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SULFURATION TREATMENT OF ELECTROPLATING WASTEWATER FOR SELECTIVE RECOVERY OF COPPER, ZINC AND NICKEL RESOURCE

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ABSTRACT

In the electroplating process, various metal salts are used and the residues on the surface of electroplated materials are rinsed out as wastewater, followed by hydration in a wastewater disposal step. Although a variety of metals are concentrated in the sludge, the mixed heterogeneous state of these metals in sludge makes it difficult to recycle and reuse them. From the viewpoint of environmental protection as well as resource saving, effective methods for recycling and reuse of these mixed metal sludge are required to be developed urgently.

In the present work, selective recovery of the metals from mixed-metal wastewater by sulfuration treatment is proposed. Sulfuration treatment is characterized by low solubility of metal sulfides; metal sulfides are, in general, lower in solubility than that of metal hydroxides. For the experiments, three metals of copper, zinc and nickel which are commonly used in the electroplating process were chosen. Separation of these metals from the mixed solution in various pH ranges was conducted by employing three sulfurating agents: sodium sulfide (Na_2S), sodium disulfide (Na_2S_2) and sodium tetrasulfide (Na_2S_4). Aqueous solutions of $CuSO_4$, $ZnSO_4$ and $NiSO_4$ and those of real plating wastewater, of which the initial concentrations were adjusted to 100-300 mg dm^{-3} were employed.

By sulfuration treatment of the simulated solution using each sulfurating agent without adjusting pH, CuS was first precipitated, but ZnS and NiS were also precipitated at the same time. In addition, pH value increased with the amount of sulfurating agents in the solution. The results demonstrated that the formation behavior of metal precipitates depended on pH value of the solution. For the sulfuration with three kinds of sulfurating agents, copper was first separated from the solution as CuS in pH=1.4-1.5, then ZnS was precipitated in pH=2.4-2.5, followed by the precipitation of nickel sulfide, NiS in the residual solution at pH=5.5-6.0. It was also found that Na_2S is most effective for selective precipitation of metal sulfides, among the three sulfurating agents of Na_2S, Na_2S_2 and Na_2S_4. The selectivity of CuS in the filtrated cake obtained by the sulfuration treatment in pH=1.4-1.5 was about 94 % and was sufficiently high, in terms of allowable metal content level for recycling. The sequent selectivity of ZnS and NiS in the cake after the sulfuration treatment in pH=2.4-2.5 were 75-77 % and about 20 %, respectively. The selectivity of NiS and ZnS in the cake after the sulfuration treatment in pH=5.5-6.0 was 64-66 % and 33-35 %, respectively.

KEYWORDS: Electroplating wastewater, Metal sulfide, Mixed metal solution, Selective recovery, Sulfuration.

1. INTRODUCTION

More than 100,000 tons of sludge per year which includes nickel, copper and zinc hydroxides, so far have been discharged and landfilled in Japan [1]. Recently, from the viewpoint of environmental protection and resource saving, effective recycling and reusing of the mixed sludge or the mixed-metal wastewater are strongly expected. The development of technology to separate each metal is necessary to fulfill such an increasing requirement. However, currently, there is no practical example of technology to recover each metal from sludge. Although there are some methods to separate a certain metal from the wastewater, such as ion exchange resin method [2]-[4], electrowinning method [5]-[7], it is difficult to apply these methods for the separation of metals from mixed-metal wastewater.

In this paper, selective separation of the metals from mixed-metal wastewater by sulfuration is presented. The sulfuration reaction of metal (Me) ions such as Cu, Zn and Ni with S^{2-} is considered to occur by the addition of sulfurating agent Na_2S_X into a solution containing Cu^{2+}, Zn^{2+} and Ni^{2+}, to produce and precipitate metal sulfide (MeS) and sulfur. Sulfuration treatment has some advantages such as lower solubility of metal sulfides than those of metal hydroxides. The metal sulfides thus produced can be separated, even if they are in coexistence with chelating agents contained in wastewater [8].

