Recovery of Cu, Zn, Ni and Cr from Plating Sludge by Combined Sulfidation and Oxidation Treatment

D. Kuchar, T. Fukuta, M. Kubota, and H. Matsuda

Abstract—The selective recovery of heavy metals of Cu, Zn, Ni and Cr from a mixed plating sludge by sulfidation and oxidation treatment was targeted in this study. At first, the mixed plating sludge was simultaneously subjected to an extraction and Cu sulfidation process at pH=1.5 to dissolve heavy metals and to precipitate Cu^{2+} as CuS. In the next step, the sulfidation treatment of Zn was carried out at pH=4.5 and the residual solution was subjected to an oxidation treatment of chromium with H_2O_2 at pH=10.0. After the experiments, the selectivity of metal precipitation and the chromium oxidation ratio were evaluated.

As results, it was found that the filter cake obtained after selective sulfidation of Cu was composed of 96.6% of Cu (100% equals to the sum of Cu, Zn, Ni and Cr contents). Such findings confirmed that almost complete extraction of heavy metals was achieved at pH=1.5 and also that Cu could be selectively recovered as CuS. Further, the filter cake obtained at pH=4.5 was composed of 91.5% Zn and 6.83% of Cr. Regarding the chromium oxidation step, the chromium oxidation ratio was found to increase with temperature and the addition of oxidation agent of H_2O_2, but only oxidation ratio of 59% was achieved at a temperature of 60°C and H_2O_2 to Cr^{3+} equivalent ratio of 180.

Keywords—Chromium Recovery, Oxidation, Plating Sludge, Sulfidation.

I. Introduction

IN Japan, an amount of 65,000 tons of plating sludge is generated annually and the content of precious metals such as copper, zinc, nickel and chromium in this amount of sludge amounts to 5,732 tons, 6,054 tons, 4,079 tons and 1,436 tons, respectively [1]. So far, these metals have been disposed of to landfills as plating sludges, but owing to the recent increase in the consumption of various metals, an increasing number of research works focusing on metal recovery from plating sludges has been observed.

D. Kuchar is with the Department of Energy Engineering and Science, Nagoya University, Nagoya, 464-8603 Japan (phone: 0081-052-789-3841; fax: 0081-052-789-3842; e-mail: d_kuchar@centrum.cz).

T. Fukuta is with Sanshin MFG. CO., LTD. 1-2 Kifuneura Haguro, Inuyama, Aichi, 484-0894 Japan (ttfukuta@ybb.ne.jp).

M. Kubota is with the Department of Energy Engineering and Science, Nagoya University, Nagoya, 464-8603 Japan (e-mail: kubota@nuce.nagoya-u.ac.jp).

H. Matsuda is with the Department of Energy Engineering and Science, Nagoya University, Nagoya, 464-8603 Japan (e-mail: matsuda@nuce.nagoya-u.ac.jp).

Regarding the recovery of chromium, sludges containing only chromium or chromium rich sludges have been targeted so far and the recovery approach mainly inhered in the chromium extraction by an acidic medium. For example, Macchi *et al.* [2] reported that the chromium extraction as high as 90% was achieved at pH value of 1.0 (adjusted by H_2SO_4) after chromium leaching for 24 hours. Similarly, Silva *et al.* [3] reported that chromium extraction of about 98% can be achieved by contacting chromium sludge with 20% HCl within 30 minutes. After the extraction, trivalent chromium was oxidized to hexavalent chromium using oxidation agents such as hypochlorite, ozone or hydrogen peroxide [2]-[3]. Specifically, Macchi *et al.* [2] investigated the chromium oxidation with H_2O_2 at pH of 10.0, at 60°C, and reaction time of 30 minutes and reported that an average oxidation ratio of 80% can be achieved. Similarly, Silva *et al.* [3] achieved a chromium oxidation ratio of about 93% after oxidation for 60 minutes at pH value of 10.0 and temperature of 60°C. Subsequently, the hexavalent chromium was separated from impurities by filtration.

