[Article ID] 1003- 6326(2001)05- 0803- 03

Separation of nickel, cobalt and copper by solvent extraction with P204①

QIAN Dong(钱 东), WANG Kai-yi(王开毅), CAI Chun-lin(蔡春林), PAN Chun-yue(潘春跃), TANG You-gen(唐有根), JIANG Jin-zhi(蒋金枝)
(College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, P. R. China)

[Abstract] Nickel, cobalt and copper were separated by solvent extraction with P204. The experimental results show that $[Co(NH_3)_6]^{3+}$ is an inert complex in extraction kinetics, therefore cobalt can be separated from nickel and copper by non-equilibrium solvent extraction. Under the conditions of temperature 25 ℃, contact time of two phases 10 min, phase ratio 1∶1, aqueous pH 10.10 and concentration of P204 20%, $[Co(NH_3)_6]^{3+}$ is hardly extracted by P204, while the percentage extractions of nickel and copper are 79.3% and 93.9% respectively. Nickel and copper are separated by equilibrium solvent extraction with P204. Under the conditions of temperature 25 ℃, contact time of two phases 1 min, phase ratio 1∶1, equilibrium pH 4.01 and concentration of P204 20%, the separation factor of copper and nickel is 216.

[Key words] non-equilibrium solvent extraction; equilibrium solvent extraction; nickel; cobalt; copper; di(2-ethylhexyl) phosphate

[CLC number] TQ 028.32; TF 804.2 **[Document code]** A

1 INTRODUCTION

Solvent extraction is generally known as a kind of equilibrium solvent extraction in thermodynamics. Non-equilibrium solvent extraction is a new kind of solvent extraction[1], which makes use of the difference of extraction speed in kinetics to separate materials such as rare metals[2~4] and rare earth metals[5,6].

The separation factor for extraction of cobalt and nickel with di(2-ethylhexyl)phosphate (P204) in sulphuric acid solution is generally below 20, therefore P204 is considered to be unfit for the separation of cobalt and nickel[7,8]. Accordingly, P204 is also an unfit extractant for the separation of nickel, cobalt and copper that people has paid attention to in hydrometallurgy since 1960s.

However, it was reported that $[Co(NH_3)_6]^{3+}$ in ammoniacal solution is an inert complex in kinetics and its extraction speed with β-hydroxyoxime N_{510}[9] or N_{530}[10] is very slow. In this paper, it was found that the extraction speed of $[Co(NH_3)_6]^{3+}$ with P204 is also very slow. So we can oxidize Co(Ⅱ) to Co(Ⅲ) in ammoniacal solution and separate cobalt from nickel and copper by non-equilibrium solvent extraction, then separate nickel and copper by equilibrium solvent extraction with P204.

2 EXPERIMENTAL

Oxidizer $(NH_4)_2S_2O_8$ was added into a mixed solution of ammoniacal sulfate of nickel, cobalt and copper (the mole ratio Ni∶Co∶Cu = 12.2∶2.4∶1). The solution was treated properly so that Co(Ⅱ) could be oxidized to Co(Ⅲ) completely and then extracted with saponified P204 to separate Co(Ⅲ) from Ni(Ⅱ) and Cu(Ⅱ). Ni(Ⅱ) and Cu(Ⅱ) stripped by solution of sulphuric acid were separated by solvent extraction with saponified P204 under proper conditions. The metal contents in the raffinate were analyzed by titration, the metal contents in the organic phase were dertermined by subtraction.

3 RESULTS AND DISCUSSION

3.1 Kinetics on extraction of Co(Ⅲ) with P204

Co(Ⅱ) in sulphuric acid solution is more easily extracted with P204 than Ni(Ⅱ)[11]. However, when Co(Ⅱ) is oxidized to Co(Ⅲ) in ammoniacal solution, the extraction speed of Co(Ⅲ) is very slow. The extraction of Co(Ⅲ) ($[Co(NH_3)_6]^{3+}$) with P204 has been investigated and the effect of contact time of two phases on the percentage extraction of Co(Ⅲ) is shown in Table 1.

From Table 1, it can be seen that the extraction of Co(Ⅲ) ($[Co(NH_3)_6]^{3+}$) with P204 does not achieve extraction equilibrium even after 12 h extraction, which shows that $[Co(NH_3)_6]^{3+}$ is an inert complex in extraction kinetics. This may be due to the difference between the stability constants of $[Co(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$ ($\lg K_{[Co(NH_3)_6]^{3+}} = 35.2$, and $\lg K_{[Co(NH_3)_6]^{2+}} = 5.11$[12]; where K

① [Foundation item] Project (99JJY20010) supported by the Natural Science Foundation of Hunan Province
[Received date] 2000- 10- 26; [Accepted date] 2000- 12- 25

Table 1 Effect of contact time of two phases on percentage extraction of Co(Ⅲ)

Contact time /min	Distribution ratio	Percentage extraction/%
1	0.0395	3.78
2	0.0417	4.00
5	0.0437	4.18
10	0.0438	4.20
15	0.0448	4.29
60	0.0695	6.50
120	0.0893	8.20
240	0.110	9.91
480	0.118	10.6
720	0.121	10.8

Extraction temperature 25 ℃; phase ratio 1:1; aqueous pH 10.13; concentration of P204 20%

symbolizes the stability constant of complex). So we can separate cobalt from nickel and copper by non-equilibrium solvent extraction.

