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# Recovery of Co(II) and Ni(II) from hydrochloric acid solution of alloy scrap

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**Abstract:** A hydrometallurgical process was developed for recovery of nickel and cobalt from the hydrochloric acid leaching solution of alloy scraps. The process consists of five major unit operations: 1) leaching with 6 mol/L hydrochloric acid under the L/S ratio of 10:1 at 95 °C for 3 h; 2) copper replacement by iron scraps under pH value of 2.0 at 80 °C, and stirring for 1 h; 3) removal of iron and chromium by chemical precipitation: iron removal under pH value of 2.0 at 90 °C by dropwise addition of sodium chlorate and 18% sodium carbonate solution, then chromium removal under pH value of 4.0 at 70 °C by addition of nickel carbonate solution, stirred by air flow for 2 h; 4) selective separation of cobalt from nickel by extraction using 30% trialkyl amine+50% kerosene (volume fraction) and tri-*n*-butylphosphate (TBP) as a phase modifier with the O/A ratio of 2:1, and stripping of cobalt with 0.01 mol/L HCl; 5) crystallization of nickel chloride and electrodeposition of cobalt. It is found that the nickel recovery of 95% and the cobalt recovery of approximately 60% with purity over 99.9% are obtained by this process.

Key words: alloy scrap; nickel; cobalt; recovery; trialkyl amine

## **1** Introduction

The demand for nickel and cobalt has recently risen for their promising use in rechargeable batteries. The increase in the industrial demand for these metals has brought forth a steady growth in the need for refining of the metals. More importantly, the recovery of nickel and cobalt from secondary sources such as alloy scraps and/or spent batteries could minimize landfill disposal and the waste of natural resources. It is also technically feasible and economical in comparison with refining cobalt and nickel from ores. To date, some typical hydrometallurgical processes have been reported for the recycling of cobalt and/or nickel from lithium ion batteries<sup>[1-3]</sup> and nickel metal hydroxide batteries<sup>[4-7]</sup> as well as Ni-Cd batteries[8]. These hydrometallurgical routes consist of acid leaching, separation of cobalt from nickel and/or lithium, and recovery as chemicals. For example, nickel has been recovered by means of both galvanostatic and potentiostatic electrowinning after separating Ni from Co by SX methods[9]. In addition, the recovery of Co(II) and Ni(II) from different sources, including polymetallic sea nodules[10–11], cobalt enriched Ni-Cu matte [12], low-grade sulfide flotation concentrates[13] and low-grade Ni-Cu sulfide tailings [14], has been achieved by different research groups. However, there have been only a handful of published works on cobalt recovery from waste alloys[15].

A variety of organic solvents or their mixtures have been tested for the extraction of nickel(II) and cobalt(II) from aqueous solutions and for separation of cobalt from nickel. Among the acidic organo-phosphoric compounds, di(2-ethylhexyl) phosphoric acid (D2EHPA) and extractant 2-ethylhexyl phosphonic acid mono-2ethylhexyl ester (EHEHPA, commercially known as PC88A or P507), have been widely used for separation of Co from Ni[11-16]. Whereas organo-phosphorous acid derivatives such as bis(2, 4, 4-trimethylpentyl) dithiophosphinic acid (Cyanex 301) extractant can extract cobalt and nickel at very low pH value as well as the ability to reject metals such as calcium, manganese and magnesium, holding a position for separation of cobalt and nickel[17–18]. The investigation on the purification of nickel showed that di-2, 4, 4-trimethylpentyl phosphinic (Cyanex 272) was most effective for selecting

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cobalt over nickel[19]. Some investigations show that the mixtures of extractants seem to give faster kinetics for the cobalt extraction[16–20, 21]. Moreover, numerous binary extractant systems have been investigated, which include mixtures of organophosphorus acids with amines [22–23], organophosphorus acids with solvating extractants such as tributylphosphate (TBP) and trioctylphosphine oxide (Cyanex 921)[24] and alcohols [25]. More recently, a systematic investigation for the Co(II)-Alamine 336-m-xylene mixtures has been performed to reveal the effect of hydrochloride acid concentration on cobalt extraction. It was found that the extractability of Co(II) increases with the increase of acidic molarities[26].

