Selective Sulfidation of Copper, Zinc and Nickel in Plating Wastewater using Calcium Sulfide

K. Soya, N. Mihara, D. Kuchar, M. Kubota, H. Matsuda, and T. Fukuta

Abstract—The present work is concerned with sulfidation of Cu, Zn and Ni containing plating wastewater with CaS. The sulfidation experiments were carried out at a room temperature by adding solid CaS to simulated metal solution containing either single-metal of Ni, Zn and Cu, or Ni-Zn-Cu mixture. At first, the experiments were conducted without pH adjustment and it was found that the complete sulfidation of Zn and Ni was achieved at an equimolar ratio of CaS to a particular metal. However, in the case of Cu, a complete copper sulfidation was achieved at CaS to Cu molar ratio of about 2. In the case of the selective sulfidation, a simulated plating solution containing Cu, Zn and Ni at the concentration of 100 mg/dm^3 was treated with CaS under various pH conditions. As a result, selective precipitation of metal sulfides was achieved by a sulfidation treatment at different pH values. Further, the precipitation agents of NaOH, Na$_2$S and CaS were compared in terms of the average specific filtration resistance and compressibility coefficients of metal sulfide slurry. Consequently, based on the lowest filtration parameters of the produced metal sulfides, it was concluded that CaS was the most effective precipitation agent for separation and recovery of Cu, Zn and Ni.

Keywords—Calcium sulfide, Plating Wastewater, Filtration characteristics, Heavy metals, Sulfidation.

I. INTRODUCTION

PLATING wastewater containing toxic heavy metals such as Ni, Zn and Cu is discharged from plating industry. To ensure the environmental protection, the wastewater is commonly treated with NaOH or Ca(OH)$_2$, and the resulting metal hydroxide sludge is separated from the wastewater by a filtration process. Presently, the amount of metal sludges generated in Japan amounts to about 65,000 tons (containing 5,500 tons of metals) per year, and the majority of the sludges, so far, has been disposed of to landfills without any attempt to recover heavy metals. Additionally, in recent years, the prices of non-ferrous metals have risen drastically on increased global demand, and thus it is necessary to realize a "zero-waste society" which minimizes the disposal of metallic resources into the environment.

To achieve metals recovery from plating wastewater, the precipitation of metal ions as metal sulfides was used in the present study since the sulfidation treatment of plating wastewater with sulfidation agent such as Na$_2$S or H$_2$S has an advantage of high degree of metal removal even at low pH, low reactor detention time requirements due to the high reactivity of sulfides, possibility of selective metal removal and recovery by pH control during sulfidation treatment, and higher dewaterability of metal sulfides compared to metal hydroxide sludge [1-3].

To continue the research on the metal precipitation with sulfides, CaS, which can be produced at the recycling process of gypsum boards [5-6], was used in this study to investigate sulfidation behaviors of Ni, Zn and Cu as well as filtration characteristics of metal sulfide slurry. Regarding the CaS, it was considered that the addition of solid CaS could lead to generation of easily settleable precipitates compared to Na$_2$S or H$_2$S since CaS particles act as nuclei for production of metal sulfide particles and dissolved calcium ion functions as a coagulant [4]. Moreover, the utilization of CaS obtained by recycling gypsum boards was expected to solve a problem of the additional treatment costs as well as the difficulty of controlling the delivery of sulfide ions in the sulfidation process [4].

II. EXPERIMENTAL

A. Materials

K. Soya is with the Department of Energy Engineering and Science, Nagoya University, Japan (e-mail: k-soya@ees.nagoya-u.ac.jp).

N. Mihara is a graduate doctor course student of Department of Energy Engineering and Science, Nagoya University, Japan (e-mail: nam_sagggi @yahoo.co.jp).

D. Kuchar is with the Department of Energy Engineering and Science, Nagoya University, Japan (e-mail: dalikuchar@hotmail.com).

M. Kubota is with the Department of Energy Engineering and Science, Nagoya University, Japan (e-mail: kubota@nuce.nagoya-u.ac.jp).

H. Matusda is with the Department of Energy Engineering and Science, Nagoya University, Japan (e-mail: matsuda@nuce.nagoya-u.ac.jp).

