Separation of Nickel from Plating Solution by Sulfuration Treatment

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Precipitation by sulfuration of nickel was used to recover nickel from the waste plating solution. Three kinds of sulfurating agents—sodium sulfide (Na_2S), sodium disulfide (Na_2S_2), and sodium tetrasulfide (Na_2S_4)—were compared for the sulfuration behavior and the precipitation characteristics of the nickel sulfide (NiS) produced. Results showed that the nickel concentration in the filtrate was reduced from the initial concentration of 100 mg_{-N}/L to about 0.594–3.37 mg_{-N}/L with the addition of each sulfurating agent. The average specific filtration resistance of the slurry produced by adding each sulfurating agent was smaller than that in the nickel hydroxide (NiOH) slurry. In particular, the average specific filtration resistance of the slurry produced by adding Na_2S_4 was greatly reduced under controlled pH values of 7 ± 1. The good filtration property obtained from the proposed sulfuration treatment was attributed to the larger particle-size distribution of NiS produced by the sulfuration agent Na_2S_4. It was further confirmed that the proposed sulfuration treatment using Na_2S was applicable for the separation of nickel, zinc, and copper in mixed-metal solutions.

INTRODUCTION

In the plating industry, wastewater containing valuable metals, such as nickel, zinc, and copper, is discharged in the rinsing process, in which extra plating solution is rinsed out with water from the surface of the plated product.

To remove these metals from wastewater, sodium hydroxide (NaOH) is commonly used because the hydroxide ion reacts with the metal to form insoluble metal hydroxide in water (Kosaka 1997). In this treatment, however, a sludge containing various metals and more than 85% water is formed. Over 100,000 tons per year of the sludge is generated in Japan (Federation of Electroplating Industry Association of Japan [FEIAJ] 1993); and, so far, most of which are dumped into landfills without any metal recovery.

For the purpose of recovering metal from wastewater generated by the plating industry, precipitation by sulfuration of metals is proposed in this present study. By applying existing sulfuration techniques, the metals contained in the plating solution are recovered easily as metal sulfides in the sludge (Chemical Society of Japan [CSJ] 1993). Moreover, precipitation by sulfuration is better than the conventional means of recovering metals using NaOH in terms of reduced sludge volume and the possibility of metal separation from mixed-metal solutions.

In the filtration process, however, it is difficult to separate the metal sulfide from the slurry obtained by the addition of sodium sulfide (Na_2S) or sodium hydrosulfide (NaHS) to the wastewater, since metal sulfides formed in the precipitation consist of fine particles. It is, therefore, important to form metal sulfides with the largest particle possible during the precipitation process (Tels 1997). In order to improve the filtration property, the proponents employed two kinds of sodium polysulfides as sulfurating agents, sodium disulfide (Na_2S_2) and sodium tetrasulfide (Na_2S_4).

In this study, they chose nickel as the target metal among the other metals contained in the dumped sludge. Nickel is one of the most valuable metals discharged in large amounts by the plating industry. According to the report of the Federation of Electroplating Industry Association of Japan (1997), about 0.212 wt% of nickel is contained in the dumped sludge, and only 0.171 and 0.089 wt% of copper and zinc, respectively.

For the purpose of recovering these metals by the proposed sulfuration treatment, the proponents studied the mechanism of sulfuration reaction between nickel and the sodium-based sulfurating agents—Na_2S, Na_2S_2, and Na_2S_4. The average specific filtration resistances of the slurries formed by sulfuration with these sulfurating agents were determined using simulated rinsing water.

The properties of both the slurries and the sludge, such as particle-size distribution, average porosity, and density, were likewise determined. The sulfuration treatment was also applied to the separation of metals from mixed-metal solutions containing nickel, zinc, and copper. Then, the applicability of the proposed sulfuration treatment

for effective recovery of nickel from mixed-metal solutions was examined.

