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Extraction studies of cobalt (Ⅱ) and nickel (Ⅱ) from chloride solution using PC88A

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Abstract: Solvent extraction study of cobalt and nickel were carried out from a chloride solution with a high ratio of Co to Ni using the sodium salt of PC88A as extractant diluted in kerosene. The solution was generated in batches by leaching a tungsten super alloy scraps. The results show that extraction rate of metal ions increases with increase of aqueous phase pH value. The $pH_{0.5}$ value difference of 1.40 with PC88A indicates the possible separation of cobalt and nickel. Increase of the concentration of the solvent can enhance the percentage extraction of both metal ions. Improvement of temperature is beneficial to extraction separation of cobalt and nickel. Extraction and stripping processes were also studied in a cross-current solvent extraction unit and the results were also given.

Key words: cobalt; nickel; solvent extraction; PC-88A

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1 Introduction

Since the first commercial process using di-2-ethyl hexyl phosphoric acid (D2EHPA) was developed by RITCEY et al[1], the organophosphorus extractants have been proved to be primary solvents for separation cobalt from nickel in acidic media solution[2−5]. 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester was developed and marketed as PC-88A by the Daihachi Chemical Industry, and as SME 418 by Shell used by the Nippon Mining[6−8]. Under the same extraction condition, this reagent gives a Co/Ni separation factor about 200 times greater than that of D2EHPA. A similar solvent with PC-88A, named as P507, was produced in early 1970s and found commercial application of Co/Ni separation in one Chinese metallurgical enterprises in 1981[9]. Several phosphinic acids, such as Cyanex272, Cyanex301 and Cyanex302, were developed by Cytec Chemicals. Cyanex272 is being used in the Outokumpu Plant in Finland[10].

A survey of literature has reviewed the cobalt-nickel separation factors from sulphate media using phosphoric, phosphonic and phosphinic acids[11]. The separation ability of cobalt and nickel increases in the order phosphinic＞phosphonic＞phosphoric acid due to the increasing stabilization of tetrahedral coordination compound of cobalt with the extractant in the organic phase, because the tetrahedral compound is more stable than the octahedral one. Out of the three types of extractants, Co-Ni separation factor of phosphoric acid, such as D2EHPA, is usually below 10. Cyanex solvents are usually most expensive in despite of most selective. Therefore, PC-88A was chosen as extractant for separation cobalt from nickel in this study. Recently, PC88-A has been reported to be rather effective in separating cobalt from nickel in sulphate media.

Much basic research has been carried out on the extraction of cobalt and nickel from sulphate solution. FUJIMOTO et al[12] have patented a process for cobalt-nickel separation using PC-88A. The date shows 45.8 g/L cobalt extraction at pH 4.5 from a solution containing 30 g/L each of Co and Ni using 20%(volume fraction, the same below if not mentioned) PC-88A. DEVI et al[13] studied the Co-Ni separation effects of D2EHPA, PC-88A and Cyanex272 from a sulphate solution containing 0.01 mol/L metal ions each and 0.1 mol/L Na_2SO_4. In the case of extractions with 0.05 mol/L

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Na-PC88A, the separation factor can reach over 1 000 at equilibrium pH range of 5.75−6.2, but was extremely pH sensitive.

However, studies concerning extraction separation of cobalt and nickel using PC-88A from chloride media are little. SARANGI et al[11] indicated that the Co-Ni separation factor can reach 37−72 at equilibrium pH range of 5.5−5.7 using different concentrations of PC-88A from a chloride solution. Separation factors obtained with binary mixture of extractants gave a value 5.6 times higher in the case of Na-PC88A as extractant and Na-Cyanex 272 as synergist than that for Na-Cyanex 272 alone. LIU et al[9] reported Co-Ni separation using P507 as extractant in sulfate and chloride solution. It was proved that P507 (PC-88A) has good chemical stability, low toxicity and low solubility in water and can be applicable to the effective recovery of cobalt from various sulfate and chloride solutions with wider range of Ni/Co ratios.

In the present study, the extraction and separation of cobalt and nickel from the chloride leach solution of a super alloy scraps using the sodium salt of PC-88A were reported. The effect of equilibrium pH, extractant concentration, temperature, phase ratio on extraction of cobalt and nickel were studied in addition to stripping and counter-current extraction studies.

