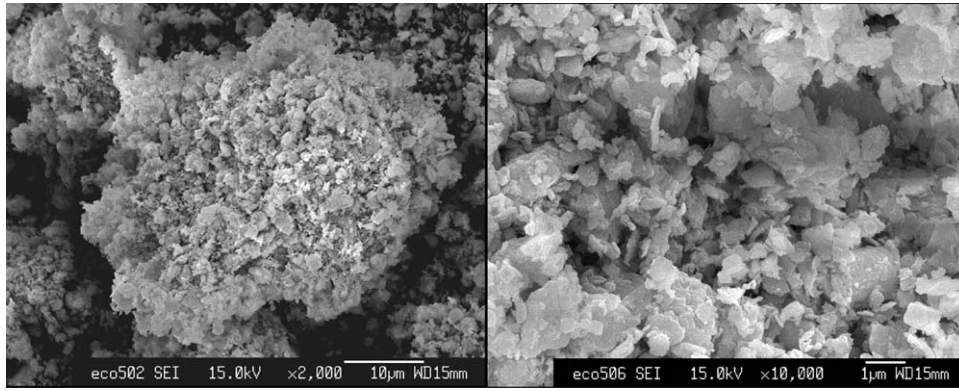
Fig. 2. SEM images of simulated zinc plating sludge.

of the reacting system. The significance of pH arises from an increase in the solubility of Zn compounds with an increase in pH, owing to the formation of more soluble zincates, according to Eqs. (3) and (4) [24].

$$Zn^{2+} + 3OH^- \rightarrow Zn(OH)_3^- \tag{3}$$

$$Zn^{2+} + 4OH^- \rightarrow Zn(OH)_4^{2-} \tag{4}$$

Based on the increase in conversion of zinc compounds to ZnS with an increase in pH of the reacting system, it is considered that the solubility of zinc compounds is influential in the sulfidation of Zn to ZnS in the simulated zinc plating sludge.

On the contrary, the precipitation of Zn^{2+} ions as insoluble ZnS according to Eqs. (5)–(7) is supposed to be instantaneous and thus having negligible effect on reaction rate, since the concentrations of Zn^{2+} ions in all filtrates measured by ICP were found to be less than 1 mg/L.

$$Zn^{2+} + S^{2-} \rightarrow ZnS(s) \tag{5}$$

$$Zn(OH)_3^- + S^{2-} \rightarrow ZnS(s) + 3OH^- \tag{6}$$

$$Zn(OH)_4^{2-} + S^{2-} \rightarrow ZnS(s) + 4OH^- \tag{7}$$

3.3. Analyses of treated zinc plating sludge

After the sulfidation treatment, the simulated zinc plating sludge was subjected to XRD analysis. Fig. 4 shows the XRD patterns of zinc compounds in the treated sludge. It was confirmed that ZnS was formed as a product of sulfidation of zinc compounds. As indicated in the XRD diagram, characteristic zinc sulfide peak became higher with an increase in sulfidation time as well as with an increase in S:L ratio. It can be observed
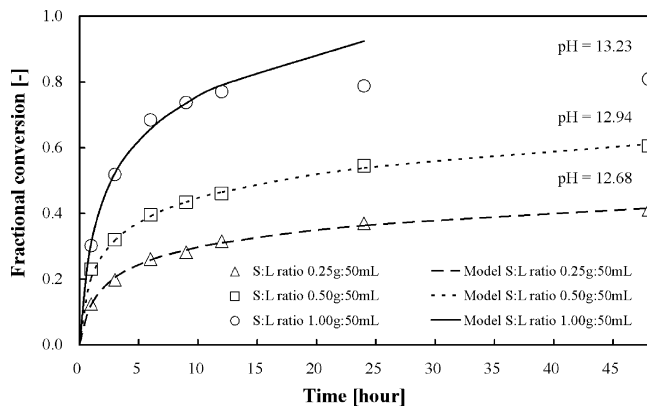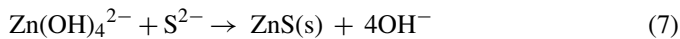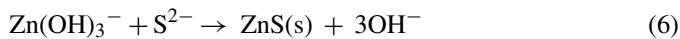