T. Fukuta is with Sanshin MFG. Co., LTD (e-mail: ttfukuta@ybb.ne.jp).

TABLE I
SAMPLE METAL SOLUTION EMPLOYED

Sample Solution	Sample No	Metal Concentration [mg/dm³]		Ingredient
Simulated wastewater (Single Metal)	1-1	Cu	100	CuSO$_4$
	1-2	Zn	100	ZnSO$_4$
	1-3	Ni	100	
	1-4	Ni	200	NiSO$_4$
	1-5	Ni	500	
	1-6	Ni	1000	
	1-7	Ni	2000	
Simulated wastewater (Mixed Metal)	2-1	Cu	100	CuSO$_4$
		Zn	100	ZnSO$_4$
		Ni	100	NiSO$_4$

Table I shows the composition of simulated electroplating wastewater used in the experiments. The simulated plating wastewaters were prepared by dissolving metal sulfates of $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ of reagent grade in distilled water, since metal sulfates are generally used in the electroplating process.

B. Sulfidation Treatment of Single Metal Solution using CaS

At first, the experiments were carried out by adding solid CaS (purity higher than 99%) to 100 ml of sample solutions (Sample No. 1-1 to 1-3) without pH adjustment. The precipitation was allowed to proceed for 10 minutes, and then the solution containing metal sulfide slurry was filtered using a filter paper with pore size of 0.45μm. In addition, to investigate the possibility of selective precipitation, the sulfidation treatment of single-metal solution using CaS was conducted at pH range of 2.0 to 7.5. All experiments were carried out at a room temperature, and to maintain pH value at a constant value, 0.5 M or 0.1 M H_2SO_4 solution was used. The residual metal concentration in the filtrate was measured using an ICP (ICP, Vista-MPX Simultaneous ICP-OES, Varian, Inc.). The filter cake was dried at a temperature of 378K, and the dried filter cake was subjected to an X-ray Powder Diffraction Analysis (RINT-2500 TTR, Rigaku Model) in order to identify the crystallographic composition.

C. Sulfidation Treatment of Mixed Metal Solution using CaS

In the case of the selective sulfidation of Cu-Zn-Ni, a simulated plating solution (Sample No. 2-1) was treated with CaS in a cascade manner at pH of 2.0 for precipitation of Cu; pH of 4.0, 4.5, 5.0 and 5.5-6.0 for precipitation of Zn and pH over 6.0 for precipitation of Ni. Similarly, the metal concentrations in filtrates were analyzed using an ICP. At the end of the experiment, the filter cakes were dissolved in aqua regia (a mixture of HCl and HNO_3 at the ratio of 3:1) and the elemental composition of the leachates was analyzed by an ICP.

D. Evaluation of Filtration Characteristics

Filtration test apparatus was used to determine the average specific filtration resistance and compressibility coefficients of the slurry obtained by sulfidation treatment of nickel solution (Samples No. 1-3 to 1-7) using CaS at an Ni/CaS molar ratio of 1.0. In these experiments, a membrane filter with filtration area of 2.4×10^{-3} m^2 and a mean pore size of 0.45 μm was used. Solvent was separated from the slurry at a constant pressure and filtration time was determined. The relation between filtrate volume (V) and filtration time (θ) is given in (1)

$$\frac{d\theta}{dV} = \frac{\mu \rho s \alpha}{A^2 (1-ms) p}(V + V_m) \tag{1}$$

where μ is the filtrate viscosity, ρ is the filtrate density, s is the concentration of the slurry, A is the filtration area, p is the filtration pressure and Vm is the theoretical filtrate volume required to form a filter cake of resistance equal to medium resistance [7]. In the determination of average specific filtration resistance (α), $d\alpha/dV$ was plotted against V and the value of coefficient on the right side of (1) was determined from the slope of this plot. Consequently, the average specific filtration resistance (α) was calculated.

Further, in order to determine the compressibility coefficients (n), filtration resistance under different filtration pressure was measured, and then the compressibility coefficients were calculated using (2)

$$\alpha = \alpha_0 + \alpha_1 \cdot p^n \tag{2}$$

where α_0 and α_1 are constants.

For a comparison, the average specific filtration resistance and the compressibility coefficients of the slurry generated either by adding NaOH with a flocculant ($FeCl_3$: 500 mg-Fe/dm^3) or Na_2S as commonly used sulfidation agent were also determined.