EXPERIMENTAL METHODS

Chemicals
Nickel sulfate hexahydrate aqueous solution of 100 mg_{-Ni}/L (1.7 x10^{-3}mol/L) was used as simulated wastewater. Aqueous solutions of Na_2S, Na_2S_2, and Na_2S_4 of 6.8x10^{-4} mol/L concentration were used as sulfurating agents.

Precipitation procedure
Nickel sulfate hexahydrate, zinc sulfate heptahydrate, and copper sulfate pentahydrate of reagent grade (Wako Chemicals) were employed. The metal sulfates were dissolved in distilled water to prepare 100 mg/L of nickel sulfate solution and 300 mg/L of the mixed solution containing the same weight of nickel sulfate, zinc sulfate, and copper sulfate, as the model samples of plating solution. The amount of solution of sodium sulfides, which was added to 1.0x10^{-4} (or 3.0 x10^{-3}) m^3 nickel sulfate solution, or nickel, zinc, and copper mixed solution, was regulated so that the molar ratios of sodium sulfides to metals (Ni^{2+}, Zn^{2+}, and Cu^{2+}) could be adjusted as 0.5, 1.0, 1.5, 2.0, and 3.0. The slurries, which were formed by the precipitation of metal sulfides by the sulfuration of Ni^{2+}, Zn^{2+}, or Cu^{2+} with sodium sulfides were mixed for 600 s and then allowed to stand for another 600 s. The pH value of the sample solution was controlled by adding 10% H_2SO_4 aqueous solution in order to keep the pH value of the slurry within 7 ± 1.

The slurry obtained was filtered using filter paper with a mean pore size of 1 μm (ADVANTEC No. 5C) to separate the filtrate and the precipitate from the slurry. The nickel concentration of the filtrate was measured using an Induction Coupled Plasma (Perkin Elmer Japan, Optima3300DV). The sludge (*precipitate*) was allowed to dry in a muffle furnace at 378 K for 2 h before its chemical composition was analyzed by X-ray diffraction (Rigaku, RINT–2599DDV).

Filtration test
Figure 1 shows the experimental filtration testing apparatus employed to measure the

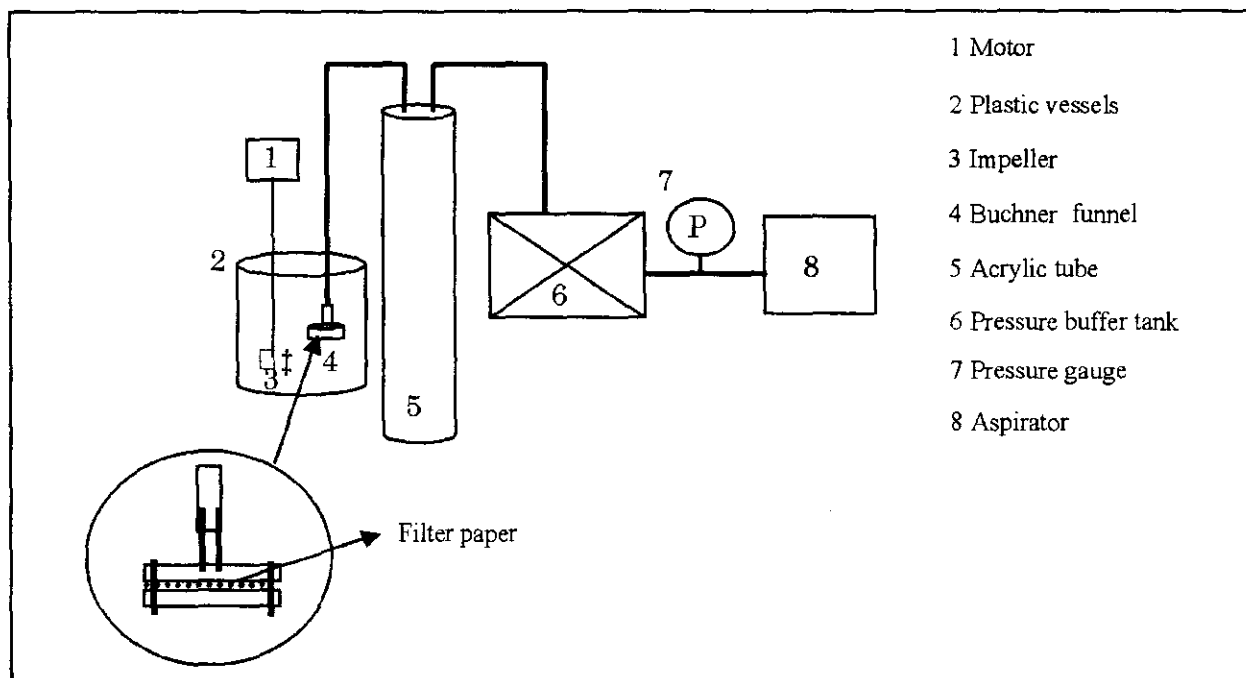| 1 Motor |
| 2 Plastic vessels |
| 3 Impeller |
| 4 Buchner funnel |
| 5 Acrylic tube |
| 6 Pressure buffer tank |
| 7 Pressure gauge |
| 8 Aspirator |

