

## Copper and Nickel Recovery from Electroplating Sludge by the Process of Acid-leaching and Electro-depositing

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**ABSTRACT:** In this work, we developed a method which combined the processes of acid-leaching, ammonium jarosite precipitating and electro-depositing to recover copper and nickel from electroplating sludge. Residual sludge from an electroplating plant located in Qingdao was used for acid-leaching, and more than 95% of copper, nickel, zinc, chromium and iron were extracted from the sludge. After acid-leaching, the extracted solution was put into an electrolytic cell for copper recovery by electro-depositing process, and about 95% of copper was recovered under the optimized operation parameters such as cell voltage, pH and electrode material. After copper recovery, the extracted solution was treated with ammonium jarosite precipitating process. About 99% of chromium and iron could be deposited as chromium ferrite in this process. Finally, the left solution was treated with electro-depositing process again for nickel recovery, and about 57% of nickel could be recovered in this process under the condition of pH 5.5 and voltage 5.5V.

**Key words:** Electroplating sludge, Heavy metal recovery, Acid-leaching, Electro-depositing, Ammonium

### INTRODUCTION

Electroplating wastewater generated from electroplating and acid-alkali washing process (Armstrong *et al.*, 1996). Chemical precipitation is the most commonly used method for the removal of dissolved metals from wastewaters. However, it can produce the precipitation sludge that leads to secondary pollution, a troublesome problem hard to be solved (Asavapisit and Chotklang, 2004; Chang *et al.*, 2008). Since the component of electroplating sludge is very complex (Venkateswaran *et al.*, 2007), conventional treatment methods such as land-filling, ocean-dumping, incineration, stabilization or solidification cannot dispose it effectively (Shapouri *et al.*, 2007; Chen *et al.*, 2008; Dutra *et al.*, 2008 and Naim *et al.*, 2010), even bring the surroundings more serious secondary pollution (Peng *et al.*, 2002). Now, some new techniques, such as ferrite process, fractional precipitation, extraction separation, membrane techniques, have been developed to manage these toxic sludge or recover the heavy metals in more economical ways (Peng *et al.*, 2004; Wodzki *et al.*, 1999; Wu, 2005 and Yan, 2005), these methods have their own advantages and disadvantages. However, few studies have been published for total heavy metals recovery, including

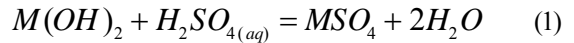
Cu, Fe, Cr, and Ni, from electroplating sludge. Over thirty heavy metals can be recovered from aqueous solutions by electrolysis including many precious metals and heavy metals (Zhu and Yang, 1996). In this paper, we developed a process combined with acid-leaching, ammonium jarosite precipitating, and electro-depositing to recover Cu, Fe, Cr, and Ni from electroplating sludge. This study provides a theoretical basis and technical support for the development of a new electroplating sludge treatment.

### MATERIAL & METHODS

The electroplating sludge was collected from an electroplating plant in Qingdao, China. Some physical and chemical properties of the sludge are summarized in Table 1. Reagents used in the experiments were displayed in Table 2. All the chemicals used for the chemical analysis were from Nanjing Chemical Reagent Ltd. The concentration of metals was measured by atomic absorption spectrometry (Solar M6, Thermo Elemental, USA). A pH meter and a conductivity meter (PH-3D, DDS-307, Shanghai Leici Ltd., China) were used for the determination of pH and conductivity. Electric voltage and current were monitored by multimeter (A830, Shenzhen Focus Ltd., China). The

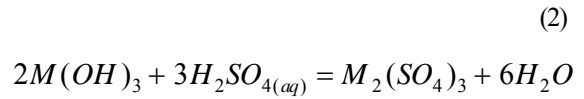
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entire acid-leaching and heavy metal recovery process is shown in Fig.1.



**RESULTS & DISCUSSION**

According to the following two equations, we can calculate the required amount of H<sub>2</sub>SO<sub>4</sub> for the sludge acid-leaching.