Finally, to investigate the effect of initial concentration of nickel on the specific filtration resistance, filtration tests were also carried out for slurry generated by sulfidation treatment of sample solutions (Sample No. 1-3 to 1-7).
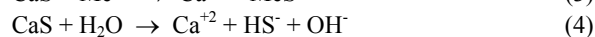
III. RESULTS AND DISCUSSION

A. Reaction Mechanism of Sulfidation of Ni, Zn and Cu

Fig. 1 shows the changes in the Ni, Zn and Cu concentrations in filtrates obtained at different molar amounts of CaS added to the sample solution. In the case of Ni and Zn, it can be seen that the metal concentrations in filtrate were reduced to a value below 1.0 mg/dm^3 when the molar ratio of CaS to metal exceeded a value of about 1.3. By contrast, the addition of the CaS agent at CaS to Cu molar ratio of 2.0 was necessary to reduce the Cu concentration in the filtrate below 1 mg/dm^3.

In the next step, the filter cakes obtained at CaS to metal molar ratio of 1.0 for Zn and Ni and CaS to Cu metal molar ratio of 2.0 were subjected to XRD analyses. In the case of Zn and Ni, only characteristic peaks of ZnS and NiS were obtained. However, the characteristic peaks of CuS and CaS were identified in the filter cake of copper sulfide slurry. This result was attributed to rapid precipitation of CuS on the CaS particles, which brought about an enclosure of unreacted CaS inside the CuS particles. As a consequence, a higher molar ratio of CaS to Cu was needed to achieve the reduction of Cu concentration to a value below 1 mg/ dm^3.

Regarding the reaction mechanism, it was considered that the reactions given by (3) - (7) might take place in the sulfidation of a given metal in wastewater [4], [8]:

$$CaS + Me^{2+} \rightarrow Ca^{2+} + MeS \tag{3}$$
$$CaS + H_2O \rightarrow Ca^{+2} + HS^- + OH^- \tag{4}$$
$$HS^- \leftrightarrows H^+ + S^{2-} \tag{5}$$
$$HS^- + Me^{2+} \rightarrow MeS + H^+ \tag{6}$$
$$S^{2-} + Me^{2+} \rightarrow MeS \tag{7}$$

In accordance with the proposed mechanism, pH value of the filtrates was observed to increase as the CaS/Me molar ratio was increased, owing to the generation of OH⁻ from CaS as expected by (4).

As described above, sulfidation of Cu using solid CaS was characterized by a low reactivity at a pH value of about 6.0. Therefore, sulfidation of Cu was conducted at the fixed pH value of 2.0 to increase the efficiency of the Cu sulfidation treatment owing to an improvement in CaS hydrolysis [9]. Fig. 2 shows the effect of CaS addition on the copper concentration in the filtrate at controlled pH. It can be seen that Cu was almost completely precipitated at pH = 2.0 when CaS to Cu molar ratio was adjusted to 1.2. After the precipitation experiment, the dried filter cake obtained at pH = 2.0 was analyzed by XRD and CuS was identified as the main component. Thus, it was concluded that sulfidation of Cu with CaS was dependent on pH and equations (8), (9) were considered to take place in the sulfidation of Cu in the acidic solution [9].

$$CaS + 2H^+ \rightarrow Ca^{2+} + H_2S(aq) \qquad (8)$$
$$Me^{2+} + H_2S(aq) \rightarrow MeS + 2H^+ \qquad (9)$$
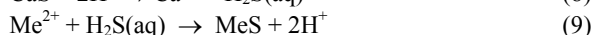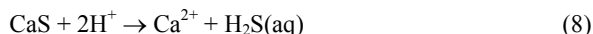
Subsequently, chemical reaction and equilibrium software (HSC Chemistry Ver.6.12) was used and Gibbs free energy of reaction (8) was found to be -112.4 kJ/mol, which was about 120 kJ/mol less than the Gibbs free energy of the reaction given by (4) (ΔG = 7.5 kJ/mol). Thus, from thermodynamic point of view, it was considered that the dissolution reaction of CaS in the acidic solution should proceed via (8) rather than (4). Based on this result, it was assumed that, in acidic pH, CaS was almost fully dissolved and reacted with Cu to form copper sulfide.
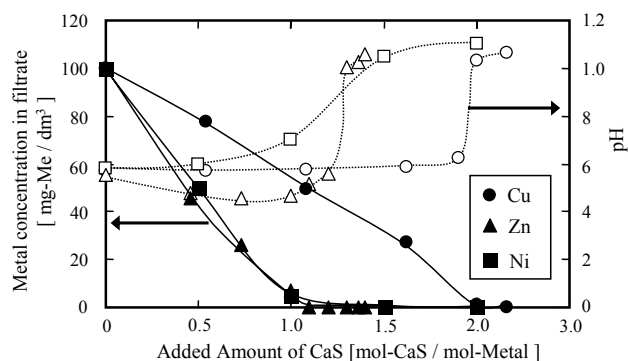