Selective recovery of three metals namely, Cu, Zn and Ni, which are often used in the electroplating process, from the mixed solution containing the metals was investigated through sulfuration by adding sulfurating agents. Three kinds of sulfurating agents, namely, sodium sulfide (Na_2S), sodium disulfide (Na_2S_2) and sodium tetrasulfide (Na_2S_4) were employed for the sulfuration treatment of Cu, Zn, and Ni solution. We examined the influence of the amount of sulfurating agent added and the pH on the formation of metal sulfides precipitated.

2. EXPERIMENTAL

2.1 Samples

Table 1 shows the composition and concentration of the actual and the simulated electroplating wastewater used in the experiment. The metal sulfates, generally used in the electroplating process, $Cu(SO_4)\cdot 5H_2O$, $Zn(SO_4)\cdot 7H_2O$ and $Ni(SO_4)\cdot 6H_2O$ were dissolved in distilled water to prepare the simulated wastewater, and the concentrations of solutions were adjusted in the range of 100-300 mg dm^{-3}.

The electroplating wastewater, that is, Cu, Zn and Ni plating solution, was obtained from a plating shop in operation, and was diluted to 300 mg dm^{-3} for each solution of Cu, Zn and Ni. Table 1 also shows the other compounds present in electroplating wastewater. The concentrations of aqueous solution of the three kinds of sulfurating agents, Na_2S, Na_2S_2 and Na_2S_4, were adjusted to a constant concentration of $6.8x10^{-2}$ mol dm^{-3}.

Table 1. Employed metal solution sample

Sample solution	Sample No	Metal Concentration (mg dm^{-3})		Ingredient
Simulated waste water (single)	1-1	Cu	105	$CuSO_4$
	1-2	Zn	101	$ZnSO_4$
	1-3	Ni	100	$NiSO_4$
Simulated waste water (mixed)	2-1	Cu	109	$CuSO_4$
		Zn	105	$ZnSO_4$
		Ni	90.3	$NiSO_4$
	2-2	Cu	320	$CuSO_4$
		Zn	256	$ZnSO_4$
		Ni	316	$NiSO_4$
Electroplating waste water	3-1	Cu	97.5	$CuSO_4$
		Zn	85.3	$ZnSO_4$
		Ni	222.3	$NiSO_4$
		Fe	1.7	
				$NH_4(OH)$, EDTA
				pH 2.0
				TOC 55 mg dm^{-3}

2.2 Experimental procedure

Figure 1 shows the experimental flow chart employed in this study for sulfuration treatment of wastewater which contains Cu, Zn and Ni. Aqueous solutions of sulfurating agents were added into 250 ml of each sample solution. For a rough adjustment of the pH value of the initial metal solution, either 10wt% H_2SO_4 or 10wt% NaOH solution was used to keep the pH value in the predetermined range for precipitation of a specific metal sulfide. For a precise control of the pH value after sulfurating agents were added, 0.5 mol dm^{-3} H_2SO_4 was used. After the addition of sulfurating agent to the sample solution up to a prescribed amount, the solution was stirred for a time range of 30 to 60 min, and the metal sulfide formed was filtered by using a paper filter with a mean pore size of 1 µm. The metal concentration of the filtrate was measured by using an ICP(P-4010, HITACHI). The sludge was dried at 378 K for 2 hrs, then the chemical compositions were analyzed with an XRD (Rint-2500TTR Rigaku).