Fig. 3. Dependence of the fractional conversion of zinc in simulated zinc plating sludge on time, and the results of conversion rate modeling using Elovich kinetic equation.
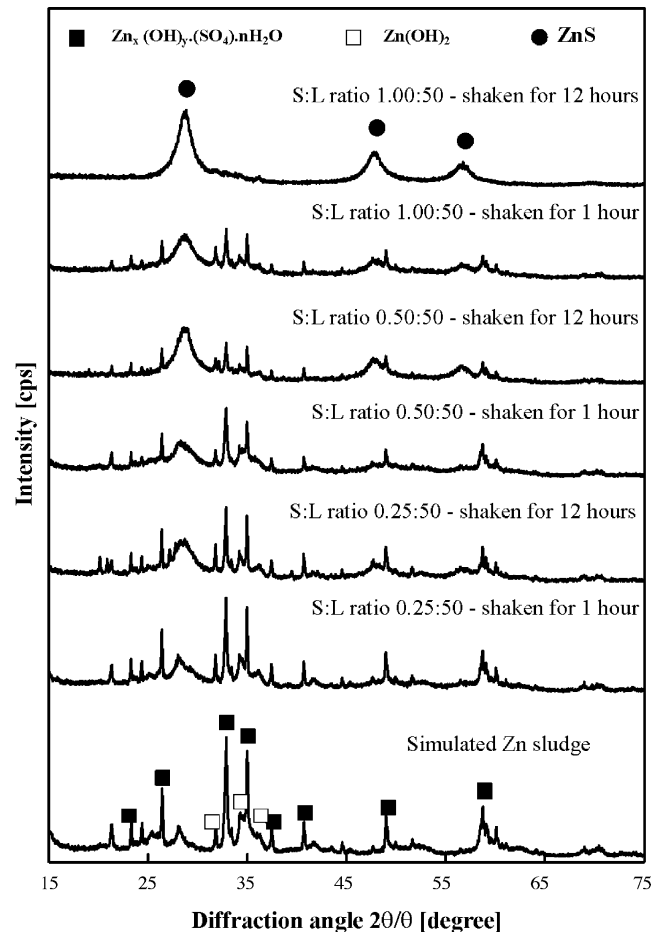

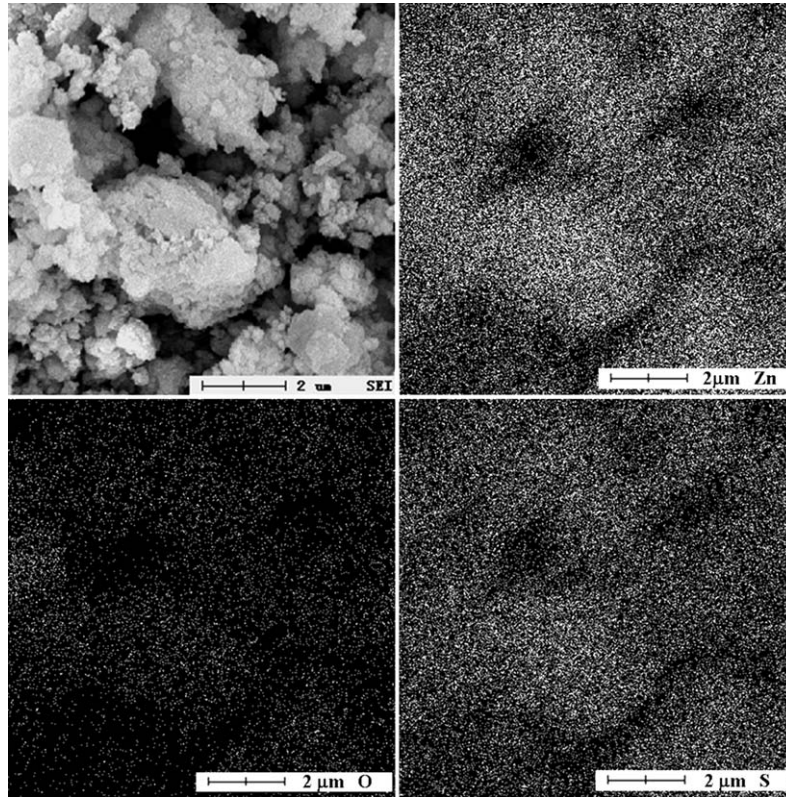Fig. 4. XRD patterns of simulated zinc plating sludge before and after sulfidation treatment.