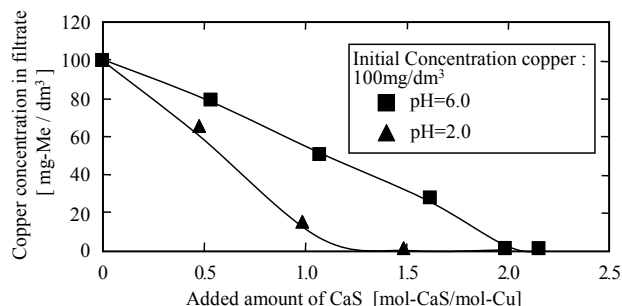Fig. 1 Effect of CaS addition on metal concentration in filtrate

Fig. 2 Effect of CaS addition on copper concentration in filtrate with pH control

B. Selective Sulfidation of Mixed Metal Solution with CaS

The pH values required for selective sulfidation of Cu, Zn and Ni in mixed metal plating wastewater were determined based on the results obtained in single metal systems. At first, selective sulfidation of Cu was carried out at pH range of 1.9-2.0. Fig. 3 shows the concentration change of Cu, Zn and Ni in the filtrate of mixed metal solution and it can be seen that the copper concentration was reduced to a value below 1.0 mg/dm³ at a molar ratio of CaS to Cu of about 1.2.

In the next step, selective sulfidation of Zn was carried out for the residual solution containing Zn-Ni mixture in a pH range of 4.0 to 6.0, based on ZnS solubility as a function of pH [1], [10]. Fig. 4 shows the change of metal concentration in the mixed metal solution and it can be seen that the zinc concentration decreased with an increase in pH. Specifically, the zinc concentration in filtrate was reduced to 5.0 mg/dm³ at a molar ratio of CaS to Zn of about 1.5 and to 2.0 mg/dm³ at a molar ratio of CaS to Zn of about 2.0 at controlled pH = 5.5-6.0. From these results, it was considered that at low pH conditions (pH < 4), H₂S(aq) was the predominant species [9-10], and part of the H₂S was released from the solution as H₂S gas due to the poor precipitation of ZnS in an acidic solution compared to CuS. Such assumption is further supported by lower Gibbs free energy of Zn sulfidation in an acidic solution shown by reaction (9) (ΔG = -23.6 kJ/mol) compared to Gibbs free energy of Cu sulfidation reaction (ΔG = -94.0 kJ/mol). To conclude this part, it was considered that an optimum pH value for selective sulfidation of Zn was 5.5-6.0.

Finally, sulfidation of single nickel solution was carried out at controlled pH using CaS, and the nickel concentration was observed to decrease rapidly at a pH value higher than 6.0, so that it was considered that the optimum pH value for selective sulfidation of zinc in mixed metal solution was about 6.0.