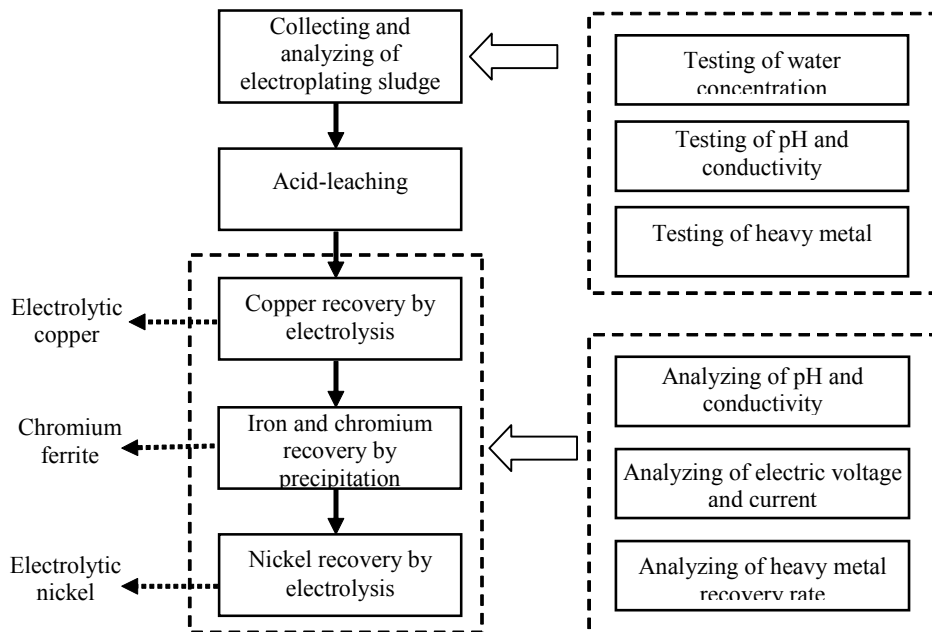
**Table 1. Chemical properties of the electroplating sludge**

Colour	Sap green					
Water content (%)	84.3					
Initial pH <sup>a</sup>	9.3					
Initial conductivity <sup>b</sup> (μs/cm)	4250					
Heavy metal	Cu	Ni	Zn	Cr	Fe	others
Concentration (mg/kg)	114133	99967	16217	13820	12730	---

<sup>a</sup> water: sludge=10:1; <sup>b</sup> water: sludge=10:1.

**Table 2. Reagents used in the experiments**

Reagent name	Grade	Chemical formula	Pur pose
Hydrochloric acid	GR/AR	HCl	Digest/acid-leaching
Nitric acid	GR/AR	HNO <sub>3</sub>	Digest/acid-leaching
Sulfuric acid	AR	H <sub>2</sub> SO <sub>4</sub>	Acid-leaching/adjust pH
Perchloric acid	GR	HClO <sub>4</sub>	Digest
Hydrofluoric acid	GR	HF	Digest
Standard solution	SP	Cu/Ni/Cr/Zn/Fe	Testing
Sodium hydroxide	AR	NaOH	Precipitant/adjust pH
30% Ammonia	GR	NH <sub>3</sub> ·H <sub>2</sub> O	Adjust pH
Boric acid	AR	H <sub>3</sub> BO <sub>3</sub>	Buffer reagent



**Fig. 1. Flow-sheet of acid-leaching and heavy metal recovery process**

The required amount of  $H_2SO_4$  could be:

$$V_{ml} = 100n_{M(OH)_2} / 1.84$$

or (3)

$$V_{ml} = 150n_{M(OH)_3} / 1.84$$

Where n is the metal hydroxides' amount of substance (mol), V is the required amount of  $H_2SO_4$  (mL).

Combined with the content of Cu, Ni, Zn, Cr and Fe in the electroplating sludge, which were already listed in Table 1, we calculated from equation (3) that about 0.242 mL  $H_2SO_4$  required for acid-leaching the sludge 1g. This experiment was carried on 25°C, an amount of 2g dried electroplating sludge was weighed and transferred to a 50mL small beaker, adding into a certain amount of  $H_2SO_4$  and magnetic stirring for 0.5h, then put it aside for 0.5h and was centrifuged at 4000rpm for 7 minutes, the solution was then filtered into a 25mL volumetric flask, the remaining residue was washed twice, all the solution was poured into the flask, and the volume completed with distilled water. Five kinds of  $H_2SO_4$  solutions with the concentrations of 5%, 10%, 15%, 20%, 30% were prepared for these experiments, and the results were shown in Fig.2. It can be seen from Fig.2 that the metal leaching rates increased with the acid concentration, and the maximum appeared at the  $H_2SO_4$  concentration of 10%. Here, 0.98mL  $H_2SO_4$  was used for 2g sludge, which was somewhat different from theoretical calculation. Because the latter was only calculated by a chemical reaction formula, while the actual leaching process is related to leaching mechanism [8], which would consume more  $H_2SO_4$ . There was large number of bubbles around the sludge sample when the  $H_2SO_4$  concentration was 30%, forming massive, which made against the contact between  $H_2SO_4$  liquid and sludge particle, so the leaching rate would decline. Take into the account the cost and the follow-up process, 10%  $H_2SO_4$  concentration was appropriate. 10%  $H_2SO_4$  was used for this experiments. Six ratios of acid to sludge,