Fig. 5. SEM-EDS images of treated simulated zinc plating sludge.

that only ZnS was present, when the sample was contacted with Na$_2$S solution for 12 h at S:L ratio of 1.00:50. Based on the XRD results and the results of fractional conversion (Fig. 3), it was concluded that some of the unreacted zinc hydroxide and zinc sulfate hydroxide hydrate were enclosed inside the agglomerates of ZnS.

Fig. 5 shows the SEM-EDS results of the zinc sludge treated with Na$_2$S for 12 h at the S:L ratio of 1.00:50. SEM image shows that the sulfidation product is composed of fine particles of ZnS. From the EDS maps, zinc, sulfur and oxygen atoms are located at a nearly the same positions, but the number of oxygen atoms detected is significantly lower than those of zinc and sulfur. This result may support the above-mentioned conclusion that some unreacted zinc hydroxide or zinc sulfate hydroxide hydrate was enclosed inside the agglomerates of ZnS.

From the point of view of zinc recovery from mixed plating sludges, it is supposed that the agglomerates of ZnS enclosing unreacted zinc plating sludge should be separable by flotation, since the flotation is based on the surface interactions of particles with flotation agents. Thus, the proposed sulfidation treatment followed by flotation could be used to selectively recover zinc from mixed plating sludges.

3.4. Evaluation of controlling factors for sulfidation of zinc compounds

As mentioned in Section 3.2, the fractional conversion of zinc compounds involved in plating sludge to zinc sulfide increased with an increase in S:L ratio and with an increase in the pH

value of the reacting system. It is therefore important to evaluate the effect of these two parameters on the sulfidation of zinc compounds. For this aim, the zinc simulated plating sludge was treated with Na$_2$S solution for 24 h at a constant S:L ratio of 0.25:50, while the pH value was adjusted with 1 M NaOH in the range of 12.68 (without NaOH addition) to 13.30.

Fig. 6 shows the change in the fractional conversion of zinc compounds involved in plating sludge obtained at the fixed S:L ratio of 0.25:50, while changing pH of the reacting system with NaOH (dashed line). In this figure also, the fractional conversions obtained at the S:L ratios of 0.25:50, 0.50:50 and 1.00:50 after 24 h are plotted against the pH value of the reacting systems (solid line). In the latter case, the increase in pH value naturally
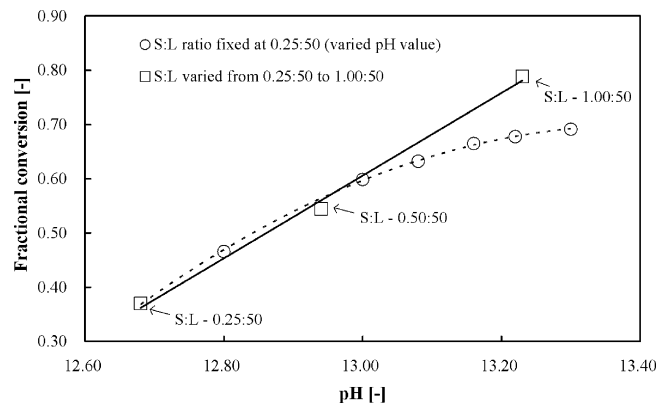

Fig. 6. Dependence of fractional conversion on pH value of reacting system.

resulted from an increase in the amount of $Na_2S \cdot 9H_2O$ dissolved in distilled water to adjust the molar ratio of S^{2-} to Zn^{2+} to 1.5 and no pH adjustment was made.