At the end of sulfidation experiments, the filter cakes obtained at each sulfidation step were analyzed and the composition of filter cakes in terms of Cu, Zn, Ni and Ca is given in Fig. 5. It is shown that the filter cake obtained by sulfidation of mixed metal solution at pH=2.0 was almost completely composed of copper confirming that high precipitation selectivity can be achieved for Cu. Further, the filter cake obtained at pH-5.5-6.0 contained 81.4% Zn and Ni 18.2% Ni, and thus further experiments should be considered to increase the selectivity of zinc precipitation.
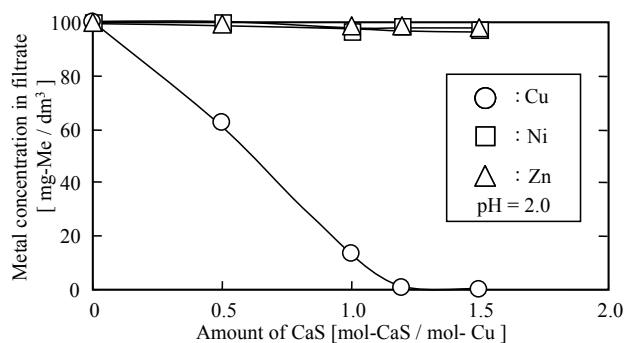
Fig. 3 Change of metal concentration in filtrate of simulated mixed metal solution at controlled pH, Temperature : 293－298 K
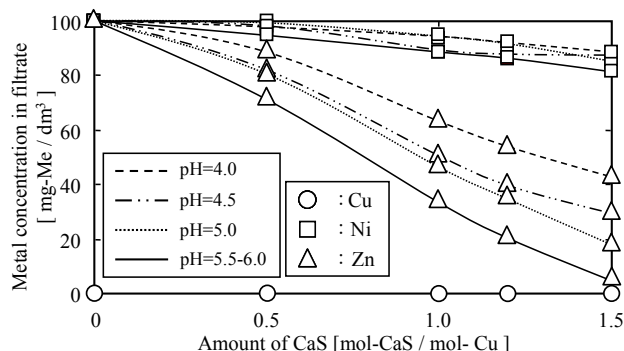

Fig. 4 Change of metal concentration in filtrate of residual metal solution after selective precipitation of copper at controlled pH, Temperature: 293－298 K
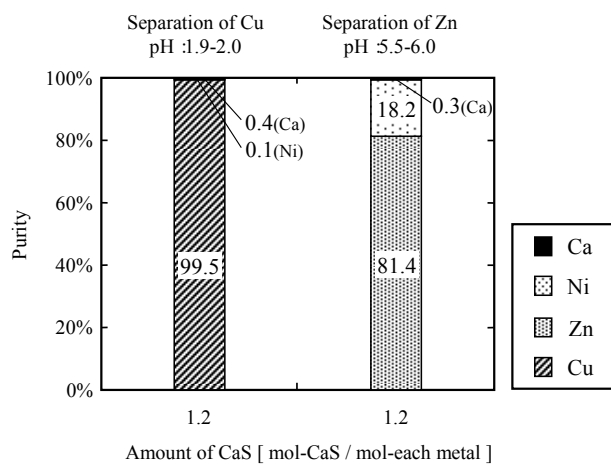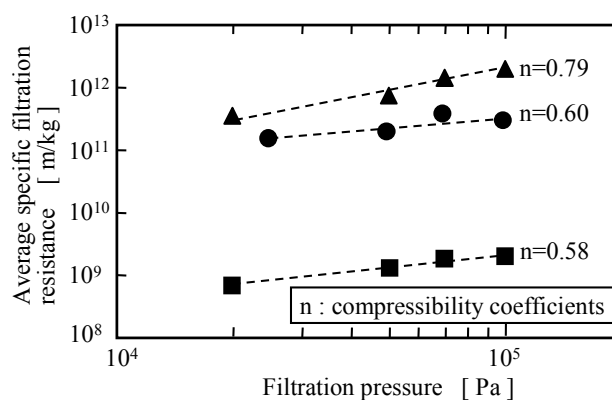

Fig. 5 Composition of filter cake

C. Average Specific Filtration Resistance

Fig. 6 shows the average specific filtration resistances and the compressibility coefficients of the nickel slurries obtained by sulfidation of sample solutions (Sample No. 1-3 and 1-7) without pH control plotted against filtration pressure. The results confirmed that the average specific filtration resistance and the compressibility coefficients of metal sulfide slurries

obtained with CaS were lower than that of slurry obtained with NaOH. Furthermore, the average specific filtration resistance of metal sulfide slurry generated was found to decrease with an increase in metal concentration.