say 5mL, 6mL, 7mL, 8mL, 10mL and 12mL of  $H_2SO_4$  to 2g dried sludge, were tested for acid-leaching, and the results were shown in Fig. 3. It can be seen from Fig. 3 that the extraction of metals increased sharply with the increasing of  $H_2SO_4$  volume. More than 95% of Cu, Ni, Zn, Cr and 80% of Fe have been extracted from the sludge after the volume of 10mL. Considering the balance between leaching efficiency and leaching cost, 10% the concentration of  $H_2SO_4$  and 10mL to 2g the ratio were decided the optimal acid-leaching conditions. Based the optimal conditions, we amplified the acid-leaching experiment and got the extracted solution as shown in Table 3.

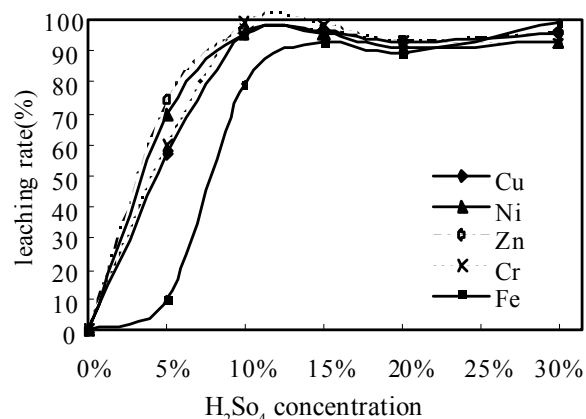


Fig. 2. Effect of  $H_2SO_4$  concentration on acid-leaching rate

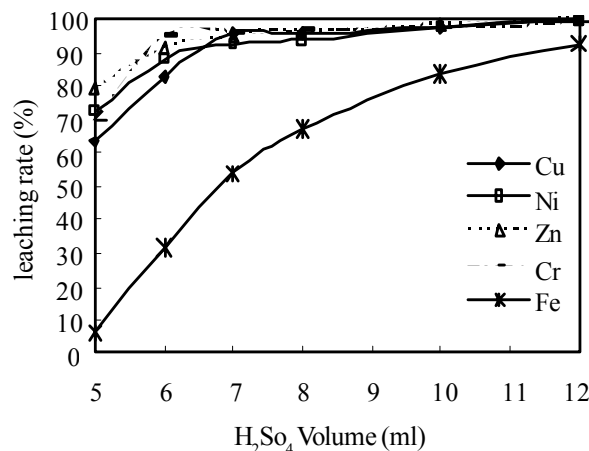


Fig. 3. Leaching rate changes under different  $H_2SO_4$  Volume

Table 3. The concentration of metals in the extracted solution of acid-leaching

Heavy metals	Cu	Ni	Zn	Cr	Fe
Concentration (g/L)	21.734	19.308	3.038	2.512	2.188
Leaching rate (%)	95.21	96.57	93.67	90.88	85.94