It can be seen that the fractional conversion increased linearly with an increase in the pH value resulting from an increase in S:L ratio (solid line). On the contrary, a two stage behavior was observed when the pH value was adjusted with 1 M NaOH at fixed S:L ratio of 0.25:50 (dashed line). In the first stage (pH range of 12.68–13.00), the fractional conversion increased almost linearly with an increase in pH, which corresponded to the results obtained when S:L ratio was varied. This suggests that at an S:L range of 0.25:50 to about 0.50:50, the pH of the reacting system was the main controlling factor, while the effect of change in S:L ratio on the fractional conversion was almost negligible. Then, in the second stage (pH range of 13.00–13.30) lower values of fractional conversion were obtained at fixed S:L ratio of 0.25:50 compared to the results obtained when varying S:L ratio (solid line). The result indicates the importance of S:L ratio on the conversion of zinc compounds to ZnS at an S:L ratio higher than 0.50:50.

The S:L ratio is related to the weight concentration of the zinc plating sludge in the reacting system and thus to the number of solid particles in the reacting system. It is assumed that the higher number of particles present in the same volume of the reacting system led to a higher number of mutual collisions at the S:L ratio of 1.00:50 compared to the number of mutual collisions at the S:L ratio of 0.25:50. Consequently, the ZnS agglomerates, in which unreacted zinc compounds were enclosed, disintegrated. Hence, the fractional conversion of sulfidation of zinc compounds at a higher S:L ratio became higher, compared with that obtained at a lower S:L ratio at the same pH value.

3.5. Modeling of the sulfidation of zinc plating sludge

For describing the conversion of Zn compounds in the plating sludge to ZnS, the Elovich kinetic model, which has been used in modeling of adsorption of gases on solid adsorbents [20], removal of copper and zinc from effluents [21], extraction of arsenic from contaminated soils [22] and the thermal decomposition of solid oxygenated complexes formed by coal oxidation [23], was applied to our experimental results. The Elovich equation is an empirical model which in terms of the fractional conversion is expressed by Eq. (8),

$$\frac{dX}{dt} = a\,e^{-bX} \tag{8}$$

where X is the fractional conversion, t the time [h] and a, b are the constants—Elovich parameters. The integration of Eq. (8) with the boundary conditions of $X = 0$ at $t = 0$, $X = X$ at $t = t$ gives Eq. (9):

$$X = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t + t_o) \tag{9}$$

where t_o is the Elovich time constant [h].

The relation between the conversion X and $\ln(t + t_o)$ obtained from Eq. (9) is shown in Fig. 7 for different S:L ratios. The
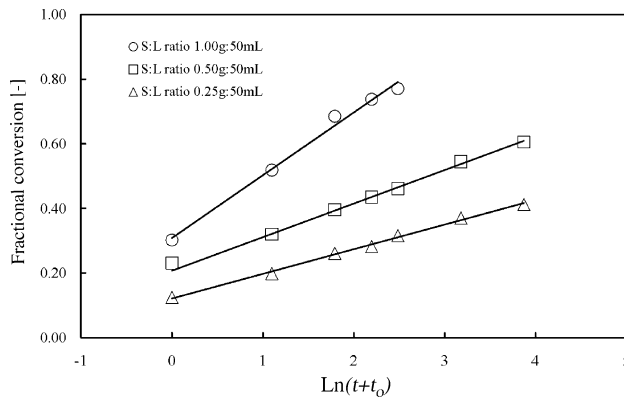

Fig. 7. Dependence of fractional conversion on $\ln(t + t_o)$—Elovich kinetic equation.

Elovich constants a and b were obtained from the slope and the intercept of the linear regression plot of X against $\ln(t + t_o)$. The constant a and b correspond to the initial reaction rate and the extent of conversion, respectively. In Fig. 8, the Elovich constants a and b were plotted against S:L ratio. The constant b decreases with an increase in S:L ratio due to a higher conversion ratio achieved at higher S:L ratios. The higher value of the constant a at a higher S:L ratio is attributed to an increase in solubility of zinc compounds in the sludge due to a higher pH value of the reacting system.

The conversion-time curves obtained according to Eq. (9) are represented in Fig. 3, in which the solid-, dotted- and dashed-lines are those calculated for S:L ratio of 1.00:50, 0.50:50 and 0.25:50, respectively. The Elovich equation describes the data points fairly well.