Precipitation agent	▲	●	■
	NaOH (pH=12)	CaS (Powder)	
Initial concentration [mg-Ni / dm^3]	100	100	2000

Fig. 6 Average specific filtration resistances and compressibility coefficients obtained at each filtration pressure

To investigate the dependence of filtration characteristics on initial metal concentration, the filter cakes were subjected to XRD analysis and as a result, only peaks of nickel sulfide were obtained in the case of 100 mg/dm^3 nickel solution. Meanwhile, the characteristic peaks of nickel sulfides and calcium sulfate were identified in the case of 1000 mg/dm^3 nickel solution. To understand this phenomenon, the residual concentrations of Ca^{2+} and SO_4^{2-} in the filtrates obtained at different nickel concentrations were determined and the results are shown in Fig. 7. It can be seen that the residual ratios of calcium and sulfate in the filtrate started to decrease at a nickel initial concentration of about 500 mg/dm^3. From these results, it was considered that the nickel sulfide was efficiently precipitated by the flocculating effect of $CaSO_4$ and CaS. Thereby, the average specific filtration resistance of the nickel slurries was reduced [11-12]. Meanwhile, it was also considered that a higher average specific filtration resistance obtained at low initial nickel concentration could be attributed to the generation of fine particles owing to the colloidal properties of nickel sulfide [13-14], and as the initial nickel concentration increased, NiS particle size also increased owing to the flocculation supported by the presence of cation (Ca^{2+}, Ni^{2+}) in the solution [10], [15-17].

To summarize these findings, it was recognized that sulfidation in highly concentrated metal solution had advantages of low specific filtration resistance and easy metal removal, however, had a disadvantage of the increased content of impurities in nickel precipitate.
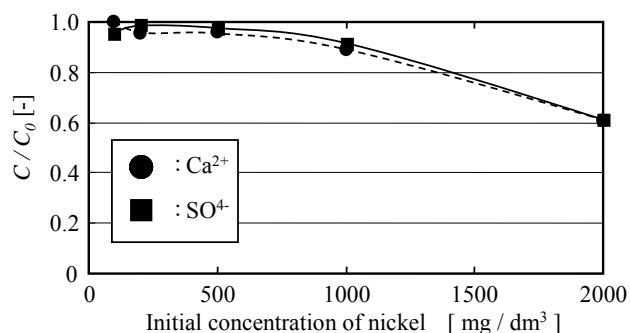
Fig. 7 Residual ratio of calcium and sulfate in filtrate of nickel single solution at different initial nickel concentrations, Temperature: 293−298 K

IV. Conclusion

In this work, sulfidation behaviors of Cu, Zn and Ni in single metal solution with and without pH control and possibility of selective precipitation of Cu, Zn and Ni from mixed metal solution were investigated.

In the case of single metal solution without pH control, Ni and Zn concentrations were reduced from $100 mg/dm^3$ to less than $1 mg/dm^3$ respectively when the CaS was added to the simulated wastewater at CaS to metal molar ratio of 1.3. By contrast, the copper concentration in filtrate was reduced below $1 mg/dm^3$ when the molar ratio of CaS to Cu exceeded a value of 2.0. On the other hand, when the experiments were carried out at a fixed pH value of 2.0, Cu was almost completely precipitated at CaS to Cu molar ratio of 1.2.

Further, regarding the selective precipitation of Cu, Zn and Ni from mixed metal solution, copper concentration in the filtrate was reduced to a value below $1.0 mg/dm^3$ at pH=1.9-2.0 and at a molar ratio of CaS to Cu of about 1.2. Then, the zinc concentration was reduced to $5.0 mg/dm^3$ at pH-5.5-6.0 and a molar ratio of CaS to Zn of about 1.5. Subsequently, the selectivity of copper precipitation at pH=1.9-2.0 was determined to be 99.5%, while the selectivity of zinc precipitation obtained at pH=5.5-6.0 was only about 81.4%.

Finally, the determination of average specific filtration resistance and compressibility coefficients showed that better filtration characteristics can be obtained in the case of CaS than in the case of commonly used NaOH. Furthermore, it was found that the average specific filtration resistance of metal sulfide slurry generated in high metal concentration was smaller than in low metal concentration owing to the presence of $CaSO_4$ and cation (Ca^{2+}, Ni^{2+}) which enhanced sedimentation ability of nickel sulfide slurry.