As for the recovery of copper, zinc and nickel, the recent focus has been put on selective sulfidation treatment. In one of ours previous works, the possibility of selective precipitation of heavy metals of Cu, Zn and Ni with Na_2S was studied and the precipitation selectivities as high as 94.5% for Cu (pH=1.5), 75.9% for Zn (pH=2.5) and 65.9% for Ni (pH=5.5-6.0) were achieved [4]. Moreover, in our subsequent research study, the applicability of H_2S gas for selective heavy metals precipitation was investigated and higher precipitation selectivities were obtained with H_2S compared to Na_2S. More precisely, the precipitation selectivity was 95.5% for Cu at pH=1.5, 87.4% for Zn at pH=4.5 and 94.7% for Ni at pH=6.7±0.2 [5].

However, the research works given above focused either on recovery of only chromium or on recovery of heavy metals such as copper, nickel, zinc, but no study for selective recovery of all these metals was performed. Therefore, in this work, an attempt was made to separate copper and zinc from nickel and chromium by selective sulfidation at controlled pH value. Subsequently, an oxidation treatment with H_2O_2 was used to convert Cr^{3+} to Cr^{6+} and thus to achieve separation of chromium and nickel in the residual solution. In this oxidation treatment, the effect of temperature, reaction time and H_2O_2/Cr equimolar ratio on chromium oxidation ratio was evaluated. After the

oxidation treatment, nickel precipitated as $Ni(OH)_2$ is expected to be recovered at smelters together with CuS and ZnS. Meanwhile, chromium (Cr^{6+}) solution will be further concentrated and reused in plating process.

II. EXPERIMENTAL

A. Plating Sludge

Plating sludge used in this study was dried in a muffle furnace at a temperature of 105°C for 24 hours, and then thoroughly ground and screened to particle size diameter of 125 μm to 300 μm. Subsequently, to determine the sludge composition, an amount of 0.5 g of plating sludge was dissolved in aqua regia (a mixture of HCl and HNO_3 at a ratio of 3:1). The solution was analyzed using an inductively coupled plasma (ICP, Vista-MPX Simultaneous ICP-OES, Varian, Inc.). Table I shows the contents of Cu, Zn, Ni and Cr determined in the mixed plating sludge.

TABLE I
CONTENT OF CU, ZN, NI AND CR IN PLATING SLUDGE

Element	[mg/g-dry sludge]
Cu	75.50±1.613
Zn	77.50±1.754
Ni	35.33±0.803
Cr	56.05±0.777

B. Approach to Selective Metal Recovery

The idea for recovery of from plating sludge is given by the flow chart shown in Fig. 1.
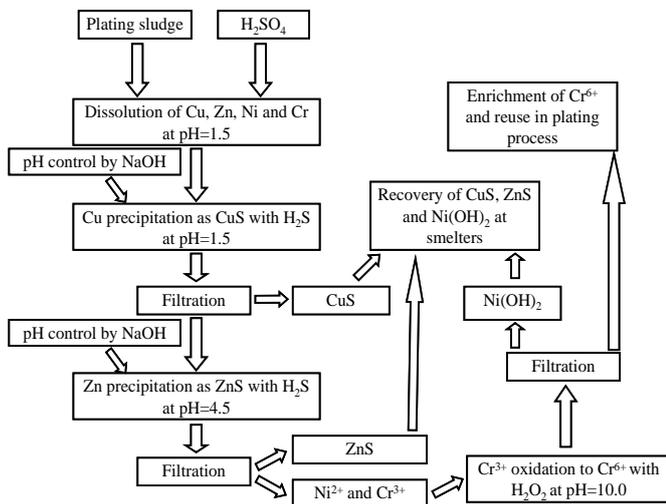

Fig. 1 Experimental procedure

At first, sludge suspension (2 g/L) was prepared and pH was adjusted to 1.5. At this pH, the heavy metals were extracted and simultaneous sulfidation treatment with H_2S was carried out to precipitate CuS. After CuS separation by filtration, the pH was increased to 4.5 to precipitate Zn as ZnS, which was then separated by filtration. Finally, the residual solution was

subjected to the oxidation treatment in order to convert Cr^{3+} to Cr^{6+}. After oxidation treatment, the pH was adjusted to pH of 9.5 and chromium was separated from $Ni(OH)_2$ and recovered in the form of $Cr_2O_7^{2-}$ which will be reused in the plating industry.

