

Separation and Recovery of Nickel and Copper from Multi-Metal Electroplating Sludge by Co-Extracting and Selective Stripping

Taihong Shi^{1*}, Shujian Zou¹, Jinfeng Liu¹, Lina Zuo¹, Can Lv¹, Shiguo Jia¹ and Rong Liang Qiu²

¹School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, P.R. China

²Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, Guangzhou 510275, P.R. China

Abstract

N902 diluted with kerosene was used to co-extract copper and nickel from the ammoniac-carbonate leaching liquor of multi-metal electroplating sludge. The influence factors of the ammoniac-carbonate leaching and the extracting process on the recovery of copper and nickel were studied. The leaching rate of copper and nickel can reach to 90 % and the other metal ions are less leached under the optimal leaching condition. In order to optimize the extraction condition, the $L_g(3^4)$ intersecting experiment of co-extraction of copper and nickel ions was tested. For a typical ammonium carbonate leaching solution containing Cu^{2+} 2.23 g/L, Ni^{2+} 3.31 g/L, $\text{Cr} < 0.02$ g/L and pH 9.0-9.5, the optimal conditions of co-extraction, NH_3 escape and selective stripping of nickel and copper were established. The percentage of extraction was more than 97.0 % for both copper and nickel, and the stripping percentages were 99.0 % and 99.3 % for copper and nickel, respectively. This study clearly demonstrates that N902 is suitable for the selective separation and recovery of copper and nickel from the multi-metal electroplating sludge in pure sulfate product as an extractant.

Keywords: Co-extraction; Electroplating sludge; Copper and Nickel; Recovery; Selective stripping; N902

Introduction

Electroplating sludge contains a great number of valuable chromium, nickel and copper. In china, 4×10^8 tons of plating waste water containing heavy metals was generated annually and the content of Cu, Ni and Cr in the amount of sewage amount to 5,000 tons, 4,000 tons and 20,000 tons, respectively [1]. So far, plating sludge and metals in it have been regarded as solid wastes and been disposed by means of landfill site. However, the way to dispose plating sludge leads to serious disadvantages, as it has great effect on the surface of the earth as an environmentally hazardous material. On the other hand, the reuse of heavy metals might bring great potential profits. With the increase in the consumption of various metals in recent years, increasing disquisitions focusing on metals recovery from plating sludge and wastewater have been observed [2-4].

In order to protect the environment and recover the valuable metals, techniques based on physical and chemical mechanisms (such as adsorption, ion exchange, membrane and extracting processes) were used. The recovery of Cr from electroplating effluent has been reported in our previous work [2]. From an economical point of view, Cu and Ni are the most valuable metals value to recycle. As for the recovery of Cu and Ni from multi-metal electroplating sludge, the previous investigation focuses on selective chemical precipitation of Cu and Ni with Na_2S or NaOH by controlling pH of solution. Kuchar et al. [3] reported the selective recovery of Cu and Ni from a mixed plating sludge by sulfidation treatment. As a result, it was found that the precipitation selectivity was 95.5 % for Cu as CuS at pH = 1.5 and 94.7 % for Ni as NiS at pH = 6.7 ± 0.2 . Silva et al. [4] reported a hydrometallurgical treatment involving the solvent extraction and recovery of Zn and Ni from a sulfuric acid leach solution of galvanic sludge using di-(2-ethylhexyl)-phosphoric acid (D_2EHPA) and bis-(2,4,4-trimethylpentyl) phosphoric acid (Cyanex272). The preliminary tests revealed the necessity to remove other metals from the leaching solution prior to solvent extraction, and therefore it comes into being chromium precipitate sludge. Literatures [5-8] reported the series results of the extraction and recovery of Cu and Ni from the ammoniac leaching solution obtained from the processing of manganese nodules containing Cu, Ni and cobalt, and it was treated for Cu-Ni

separation using LIX64N as extractant. Ni was selectively recovered from the loaded organic phase through pH controlled stripping using dilute H_2SO_4 solution and Cu was stripped subsequently with a more concentrated H_2SO_4 solution [6].

Rhoads et al. [9] applied the co-extraction and selective stripping process to treat leaching liquor of Ni laterites. An ammoniac ammonium sulfate solution containing (in kg/m^3) 1.00 Ni, 0.03 Cu, 0.3 Co, 0.02 Zn, 17.8 NH_4OH and 294 $(\text{NH}_4)_2\text{SO}_4$ was used to co-extract Cu and Ni in three stages with a 12 vol. % LIX64N extractant. After ammonia washing, Cu and Ni were selectively stripped in three stages. Sandhibigraha and Bhaskara Sarma [10] reported that the extraction and stripping from ammoniac carbonate solution and the influence of pH and extractant concentration on the co-extraction have been studied. For a typical solution containing about 3 kg/m^3 Cu and Ni and 60 kg/m^3 of ammonium carbonate, the percentage of extraction was about 100 % for both Cu and Ni, and the percentages of stripping were about 100 % and 99.2 % for Cu and Ni, respectively.