Figure 1. Experimental Filtration Testing Apparatus

average specific filtration resistance of the slurry. The filter paper used has a filtration area of 2.4×10^{-3} m^2 and a mean pore size of 1 μm was used.

The volume of the filtrate, V and time, θ are related as follows:

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

where

μ [Pa·s] is the viscosity of the filtrate,

ρ [kg·m^{-3}] is the density of the filtrate,

s[kg·m^{-3}] is the concentration of the slurry,

A [m^2] is the filtration area,

p [Pa] is the filtration pressure, and

V_m [m^3] is the fictitious filtrate volume

required to form a filter cake with the resistance equal to medium resistance (The Society of Chemical Engineers 1995).

The slope obtained in the plot of dθ/dV versus V gives the value of the coefficient in the right hand side (RHS) of Eq. (1). Hence, the average specific filtration resistance α [m·kg^{-1}] can be obtained using Eq. (1).

RESULTS AND DISCUSSION

Reaction mechanism between nickel and the sulfurating agents— Na_2S, Na_2S_2, and Na_2S_4

Figure 2 shows typical examples of the change in nickel concentration in a filtrate for each amount of sulfurating agent added to the nickel sulfate solution of 100 mg$_{-Ni}$/L. It is recognized that nickel concentration in filtrate decreases in proportion to the amount of sulfurating agent added. The decrease in nickel concentration could
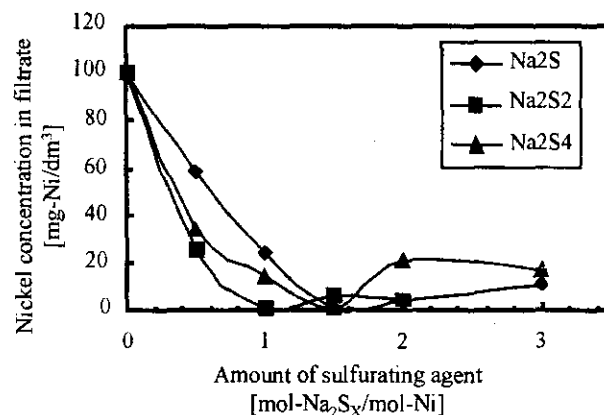

Figure 2. Nickel Concentration vs. Amount of Sulfurating Agents

be attributed to the precipitation of NiS produced by the sulfuration of nickel using sodium sulfides. In particular, low concentrations of nickel (less than 1 mg$_{-Ni}$/L), within the range of 1.0–1.5 molar ratios of sulfurating agents to nickel, were obtained for all the sulfurating agents.

On the one hand, the addition of sulfurating agents causes an increase in pH value, resulting from the increase in OH- formed by the hydrolysis of sulfurating agents. The OH- is liable to react with nickel ion to produce nickel hydroxide. The resulting change in nickel concentration (see Figure 2) that was obtained without pH control could be attributed to the fact that a percentage of nickel was precipitated as nickel hydroxide.