C. Sulfidation Experiments

Based on our previous study [6], the sulfidation experiments were carried out at a pH value of 1.5 for copper precipitation and pH value of 4.5 for precipitation of zinc. The sulfidation experiments were conducted in the experimental apparatus shown in Fig. 2.

At first, a volume of 1300 mL of plating sludge slurry (weight concentration of 2 g/L) of which the pH value was adjusted to 1.5 by H_2SO_4 was poured into the cylindrical reaction vessel. During the sulfidation, the pH was kept at a constant value of 1.5 by using 0.1 M NaOH solution. After the CuS separation by filtration, the pH value was increased to 4.5 and zinc sulfidation experiments were conducted. At the end of zinc sulfidation, ZnS was separated by filtration. Regarding the reaction conditions, N_2/H_2S gas was introduced to the reactor at the bottom of the cylindrical reaction vessel and the concentration of H_2S gas was set at 5000 ppm (v/v), N_2/H_2S flow rate was set at 350 mL/min and bubble diameter of N_2/H_2S of 1.64 mm was used. In the experiments, the samples were withdrawn at the bottom of reactor using sampling tap and then analyzed by means of inductively coupled plasma (ICP-OES, VISTA-MPX, Varian).
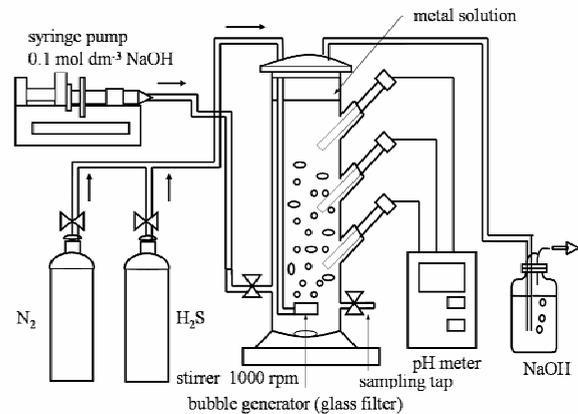

Fig. 2 Experimental apparatus for sulfidation experiments

D. Chromium Oxidation with H_2O_2

In the preliminary experiments, $CrCl_3 \cdot 6H_2O$ of reagent grade (Wako Pure Chemical Industries, Ltd.) was used to prepare 100 mg/L solution of Cr^{3+}. Then, 100 mL of Cr^{+3} was transferred to a beaker and pH value was adjusted to 10.0 using NaOH. In the next step, the solution prepared in this way was poured into a 200 ml Teflon-coated reactor placed in a jacket heater equipped with propeller stirring. Subsequently, the reactor was heated to a given temperature from a temperature range of 25°C to 90°C, and upon achieving the given temperature, a volume of 3.5 mL

H_2O_2 solution of a given concentration was added to the solution and chromium oxidation was investigated at a time period varying up to 2 hours. At the end of the experiments, the solution was filtered using 0.45 μm pore size filter and the content of Cr^{6+} was analyzed using diphenylcarbazide method at 540 nm (UV-VIS, Optima SP-300 Spectrophotometer). Consequently, the oxidation ratio was determined based on the initial concentration of Cr^{3+} and concentration of Cr^{6+} determined after experiments.

III. RESULTS AND DISCUSSION

A. Separation of Copper and Zinc

The sulfidation of copper was carried at pH value of 1.5 using H_2S as a sulfidation agent. The flow rate of H_2S/N_2 gas was set at 350 mL/min and H_2S concentration in H_2S/N_2 gas was 5000 ppm (v/v). Fig. 3 shows the results of copper precipitation plotted against the sulfidation time.
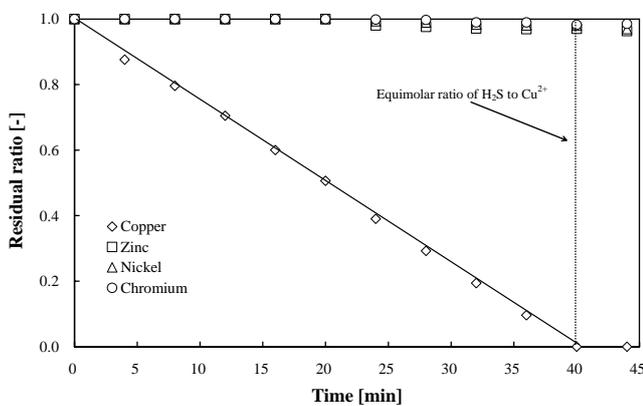