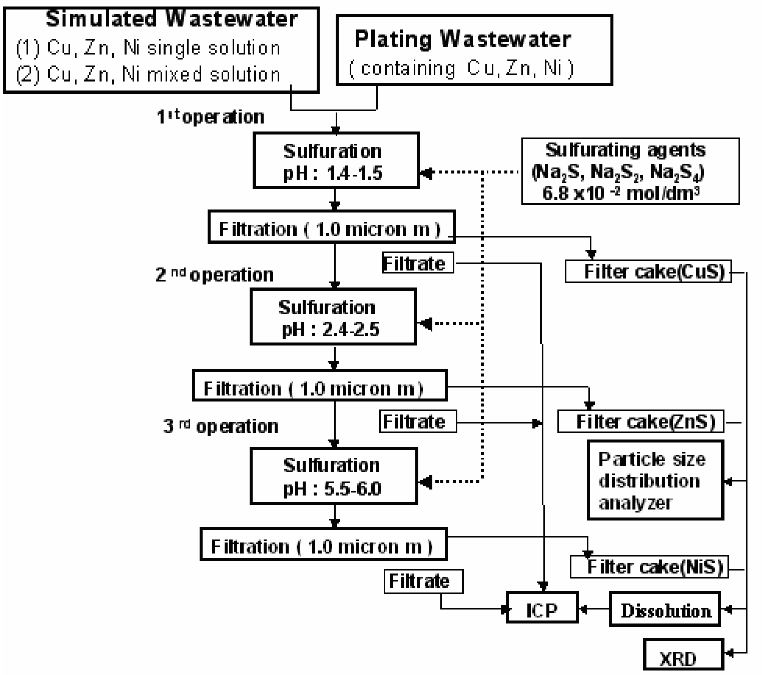


Figure 1. Experimental scheme

3. RESULTS AND DISCUSSION

3.1 Mechanism of selective sulfuration of Cu, Zn and Ni mixed metal solution

The sulfuration reaction of metal (Me) ions such as Cu, Zn and Ni with S^{2-} is considered to occur by the addition of sulfurating agent Na_2S_X into a solution containing Cu^{2+}, Zn^{2+} and Ni^{2+}, to produce metal sulfides (MeS) and sulfur (S). In general, it is known that the reaction of Me ions with Na_2S_X proceeds as follows.

$$Me^{2+} + Na_2S_x \rightarrow MeS\downarrow + Na^+ + (X-1)S\downarrow \quad (1)$$

In the case of sulfuration of Cu, the following two reactions may hold;

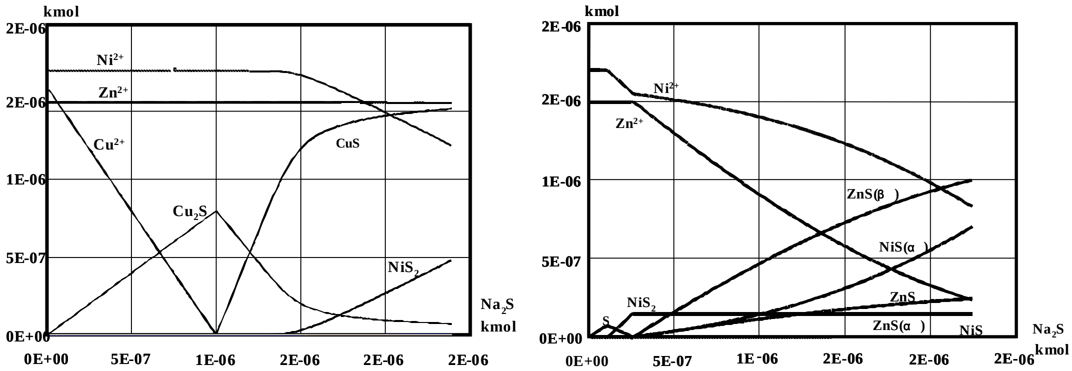
$$Cu^{2+} + Na_2S \rightarrow CuS + 2Na^+ \quad (2)$$

$$2Cu^{2+} + Na_2S_x \rightarrow Cu_2S\downarrow + 2Na^+ + (X-1)S\downarrow \quad (3)$$

In accordance with the solubility products[9], there exists the minimum pH values of pH=-4.75, pH=2.5 and pH=3.75 for the precipitation of CuS, ZnS and NiS, respectively. Taking into account the effect of pH on the formation of metal sulfide, thermodynamic calculation of sulfuration of Cu, Zn and Ni was conducted at pH 1.4-1.5, pH 2.4-2.5 and pH 5.5-6.0, respectively, by the use a chemical equilibrium calculation software(HSC Chemistry, Outokumpu Research Oy Information Service).