The main objective of this work is to evaluate the recovery of nickel and cobalt from the leaching solution of the alloy scraps with hydrochloride acid by the solvent extraction and the separation of Co(II) from Ni in the chloride solutions using the mixtures of trialkyl amine and TBP.

#### 2 Experimental

#### 2.1 Material and reagents

The alloy scraps used in this investigation were imported from South Africa. The chemical composition was (mass fraction): 40.10% Co, 13.04% Ni, 28.76% Fe, 17.84% Cr, 0.45% Cu, < 0.01% Al. The fuming hydrochloric acid, sodium chlorate, sodium carbonate and sodium chloride were all of analytical grade and without further purification. Trialkyl amine was purchased from Dalian Chemical Plant, China. The active component of trialkyl amine was C<sub>8</sub> aliphatic substituted ternary amine (mass fraction >98%, density 0.82 g/cm<sup>3</sup>, commercially as N235 in China). The chemical structure is shown as follows:

$$R \rightarrow R$$
 where  $R = CH_3 \rightarrow CH_2$ .

In experiment, the TBP and low odour kerosene were used as phase modifier and diluent, respectively.

#### 2.2 Procedure

In each run of a batch of leaching test, 200 g alloy scraps were leached with 2 L of 6 mol/L HCl in a 5 L round bottom glass flask with three openings serving for a feed tube, a thermometer and an overhead stirrer driven by a variable-speed motor. After 3 h of reaction time at 95 °C, the leaching liquor after filtration was analyzed for cobalt, nickel, iron, copper and chromium. Superfluous iron scraps were added to 1 L of the leaching solution to precipitate copper at 90 °C with 0.1–0.3 mol/L HCl at stirring of air flow for 2 h. The main proportion of iron was precipitated as goethite by adding a dilute sodium carbonate and stoichiometric amounts of sodium chlorate. Thereafter, the pH value was adjusted to 4.5 for the removal of chromium at 70 °C. The contents of each metal in the filtrate and the purified solution were measured. The organic solution was prepared by dissolving appropriate trialkyl amine (hereafter as N235) and TBP in 50% distilled kerosene (bp 165–190 °C). The effect of HCl concentration and chlorine concentration was respectively examined within the 2-8 mol/L range and 200-300 g/L. At the desired organic/aqueous (O/A) volume ratios, selective cobalt extraction was carried out by mixing two phases in sealed flasks and shaken for 10 min with a wrist action shaker at  $(35\pm1)$  °C. The stripping experiments of cobalt from the loaded organic phase were performed with HCl solution.

The analysis of metal ions in the solution and solid samples was performed using the Perkin-Elmer Model 800 atomic absorption spectroscopy(AAS). Chlorine ion concentration was determined by titration with AgNO<sub>3</sub>. The analysis for the organic phase was carried out by filtering through phase separation paper and a suitable aliquot of it was stripped with 0.5 mol/L HCl followed by its dilution and analysis using AAS.

## **3 Results and discussion**

#### 3.1 Leaching

The results showed that the high L/S ratio, high hydrochloric acid concentration and high temperature can result in high leaching efficiency. Accordingly, the leaching procedure was conducted at an L/S ratio of 10:1 with 6 mol/L hydrochloric acid at 95 °C for 3 h. Under these conditions, the average composition of the leach liquor was found to be 24.85 g/L Co, 12.55 g/L Ni, 28.62 g/L Fe, 13.97 g/L Cr, and 0.44 g/L Cu. In comparison with the chemical composition of the alloy scraps, 62% of Co, 96% of Ni, 99% of Fe, 78% of Cr and 98% of Cu were extracted from the scraps. It is under further consideration whether the residue should be leached in  $H_2SO_4$  by the pressure to extract the remnant cobalt.