On the other hand, the nickel concentration in filtrate increased with each increase in the amount of sulfurating agent exceeding 1.0–1.5 mol$_{-Na2SX}$/mol$_{-Ni}$. It is considered that a part of the precipitated particles in a slurry passed through the filter. These precipitated particles, however, could be collected when the filter paper was replaced with one having a mean pore size of 0.45 μ m. Metal sulfides are liable to undergo particulation with the excessive addition of sulfurating agent. Figure 2 shows that particulates of nickel sulfides of less than 1- μ m diameter were formed when the amount of sulfurating agent exceeded 1.5 mol/mol-Ni.

To determine the chemical composition of the sludge, it was subjected to X-ray diffraction (XRD) analysis. Figure 3 shows the XRD patterns of the cakes obtained by adding Na$_2$S at 1.5 mol$_{-Na2SX}$/mol$_{-Ni}$ (a), Na$_2$S$_2$ at 1.0mol$_{-Na2SX}$/

mol$_{-Ni}$ (b), and Na$_2$S$_4$ at 1.5mol$_{-Na2SX}$/mol$_{-Ni}$ (c). There were no characteristic X-ray peaks of nickel compounds detected.

It was considered that the crystallinities of nickel sulfides formed in this experimental condition might be relatively low. On the contrary, sulfur peaks were found in the X-ray patterns for the case of (b) and (c). From these results, it was considered that the reaction between nickel and sodium sulfides proceeded as follows:
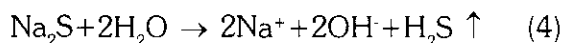
$$Na_2S_X \leftrightarrow 2Na^+ + S^{2-} + (X-1)S \qquad (2)$$

then

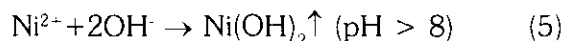$$Ni^{2+} + S^{2-} \leftrightarrow NiS\downarrow \qquad (3)$$
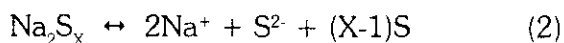
It is known that the sulfuration of zinc with sodium polysulfides occurs in a similar manner (Meux et al. 1995).

Likewise, the following hydrolysis of Na$_2$S is well known:

$$Na_2S+2H_2O \rightarrow 2Na^++2OH^-+H_2S \uparrow \qquad (4)$$

Once the hydroxide ion is present in the nickel solution, the precipitation of NiOH is supposed to occur as:

$$Ni^{2+}+2OH^- \rightarrow Ni(OH)_2\uparrow \ (pH > 8) \qquad (5)$$

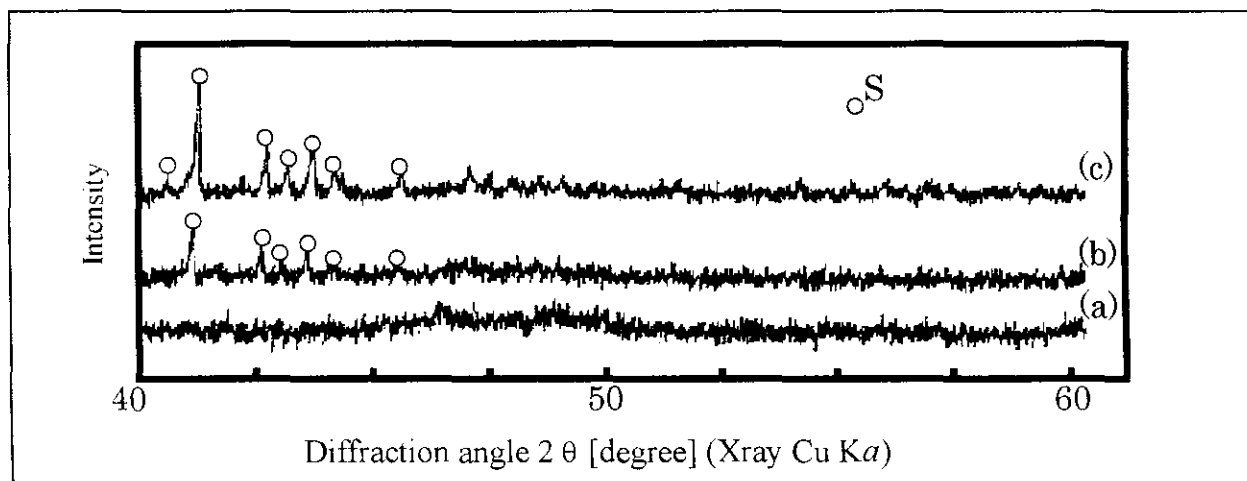In the present experiment, the hydrolysis of sodium sulfides was expected to occur since a