2 Experimental

2.1 Sample solution

A tungsten alloy scrap was roasted together with air and Na_2CO_3, and then dissolved by caustic alkali solution. The tungsten bearing solution, also containing V, Mo and some impurities, was then delivered to production of APT or WC. This study has been completely reported in LUO's other papers[14−16]. The leach residue containing Co and Ni, also Ta, Nb, Fe, was further dissolved by a 4 mol/L HCl solution at 80 ℃ for 2 h. Co, Ni, and Fe can get into the leach solution and leave other metal values in residue. This chloride leach solution in this study contained 56.65 g/L Co, 151.50 mg/L Ni and 364.10 mg/L Fe. Purification of the solution is necessary before it is contacted with solvent, because iron value can be extracted by PC88A previous cobalt and nickel values. Over 99% iron values, which exist in the solution as ferric ions state, can be removed from the leach solution only by raising pH from below 1 to 3.5−5.0. The purified chloride solution contained 56.78 g/L Co, 140.78 mg/L Ni and 1.2 mg/L Fe.

2.2 Reagents and apparatus

The commercial solvent, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), was supplied by Daihachi Chemical Industry Co Ltd, and used as such without any purification. Distilled kerosene (bp165-190 ℃) was used as the diluent. The solvent, sodium salt of PC-88A, was prepared (60% neutral) by adding the requisite quantities of a concentrate and standard NaOH solution and mixing the phases intimately to form a single phase.

ICP spectrophotometer (SPS3000) was used for analysis of metal values in aqueous solution and a thermostat with a stirrer was used for the study of temperature effect.

2.3 General extraction procedure

For the extraction experiments of single stage, the chloride solution was primarily diluted to 10 times for a suitable extraction concentration. Ten milliliters of this diluted solution containing metal ions were equilibrated with a certain volume of solvent by mechanical shaking in a 100 mL separating funnel for 5−10 min. Initial experiments on effect of time on metal extraction indicated that 2−3 min was sufficient to reach equilibrium reaction. The initial pH of the solution was adjusted to a desired value by adding dilute HCl or NaOH solution before the equilibrations. After phase separation, the equilibrium pH of raffinate was measured. The raffinates were diluted as required concentration and analysis of the metal values was carried out by ICP. The stripping studies of cobalt and nickel were carried out with diluted HCl solution. The concentrations of metal ions in the organic phase were calculated from mass balance.

The cross-current extraction tests were carried out in a thermostat (±0.5 ℃) with magnetic stirring for 10 min. The raffinate was always contacted with a fresh organic phase in the next extraction stage. The loaded organic solution were collected and contacted with HCl solution for stripping metal values. The equilibrium pH of each stage was measured. Analysis of metal values in the final raffinate and striping solution were carried out by ICP.

3 Results and discussion

PC-88A is usually thought as a weak organic acid, which can extract metallic ions by cation exchange. Its total extraction reaction can be expressed as Eqn.(1) according to the study of ZHANG[17]:

$$n\overline{\mathrm{HR}} + \mathrm{M}^{n+} = \overline{\mathrm{MR}}_n + n\mathrm{H}^+ \tag{1}$$

where $\overline{\mathrm{HR}}$ is PC-88A and M^{n+} is metallic ion in aqueous solution. The extraction equilibrium constant (K) of the reaction can be written as

$$K=\frac{[\overline{\mathrm{MR}}_n]\cdot a_{\mathrm{H^+}}^n}{[\overline{\mathrm{HR}}]^n\cdot[\mathrm{M}^{n+}]} \tag{2}$$

where $\overline{\mathrm{MR}}_n$ stands for extracted compound and $a_{\mathrm{H^+}}$ means activity of $\mathrm{H^+}$ in aqueous phase. Therefore, distribution ratio of metal (D) can be expressed as

$$D=\frac{[\overline{\mathrm{MR}}_n]}{[\mathrm{M}^{n+}]}=K\times\frac{[\overline{\mathrm{HR}}]^n}{a_{\mathrm{H^+}}^n} \tag{3}$$

Then

$$\begin{aligned}\lg D&=\lg K+n\lg[\overline{\mathrm{HR}}]-n\lg a_{\mathrm{H^+}}\\&=\lg K+n\lg[\overline{\mathrm{HR}}]+n\mathrm{pH}\end{aligned} \tag{4}$$

The value D under different pH values can be calculated by Eqns.(3) or (4). In the meantime, we can find from Eqn.(2) and Eqn.(3) that influence factors on extraction are acidity of solvent, solubility of solvent and extracted compound, concentration of free solvent, acidity of aqueous phase and others which can affect stability of extracted compound.

The separation factor between cobalt and nickel can be calculated by the ratio of the distribution ratios of two metals.