References

[1] R. W. Peters, and Y. Ku, "Batch precipitation studies for heavy metal removal by sulfide precipitation," *AIChE Symp. Ser.*, vol. 81, 1985, pp. 9-26.
[2] T. Fukuta, T. Ito, K. Sawada, Y. Kojima, H. Matsuda, and F. Seto, "Separation of Cu, Zn, and Ni from plating solution by precipitation of metal sulfides," Kagakukougaku- ronbunshu vol. 30, 2004, pp. 227-232 (in Japanese).
[3] H. Kondo, T. Fujita, D. Kuchar, T. Fukuta, H. Matsuda, and K. Yagishita, "Separation of metal sulfides from plating wastewater containing Cu, Zn and Ni by selective sulfuration with hydrogen sulfide," Hyomengijutsu vol. 57, 2006, pp. 901-906 (in Japanese).
[4] B. M. Kim, "Treatment of metal containing wastewater with calcium sulfide," *AIChE Symp. Ser.,* vol. 77, No. 209, 1980, pp. 39-48.
[5] N. Mihara, K. Soya, D. Kuchar, T. Fukuta and H. Matsuda, "Utilization of calcium sulfide derived from waste gypsum board for metal-containing wastewater treatment," Global NEST Journal, vol. 10, 2008, pp. 101-107.
[6] B. Kamphuis, A. W. Potma, W. Prins, and W. P. M. Van Swaaij, "The reductive decomposition of calcium sulphate–I. Kinetics of the apparent solid–solid reaction," *Chem. Eng. Science*, vol. 48, 1993, pp. 105–116.
[7] (Handbook style) *The Society of Chemical Engineers, Japan, Kagaku Kogaku Binran*, Maruzen Co., Tokyo, 1999, pp. 789-819 (in Japanese).
[8] B. M. Kim and P. A. Amodeo, "Calcium sulfide process for treatment of metal-containing wastes," *Environ. Prog.*, vol. 2, No. 3, 1983, pp. 175–180.
[9] M. García-Calzada, G. Marbán and A. B. Fuertes; "Decomposition of CaS particles at ambient conditions," *Chem. Eng. Science*, vol. 55, 2000, pp. 1661-1674.
[10] R. W. Peters, Y. Ku and T.- K. Chang, "Heavy metal crystallization kinetics in an MSMPR crystallizer employing sulfide precipitation," *AIChE Symp. Ser.*, vol. 80, 1984, pp. 55-75.
[11] K. Yahikozawa, T. Aratani, R. Ito, T. Sudo, and T. Yano, "Kinetic studies on the lime sulfurated solution (calcium polysulfide) process for removal of heavy metals from wastewater," *Bulletin of the Chemical Society of Japan*, vol. 51, No. 2, 1978, pp. 613-617.
[12] Y. Sano, M. Shimada, Y. Nagahama, and Y. Sugimoto, (1984). "Filtration characteristics of calcium polysulfide suludge containing sime heavy metals," *Bull. Environ. Conserv., Shinshu Univ.,* vol. 6, pp.40-45 (in Japanese).
[13] T. Aratani, K. Yahikozawa, H. Matoba, S. Yasuhara, and T. Yano, "Condition for the Precipitation of Heavy Metals from Wastewater by the Lime Sulfurated Solution (Calcium Polysulfide) Process," *Bulletin of the Chemical Society of Japan,* vol. 51, No. 6, 1978, pp. 1755-1760.
[14] H. Deng, C. Chen, Q. Peng and Y. Li, "Formation of transition-metal sulfide microspheres or microtubes," *Materials Chemistry and Physics,* vol.100, 2006, pp.224-229.
[15] Y. F. Nicolau and J. C. Menard, "An electrokinetic study of ZnS and CdS surface chemistry," *J. Colloid Interface Sci*, vol. 148, No. 2, 1992, pp. 551–570.
[16] W. Gan and Q. Liu, "Coagulation of bitumen with kaolinite in aqueous solutions containing Ca^{2+},Mg^{2+} and Fe^{3+}: Effect of citric acid," *J. Colloid Interface Sci*, vol. 324, 2008, pp. 85–91.
[17] D. Feng, C. Aldrich and H. Tan, "Treatment of acid mine water by use of heavy metal precipitation and ion exchange," *Miner. Eng.*, vol. 13, No. 6, 2000, pp. 623–642.