As a whole, the chemical processing method of multi-metal electroplating sludge for recovery of valuable metals is difficult because of its multi-step process and environmental issue, and it is economical only under favorable conditions. Up to date extracting technology can be a good choice to treat and utilize multi-metal electroplating sludge for its economically and environmentally suitable way to recover valuable metal elements. Solvent extraction is now a very well-established process in hydrometallurgy. It is used for the separation and recovery of Cu, Ni, Co, Zn, rare earths and the platinum group metals etc. In this work, an ammonium leaching solution, which comes

***Corresponding author:** Taihong Shi, School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, P.R. China, Tel: 0086-020-84115065; Fax: 0086-020-39332690; E-mail: eesshth@mail.sysu.edu.cn

Received November 02, 2011; **Accepted** December 12, 2011; **Published** December 14, 2011

Citation: Shi T, Zou S, Liu J, Zuo L, Lv C, et al. (2011) Separation and Recovery of Nickel and Copper from Multi-Metal Electroplating Sludge by Co-Extracting and Selective Stripping. J Civil Environment Engg 1:103. doi:10.4172/2165-784X.1000103

Copyright: © 2011 Shi T, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

from the first stage of two-stage leaching of multi-metal electroplating sludge, was used to recover Cu and Ni with co-extracting and selectively stripping technology of more economical and easy operation. A cheap and effective extractant N902 (made in China) was applied. The ammoniac leaching solution mainly containing Cu and Ni was obtained from multi-metal electroplating sludge through ammoniac ammonium carbonate leaching to solubilize Cu and Ni as their ammine carbonate complexes and reject Fe and Cr in the residue. The parameters of extracting process were optimized for the co-extraction of Ni and Cu, ammonia scrubbing from the loaded organic phase and selective stripping of Ni and Cu with sulfuric acid from the ammonia-free organic phase.

Experimental

Reagents

A stock solution of Cu^{2+} and Ni^{2+} for batch extracting test was prepared by dissolving $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (obtained from Guangzhou Chemical Reagent Factory, China) into distilled water and diluting to content volume. N902 (obtained from Yashi Chemical Co. Shanghai, China) was used as an extractant, and kerosene (mostly aliphatic) was used as the diluents to obtain the desired concentration of the extractant. The chemical agents of $\text{NH}_3 \cdot \text{H}_2\text{O}$, NH_4HCO_3 , $\text{Al}(\text{OH})_3$, HCl and H_2SO_4 were got from the Chemical Reagent Factory, Guangzhou. All the reagents were analytical grade.

Ammonium leaching of electroplating sludge

A representative sample of 1 kg multi-metal electroplating sludge (obtained from the Ming Run Electroplating Plant, Guangdong, Foushan City, China) was homogenized after been dried, mixed and sieved (≤ 160 mesh). Chemical analysis of the multi-metal electroplating sludge was determined by ICP (IRIS-HR, U.S.A).

Leaching batch experiment was performed in a 500-mL closed glass container immersed in a thermostatically controlled water bath equipped with mechanical stirrer [1]. The sample was leached with 8 mol/L NH_3 and 5 mol/L NH_4HCO_3 at 75°C by liquid/solid ratio of 20:1 for 3.5 hrs. A stirring speed of 800 rpm, with a magnetic stirrer, was set up to ensure the full suspension of particles and to improve the liquid-to-solid phase contact. The reaction mixture was filtrated and washed with deionized water. The ammonium solubility metal ions (i.e. Cu^{2+} and Ni^{2+} ions mainly) were dissolved into the filtrate, and the other metal ions (i.e. Cr^{2+} and Fe^{3+} ions) were blocked into the residue. Then Cu^{2+} and Ni^{2+} ions were separated from the Cr/Fe and other impurity ions which may be depressed on the extracting rate of Cu^{2+} and Ni^{2+} ions. The concentration of metals in leaching solution was determined by ICP.

Scheme 1 shows the procedures to follow in this work for the leaching of electroplate sludge.

Extracting experimental

All the experiments were carried out in shake flasks at room temperature ($30 \pm 0.5^\circ\text{C}$). N902 was mixed with Kerosene (as the diluent) to obtain the desired concentration of the extractant. The aqueous and organic phases were contacted for the desired time.

UV 751-Vis Spectrophotometer (Precision Scientific Instruments Ltd., Shanghai, China) was used for the measurement of metal ions concentration of Cu, Ni, Cr, Zn and Fe in aqueous phase and pHs-3C meter (Shanghai Precision & Scientific Instrument Co. Ltd.) for the measurement of the pH. The concentration of Cu^{2+} and Ni^{2+} ions in organic phase was calculated by law of conservation of matter.

The computing formula of extraction percentage is as follows:

$$E = \frac{C_0 - C_{\text{eq}}}{C_w} \cdot 100\% \quad (1)$$

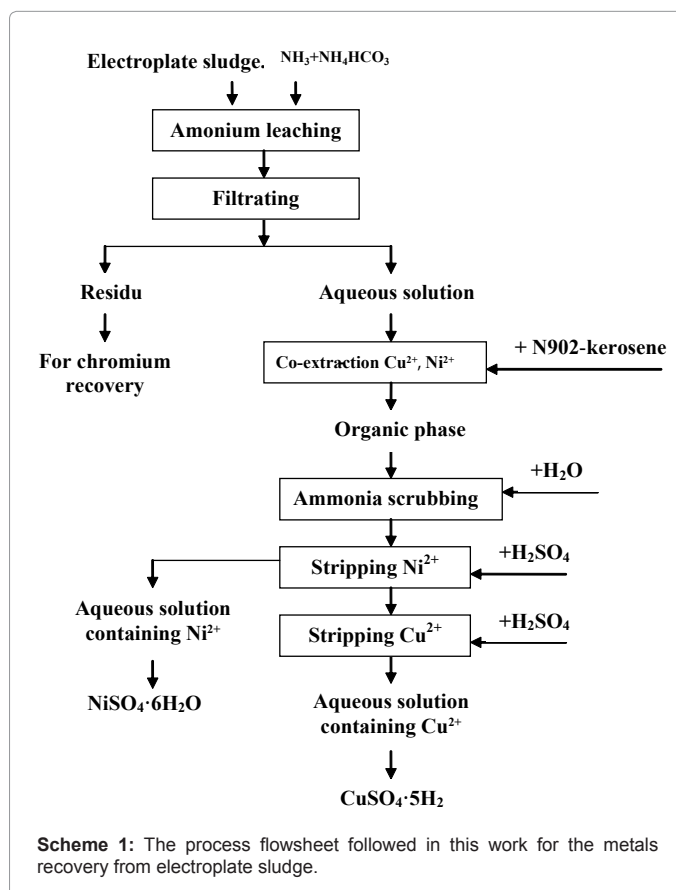
Where E is the extracting percentage (%), C_0 for the concentration of metal ion in organic phase (mg/L), C_{eq} for the concentration of metal ion in aqueous phase (mg/L) and C_w is the initial concentration of metal ion (mg/L).

Ultimately, the stripping metal salt from the organic phase was concentrated by evaporating and crystallizing with the pure product as $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ forms.

Results and Discussion

Separation of Cu and Ni from other metals

Physico-chemical characteristic of multi-metal electroplating sludge: The sludge used in this study was got from a Cu/Ni/Cr plating plant in Fushan City, in the south China, which was produced by the physico-chemical treatment of wastewater. This sludge was mostly composed of metal hydroxide gels, sulphate salts and some chlorides, thus it had a relatively complex structure and a reasonable high chemical variability which determined by producing address, time, product



Density(g cm ⁻³) 3.41 H ₂ O(%) 61.8% Blue and black solid					
Elements in the dried sludge (wt.%)					
Al	1.35	Fe	16.64	Pb	0.21
Ca	1.89	Ni	7.08	Si	16.83
Mg	1.45	Cu	4.65	K	0.84
Cr	11.16	Zn	2.47	S	8.26

Table 1: Relevant physical-chemical characteristics of the sludge.

specifications, processing/operation variations. The main metal species exist in the form of nitro at 105°C, and then comminuted and sieved. Particles of a size<160 mesh were selected. The powdered material was thoroughly homogenized, and the representative samples were

taken for chemical characterization and subsequent leaching tests. The chemical composition (major elements) of the sludge was determined by submitting three small representative samples to digestion with aqua regia. The resulting solutions were analyzed by atomic absorption

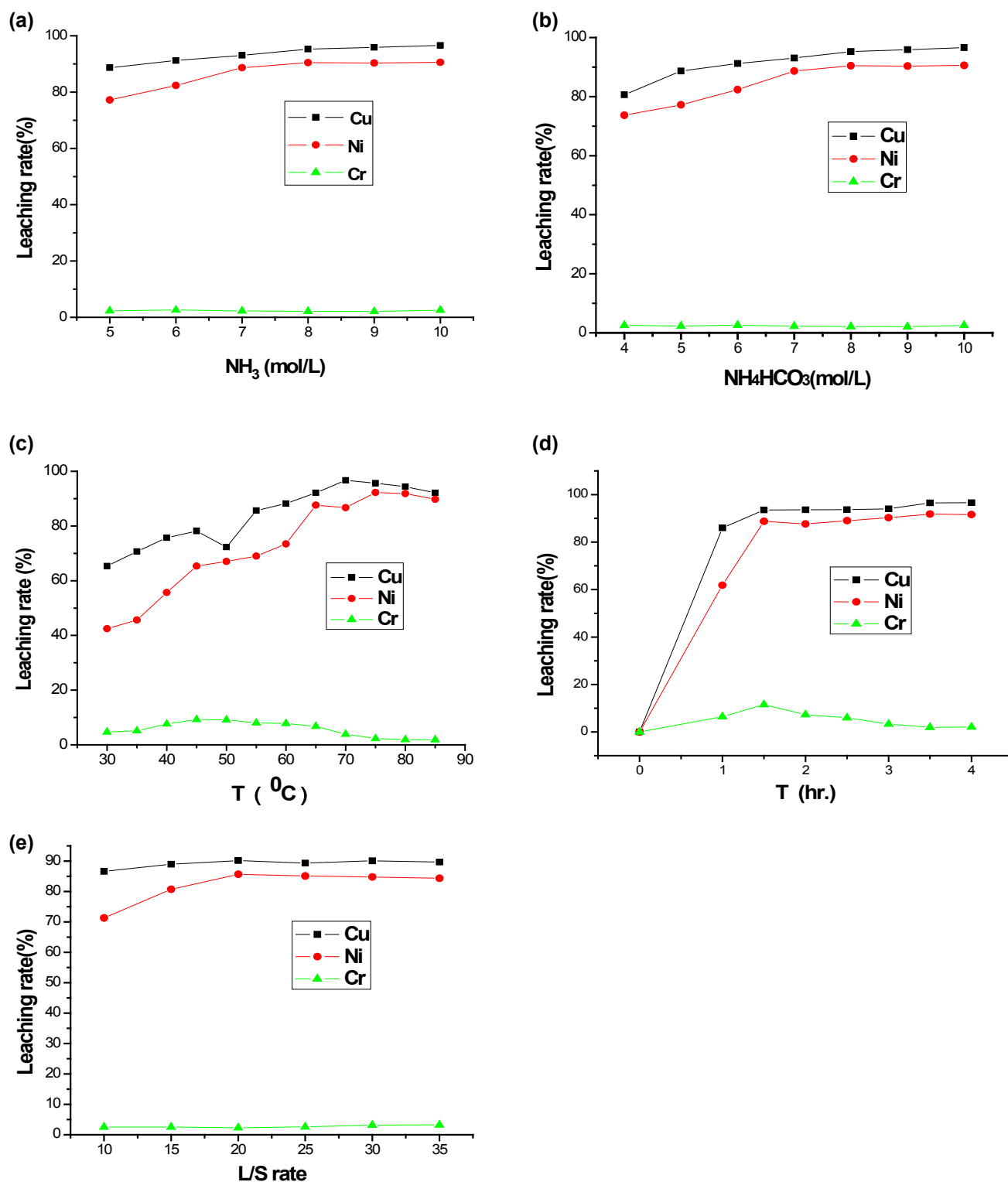
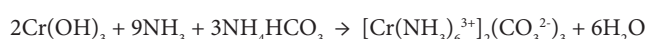