#### 3.2 Elimination of copper, iron and chromium

By adding iron powder into the above filtrate, the copper in the solution was precipitated via replacement at 80  $^{\circ}$ C,

$$Cu^{2+} + Fe = Fe^{2+} + Cu \tag{1}$$

When the reaction was in equilibrium, the Nernst equation [27] should be satisfied:

$$\phi_{\text{Cu}}^{0} + \frac{2.303RT}{nF} \lg a(\text{Cu}^{2+}) = \phi_{\text{Fe}}^{0} + \frac{2.303RT}{nF} \lg a(\text{Fe}^{2+}) (2)$$

where  $\phi^0$  is the standard equilibrium potential, *a* is the activity of respective cation in the solution (it can be

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replaced by the concentration of metal ions in the range of low concentration). Eqn.(2) can be further deduced as follows:

$$a(\operatorname{Cu}^{2+})/a(\operatorname{Fe}^{2+}) = 10^{(\phi_2^0 - \phi_1^0)nF/2.303RT}$$
(3)

According to Eqn.(3), the remnant copper calculated was very low, i.e.  $\alpha(Cu^{2+})/\alpha(Fe^{2+})=2.0\times10^{-26}$ .

Thereafter, the precipitation processes were further conducted for the removal of iron and chromium. Three exercisable processes, i.e. jarosite, goethite and hematite, respectively, are available for the removal of iron from the solution. Investigations into the precipitation of iron (III) from the cobalt sulfate solution showed that the optimum pH range is in 3.0-3.5[28]. However, the present investigation showed that the preferred pH value is 2.0 for the iron precipitation from chloride system. To complete the goethite precipitation, Fe<sup>2+</sup> via oxidization by sodium chlorate was precipitated by adjusting the pH value to 2.0 using sodium carbonate as neutralizer. The oxidization and precipitation of Fe<sup>2+</sup> to goethite can be expressed as

$$6FeCl_2+NaClO_3+3H_2O+6Na_2CO_3=6FeOOH\downarrow+13NaCl$$
(4)

Then the solution temperature was adjusted to 70  $^{\circ}$ C and the pH value was adjusted to 4.0 using nickel carbonate dilute solution. The following reaction can be expected to occur:

$$2CrCl_3+3NiCO_3+3H_2O = 2Cr(OH)_3 \downarrow +3NiCl_2+3CO_2 \uparrow$$
(5)

Thus, chromium was also precipitated as hydroxide. The resulting solution consisted of 23.96 g/L Co, 12.63 g/L Ni, 0.001 g/L Fe, 0.005 g/L Cr, and 0.001 g/L Cu. Consequently, the percentages of Cu, Fe and Cr precipitated were about (mass fraction) 99.78%, 99.99% and 99.96%, while the loss of cobalt was about 1.5% in this stage.

Based on the experimental result, the preferred conditions for the selective separation of iron and chromium from the leaching liquor are: pH value 2.0 at temperature of 90  $^{\circ}$ C for iron and pH value 4.0 at 70  $^{\circ}$ C for chromium, stirring under air flow for 2 h. As a result, there was only 0.001 g/L Fe and 0.005 g/L Cr left in the solution.

#### 3.3 Separation of Co and Ni by solvent extraction

## 3.3.1 Chemical background

Pretreatment of N235 with HCl solution led to the formation of amine salt with the reaction:

$$R_3 N_{\text{org}} + \text{HCl} = R_3 \text{NHCl}_{\text{org}}$$
(6)

where  $R_3N$  represents N235 and subscript "org" the organic phase. The extraction of cobalt by N235 can be represented by the general equilibrium:

$$2R_{3}NHCl + CoCl_{4}^{2-} = (R_{3}NH)_{2}CoCl_{4} + 2Cl^{-}$$
(7)

According to Eqn.(7), the cobalt cation reacts with chlorine ions to form co-ordinate complex while the nickel does not. Therefore, the cobalt can be extracted by N235 from chloride solution.

The equilibrium may be characterized by the distribution coefficient of metal, *D*, defined as

$$D = [Co^{2+}]_{org} / [Co^{2+}]_{raff}$$
(8)

Thus, the percentage of the extracted metal, E, can be calculated by

$$E_{\rm Co} = \frac{[\rm Co]_{\rm org} V_{\rm org}}{[\rm Co]_{\rm org} V_{\rm org} + [\rm Co]_{\rm raff} V_{\rm raff}} = \frac{DR}{DR+1} = \frac{D}{D+1/R}$$
(9)

where R is the ratio of organic phase volume to aqueous phase volume.