Copper recovery is a static test. Home-made PVC rectangular tank (10cm×5cm×11cm) as the electrolytic bath; stainless steel plate as cathode, with the area of 9cm×10cm; the distance between electrodes is 3.5cm, plus DC voltage to recovery copper. A certain volume (1.5mL) electrolyte was taken out for the measurement of pH, conductivity and heavy metal concentration at regular time. A factorial design was employed to assess the influence of cell voltage, pH and electrode material on the copper recovery. Effect of cell voltage on copper recovery was studied at different voltages. Experimental condition as follow: pH=2, stainless steel as anode, five voltage gradient (2.0V, 2.2V, 2.5V, 2.7V, 3.0V). The changes of copper recovery rate with the electrolytic time were shown in Fig. 4. From Figure 4, the higher the voltage, the copper recovery rate was greater at the same time, because the cathode potential increases with the increasing of cell voltage, which is more conducive to the copper reduction at the cathode. When the voltage was low (U=2.0V, or U=2.2V), with the cathode potential low, so the recovery rate was lower, only less than 30% and 50%; while the voltage raised to 2.5V, copper recovery rate reached to 90% after 12h electrolysis; and the voltage was higher than 2.5V, the rate has been 99%. Solution pH was adjusted to 0.3, the relationship between the copper recovery rate and voltage was shown in Fig. 5. Comparing Figure 4, under the same voltage and the same time, the current (pH=0.3) was bigger than that when the pH=2. Lower pH value, even if the voltage was low, the copper recovery rate was also higher, and better recovery effect could be achieved less than 12h electrolysis time. Thus, low pH was conducive to copper electrolysis. Copper recovery rate reached 93.32% under 2.7V voltage for electrolysis 8h. Two kinds of electrode materials were used as anode in these experiments, one is stainless steel, and the other is Ti coated with Ru and Ir. pH is 0.3, cell voltage is 2.7V, electrode distance is 3.5cm to determine the appropriate electrode material. From the Fig. 6, we can see that the copper recovery rate using Ti coated with Ru and Ir anode was little different from that using stainless steel anode, and the latter was not easy to be passivated and corroded, so Ti coated with Ru and Ir anode was suitable as an anode. Fig. 7 shows the variation curves of other heavy metal content using different anodes. Ni content remained unchanged basically, that was because cell voltage was not high enough to meet the actual decomposition potential leading to Ni Electro-depositing. (a) shows the situation using stainless steel anode. The content of Fe and Cr increased significantly with time, because with the electrolysis process carried out, pH decreased rapidly, stainless steel was corroded, Fe and Cr of which released. (b) shows the situation using Ti coated with Ru and Ir anode, we can see that the contents of Ni, Fe,

Cr, Zn hold a line on the whole, which would take no impact on the follow-up process. So Ti coated with Ru and Ir plate was chosen as anode in this experiment. Two different impurity removal processes (Hydroxide precipitation and ammonium jarosite precipitation) were compared to remove Fe and Cr and choose an appropriate one. The former was carried out at room temperature. Five identical liquid (50mL) was taken into 100mL beaker, in which the metal contents were known. Then their pH values were adjusted to 3.0, 3.2, 3.5, 3.8, 4.0 respectively and the stirring settling time was 2h. Reaction solution was filtered after the test and the residual heavy metal contents were measured by AAS to calculate the Fe, Cr, Zn, Ni removal rate; the latter was carried out at high temperature, take 50mL mixed-model liquid (50mL, no copper) as reaction solution, which pH was adjusted to 1.6 by 1mol/L sodium hydroxide, and then added different amounts of ammonia, constantly stirred at the speed of 150r/min, 95°C for 3h. At last, the precipitation was centrifugal separated to analyze the filtrate liquid. Fig. 8 shows the comparison of heavy metal removal rates with two different approaches. From Fig. 8a, we can see that with the increasing of amount of NaOH, pH increased and the heavy metals removal rates were also increased, in which Fe removal rate was the largest. When 50mL solution added 5.6mL NaOH, the Fe removal rate reached 83%, the concentration of iron was 64.46mg/L at this time; although Cr, Zn and Ni content also decreased, the removal rate was not large, the largest rate of which were 25%, 14% and 15%, respectively. Figure 8b shows the method of ammonium jarosite precipitation, we can see that this method was very effective to Fe and Cr removal. Adding 1mL ammonia per 50mL solution, the two heavy metals removal rates reached to 99%; the removal of Zn and Ni increased gradually, when adding 2.5mL ammonia per 50mL solution, which rates were 53% and 15%, respectively. And the precipitation with the method (b) was similar with earthy clay, with large particle size and easy to collect. Therefore, yellow ammonium jarosite precipitation is more suitable for Fe and Cr removal. And the amount of 1mL ammonia per 50mL solution was appropriate, when the Fe and Cr removal rate reached 99% and the adsorption of Zn and Ni were less. After impurity removal process, the main heavy metal ions in the solution are Zn<sup>2+</sup> and Ni<sup>2+</sup>. Here electrolysis was still chosen to recovery nickel, but because the standard electrode potential of Ni<sup>2+</sup>/Ni is much lower than that of Cu<sup>2+</sup>/Cu, it is more difficult for nickel electro-depositing than that of copper. In this test, the effect of cell voltage, the initial pH value and the dose of boric acid on the nickel recovery were preliminary researched in order to provide technical support for practical application. The experimental