Figure 1: Effects of the factors on the leaching rate of Cu, Ni and Cr. (a) Effect of concentration of NH_3 ; (b) Effect of concentration of NH_4HCO_3 ; (c) Effect of temperature; (d) Effect of leaching time; (e) Effect of Liquid/Solid rate.

spectrometry (AAS method, Z-5000AA device). The main physical-chemical characteristics of the sludge are presented in Table 1.

Optimizing condition of ammonium leaching for multi-metal electroplating sludge: To separate Cu and Ni from the other metals (Cr and Fe et al.) and eliminate the effect of existing ions, the multi-metal electroplating sludge was leached with alkaline ammonium solution. Ammonia leaching can make metal ions and ammonia molecular to form a stable conjugate ion with $\text{Me}(\text{NH}_3)_n^{z+}$ into the solution to separate Cu^{2+} and Ni^{2+} ions from the other impurities ions which are insoluble or cannot react with ammonia. The advantages of the leaching are the efficiency of the selective dissolving Cu and Ni and other insoluble metals (such as Fe, Cr etc.) exist mostly in the leaching residue. By the ammonia leaching, a valuable metal ions solution with low impurity content and less consumption of leaching agent can be obtained from the multi-metal electroplating sludge. Between the same kinds of metals, the complex of high coordination number is generally more stable than that of low coordination number at the high concentration of ammonia. As long as high concentration of ammonia exists, the highest allocation of ammonia ligand ions are the vast majority of the existence in solution, then the low coordination number of ions could be neglected. The chemical process of ammonia leaching system for division of each divalent metal is as follows:



In addition, the study suggests that the activity state $\text{Cr}(\text{NH}_3)_6^{3+}$ of Cr can speed up the oxidizing hydrolysis into hydroxyl passivation state $\text{CrO}(\text{OH})$ in the ammonia leaching process by adding a catalyst $\text{Al}(\text{OH})_3$, and thereby inhibits the leaching of Cr to achieve a better separation efficiency with Cu and Ni.

A series of tests for ammonium leaching of multi-metal electroplating sludge were carried out in order to optimize the conditions which contain NH_3 concentration, NH_4HCO_3 concentration, the reactive temperature and time, the liquid-solid ratio (L/S) and catalyst and so on. The results are shown in Figure 1.

Figure 1(a) and Figure 1(b) suggest that the leaching rates of Cu and Ni are increasing gradually with the increasing concentration of NH_3 and NH_4HCO_3 , which owing to the quickly reaction between more ammonium molecular and metals. However, the rates increase slowly when the concentration of NH_3 and NH_4HCO_3 are more than 8 mol/L. The effect of temperature to leaching rates of Cu and Ni are greater than that of the others Figure 1(c). With the quickly enhancement of temperature, leaching rates of Cu and Ni are increasing gradually, and the maximum leaching rates of Cu and Ni achieve within 2 hrs at the 75 °C Figure 1(d). The ratio of solid to liquid affects scarcely to Cu, and a few to Ni between 10 and 35 Figure 1(e). The leaching rate of Cr is below to 8% for all experiments, which suggests that Cu^{2+} and Ni^{2+} ions can be separated effectively from Cr^{2+} ion.

Through multi-group conditions of single factor ammonia leaching experiments for NH_3 - NH_4HCO_3 leaching system, optimal leaching conditions of multi-metal electroplating sludge are as follows: temperature at 75°C, the time $t = 3.5$ hrs, NH_3 concentration of 8 mol/L, NH_4HCO_3 concentration of 5 mol/L, liquid-solid ratio $\text{L/S} = 20$, catalyst of 0.25 g/L, and the characteristics of the ammonium leaching solution of the sludge under the optimizing condition are shown in Table 2.

It was clear indicated that the metal ions of Ni and Cu has been separated from Cr and Fe, and the impurity affect was eliminated. But about 90 g/L NH_4OH and 45 g/L NH_4HCO_3 would remain in the leaching liquor.