Figure 2 shows the calculation results obtained in specific conditions. From Fig. 2, it is found that CuS started to precipitate when Na_2S of 1.0×10^{-6} kmol was added to the mixed solution of Cu^{2+}, Zn^{2+} and Ni^{2+} at an initial pH of 1.5. However, Zn^{2+} and Ni^{2+} was kept unreacted, except that NiS_2 was formed when Na_2S of 1.5×10^{-6} kmol was added to the mixed solution. From this calculation result, it is predicted that CuS can be selectively recovered from the mixed solution of Cu^{2+}, Zn^{2+} and Ni^{2+}. After CuS was separated by the precipitation from the mixed solution, it was found that both ZnS and NiS were formed to coprecipitate at pH=2.5. It was nevertheless expected that

Zn-rich precipitate was recovered, since the amount of ZnS precipitated was about 2 times larger than that of NiS coexisted with ZnS.



Cu, Zn and Ni mixed solution
Cu^{2+} : 1.6x10^{-6} kmol, Zn^{2+} : 1.5x10^{-6} kmol,
Ni^{2+} : 1.7x10^{-6} kmol, Na_2S : 2.4x10^{-6} kmol
SO_4^{2-} : 5.0x10^{-5} kmol (pH: 1.5)

Zn and Ni mixed solution
Zn^{2+} : 1.5× 10^{-6} kmol, Ni^{2+} : 1.7× 10^{-6} kmol,
Na_2S : 2.25× 10^{-6} kmol
SO_4^{2-} : 5.0x10^{-6} kmol (pH: 2.5)

Figure 2. Equilibrium on the formation of CuS, ZnS and NiS

3.2 Optimum pH range for sulfuration of Cu, Zn and Ni

For determining the optimum pH range of sulfuration of Cu, Zn and Ni, we referred to Charlot[9], in terms of the relation of solubility products with pH value. According to Charlot [9], the pHs for the precipitation of copper sulfide, zinc sulfide and nickel sulfide were pH= - 4.75, pH=2.5 and pH=3.75, respectively. In our preliminary test, it was found that the separation of ZnS and NiS was insufficient in this set of pH values. Hence, we adjusted the pH value for the sulfuration of copper at pH=1.4-1.5, then after precipitation of CuS, the pH value was increased to pH= 2.4-2.5 for the sulfuration of zinc. Finally, after precipitation of ZnS, the pH value was further increased to pH= 5.5-5.6 for the sulfuration of nickel to NiS. This set of pH values was most effective for selective sulfuration of copper, zinc and nickel, under the experimental condition employed.

3.3 Selective sulfuration of simulated wastewater with Na_2S, Na_2S_2 and Na_2S_4

Based on thermodynamic calculations of sulfuration of Cu, Zn and Ni, we tried selective sulfuration of these metals by fixing pH at a certain constant value. Figure 3 shows the result of sulfuration treatment of simulated wastewater (sample No. 2-1) under a constant pH of 1.4-1.5, 2.4-2.5 and 5.5-6.0, for Cu, Zn and Ni, respectively by using Na_2S, Na_2S_2 and Na_2S_4 as sulfurating agents. In the pH range of 1.4-1.5, the ratios of the concentration to the initial concentration, C/C_0 of Zn were 0.82, 0.70 and 0.60 with the addition of Na_2S, Na_2S_2 and Na_2S_4, respectively, when the concentration of Cu in the filtrate became zero.