3.1 Effect of equilibrium pH

The extraction of cobalt and nickel from the chloride solution was studied using the PC-88A within the pH range 3.0−6.0 corresponding to the change in the equilibrium pH in the range 3.0−7.0, respectively. As shown in Fig.1 that percentage extraction increases with increase in the equilibrium pH of the aqueous phase. The $\mathrm{pH}_{0.5}$ values are 3.39 and 4.58 for cobalt and nickel, respectively, which indicate that cobalt is extracted at lower pH value than nickel. The difference of $\mathrm{pH}_{0.5}$ (1.4) states that it is possible to separate cobalt from nickel in a suitable pH range. The observed $\mathrm{pH}_{0.5}$ difference value of 1.4 is slighted different from the reported value from sulphate solution.

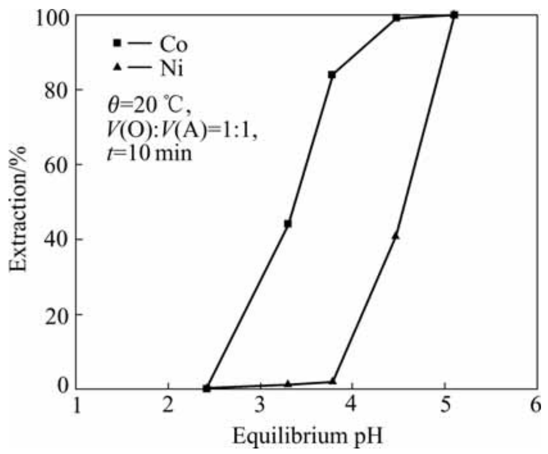

Fig.1 Effects of equilibrium pH on extraction of cobalt and nickel by 20%(volume fraction) PC-88A in kerosene

As shown in Fig.2 that the separation factor (Co/Ni) increases as pH value increases from 2.42 to 4.48, and then decreases over pH of 4.48. This shows almost same trend with one in sulfate solution.

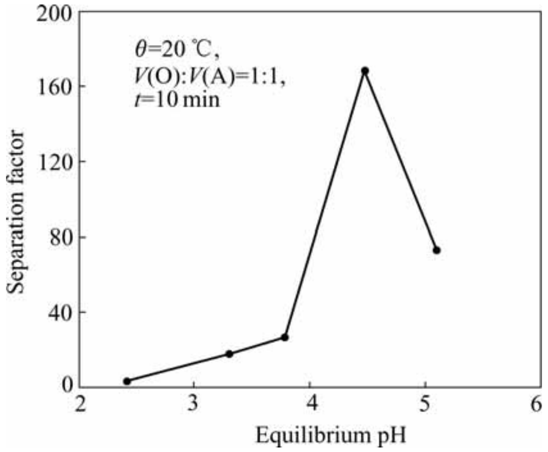

Fig.2 Effects of equilibrium pH on separation factor of cobalt and nickel by 20% PC-88A in kerosene

3.2 Effect of temperature

To study the effect of temperature on extraction of cobalt and nickel, experiments were carried out in a thermostat (±0.1 ℃) with mechanical stirring for 10 min. Temperature varies in the range 20-80℃. It can be observed from Fig.3 that for nickel, percentage extraction decreases with increase of temperature throughout the temperature range. In the case of cobalt, percentage extraction rises up to 35 ℃ and reaches an extraction plateau when the temperature is higher than 35 ℃.

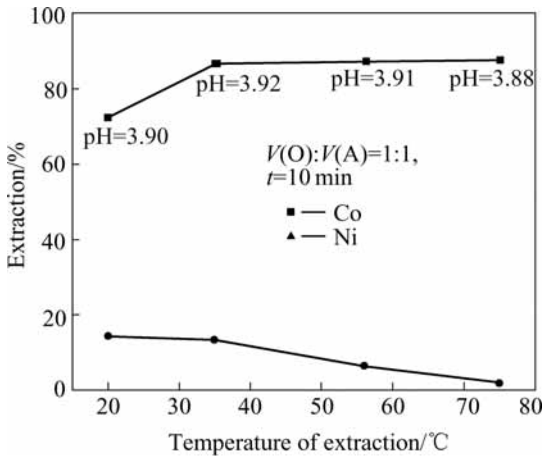

Fig.3 Effects of temperature on extraction of cobalt and nickel by 20% PC-88A in kerosene

Increase of temperature can improve reaction dynamic, benefiting extraction of metal ions, conversely decrease stability of the loaded complex. LIU et al[9] stated that the viscosity of PC-88A complex (Co) was much higher than that of PC-88A complex (Ni). The result also shows that the viscosity of Co-loaded complex rises sharply to over 30 centipoise when the cobalt concentrate in organic phase goes up to 18 g/L. In the case of this study, sample solution contains high concentration of cobalt and low concentration of nickel, so temperature ascent increases extraction of cobalt, whereas decreases extraction of nickel. Fig.4 shows that separation factor (Co/Ni) increases with temperature ascent throughout the temperature range of 20−80 ℃.