Co-extracting of Cu and Ni from ammonia-leaching aqueous

With the ammonium leaching aqueous containing Cu and Ni, the effects of single factor on extraction capacity of Cu^{2+} and Ni^{2+} ions were studied. It can be learned that pH, N902 concentration in organic phase and the contact time have intensive influence on the rate of metal extraction, but the influence of temperature is less obvious. Extraction temperature can be controlled at 20-30°C, that is, at room temperature. However, the actual ammonia leaching aqueous is complicated, and the various influence factors on the extraction are not isolated, that is, extraction is affected by the above-mentioned factors, as well as

Leaching Test	Leaching metal ions (g.L ⁻¹)(%)				
	Cu	Ni	Cr	Fe	[Cu+Ni]/[Cr+Fe]
1	2.260(96.23) ^b	3.383(91.76)	0.015(3.86)	0.063(1.56)	73.6
2	2.233(95.22)	3.275(89.65)	0.013(3.35)	0.045(1.15)	94.9
3	2.252(96.03)	3.335(91.12)	0.014(3.68)	0.054(1.43)	82.2
average	2.248(95.82)	3.332(90.81)	0.014(3.63)	0.054(1.38)	83.6

^aLeaching conditions: $t = 3.5$ h; L/S ratio = 20:1; stirring speed = 100 rpm, $T = 75^\circ\text{C}$,

^bValues in brackets give the percentage of dissolution for each metal species

Table 2: Result of comprehensive test conditions of ammonia-leaching^a.

Sequence number	pH /A	Phase ratio(O/A) /B	N902 conc.(%) /C	Time (min.) /D	Inspection targets	
					Cu extraction rate(%)	Ni extraction rate(%)
1	8.5	1:2	10	2	72.6	39.7
2	8.5	1:1	20	4	98.6	97.1
3	8.5	2:1	30	6	95.2	92.7
4	9.0	1:2	20	6	98.3	96.4
5	9.0	1:1	30	2	95.6	83.4
6	9.0	2:1	10	4	94.4	90.9
7	9.5	1:2	30	4	98.7	95.3
8	9.5	1:1	10	6	93.2	89.4
9	9.5	2:1	20	2	91.7	81.7

Table 3: The results of $\text{L}_9(3^4)$ intersect experiment of Cu and Ni extraction.

Range of copper extraction rate				
K_1	266.4	269.6	260.2	259.9
K_2	288.3	287.4	290.6	291.7
K_3	285.6	283.3	289.5	286.7
k_1	88.8	89.9	86.7	86.6
k_2	96.1	95.8	96.9	97.2
k_3	95.2	94.4	96.5	95.6
R	7.3	5.9	10.2	10.6
Optimal decision	A_2	B_2	C_2	D_2

Table 4: Analysis of range of copper extraction rate.

Range of nickel extraction rate				
K_1	229.5	231.4	220	204.8
K_2	270.7	269.9	275.2	283.3
K_3	266.4	265.3	271.4	278.5
k_1	76.5	77.1	73.3	68.3
k_2	90.2	90.0	91.7	94.4
k_3	88.8	88.4	90.5	92.8
R	13.7	12.9	18.4	26.1
Optimal decision	A_2	B_2	C_2	D_2

Table 5: Analysis of range of nickel extraction rate.

the interference of impurity ions. In order to further understand the effect of factors mentioned above on the co-extraction of Cu and Ni, an orthogonal experimental design was used to explore these factors on extraction equilibrium and selectivity.