apparatus for Ni electrolysis is similar to Cu electrolysis. The difference lies in the water-bath wok outside the Ni electrolytic bath to control the temperature at about 60; the test method is similar too, focusing on the effect of cell voltage, the initial pH value and the dose of boric acid on the nickel recovery. Recovery rate formula is shown as copper recovery. In pH Effect experiment, the electrolysis under three pH gradients (pH=3.64, pH=4.65, pH=5.5) was mainly considered. 8g boric acid was added into 400mL solution containing Zn and Ni, which was used as a buffer. Fig. 9 indicated the changes of Ni and Zn removal rates in different pH, which indirectly said the recovery effects. In the Figure, the trend of Ni recovery rate was that it rose to maximum rapidly in the first 1 hour, then rose slightly but remain unchanged basically, which indicated that the nickel electro-deposition in the cathode reached the maximum in the first 1 hour, then with the pH decreasing, hydrogen evolution reaction were serious in cathode, leading to the current efficiency of Ni electrolysis falling down. pH value increased in the hydrogen evolution reaction process, and  $Ni^{2+}$  and  $OH^-$  generated colloidal nickel hydroxide precipitation, so the formation of hydroxides and self-dissolution alternately, which was the reason that the Ni recovery rate was stable basically. The greater the original pH was, the Ni recovery rate was higher. The maximum recovery rates were 31%, 38% and 42% when the original pH were 3.64, 4.65 and 5.5, which is also related with the pH was high, the hydrogen evolution reaction in cathode would lag. After a few exploration tests, results were showed that when the cell voltage was less than 5V, no metal electro-deposited in the cathode. So the main considerations in this study were two voltage gradients (5V and 5.5V). Original pH was 5.5, 8g boric acid as a buffer was added into 400mL solution containing Zn and Ni. Fig.10 indicated the changes of Ni and Zn removal rates under different cell voltages, the overall trend of Ni was similar to the situation in different pH, which rose rapidly at first, then keep stable. So conclusion can get that when the cathode potential reached to the heavy metal evolution potential in the cathode, but the current density didn't meet the current limits, higher the voltage was, it was more conducive to the heavy metal electro-deposition in the cathode. Overall the Ni recovery rate was low, which was only 48% under 5.5V electrolysis. Boric acid used as a buffer to keep the solution pH at a certain range. 5.5V voltage were applied in this experiment, the original pH was 5.5, the effect on the heavy metal recovery rate adding different amount of boric acid (0g, 8g, 12g) to 400mL electrolyte was considered. From Fig. 11, we can see that the Ni recovery rate increased with the amount of boric acid increasing. Because of the buffer effect of boric acid to pH and inhibition on

$H^+$  discharge, it was beneficial to the Ni electro-deposition in the cathode. Ni recovery rate was not very high, only 57% of maximum. In the whole Ni recovery experiments, the Zn recovery rates were very low. It was related to the low cell voltage, for which the cathode potential didn't reach to the Zn electro-deposit potential.