3.2 Separation of cobalt from nickel and copper

The effects of aqueous pH and contact time of two phases on the percentage extraction of Ni(Ⅱ), Co(Ⅲ) and Cu(Ⅱ) are shown in Table 2 and Table 3 respectively.

From Table 2, Co(Ⅲ) is hardly extracted with P204 when the aqueous pH is 10.10, while the percentage extractions of Ni(Ⅱ) and Cu(Ⅱ) are 79.3% and 93.9% respectively. Thus, we can separate cobalt from nickel and copper by non-equilibrium solvent extraction when the aqueous pH is above 10.10.

Table 3 shows that the extraction equilibriums of Cu(Ⅱ) and Ni(Ⅱ) are achieved after extracting 1 min and 10 min respectively, while the percentage extraction of Co(Ⅲ) is approximately 0.504% after 15 min extraction. So the contact time of two phases is selected to be about 10 min to separate cobalt from nickel and copper by non-equilibrium solvent extraction with P204.

Table 2 Effect of aqueous pH on percentage extraction of Ni(Ⅱ), Co(Ⅲ) and Cu(Ⅱ)

pH	Percentage extraction/%		
	Co	Ni	Cu
8.90	1.81	87.1	95.3
9.61	1.10	83.2	94.2
10.10	≈0	79.3	93.9

Extraction temperature 25 ℃; contact time of two phases 10 min; phase ratio 1:1; concentration of P204 20%

Table 3 Effect of contact time of two phases on percentage extraction of Ni(Ⅱ), Co(Ⅲ) and Cu(Ⅱ)

Contact time/min	Percentage extraction/%		
	Co	Ni	Cu
1	≈0	75.0	93.4
2	≈0	77.6	93.5
5	≈0	78.7	93.6
10	≈0	79.2	93.6
15	0.504	79.1	93.6

Extraction temperature 25 ℃; phase ratio 1:1; aqueous pH 10.01; concentration of P204 20%

3.3 Separation of nickel and copper

Nickel and copper are separated by equilibrium solvent extraction with P204 in experiments. The effects of equilibrium pH, phase ratio, extraction temperature and contact time of two phases on the separation of Ni(Ⅱ) and Cu(Ⅱ) are shown in Table 4 ~ 7.

Table 4 Effect of equilibrium pH on separation of Ni(Ⅱ) and Cu(Ⅱ)

pH	Percentage extraction/%		Separation factor
	Cu	Ni	
5.90	99.0	68.1	46.6
5.34	98.3	49.3	59.8
4.62	97.8	24.6	136
3.96	93.2	7.40	172
3.41	85.9	4.30	136

Extraction temperature 25 ℃; contact time of two phases 1 min; phase ratio 1:1; concentration of P204 20%

Table 5 Effect of phase ratio on separation of Ni(Ⅱ) and Cu(Ⅱ)

Phase ratio (O/W)	Percentage extraction/%		Separation factor
	Cu	Ni	
1:2	97.4	23.0	125
1:1	97.8	24.6	136
2:1	98.1	32.0	109

Extraction temperature 25 ℃; contact time of two phases 1 min; equilibrium pH 4.62; concentration of P204 20%

Table 6 Effect of extraction temperature on separation of Ni(Ⅱ) and Cu(Ⅱ)

Extraction temperature/℃	Percentage extraction/%		Separation factor
	Cu	Ni	
25	97.8	24.6	136
35	97.9	28.4	117
45	98.0	32.0	104
55	98.1	35.2	95.0
65	98.1	39.4	83.9

Contact time of two phases 1 min; phase ratio 1:1; equilibrium pH 4.62; concentration of P204 20%

Table 7 Effect of contact time of two phases on separation of Ni(Ⅱ) and Cu(Ⅱ)

Contact time/s	Percentage extraction/ %		Separation factor
	Cu	Ni	
20	93.2	6.79	188
30	94.2	7.20	195
60	94.8	7.78	216
120	94.8	7.80	215

Extraction temperature 25 ℃ ; phase ratio 1∶1; equilibrium pH 4.01; concentration of P204 20%

From Table 4, it is shown that the percentage extractions of Ni(Ⅱ) and Cu(Ⅱ) decrease with decreasing equilibrium pH. When the equilibrium pH is about 3.96, the separation factor of Cu(Ⅱ) and Ni(Ⅱ) is the biggest.