Fig. 3 Sulfidation treatment of Cu at pH value of 1.5

It can be seen that copper was removed from the solution as the sulfidation treatment proceeded and at H_2S to Cu^{2+} molar ratio of 1.0, which corresponded to reaction time of approximately 40 minutes, the Cu concentration in the solution was reduced below 1.0 mg/L. Meanwhile, the residual ratio of Zn, Cr and Ni was higher than 96%.

In the next step, the sulfidation treatment of zinc was conducted. At first, the pH value of residual solution, obtained after separation of CuS by filtration, was adjusted to 4.5 using NaOH solution and the volume was adjusted to 1300 mL. Then, the experiments were carried out under the same conditions as in sulfidation of copper and the results are shown in Fig. 4.

In this experiment, the Zn concentration was reduced to a value below 1.0 mg/L after 40 minutes, which corresponded to a ratio of H_2S to Zn^{2+} of 1.14. The need for higher supply of H_2S resulted from co-precipitation of nickel as also seen from Fig. 4. As a result of co-precipitation of NiS, Ni residual ratio was reduced to 88% at the end of the experiments. Similarly to Ni, precipitation of Cr^{3+} was observed and it was concluded that Cr^{3+} was partially precipitated as $Cr(OH)_3$. After the experiments, the ZnS was separated by filtration and the residual solution was subjected to chromium oxidation treatment with H_2O_2.
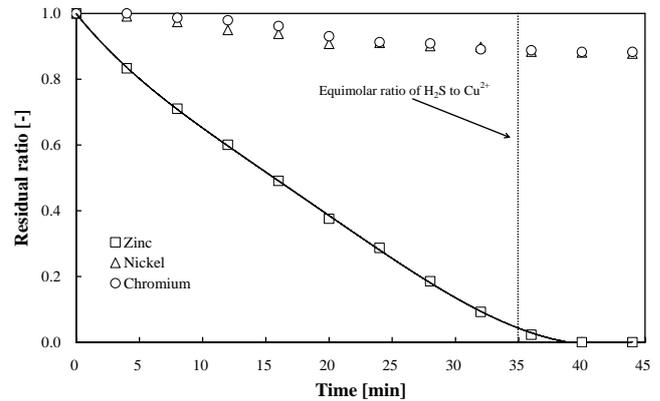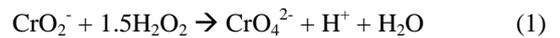

Fig. 4 Sulfidation treatment of Zn at pH value of 4.5

B. Chromium Oxidation

The chromium oxidation was carried out using an oxidation agent of H_2O_2 and the oxidation reaction is given by (1).

$$CrO_2^- + 1.5H_2O_2 \rightarrow CrO_4^{2-} + H^+ + H_2O \qquad (1)$$

At first, preliminary experiments were conducted to confirm the results of Macchi et al. [2] and Silva et al. [3] in our experimental apparatus. For these experiments, a chromium model solution of which the concentration was adjusted to 100 mg/L was prepared by dissolving chromium chloride. Subsequently, the experiments were conducted at pH value of 10.0 and at the reaction time of 60 minutes. The H_2O_2 concentration in the reaction solution was set to 0.039 mol/L, which gave an H_2O_2 to Cr equivalent ratio of about 14.2 (the equivalent ratio of 1.0 corresponded to the stoichiometric molar ratio of 1.5, according to (1)). As a result it was found that in accordance with the results of previous reports [2]-[3], the chromium oxidation ratio increased with an increase in the temperature and an oxidation ratio of about 76% was achieved at 60°C, as shown in Fig. 5. However, when the temperature was further increased up to 90°C, no significant rise in oxidation ratio was observed.