For the actual ammonia leaching liquid, a set of four factors and

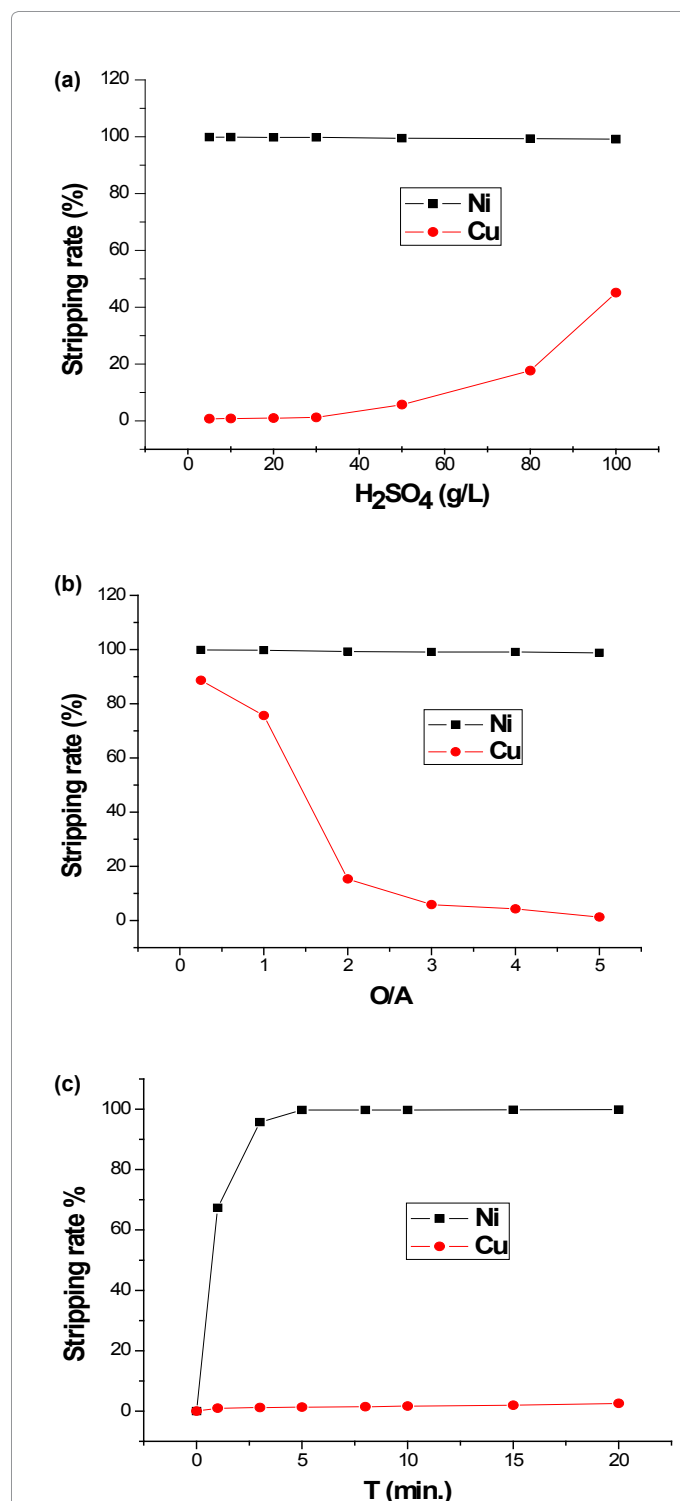


Figure 2: Effects of the factors on Ni selective stripping. (a) Effect of concentration of H_2SO_4 ; (b) Effect of O/A rate; (c) Effect of contacting time.

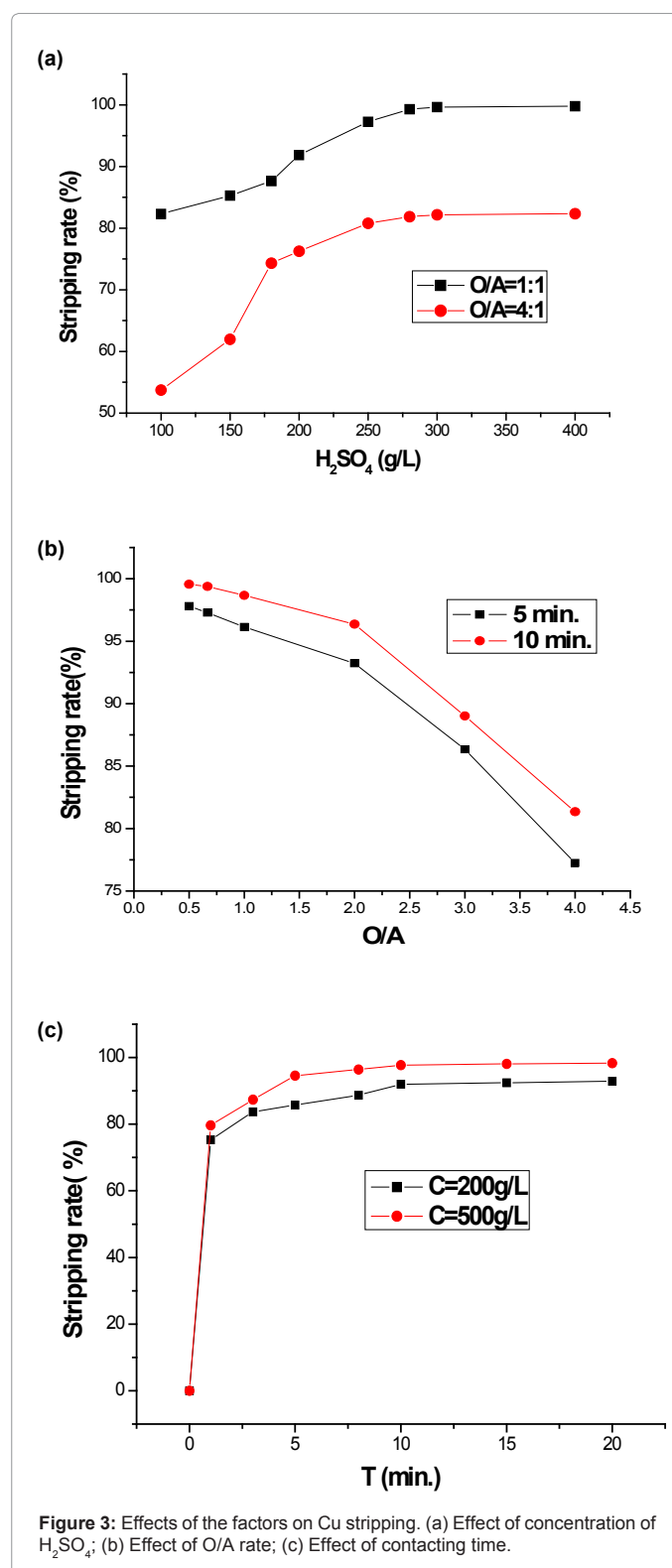


Figure 3: Effects of the factors on Cu stripping. (a) Effect of concentration of H_2SO_4 ; (b) Effect of O/A rate; (c) Effect of contacting time.

three levels L_9 (3^4) orthogonal test was designed to select pH value, initial concentration of extractant, phase ratio (Organic/Aqueous) and the contact time. The results of orthogonal experiment are shown in Table 3.

According to Table 3, the results of the analysis of experimental

data are shown in Table 4, 5. From these tables, it can be seen that the initial concentration of N902 and the O/A play a very important role in the extraction rate of Cu and Ni. The oscillation time also affects it to some extent, but the effect of pH value is relatively small.