On the other hand, C/C_0 of Ni was 0.83, 0.80 and 0.75 with the addition of Na_2S, Na_2S_2 and Na_2S_4, respectively. In the pH range of 2.4-2.5, when zinc in filtrate was no more detected, C/C_0 of Ni was about 0.65 for Na_2S and Na_2S_2, and 0.55 for Na_2S_4. It was found that Na_2S is the most effective sulfurating agent for selective recovery of the three metals present in the solution. A similar behavior of sulfuration of a simulated wastewater containing 300 g dm^{-3} of each metal (sample No. 2-2) was obtained.

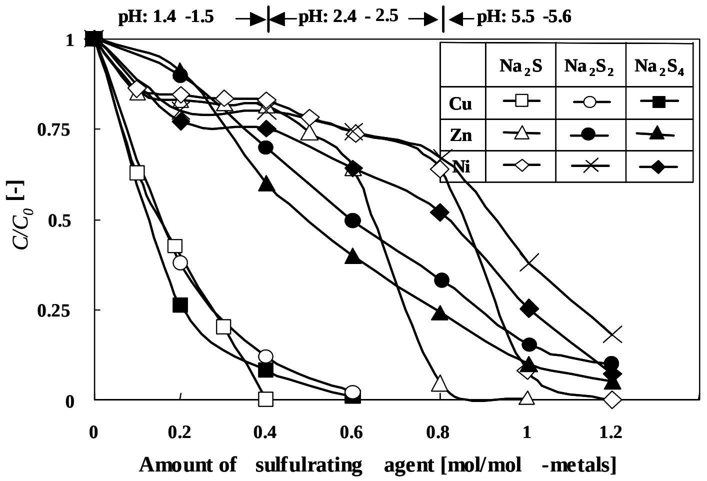


Figure 3. Concentration change of metal in filtrate of simulated mixed wastewater with addition of sulfurating agents under a constant pH contition

3.4 Selective sulfuration of electroplating wastewater with Na_2S and metal yield

The electroplating wastewater (sample No. 3-1) of the pH value of 2.0, which contained ammonia, EDTA and other organic components, was treated with Na_2S as the sulfurating agent under the same pH condition applied to the sulfuration treatment of the simulated solution; pH 1.4-1.5 for copper sulfide precipitation, pH 2.4-2.5 for zinc sulfide precipitation and pH 5.5-6.0 for nickel sulfide precipitation. The result is shown in Figure 4. For the sulfuration treatment of electroplating wastewater, the behaviors of concentration change C/C_0s of Cu, Zn and Ni in the filtrate were similar to those obtained in the sulfurating treatment of simulated solution (sample No. 2-1). There was no effect of the presence of organic components on the sulfuration of Cu, Zn and Ni in the electroplating wastewater. After sulfuration treatment of samples No.2-2 and No.3-1, we measured not only the concentration of metals, Cu, Zn and Ni, in the filtrate, but also the amount of metals contained in the filter cake. The selectivity of metals, Cu, Zn and Ni contained in the filtrated cake was evaluated, which is defined as the ratio of the amount of Cu, Zn or Ni to the total amount of metals of Cu, Zn and Ni in the filtrated cake.

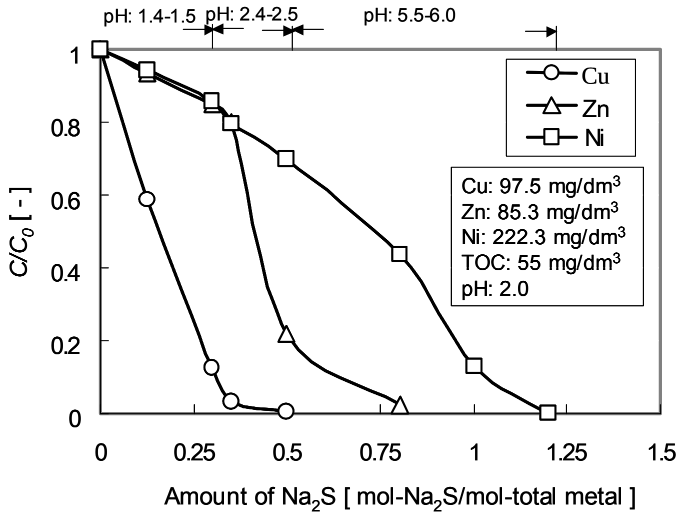


Figure 4. Concentration change of Cu, Zn and Ni in fitrate of electroplating wastewater with the addition of Na_2S under a constant pH condition