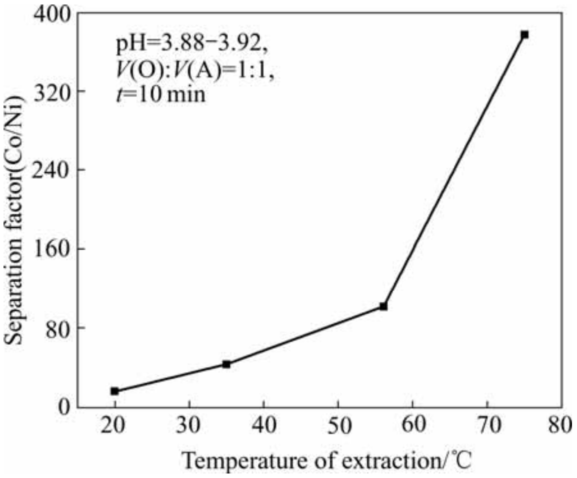

Fig.4 Effects of temperature on separation factor (Co/Ni) by 20% PC-88A in kerosene

3.3 Effect of concentration of solvent in organic phase

The effect of the solvent concentration in organic phase was investigated by varying the concentration of solvent from 10% to 25% in initial pH of 5.2 corresponding to the change in the equilibrium pH in the range of 4.20−4.28. The extraction separation factor is shown in Fig.5. Percentage extraction of both cobalt and nickel increases throughout solvent concentration range of 10%−25%. However, separation factor (Co/Ni) increases from 28.45 to 118.61 as solvent concentration rises from 10% to 20%, and decreases above the concentration of 20%.

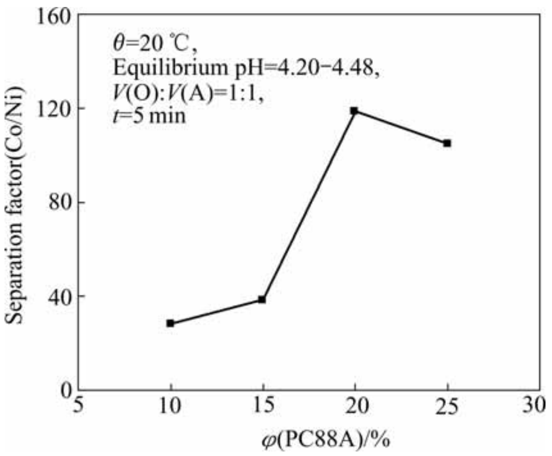

Fig.5 Effects of solvent concentration in organic phase on extraction of cobalt and nickel

3.4 Effect of phase ratio (O/A)

The effect of the organic to aqueous volume ratio (O/A) was investigated by varying the O/A ratio from 1/3 to 3/1 keeping the total volume of phase constant. The results are shown in Fig.6.

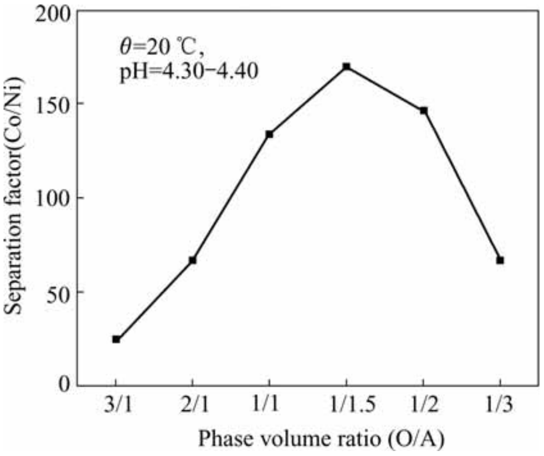

Fig.6 Effect of phase volume ratio (O/A) on separation factor (Co/Ni) 20% PC-88A in kerosene

The separation factor increases from 24.58 to 169.37 as the phase volume ratio (O/A) descends from 3/1 to 1/1, but decreases from 169.37 to 67.16 as the phase volume ratio further drops to 1/3. The highest separation factor is achieved at O/A ratio of 1.5. It is also found that when equilibrium pH is controlled in lower pH range of 2.92−3.40, separation factor decreases from 77.18 to 5.09 as phase ratio (O/A) increases from 1/3 to 2/1. At low pH range below 3.5, nickel extraction is usually below 2%, as it is beneficial to obtaining pure cobalt loaded complex.