From the analysis on extraction rate of Cu and Ni above, it makes clear that the optimal conditions of the Cu^{2+} and Ni^{2+} ions co-extracting are the same for $\text{A}_2\text{B}_2\text{C}_2\text{D}_2$. Under the optimal conditions ($\text{A}_2\text{B}_2\text{C}_2\text{D}_2$), several sets of multi-stage extraction test were conducted, and the results are shown in Table 6. The level of Cu and Ni extraction rate are both more than 96 %.

Ammonia removal from the loaded organic phase

After extracting Cu and Ni by N902 from the ammonia solution, a small amount of ammonia with Cu and Ni together came into the organic phase due to ammonia with the stripping agent (H_2SO_4) to form ammonium sulfate, even to form $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ complex Ni salt in the Ni stripping solution, which had an impact on follow-up treatment. Therefore, in order to reduce the consumption of sulfuric acid, it was necessary to remove ammonia from organic phase after the extraction of Ni and before the stripping process. Based on the existing literature [11], the distilled water was selected to remove ammonium agent. The test showed that the elution effect of ammonia would take more than 10 min, but it slowed down the phase separation, under the condition of O/A = 5/1, mixing time 5 min. After washing the loaded organic phase, the rate of ammonia removal can be as high as 98 %, and the loss of Cu and Ni be ignored.

Ni selectively stripping and recovery from the loaded organic phase

Literature [12] and experiments show that Ni and Cu can be separate recovery by selectively stripping from the loaded organic phase because of the complex instability of Ni with the N902 under condition of low acid.

The effect of sulfuric acid on Ni selectively stripping: The effect result of sulfuric acid on Ni selectively stripping is shown in Figure 2(a). It suggests that the sulfuric acid concentration ranges from 5 g/L to 100 g/L should be used to obtain reasonably sufficient Ni stripping in a single stage (~100 %), so that nearly complete stripping is possible. When the sulfuric acid concentration is 30 g/L, better separation efficiency can be achieved for Ni and Cu which stripping rates are 99.77 % and 1.23 %, respectively.

However, with the increasing concentration of sulfuric acid, Cu stripping rate is getting higher and higher. When the sulfuric acid concentration is 50 g/L, the Cu stripping rate is 5.68 %, and when the sulfuric acid concentration up to 100 g/L, the Cu stripping rate has reached 45.12 %. It is not benefit for the separation of Ni and Cu. Therefore, sulfuric acid concentration of 30 g/L is the optimal concentration of stripping agent.

The effect of O/A and contact time on Ni selectively stripping: Compared with sulfuric acid, ratio of O/A does less effect on Ni

stripping. Figure 2(b) shows that reasonably sufficient Ni stripping in a single stage (~100 %) can be achieved in the range of 1-5 of O/A. With the increase of O/A, the back-extraction rate of Cu decreases sharply, while the back-extraction rate of Ni is relatively stable. With the 5/1 of O/A, the Cu stripping rate decrease by 1.27 % and the Ni back-extraction rate is 98.83 %, which means Cu-Ni separation is effective.

Figure 2(c) indicates that with the increase of contact time, the back-extraction rate of Ni changes sharply, while the back-extraction rate of Cu is relatively stable, less than 2 %. Within 5 min of contact time, the satisfied Ni stripping rate can be achieved. Cu-Ni separation is effective.

After the Ni back-extraction experiment, the optimal stripping conditions of Ni are as follows: temperature at $30 \pm 2^\circ\text{C}$, stripping agent for the sulfuric acid concentration of 30 g/L, O/A = 5:1, contact time of 5 min. From the experiment, we can find that more than 99 % of Ni stripping rate can be achieved by the two-stage counter-current stripping, concentration of Ni is 15.95 g/L in stripping solution, concentration of Cu is less than 0.03 g/L and Cu is not striped.

Cu stripping from the Ni-free loaded organic phase

The Ni-free loaded organic phase was used for carrying out Cu stripping study. Using the loaded organic phase containing 2.26 g/L Cu and 0.002 g/L Ni and sulfuric acid as stripping agent, single stage experiments were designed, and the other conditions were shown as follows: the deferent phase ratios of 1:1 to 4:1 of O/A, the concentration of sulfuric acid of 100-400 g/L, temperature at $30 \pm 2^\circ\text{C}$, contact time from 1 to 15 min. The stripping efficiency of Cu is in the range of 50 % to 99 % Figure 3. The optimal stripping conditions of Cu are as follows: temperature at $30 \pm 2^\circ\text{C}$, stripping agent for the sulfuric acid concentration of 250 g/L, O/A = 1:1, contact time of 8 min. From the experiments, we can find that more than 99 % of Cu stripping rate can be achieved by the three-stage counter-current stripping under the optimal stripping conditions of Cu. The concentrations of Cu in stripping solution and in organic phase are 2.25 g/L and less than 0.05 g/L, respectively.

Recovery of Cu and Ni products

After stripping process, the stripping solution was heated, evaporated and crystallized. Cu was recovered as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ purity blue crystal product (99.3 % in purity). Ni was recovered as $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ green crystal product (98.4 % in purity).