As shown in Figure 5, the selectivity of Cu in the filter cake obtained by the sulfuration treatment in the pH range of 1.4-1.5 was about 94 %, and was sufficiently high to yield Cu acceptable for recycling. Moreover, the selectivity of Zn and Ni in the cake obtained by the sulfuration treatment

in the pH range of 2.4-2.5 was 75-77 % and about 20 %, respectively.
The selectivity of Zn and Ni in the cake obtained by the sulfuration treatment in the pH range of 2.4-2.5 was 64-66 % and 33-35 %, respectively. For the improvement of selectivity of Zn and Ni, further investigation is necessary by considering more precise control of pH as well as controlling the concentration of sulfurating agent, etc.

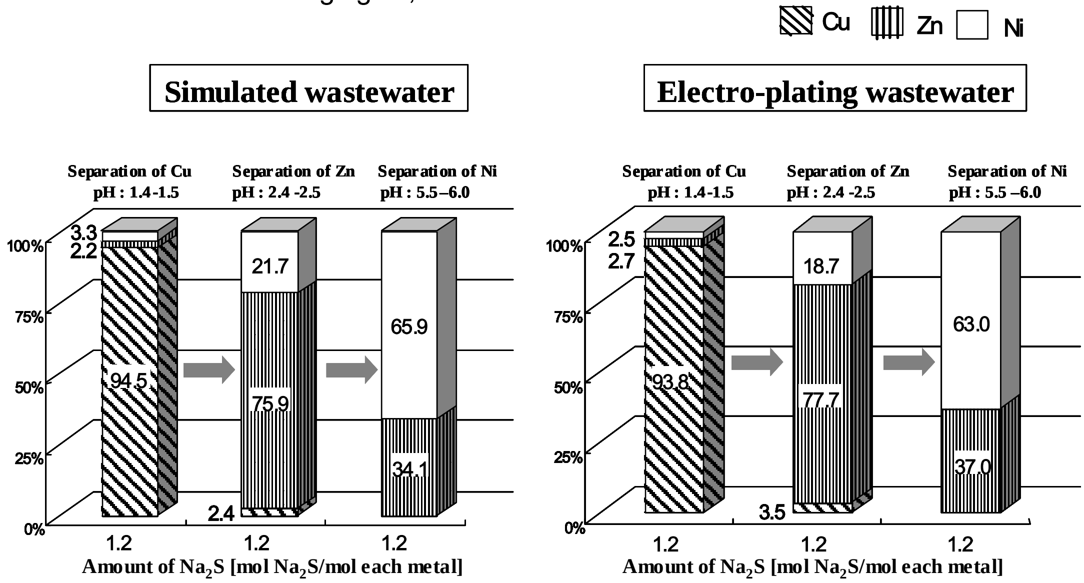


Figure 5. Yield of metal recovery from filtrate cake

4. CONCLUSIONS

An attempt was made for selective recovery of copper, zinc and nickel from plating wastewater by the sulfuration treatment. In this paper, the effects of pH condition and sulfurating agents (Na_2S, Na_2S_2 and Na_2S_4) on selective sulfuration of copper, zinc and nickel were studied
A high selectivity of 94% of copper from a plating wastewater was obtained for the sulfuration of sample solution in the pH range of pH=1.4-1.5. On the other hand, in the pH ranges of 2.4-2.5 and 5.5-6.0, the selectivity of zinc and nickel was 75 % and 65%, respectively.
It was found that Na_2S was more effective compared with Na_2S_2 and Na_2S_4, in terms of higher selectivity of the three metals involved in the model solutions and the real plating solution.

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