In Table 1, the experimental data on the conversion of zinc compounds in the sludge were compared with those obtained from Eq. (9). For this, S:L ratios of 0.375:50 and 0.75:50 were employed for the reaction time of 3 h, 12 h and 48 h. It can be seen from Table 1 that the experimental data of the fractional conversion (X_{exp}) were in good agreement with those determined by Elovich kinetic equation (X_{calc}) for the reaction time of 3, 12 and 48 h, except for S:L ratio of 0.75:50 after 48 h. It is supposed that at S:L ratio higher than 0.50:50, the sulfidation reaction almost stopped after 12 h, since the unreacted zinc compounds had been enclosed inside the agglomerates of ZnS.
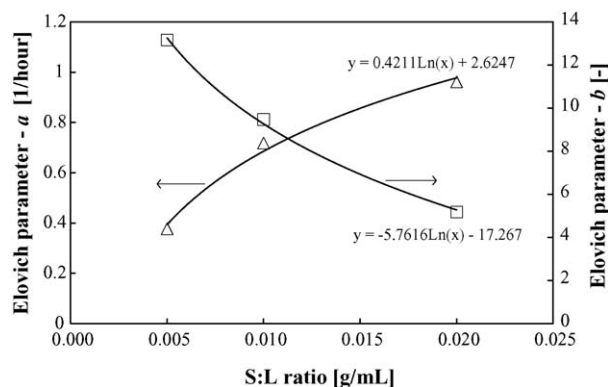

Fig. 8. Correlation of Elovich parameters a and b.

Table 1

Comparison of conversion predicted by Elovich kinetic equation and experimentally obtained conversion

Shaking time [h]	S:L ratio			
	0.375:50		0.75:50	
	X_{calc}	X_{exp}	X_{calc}	X_{exp}
3	0.266	0.253	0.416	0.404
12	0.394	0.405	0.618	0.597
48	0.521	0.542	0.820	0.684

4. Conclusions

The sulfidation characteristics of zinc compounds involved in the simulated zinc plating sludge to zinc sulfide were investigated by using Na_2S as sulfidation agent. In the present study, the molar ratio of S^{2-} to Zn^{2+} was fixed at 1.5, while the solid to liquid ratio was changed from 0.25:50 to 1.00:50. As a result, the following conclusions were drawn:

- The XRD analyses of the simulated zinc plating sludge showed that simulated zinc plating sludge was mainly composed of zinc sulfate hydroxide hydrates. Using the thermogravimetric analysis, the amount of unreacted $ZnSO_4$ remaining in zinc sulfate hydroxide hydrates was estimated to be about 17 wt%.
- The conversion of zinc compounds was increased with an increase in S:L ratio as well as pH value, where the latter resulted from a higher amount of $Na_2S\cdot9H_2O$ added. The maximum conversion obtained at the S:L ratio of 1.00:50 was 80.9% after 48 h of the treatment time.
- After the sulfidation for 48 h at S:L ratio of 1:50, only ZnS was detected in the treated zinc sludge using XRD, and thus it is assumed that a part of unreacted zinc sludge remained enclosed in the agglomerates of ZnS. However, from the resource recovery point of view, the particles of ZnS enclosing unreacted sludge are supposed to be separable by flotation, and thus, the proposed treatment could be used to selectively recover zinc from mixed plating sludges. Furthermore, it is considered that the enclosure of unreacted zinc plating sludge inside the ZnS could be prevented by grinding and screening the simulated sludge to lower particle sizes, before the actual sulfidation treatment (in this experiments, the sludge was ground and screened to the particle size of 75 μm).
- The sulfidation of zinc compounds in zinc sludge was described by Elovich kinetic equation. It was found that Elovich kinetic model fitted well our experimental data and was further validated at the S:L ratios of 0.375:50 and 0.75:50.

References

[1] Federation of Electroplating Industry Association of Japan, Report on comprehensive recycle of valuable metals, Tokyo, Japan, 2004.

[2] Ministry of Environment of Japan, National Effluent Standards—Water Pollution Prevention Law, 2004.