Conclusions

Process parameters were optimized for the separation and recovery of Ni and Cu from ammoniac leaching liquor obtained by ammoniac leaching of the multi-metal electroplating sludge. Ni and Cu were quantitatively co-extracted in two counter-current stages under the conditions of 1:1 of O/A, a 20 vol. % N902 solution in mainly aliphatic kerosene, contact time of 4 min and temperature at $30 \pm 2^\circ\text{C}$. The percentage of extracting was 99.9 % both for Cu and Ni. The ammonia in the loaded organic phase was removed using a single stage scrubbing

Sequence number	Copper extraction				Nickel extraction			
	One-stage		Two-stage		One-stage		Two-stage	
	Cu^{2+} extra. rate (%)	Cu^{2+} conc. in aqueous(mg/L)	Cu^{2+} extra. rate (%)	Cu^{2+} conc. in aqueous(mg/L)	Ni^{2+} extra. rate (%)	Ni^{2+} conc.in aqueous(mg/L)	Ni^{2+} extra. rate (%)	Ni^{2+} conc. in aqueous(mg/L)
1	97.8	51.26	>99.9	0.18	97.3	89.37	>99.9	0.3
2	98.2	41.94	>99.9	0.20	96.8	105.92	>99.9	0.4
3	98.6	32.62	>99.9	0.15	97.2	92.68	>99.9	0.3

Table 6: The results of multi-grade extraction of co-extraction.

operation with water. Selective Ni stripping was achieved in a two-stage counter-current stripping at $O/A = 5/1$, using the sulfuric acid of 30 g/L and contacting time of 5 min. The Ni stripping efficiency was 99.0 %. Cu was stripped from the Ni-free organic phase with the sulfuric acid of 250 g/L in three stages at $O/A = 1/1$, contact time of 8 min. The organic containing was recycled in the system.

As far as we know, there is no any report about co-extract Cu (II) and Ni (II) from the ammoniac-carbonate leaching liquor of the multi-metal electroplating sludge, and almost no reports about the two-stage leaching metal ions from electroplating sludge. The results of this study suggest that this technology of recovery Cu and Ni metals from electroplating sludge can be used as a suitable reutilized method of heavy metals. The technology to dispose plating sludge not only can avoid the serious problems plating sludge caused to environment, but also can get great potential profits by reusing valuable heavy metals in plating sludge. In addition, the authors believe that the work presented in this paper will prove practically useful information for design of more efficient electroplating sludge treatment processes for metal recovery. Anyway, further work at a pilot-plant level is now in progress in order to confirm the promising results already achieved.

Acknowledgement

This paper is based on the work supported by the Bureau of Science and Technology Guangdong Province, China under the project entitled "Heavy Metal Resources Recycling Technology from the industry solid waste material". Authors are thankful to the Ming Run Electroplating plant, Guangdong, Foushan City, China to supply the experimental sample.

References

1. Shi TH, Zou SJ, Chen J, Huang R, Wang ZC (2008) Research advance of the hydrometallurgical recovery of copper and nickel from electroplating sludge. *J Chin J Environ Eng* 12: 35-41.
2. Shi TH, Wang ZC, Liu Y, Jia SG, Du CM (2009) Removal of hexavalent chromium from aqueous solutions by D301, D314 and D354 anion-exchange resins. *J Hazard Mater* 161: 900-906.
3. Kondo H, Fujita T, Kuchar D, Fukuta T, Matsuda H, et al. (2006) Separation of metal sulfides from plating wastewater containing Cu, Zn and Ni by selective sulfuration with hydrogen sulfide. *J Japa Hyomengijutsu* 57: 901-906.
4. Silva JE, Paiva AP, Soares D, Labrincha A, Castro F (2005) Solvent extraction applied to the recovery of heavy metals from galvanic sludge. *J Hazard Mater* 120: 113-118.
5. Agarwal JC, Beecher N, Hubred GL, Natwig DL, Skarbo RR (1976) Metal separation by fluid ion exchange in the processing of ocean nodules. Paper presented at AIME Ann Meeting Las Vegas NV, Feb.
6. Agarwal JC, Barner HE, Beecher N, Davies DS, Kust RN (1979) Kennecott Process for recovery of copper, nickel, cobalt and molybdenum from ocean nodules. *J Min Eng* 31: 1704-1707.
7. Agarwal JC, Beecher N, Hubred GL, Natwig DL, Skarbo RR (1976) A new FIX on metal recovery from sea nodules. *J Min Eng* 177: 74-78.
8. Pandey BD, Kumar V, Bagchi D, Akerkar DD (1989) Extraction of nickel and copper from the ammoniacal leach solutions of sea nodules by LIX64N. *J Ind Eng Chem Res* 28: 1664-1669.
9. Rhoads SC, Nilsen DN, Siemens RE (1977) Solvent extraction of nickel, cobalt and copper from laterite-ammoniacal leach liquors. *Proceedings of Proc. Internat Solv Extra Conf ISEC 77 Toronto, Canada, CIM Specl.*
10. Sandhibigraha A, Bhaskara Sarma PVR (1997) Co-extraction and selective stripping of copper and nickel using LIX87QN. *J Hydrometal* 45: 211-219.
11. Wang CY (2002) The extraction and recovery of copper nickel and cobalt extraction from the Ammoniacal leaching solution. *J Chin J Non-ferrous metals* 54: 23-26.
12. Parija C, Bhaskara Sarma PVR (2000) Separation of nickel and copper from ammoniacal solutions through co-extraction and selective stripping using LIX84 as the extractant. *J Hydrometal* 54: 195-204.