Subsequently, the effect of time on the chromium oxidation was investigated using the chromium model solution at a reaction temperature of 60°C. The results obtained in this experiment are shown in Fig. 6. It can be seen that the chromium oxidation ratio of about 62% was achieved within the first 10 minutes and the ratio further increased to 78%, when the reaction time was extended up to 120 minutes. Based on these results, the reaction time and temperature for the subsequent experiments with the real mixed plating sludge were set to 60 minutes and 60°C, respectively.
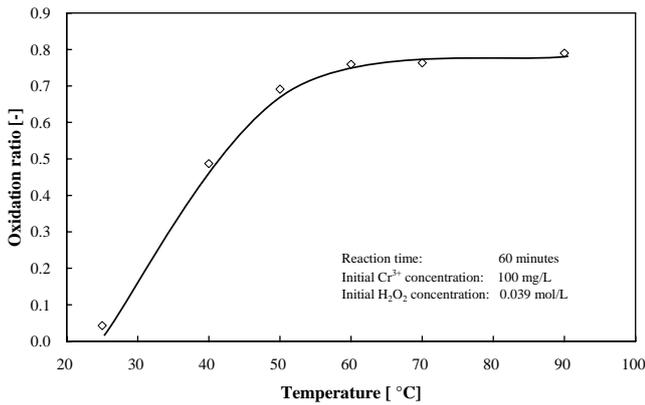
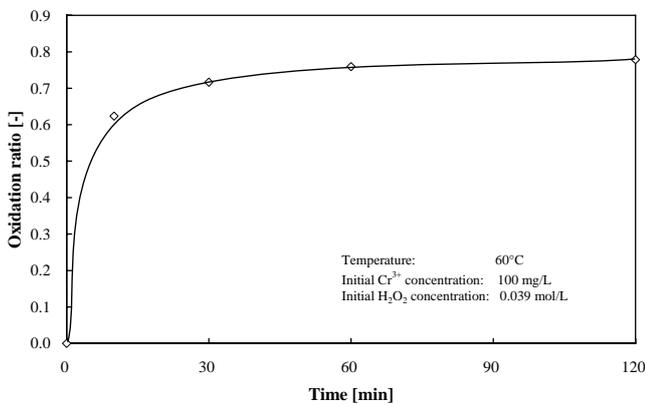Fig. 5 Effect of temperature on chromium oxidation ratio

Fig. 6 Effect of reaction time on chromium oxidation ratio

Chromium Oxidation in the Real Mixed Plating Sludge

As shown in Fig. 1, the solution obtained after sulfidation treatment of zinc was subjected to oxidation treatment and the contents of Cr and Ni in the initial solution were determined to be 77.92 and 58.88 mg/L. Then, the oxidation treatment was carried out for 60 minutes at pH of 10.0 and a temperature of 60°C. The equivalent ratio of H_2O_2 to Cr^{3+} was varied from 1.80 to 180 (the equivalent ratio of 1.0 corresponded to the stoichiometric molar ratio of 1.5, according to (1)). Fig. 7 shows the results obtained in this experiment.
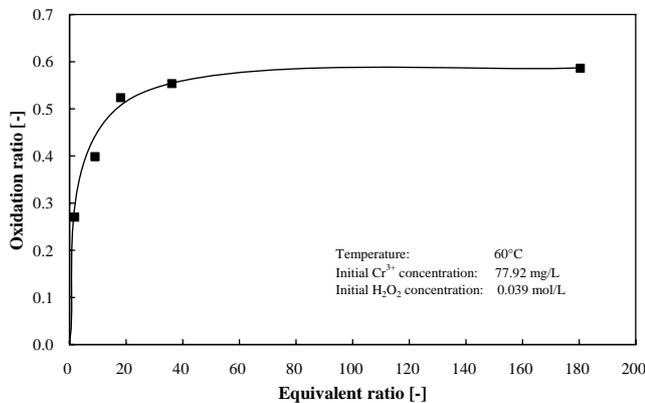

Fig. 7 Effect of H_2O_2 to Cr^{3+} equimolar ratio on chromium oxidation ratio in real plating sludge

The chromium oxidation ratio obtained for real mixed plating sludge was found to be lower than that obtained for the model chromium solution at the similar equimolar ratio of H_2O_2 to Cr^{3+} (H_2O_2 initial concentration of 0.039 mol/L). Specifically, the oxidation ratio obtained for the model chromium solution at H_2O_2 to Cr^{3+} equivalent ratio of 14.2 was 76% compared to 52% obtained for the real plating sludge at H_2O_2 to Cr^{3+} equimolar ratio of 18.0.