Figure 3. XRD Patterns of Dried Sludge: (a) Na₂S, (b) Na₂S₂, and (c)Na₂S₄

Table 1. The Lowest Nickel Concentrations Obtained

	Na_2S	Na_2S_2	Na_2S_4	Na_2S	Na_2S_2	Na_2S_4
	Without pH control			With pH control		
Amount of Na_2S_X [mol-Na_2S_X/mol-Ni]	1.5	1.0	1.5	3.0	3.0	3.0
Nickel concentration [mg-Ni/dm^3]	0.594	0.956	0.736	0.874	3.37	1.61

rise in the pH value of the slurry was observed with the addition of sodium sulfides. Therefore, NiOH may be present, to a certain extent, in the precipitate.

In order to prevent NiOH from generating, sulfurating agents were added to the nickel sulfate solution under a controlled pH value of the slurry. Figure 4 shows the changes in nickel concentration for each amount of sulfurating agent added under controlled-pH value conditions. The graph shows how the nickel concentration decreased to a value lower than
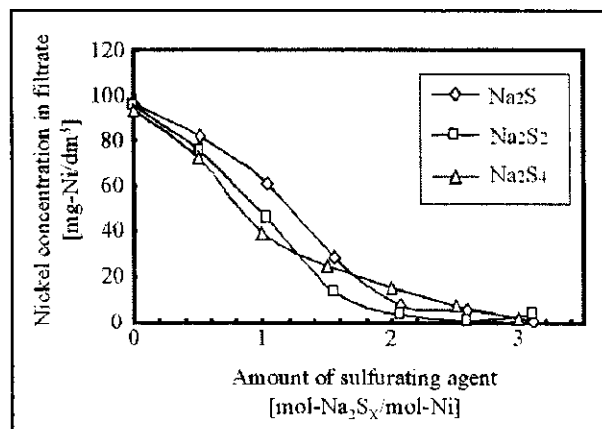
5.0 mg$_{-Ni}$/L. Compared with the results obtained when the pH value was not controlled (refer to Figure 2), a larger amount of eachof the sulfurating agents were required to achieve nickel concentrations lower than 5.0 mg$_{-Ni}$/L.

Table 1 summarizes the lowest nickel concentrations obtained under the conditions described in figures 2 and 4.

Average specific filtration resistance

The average specific filtration resistance of the slurries obtained under conditions identical to those in Table 1 were plotted against the filtration pressure found in Figure 5.

The slurry obtained by adding to the nickel solution NaOH, which is generally employed for the precipitation of metals in wastewater, was also subjected to the filtration test. Figure 5 shows that the average specific filtration resistance of all sulfide slurries was smaller than that in the hydroxide slurry. Hence, it can be concluded that the sulfide slurry has the advantage of being more effective than the hydroxide slurry in terms of filtration.