The separation factor ( $\beta$ ) is a measure of selectivity in the extraction of metal ions.  $\beta$  for Co and Ni is defined as the ratio of their distribution coefficients under identical experimental conditions:

$$\beta_{\rm Co/Ni} = D_{\rm Co} / D_{\rm Ni} = \frac{[{\rm Co}^{2+}]_{\rm org} / [{\rm Co}^{2+}]_{\rm raff}}{[{\rm Ni}^{2+}]_{\rm org} / [{\rm Ni}^{2+}]_{\rm raff}}$$
(10)

A lower nickel distribution factor gives a better separation of cobalt from nickel.

Kremser equation is a classical method for determining the number of stages, N, in counter-current mass exchange units [29]. It can be rewritten to give the following alternative form:

$$N = \frac{\lg(\eta_{C_0} + q_{C_0} - 1) - \lg q_{C_0}}{\lg \eta_{C_0}} - 1$$
(11)

where  $\eta_{Co}$  represents the extraction factor and equals the distribution ratio *D* multiplying phase ratio *R*.  $q_{Co}$ represents the remnant cobalt concentration in aqueous solution after extraction of *N* stages.

3.3.2 Selection of phase modifier

Investigation into the cobalt extraction with N235 diluted by kerosene showed that the phase separation was somewhat difficult. Consequently, the alcohol with relatively long carbon chain or acidic organophosphoric compound was used as the phase modifier to promote the kinetics of phase separation. Using the organic phases (30% N235 + kerosene+(5%-40%) phase modifier) to contact the aqueous phase containing 23.96 g/L Co(II) and 260 g/L Cl<sup>-</sup> with 6 mol/L acidity, the effect of phase modifier on the cobalt extraction was studied at O/A=2. The results were compared graphically by plotting [Co]<sub>org</sub> versus [Co]<sub>raff</sub> as shown in Fig.1. It can be observed that the cobalt extraction increased with the

increase in TBP concentration in the organic phase. In contrast, a reverse trend occurred for isooctanol. For instance, the extraction rate for cobalt was 73% by using 20% TBP as phase modifier. However, under the identical experimental conditions, only 42% of cobalt was obtained using the same amount of isooctanol as modifier (Fig.1).



**Fig.1** Effect of modifier on metal extraction (Organic phase (volume fraction): 30% N235+70% (Phase modifier+ Kerosene))

It was also found that the amount of phase modifier affects the phase separation seriously. The phase separation became very difficult due to emulsion and cruds produced during the mixing when the content of TBP in the organic phase was less than 15%, or isooctanol less than 10% (indicated by double arrow in Fig.1). When the content of TBP was more than 15% or isooctanol more than 10%, the separation of the loaded organic phase from aqueous phase became very fast.

It can be concluded that the TBP enhanced the mass transfer rate thereby reducing the residence time required for mixing, and also modified the viscosity and the surface tension of extracting phase. As a result, a more disengagement complete phase and negligible entrainment achieved. Accordingly, were the composition of organic phase was determined as follows (volume fraction): 30% N235+20 %TBP+50% Kerosene. 3.3.3 Effect of HCl concentration on cobalt extraction

In this series of tests, by using the organic phase with the composition described above, cobalt was extracted from the aqueous chloride medium within the initial hydrochloric acid concentration range of 2–8 mol/L at A/O ratio of 2:1. It can be observed from Fig.2 that the extraction rate of the metals increased with the increase in HCl concentration of the solution. The percentage of cobalt extraction was only 23% and no nickel extraction was observed when the aqueous phase acidity was 2 mol/L. However, the percentages of cobalt and nickel extraction were respectively up to 95% and 6% at HCl concentration of 8 mol/L. This indicates that N235 is suitable for the separation of cobalt from nickel chloride solution, especially at high HCl concentration. In addition, the separation factors of cobalt over nickel also increased with the increase in HCl concentration and reached hundreds at  $[H^+]=8$  mol/L (Table 1), indicating a better separation of cobalt over nickel at higher HCl concentration. Conclusively, N235 was not very efficient for extracting Co(II) from acidic aqueous solutions at low acidity of 1 mol/L HCl, however, with increasing HCl molarities, a practically complete extraction could be achieved.