[3] T.J. Weber, Wastewater treatment, Met. Finish. 1 (1999) 797–816.

[4] T. Fukuta, T. Ito, K. Sawada, Y. Kojima, H. Matsuda, K. Yagishita, Improvement of nickel-precipitation from aqueous nickel solution by sulfuration with sodium sulfides, J. Chem. Eng. Jpn. 36 (2003) 493–498.

[5] T. Fukuta, T. Ito, K. Sawada, Y. Kojima, E.C. Bernardo, H. Matsuda, Separation of nickel from plating solution by sulfuration treatment, Asian J. Chem. Eng. 4 (2004) 24–31.

[6] N. Sapari, A. Idris, N.H.A. Hamid, Total removal of heavy metal from mixed plating rinse wastewater, Desalination 106 (1996) 419–422.

[7] P. Bose, M.A. Bose, S. Kumar, Critical evaluation of treatment strategies involving adsorption and chelation for wastewater containing copper, zinc and cyanide, Adv. Environ. Res. 7 (2002) 179–195.

[8] Ch. Peng, H. Meng, J. Zhang, S. Lu, Treatment of electroplating wastewater, J. Univ. Sci. Technol. Beijing 10 (2003) 8–11.

[9] T. Hayashi, T. Fukuta, Trends in waste treatment in electroplating in Japan, in: Conference Proceedings—Surface/Finishing 1996, Cleveland, USA, 1996.

[10] N. Levy, Sludge treatment in the metal-finishing industry, Met. Finish. 98 (2000) 80–83.

[11] J.C. Pyer, et al., Handbook of industrial residue, Noyes Publications, Park Ridge, New Jersey, 1983.

[12] S. Asavapisit, D. Chotklang, Solidification of electroplating sludge using alkali activated pulverized fuel ash as cementitious binder, Cement Concrete Res. 34 (2004) 349–353.

[13] S. Asavapisit, S. Naksrichum, N. Harnwajanawong, Strength, leachability and microstructure characteristics of cement-based solidified plating sludge, Cement Concrete Res. 35 (2005) 1042–1049.

[14] J.E. Chang, T.T. Lin, M.S. Ko, D.S. Liaw, Stabilization/solidification of sludges containing heavy metals by using cement and waste pozzolans, J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng. 34 (1999) 1143–1160.

[15] V. Bednarik, M. Vondruska, M. Koutny, Stabilization/solidification of galvanic sludges by asphalt emulsions, J. Hazard. Mater. 122 (2005) 139–145.

[16] P. Crowson, Minerals exporation: too much or too little? URL:http://www.curtin.edu.au/curtin/dept/wasm/postgraduate/courses/minecon/papers/Crowson%20Paper17203.pdf, 2003 [cit. 20 January 2006].

[17] W.J. McLay, F.P. Reinhard, Waste minimization and recovery technologies, Met. Finish. 97 (1999) 817–858.

[18] A.F. Taggart, Elements of ore dressing, John Wiley & Sons, Inc., New York, 1951.

[19] K.A. Crozier, Flotation: Theory, Reagents and Ore Testing, Oxford Pergamon Press, 1992.

[20] M.J.D. Low, Kinetics of chemisorption of gases on solids, Chem. Rev. 60 (1960) 267–312.

[21] C.W. Cheung, J.F. Porter, G. McKay, Sorption kinetics for the removal of copper and zinc from effluents using bone char, Separ. Sci. Technol. 19 (2000) 55–64.

[22] S. Tokunaga, T. Hakuta, Acid washing and stabilization of an artificial arsenic-contaminated soil, Chemosphere 46 (2002) 31–38.

[23] H. Wang, B.Z. Dlugogorski, E.M. Kennedy, Thermal decomposition of solid oxygenated complex formed by coal oxidation at low temperatures, Fuel 81 (2002) 1913–1923.

[24] Y. Zhang, M. Mamoun, Critical evaluation of thermodynamics of complex formation of metal ions in aqueous solutions VI. Hydrolysis and hydroxo-complexes of Zn^{2+} at 298.15 K, Hydrometallurgy 60 (2001) 215–236.