Among the three sulfurating agents used, Na_2S_4 was most effective for giving the smallest average specific filtration resistance. It was also

Figure 4. Nickel Concentration vs. Amount of Sulfuring Agents at Controlled pH 7±1
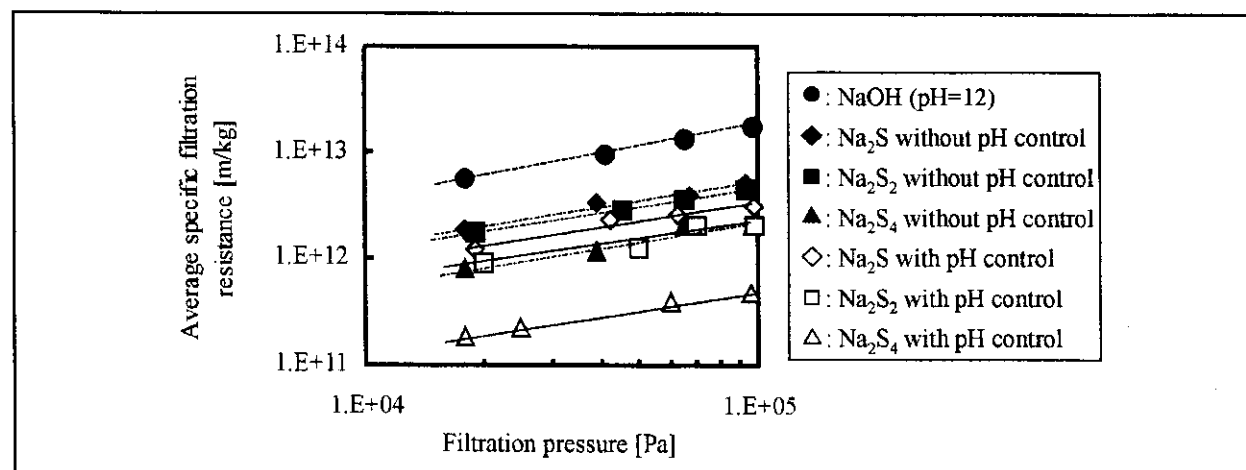

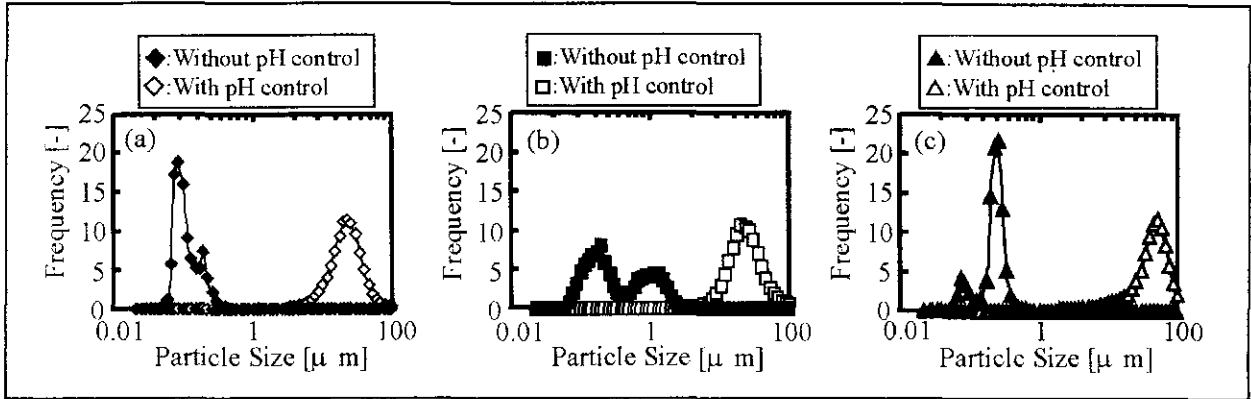**Figure 5. Average Specific Filtration Resistance**

Figure 6. Particle Size Distribution of Nickel Precipitates: (a) Na_2S, (b) Na_2S_2, and (c) Na_2S_4

observed that the average specific filtration resistance became smaller by keeping the pH value of the slurry at 7 ± 1.