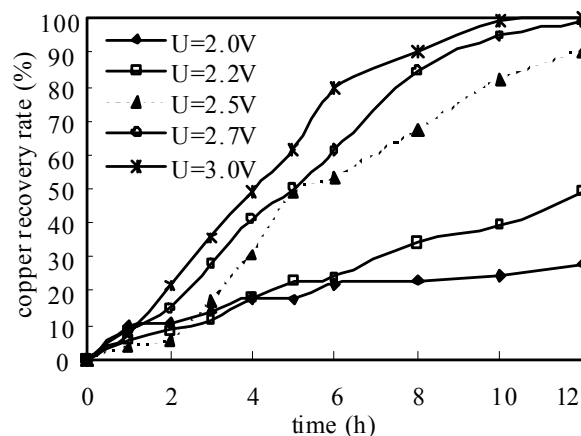


Fig. 4. Effect of cell voltage on copper recovery at pH 2

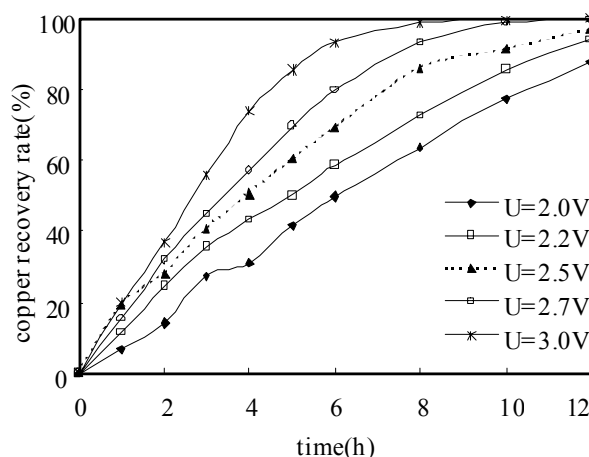


Fig. 5. Effect of cell voltage on copper recovery at pH 0.3

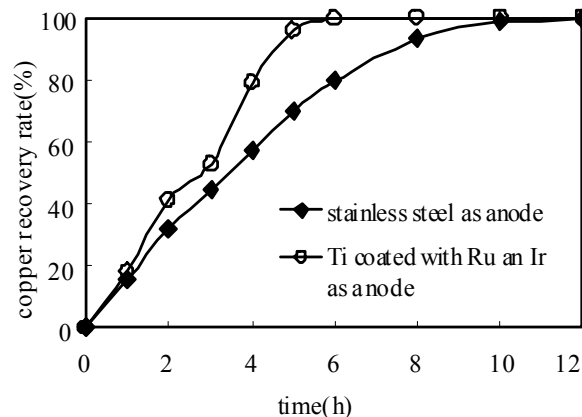


Fig. 6. Effect of electrode material on copper recovery

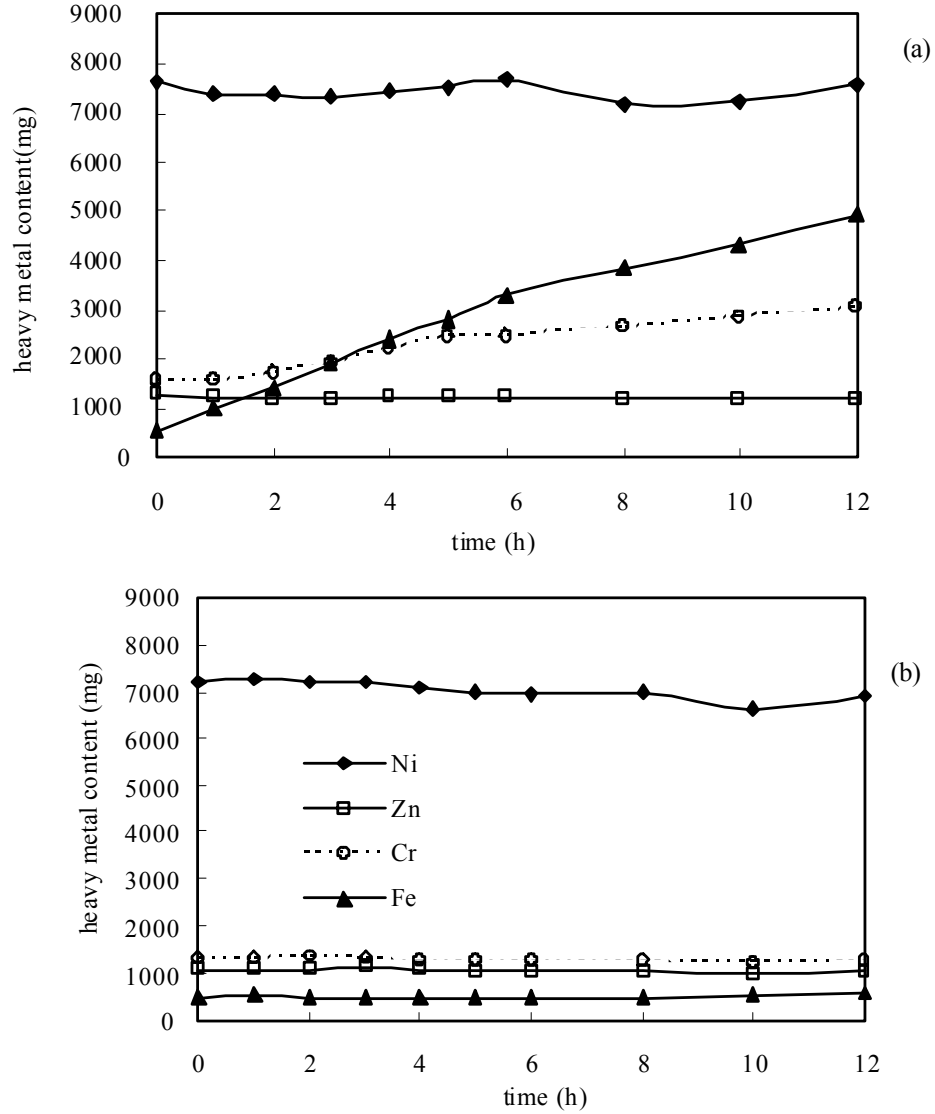


Fig. 7. Changes of other heavy metals content using different anode: (a) stainless steel, (b) Ti coated with Ru and Ir