From Table 5, it can be seen that the effect of phase ratio on the percentage extraction of Cu(Ⅱ) is smaller, while that of Ni(Ⅱ) is bigger. When the phase ratio is about 1∶1, the separation factor of Cu(Ⅱ) and Ni(Ⅱ) is the biggest.

From Table 6, it is concluded that the percentage extractions of Ni(Ⅱ) and Cu(Ⅱ) increase with the increase of extraction temperature. But the separation factor of Cu(Ⅱ) and Ni(Ⅱ) is the biggest when extraction temperature is about 25 ℃.

Table 7 shows that the extraction equilibriums of Cu(Ⅱ) and Ni(Ⅱ) are achieved after 1 min extraction and the separation factor of Cu(Ⅱ) and Ni(Ⅱ) is 216 when equilibrium pH is 4.01.

4 CONCLUSIONS

1) P204 is a cheap and facile extractant. Separation of nickel, cobalt and copper using P204 as extractant has good prospect.

2) When Co(Ⅱ) is oxidized to Co(Ⅲ) in ammoniacal solution, its extraction speed is very slow, which shows that $[Co(NH_3)_6]^{3+}$ is an inert complex in extraction kinetics. Therefore, cobalt can be separated from nickel and copper by non-equilibrium solvent extraction. Under the conditions of extraction temperature 25 ℃, contact time of two phases 10 min, phase ratio 1∶1, aqueous pH 10.10 and concentration of P204 20%, Co(Ⅲ) is hardly extracted with P204, while the percentage extractions of Ni(Ⅱ) and Cu(Ⅱ) are 79.3% and 93.9% respectively.

3) Nickel and copper are separated by equilibrium solvent extraction with P204. Under the conditions of temperature 25 ℃, contact time of two phases 1 min, phase ratio 1∶1, equilibrium pH 4.01 and concentration of P204 20%, the separation factor of Cu(Ⅱ) and Ni(Ⅱ) is 216.

[REFERENCES]

[1] MA Rong-jun. New development of solvent extraction—non-equilibrium solvent extraction [J]. Nonferrous Metals (Extractive Metallurgy), (in Chinese), 1985(5): 38 - 41.

[2] Rodriguez M A, Cote G, Bauer D. Recovery of indium (Ⅲ) from mixed hydrochloric acid—sulphuric acid media by solvent extraction with Cyanex 301 [J]. Sol Extr Ion Exch, 1992, 10(5): 811 - 827.

[3] Benedetto J S, Soares M L L, Grewal I, et al. Recovery of rare metals with a new organophosphorus extraction [J]. Sep Sci Technol, 1995, 30(17): 3339 - 3349.

[4] ZHANG Cheng-qun, ZHOU Jia-zhen, ZHOU Xiu-zhu, et al. Study on non-equilibrium extraction separating In and Fe [J]. Nonferrous Metals, (in Chinese), 1995, 47 (1): 78 - 82.

[5] Minagawa Y, Kaneko T, Yajima F, et al. Selective extraction of yttrium ions [P]. US4104358, 1978.

[6] Abdul A, Hideto M, Masaaki T. Equilibrium and non-equilibrium extraction separation of rare earth metals in presence of diethyllenetriaminepentaacetic acid in aqueous phase [J]. J Chem Eng Jpn, 1995, 28(5): 601 - 608.

[7] General Research Institute for Mining and Metallurgy of Beijing, Beijing University, Shanghai Institute of Organic Chemistry of the Chinese Academy of Sciences, et al. Separation of cobalt and nickel by extraction with P507 [J]. Nonferrous Metals (Extractive Metallurgy), (in Chinese), 1981(1): 25 - 29.

[8] ZHU Tun. The Chemistry and application of separation cobalt and nickel by extraction [J]. Nonferrous Metals (Extractive Metallurgy), (in Chinese), 1986(4): 28 - 32.

[9] SHU Wan-yin, YU Hai-ya, JIANG Man-song. Study on the extractive properties of copper, iron, cobalt and nickel by N510 [J]. Nonferrous Metallurgy, (in Chinese), 1984(2): 39 - 41.

[10] WANG Kai-yi, SHU Wan-yin. Separation of cobalt and nickel from ammoniacal solution by solvent extraction with β-hydroxyoxime N530 as extractant [J]. J Cent - South Inst Min Metall, 1988, 19(4): 467 - 674.

[11] WANG Kai-yi, CHENG Ben-cheng, SHU Wan-yin. Solvent Extraction Chemistry, (in Chinese) [M]. Changsha: Central South University of Technology Press, 1991. 76.

[12] YAO Yun-bin, XIE Tao, GAO Ying-min. Handbook of Chemistry and Physics, (in Chinese) [M]. Shanghai: Shanghai Science and Technology Press, 1985. 816.

(Edited by YUAN Sai-qian)