Particle-size distribution of filter cake

The particle size distribution and the specific surface area of the filter cake were measured using a particle-size distribution analyzer (HORIBA, LA-920). The cakes subjected to the analysis were those obtained under the conditions outlined in Table 1. Figure 6 shows the particle-size distribution of the cakes that were obtained by adding Na_2S (a), Na_2S_2 (b), and Na_2S_4 (c) to the nickel solution.

Under the condition where the pH value was not controlled, the size of the constituent particles of particles formed by sodium polysulfide was larger than that formed by Na_2S. Although it was not clear why there were differences in particle size depending on the species of surfurating agent, it was considered that the sulfur dissociated from the sodium polysulfide, as expressed in Eq. (2), might have incorporated with nickel sulfide to form a larger aggregated particle. Likewise, when the

pH value of the slurries were kept at 7 ± 1, the particle size of the precipitate became even larger than that of the precipitate formed when the pH value was not controlled. Strangely, however, it was found that the particle with a larger particle size gave a smaller specific surface area.

Average specific filtration resistance vs. average porosity, density, and specific surface area

It is well known that a cake's average porosity, density, and specific surface area (particle size) are related to its average specific filtration resistance, as shown by the Kozeny–Carman equation:

$$\alpha = \frac{(1-\varepsilon)^3}{\varepsilon^3} \cdot \frac{1}{\rho_S} k' \left(\frac{\phi}{d}\right)^2 = \frac{1-\varepsilon}{\varepsilon^3} \cdot \frac{1}{\rho_S} k' S_V^2, \quad (6)$$

where $\varepsilon[-]$ is the average porosity of the cake, $\rho_s[kg \cdot m^{-3}]$ is the density of the particle, $k[-]$ is constant, $\phi[-]$ is the specific surface shape factor of the particle, $d[m]$ is the particle size, and $S_v[m^2]$ is the specific surface area (Coulson

Table 2. Characteristics of Filter Cake Obtained at the Filtration Pressure of 0.2 MPa

	Na_2S	Na_2S_2	Na_2S_4	Na_2S	Na_2S_2	Na_2S_4
	Without pH control			With pH control		
Mass ratio of wet cake to and dry cake $m[-]$	5.12	4.70	3.87	2.17	2.13	2.10
Density of filtrate $\rho \times 10^{-3}$ [kg/m³]	0.997	0.997	0.997	0.997	0.997	0.997
Particle density $\rho^s \times 10^{-3}$ [kg/m³]	2.17	2.12	2.19	2.01	1.99	1.94
Average porosity $\varepsilon[-]$	0.900	0.887	0.863	0.702	0.693	0.682
Mean particle size $d \times 10^6$ [m]	0.388	0.500	0.854	22.0	24.9	45.3
Specific surface area $S_v \times 10^6$ [m²/m³]	6.26	6.05	4.51	3.50	3.27	2.24

and Richardson 1968). In order to explain the difference in the average specific filtration resistance $\alpha[\text{m·kg}^{-1}]$ of the nickel sulfate solution (see Figure 5), the proponents employed Eq. (6).

Prior to the evaluation of value, the density and the average porosity at filtration pressure of 0.2MPa, were measured. After dehydrating the cake at 313 K in a muffle furnace for 12 h, the cake was subjected to density measurement via water displacement technique using a pycnometer. Then, the average porosity of the cake was calculated as follows:

$$m = 1 + \varepsilon\rho / \{\rho_S(1 - \varepsilon)\}, \qquad (7)$$

where $m[-]$ is mass ratio of wet cake to dry cake. The measured values for density and average porosity are summarized in Table 2.