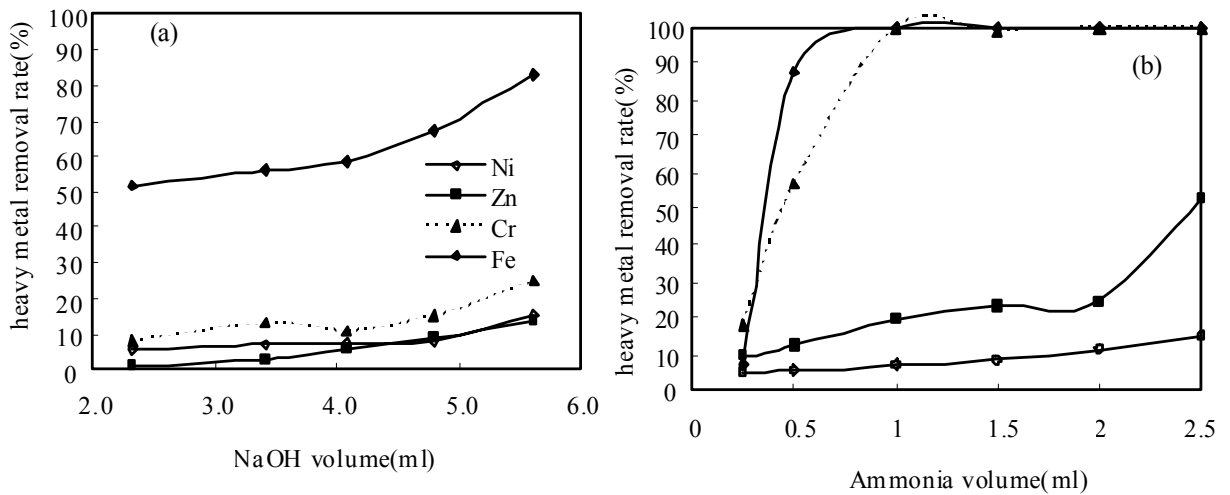


Fig. 8. Different heavy metal removal rate with two different methods: (a) Hydroxide precipitation, (b) ammonium jarosite precipitation