3.5 Stripping procedure

A loaded organic solution containing 6.21 g/L Co and 1.20 mg/L Ni was employed for stripping tests. The organic solution was obtained by contacting with the feed solution using 20% PC88A in kerosene as extractant at O/A ratio of 1/1 and 20 ℃ for 5 min. The results reveal that when contacted with a 5%(mass fraction) HCl solution at phase ratio (A/O) of 1/1, 93.74% Co and 99.5% nickel are stripped from the loaded organic phase. Over 99% stripping of Co and Ni values can be obtained when contacted with a 10%(mass fraction) HCl solution at phase ratio (A/O) of 1/1. At a phase ratio (A/O) of 1/2, a 5%(mass fraction) HCl solution can scrub 84.21% Co and 98.49% nickel. Therefore, it is easy to strip metal values from the loaded PC-88A solution.

3.6 Simulation cross-current tests

Two kinds of solutions containing different concentrations of metal ions were in the cross-current tests in order to determine the adaptability of PC-88A for different concentration solutions. One contains 7.92 g/L of cobalt and 13.7 mg/L nickel. Another one contains 54.879 g/L of cobalt and 137.213 mg/L nickel. In the case of the first solution, two stages of extraction and two stages of stripping were employed using 20% PC88A in kerosene as extractant and a 5% (mass fraction) HCl solution as stripping solution. In the case of the second solution, five stages of extraction and one stage of stripping were employed using 20% PC88A in kerosene as extractant and a 12.5%(mass fraction) HCl solution as stripping solution. The organic phase solutions were collected and contacted with a chloride solution for one stage or two stages. Test conditions and results are shown in Table 1 and Table 2, respectively.

For the first solution, extraction tests were carried out in a low pH range of 3.21−3.50 and phase volume ratio of 1/1 in order to avoid extracting nickel. Two stages extraction gives 96.72% cobalt extraction and below 2% of nickel extraction. Co in the raffinate is 0.236 g/L and Ni concentration almost has no change. A 5%(mass fraction) HCl solution can achieve to strip 97.05% of Co and 99.95% of Ni from the loaded organic phase at two stages of stripping.

For the second solution, extraction tests were carried out at a pH range of 4.20−4.80 and phase ratio of 1.5/1 in order to reduce extraction stages. Five stages of extraction give 99.69% cobalt extraction and 3.48% nickel extraction. Co in the raffinate is 0.17 g/L, while there is a little decrease for the Ni concentration. 97.61% Co and 99.86% Ni can be stripped from the loaded organic phase by a 12.5%(mass fraction) HCl solution at only one stage of stripping. It is obvious that PC-88A can be employed in effect extraction separation of cobalt and nickel from a chloride solution with different concentrations of metals.

4 Conclusions

PC-88A has been proved to be an effect solvent for extraction separation of cobalt and nickel from a chloride solution. Extraction experiments of single stage are conducted to determine influence effects of the chosen factors which are equilibrium pH, solvent concentration, temperature and phase ratio. The single extraction tests show that separation factor (Co/Ni) can reach over 350 at equilibrium pH 3.8−4.5, over 70 ℃ and a phase ratio (O/A) of 1/1−1.5/1 with 20% PC88A in kerosene as solvent. The simulation cross-current tests further verifies the adaptability of PC-88A for extraction separation cobalt and nickel from chloride solution with different concentrations of cobalt and nickel.

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Table 1 Test conditions of cross-current extraction

Solution	Stage	Extraction condition				Stripping condition		
		pH	θ/℃	V(O)/V(A)	t/min	θ/℃	V(A)/V(O)	t/min
Diluted solution	1	3.21	75	1/1	10	20	1/2	3
	2	3.50	75	1/1	10	20	1/2	3
Concentrated solution	1	4.80	75	1.5/1	10	20	1/3	10
	2	4.74	75	1.5/1	10			
	3	4.55	75	1.5/1	10			
	4	4.38	75	1.5/1	10			
	5	4.20	75	1.5/1	10			

Table 2 Test results of cross-current extraction

Item	Diluted solution		Concentrated solution	
	ρ(Co)/(g·L^{-1})	ρ(Ni)/(g·L^{-1})	ρ(Co)/(g·L^{-1})	ρ(Ni)/(g·L^{-1})
Original solution	7.920	13.703	54.879	137.213
Final raffinate	0.236	12.229	0.17	132.45
Final loaded organic phase	7.660	0.251	7.29	0.637
Final stripped solution	7.434	0.502	21.36	1.907
Final extraction/%	96.72	1.83	99.69	3.48
Final stripping/%	97.05	99.95	97.61	99.86

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