Such a result was contributed to the presence of Fe and Mg in the solution during chromium oxidation. More specifically, Macchi *et al.* [2] performed the experiments at a temperature of 60°C, reaction time 30 minutes and found that the chromium oxidation ratio increased from 70% obtained at (Fe+Mg)/Cr of 8.2 (Cr initial concentration of 109 mg/L and H_2O_2/Cr equivalent ratio of 80) to 90% at (Fe+Mg)/Cr of 0.25 (Cr initial concentration of 1260 mg/L and H_2O_2/Cr equivalent ratio of 5.

In our work, the chromium initial concentration was 77.9 mg/L and (Fe+Mg)/Cr ratio was 2.45. Therefore, the chromium oxidation ratio of 52% obtained at H_2O_2/Cr equivalent ratio of 18.0 or 59% obtained at H_2O_2/Cr equivalent ratio of 180 seems to be in good agreement with the results reported by Macchi *et al.* [2].

In addition, the results reported by Silva *et al.* [3] show that the chromium oxidation ratio was also dependent on the chromium initial concentration. In details, the chromium oxidation ratios determined at (Fe+Mg)/Cr ratio of 0.57 were 68.7%, 87.6% and 92.9% for Cr initial concentrations of 1666 mg/L, 2123 mg/L and 2253 mg/L, respectively

Selectivity of Sulfidation and Oxidation Treatment

To determine the precipitation selectivity, the respective precipitates were dissolved in aqua regia and the solution was analyzed by an ICP. The selectivity was calculated as the fraction of Cu, Zn, Ni or Cr in the Cu-Zn-Ni-Cr total amount. The results are shown in Table II and it can be seen that, by controlling precisely the pH value, selectivities higher than 91% can be obtained for Cu and Zn in the sulfidation treatment. However, only selectivity of 64% was obtained for Ni in the oxidation treatment which was attributed to an insufficient oxidation of chromium, which thus remained in the filter cake as Cr(OH)$_3$.

TABLE II
PRECIPITATION SELECTIVITIES OF CU, ZN, NI AND CR

	Selectivity (%)		
	pH		
	1.5	**4.5**	**Chromium oxidation**
Cu	96.6	1.23	0.80
Zn	0.01	91.5	4.90
Ni	1.25	0.47	64.3
Cr	2.07	6.83	30.0

IV. CONCLUSION

The possibility of selective recovery of Cu, Zn, Ni and Cr from plating sludge was investigated in this study and it was found that the sulfidation treatment for Cu and Zn separation from plating sludge. Regarding the chromium oxidation and

recovery, the oxidation ratio of less than 60% was obtained in this study, which was attributed to the presence of Fe and Mg in the sludge as well as to the low initial concentration of chromium. Therefore, in the future study, the effect of chromium initial concentration on chromium oxidation will be targeted.

REFERENCES

[1] (Handbook style) Report on comprehensive recycle of valuable metals, Federation of Electroplating Industry Association of Japan, 2004.
[2] G. Macchi, M. Pagano, M. Pettine, M. Santori and G. Tiravanti, "A bench study on chromium recovery from tannery sludge," Wat. Res., vol. 25, pp. 1019-1026, 1991.
[3] P.T. de Souza e Silva, N.T. de Mello, M.M. Menezes Duarte, M.C.B.S.M Montenegro, A.N. Araujo, B. de Barros Neto, V.L. da Silva, "Extraction and recovery of chromium from electroplating sludge," J. Hazard. Mater., vol. B128, pp. 39-43, 2006.
[4] 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, pp. 227-232, 2004 (in Japanese).
[5] 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, pp. 901-906, 2006 (In Japanese).
[6] H. Tokuda, D. Kuchar, N. Mihara, M. Kubota, H. Matsuda, and T. Fukuta, "Study on reaction kinetics and selective precipitation of Cu, Zn, Ni and Sn with H2S in single-metal and multi-metal systems," Chemosphere (Accepted for publication).