**Table 1** Extraction of Co and Ni and separation factors at selected HCl concentration values with N235 from aqueous solutions containing 23.96 g/L Co and 12.63 g/L Ni (O/A=2)

$x(\text{HCl})/(\text{m-I}^{-1})$	Extraction efficiency/%		$D_{\rm Co}$	$D_{ m Ni}$	$eta_{ m Co/Ni}$	
(III L )	Co	Ni				
2	23	_	0.298	_	_	
3	46	1	0.852	0.01	85	
4	63	1.5	1.704	0.015	112	
6	79	3	3.735	0.031	120	
7	88	4	7.378	0.042	176	
8	95	6	19.655	0.064	307	

It is well known that the optimization of the extraction operation can be interpreted as a compromise between maximum metal extraction and minimum consumption of active extractant. Low aqueous acidity facilitates the operation conditions but also makes the extracting costs increase for effective separation of metal. With the increase in HCl concentration, the improved behaviour of N235 could be due to the presence of Cl<sup>-</sup> assisting performance by varying the ion transfer and solvolytic reaction potentials of Co(II), as indicated by Eqn.(7). The underground mechanism may be due to the fact that cobalt cations react with Cl<sup>-</sup> to form the complex and then result in the co-ordinate chelate complex with extractant. Consequently, the increase of HCl concentration results in an increase in Co extraction, which is well consistent with the results presented in Fig.2. This demonstrates that the extraction of Co is predominantly governed by an anionic exchange reaction whereas that of Ni is not.

Iron, copper and chromium extraction in this series were negligible for their relatively low concentration in aqueous solution, and were not discussed in subsequent investigation.

3.3.4 Effect of chlorine ion concentration on cobalt extraction

By changing chlorine ion concentration with sodium chloride, the effect of chlorine ion concentration on the extraction of cobalt and nickel was studied in the range of 200–300 g/L. It was observed that the percentage of extraction increased considerably with the increase of chloride ion concentration (Fig.3). The increment was 48% to 93% for cobalt, which was remarkably higher than those of nickel (1%–7%). Nickel was almost not extracted when the chlorine ion concentration was less than 230 g/L. It is evident that the increase in chloride ion concentration only extremely facilitates the extraction of cobalt. In other words, the effect of chlorine ion concentration on cobalt extraction is consistent with that of HCl. Increase in the anion is



**Fig.2** Effect of HCl concentration on metal extraction (Organic phase: 30% N235+20%TBP+50%Kerosene (v/v))



**Fig.3** Effect of chlorine concentration on metal extraction (Organic phase: 30% N235+20%TBP+50%Kerosene (v/v))

helpful for both the formation and stability of  $\text{CoCl}_4^{2-}$ , which subsequently promotes the process as indicated by Eqn.(7). Most importantly, the enhanced chlorine ion concentration will be beneficial for the cobalt extraction at a relatively low acid concentration. Hence, it is feasible to separate cobalt from the nickel chloride solution by N235 extraction.