From these results, both the average porosity and the density under controlled-pH condition were smaller than those without pH control. Nevertheless, Figure 5 reveals that the average specific filtration resistance of the slurry under controlled-pH condition was smaller than that obtained under uncontrolled pH. Although the average porosity of NiS formed by Na_2S_4 was smaller than that formed by Na_2S, the average specific filtration resistance of the slurry obtained by the former was smaller than that obtained by the latter. Even if both the average porosity ε [-] and the density ρ_S [kg·m^{-3}] were small, the average specific filtration resistance also tended to be small either when the specific surface area S_V [m^2] was sufficiently small or the particle size d [m] was

Figure 7. Concentration Change of Cu, Zn, and Ni in Filtrate with the Addition of the Sulfurating Agent Na₂S

sufficiently large. It was, therefore, concluded that the average specific filtration resistance was greatly influenced by the specific surface area or the size of the particle formed in the slurry during sulfuration treatment of the nickel solution.

Separation of nickel, zinc, and copper from the mixed-metal solution

Figure 7 shows the changes in the concentration of nickel, zinc, and copper in the filtrate with the amount of sulfurating agent (Na₂S) added to 1×10^{-4} m^3 mixed-metal solution containing 10 mg of Ni, 10 mg of Zn, and 10 mg of Cu. The figure reveals that Cu was preferentially precipitated/separated from the mixed metal solution by the sulfuration treatment.

When the charged amount of Na₂S was about 0.35 mol-$_{Na2S}$/mol-$_{metals}$, Cu^{2+} was no longer detected in the filtrate, although 94–95 wt% of Zn^{2+} and Ni^{2+} still remained. The precipitation of Zn and Ni progressed with each increase in the amount of Na₂S added.

On the one hand, the complete precipitation of Zn was achieved when the amount of Na₂S added reached about 0.8 mol-$_{Na2S}$/mol-$_{metals}$. On the other hand, the complete precipitation of Ni was achieved by adding Na₂S to an excessive amount of 20–30 mol% larger than the molar amount of Na₂S, equivalent to all metal species present in the mixed metal solution.

The order of precipitation of nickel, zinc, and copper may be attributed to the differences in solubility of metal sulfides.

Nevertheless, further investigation is needed to make sure that the sulfuration treatment employed in the present study can be applied for practical use in recovering metal species from mixed-metal solutions by considering such parameters as pH value, composition, and initial concentration both of the metal solution and of the sulfurating agent.

CONCLUSIONS

The experimental results showed that nickel concentration in the simulated wastewater decreased from 100 mg$_{-Ni}$/L to 0.594–3.37 mg$_{-Ni}$/L with the addition of the sulfurating agents sodium sulfide (Na₂S), sodium disulfide (Na₂S₂), and sodium tetrasulfide (Na₂S₄).

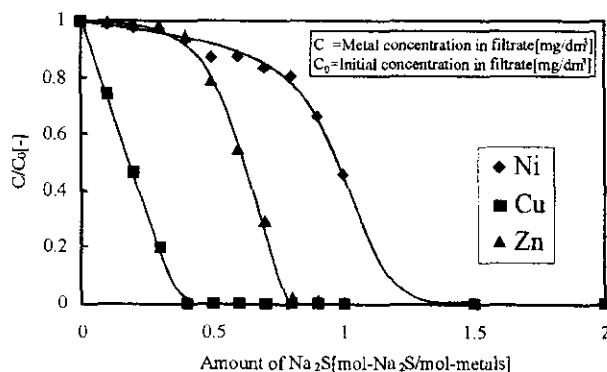Compared with the hydroxide slurry formed in the conventional precipitation treatment, all the slurries obtained by adding the aforementioned sulfurating agents had a lower average specific filtration resistance.

It was found that the filtration characteristics of the slurry improved by using sodium polysulfides since the particle size that nickel sulfide produced was larger compared to that produced by sodium sulfide. Moreover, by keeping the pH value of slurry at 7 ± 1, further improvement in filtration characteristic was obtained, owing to an increase in the particle size of the precipitate of nickel sulfide.

It was recognized that the metals nickel, zinc, and copper contained in the mixed-metal solution were effectively separated using the proposed sulfuration treatment, in which the sulfurating agent Na_2S was added to an excessive amount of 20–30 mol% larger than the molar amount of Na_2S, equivalent to all the metal species present in the mixed-metal solution of nickel, copper, and zinc.

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