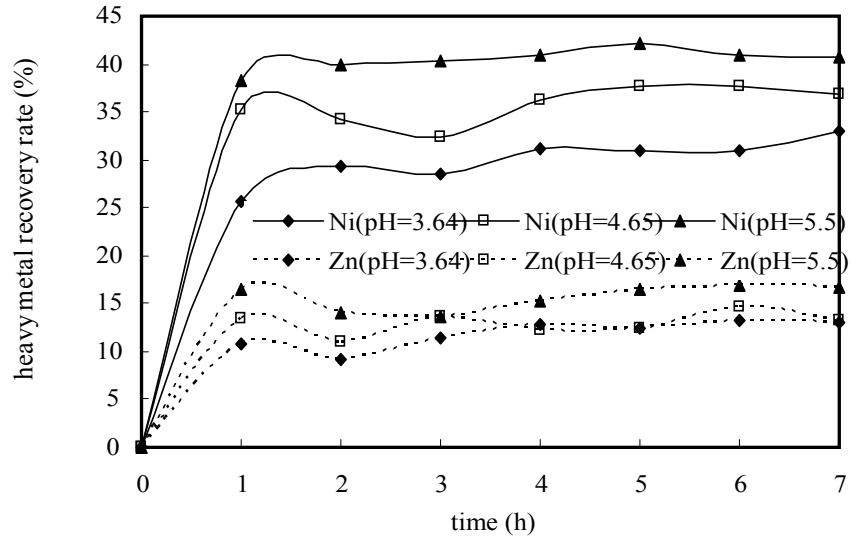


Fig. 9. Changes of heavy metal recovery rates with time in different pH

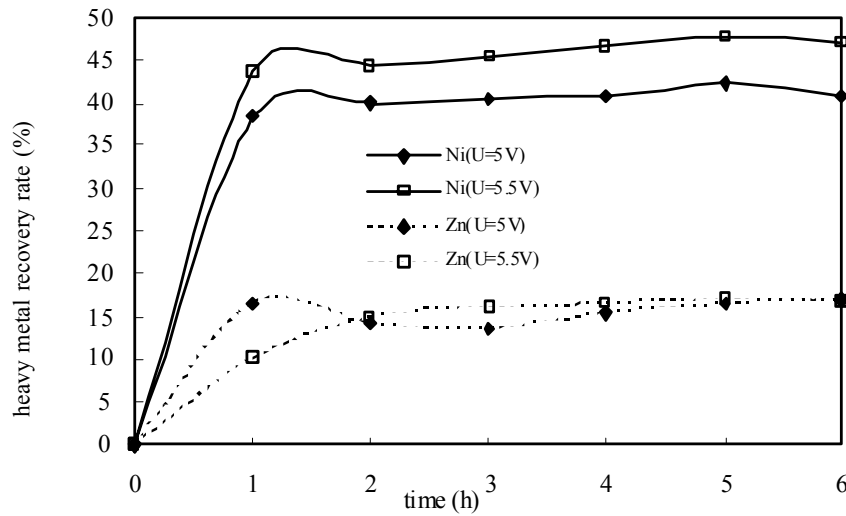


Fig. 10. Changes of heavy metal recovery rates with time under different cell voltage

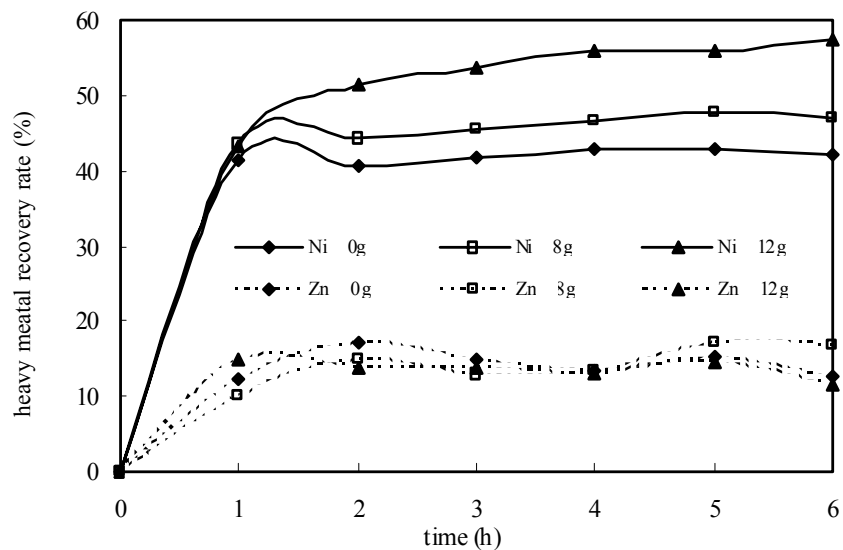


Fig. 11. Changes of heavy metal recovery rates adding different amount of boric acid

## CONCLUSION

A real electroplating sludge collected from an electroplating plant in Qingdao, and the content of metals are Cu (114133mg/kg), Ni (99967mg/kg), Zn (16217mg/kg), Cr(13820mg/kg), Fe(12730mg/kg). Under the optimum conditions of acid-leaching: 10% of the concentration, 10mL H<sub>2</sub>SO<sub>4</sub> to 2g dry sludge of the ratio, 25°C of the temperature and 0.5h of oscillating, most of Cu, Ni, Zn, Cr and Fe could be leached from the sludge. Under the optimum conditions of copper electrolysis recovery process: 2.7 V of cell voltage, 0.3 of original pH value, Ti coated with Ru and Ir as anode and stainless steel as cathode, 3.5 cm of electrode spacing and 8h of the electrolytic time, 95% of copper could be removed. About 99% of chromium and iron were deposited as chromium ferrite from the extracted solution in the process of ammonium jarosite precipitation. For the nickel electrolysis recovery, higher original pH value leads higher nickel removal rate, and higher voltage is more conducive to the reduction of heavy metals in the cathode deposition; with the adding of boric acid, the removal rate of nickel is also increased, but overall, the nickel removal efficiency is 57% of the maximum. Most of copper, chromium and iron can be recovered from extracted solution of electroplating sludge, 57% of Ni was recovered, and the left solution still containing some Zn and Ni should be treated later.

## ACKNOWLEDGEMENT

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