#### 3.3.5 Counter-current tests

For separation of Co from the Ni chloride solution using N235, the number of counter-current stages required was predicted using Eqn.(10). For O/A ratio of 2:1 and the acidity of 4 mol/L, it is calculated that 7 stages tests are necessary in order to achieve the extraction efficiency of 99.9% for cobalt. This was confirmed by the counter-current tests at the above conditions. Continuous counter-current tests were carried out in a 125 mL cone-shaped glass vessel containing 50 mL organic phase and 25 mL sample solution. The operating conditions for the extraction, scrubbing and stripping of cobalt from a nickel chloride solution were: organic phase containing 30% N235 + 20% TBP+ kerosene (volume fraction); liquor containing 23.96 g/L Co, 12.63 g/L Ni, 0.001 g/L Fe, 0.005 g/L Cr and 0.001 g/L Cu as chloride, with 4 mol/L HCl; extraction stages 7; scrubbing stages 3, with O/A ratio 10; stripping stages 3, with O/A ratio 5; temperature 35 °C; scrubbing feed 6 mol/L HCl solution; strip feed 0.01 mol/L HCl solution. Under those conditions, the raffinate contained 0.002 g/L Co, 12.57 g/L Ni, 0.000 6 g/L Fe, 0.003 g/L Cr, and 0.001 Cu. And the composition of stripped cobalt chloride solution was 115.78 g/L Co, 0.013 g/L Ni, 0.000 9 g/L Fe, 0.000 1 g/L Cr, and 0.003 g/L Cu.

The results indicate that it is possible to recovery cobalt and nickel efficiently from the chloride leaching liquor of alloy scraps. The main results are summarized in Table 2. It can be seen that the extraction rate of cobalt was 99.9% and the recovery of nickel was more than 99.7%. The very low concentrations of all metals in the final raffinate indicate that the present extraction system can be successfully used for recovery of Co and Ni in the chloride leaching solution of alloy scraps.

3.3.6 Recovery of cobalt and nickel

As indicated in Table 2, the nickel chloride and the stripped cobalt solution can be used for the further

Table	2 Main	stream	composition	and	recovery	yields

	Extraction			Scrubbing		Stripping			
Element	$\frac{\text{Feed}}{(\text{g} \cdot \text{L}^{-1})}$	$\begin{array}{c} \text{Raffinate/} \\ (g \cdot L^{-1}) \end{array}$	Loaded $organic/(g \cdot L^{-1})$	Efficiency/ %	Scrubbed organic/ $(g \cdot L^{-1})$	Efficiency/ %	Stripped organic/ $(g \cdot L^{-1})$	$\begin{array}{c} Strip\\ liquor/(g {\cdot} L^{-1}) \end{array}$	Efficiency/ %
Co	23.96	0.004	23.25	99.9	24.07	_	0.16	115.78	99.2
Ni	12.63	12.57	1.04	-	0.003	99.7	-	0.013	_

treatment. The nickel chloride solution obtained was condensed to form corresponding salt which can be used as ammonia absorbent or antiseptic. The cobalt chloride solution was contacted with activated carbon powder and then used to produce cathode cobalt for electrodeposition. The purity of resulting cathode cobalt was more than 99.9%. The chlorine gas evolved from anode was collected by a special designed instrument in the present study.

The overall recovery for Ni and Co was 95% and 60%, respectively. Based on the present study, a proposed flow-sheet for recovery of nickel and cobalt is presented in Fig.4.



Fig.4 Proposed flow-sheet for recovery of nickel and cobalt from alloy scraps by hydrochloric acid leaching and solvent extraction

# **4** Conclusions

1) The leaching efficiency for Co and Ni was 62% and 96%, respectively, under the conditions of the L/S ratio of 10:1 with 6 mol/L hydrochloric acid leaching at 95  $^{\circ}$ C for 3 h.

2) The copper in the leaching liquor under the pH value of 2.0 was deposited at 80  $^{\circ}$ C by using iron scraps, and the removal was over 99.7%. Iron and chromium were removed from the leaching liquor by formation of

goethite precipitate and/or hydroxide. The preferred conditions for the removal of iron were pH=2.0 at 90  $^{\circ}$ C and the removing rate was about 99.99%, while for chromium the conditions were pH=4.0 at 70  $^{\circ}$ C and the removing rate was 99.97%.

3) Cobalt and nickel in chloride solution can be effectively separated by choosing a suitable extractant system and controlling chlorine ions and HCl concentrations of aqueous phase. Cobalt of 99.9% can be extracted using the organic phase of 30% N235+50% kerosene +20% TBP (volume fraction) in 7 stages with A/O of 2. Stripping of cobalt was achieved effectively using diluted HCl solutions with the efficiency of 99.2%.

4) The overall recoveries for Ni and Co were 95% and 60%, respectively.

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