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Yukio Nagaosa[a]; Yao Binghua[a]
[a] FACULTY OF ENGINEERING, FUKUI UNIVERSITY BUNKYO, FUKUI, JAPAN

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Recovery and Separation of Lanthanum(III), Aluminum(III), Cobalt(II), and Nickel(II) from Misch Metal by Solvent Extraction Using Bis(2-ethylhexyl)phosphinic Acid

YUKIO NAGAOSA* and YAO BINGHUA
FACULTY OF ENGINEERING
FUKUI UNIVERSITY
BUNKYO, FUKUI 910, JAPAN

ABSTRACT

This paper describes use of bis(2-ethylhexyl)phosphinic acid as a reagent for extraction and mutual separation of lanthanum(III), aluminum(III), cobalt(II), and nickel(II) in 1.0 mol/L sodium nitrate. The extraction and stripping behavior of the four metal ions has been investigated using the extractant in Solvesso #150 as a diluent. The mutual separation and recovery of the metal ions from their mixtures has been tested by multistage extraction with a conventional separator funnel. A set of separation schemes has also been proposed for a continuous countercurrent multistage extraction which is comprised of ten extraction stages, four scrubbing stages, and seven stripping stages. Lanthanum(III) and aluminum(III) are coextracted but separated by selective stripping into different concentrations of hydrochloric acid. Cobalt(II) can be extracted with the nickel(II)-preloaded extractant solution, whereas nickel(II) remains in the aqueous phase. The successful separation of these metal ions from a misch metal-simulated sample is presented.

INTRODUCTION

Recently, rare-earth metals have been increasingly used in material industries of high-temperature superconductors and secondary batteries (1–5). Among the metals, lanthanum is an important element of misch

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* To whom correspondence should be addressed.

metals and hydrogen-absorbing alloys. However, very few papers report about the separation and recovery of rare metals that are considered to be useful for recycling resources from waste materials.

Many fundamental studies have been reported on the extraction of rare-earth metals with such organophosphorus acids as bis(2-ethylhexyl)phosphoric acid (DP-8R) and 2-ethylhexyl-2-ethylhexylphosphonic acid (PC-88A) as selective chelating extractants (6–10). It has been known that the selectivity of DP-8R is superior to that of PC-88A for separation of light rare-earth metals from heavy ones. In contrast, PC-88A is more useful for the separation of heavy metals from light ones than DP-8R (11). Dialkylphosphinic acids have also been studied for the separation of cobalt and nickel and rare-earth metals. Bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) is one of the most used phosphinic acids commercially available.

In a previous paper we examined the basic physicochemical properties of bis(2-ethylhexyl)phosphinic acid (referred to as PIA-8) as the extractant for the solvent extraction of light rare-earth and transition metals (12). The purpose of the present paper is to mutually separate lanthanum(III), aluminum(III)), cobalt(II), and nickel(II) using PIA-8 in Solvesso #150. We first examined the extraction and stripping percentages of these metal ions with the extractant solution in order to attempt continuous multistage extraction. A systematic scheme for the separation of a mixture of the four metal ions by a continuous countercurrent multistage extraction was then developed. The presented processes include coextraction of lanthanum(III) and aluminum(III) followed by selective stripping with hydrochloric acids, and then separation of cobalt(II) and nickel(II) using a nickel(II)-preloaded PIA-8 in Solvesso #150. The proposed method gives a convenient and efficient technique for the separation and recovery of the four metal ions in waste materials.

EXPERIMENTAL

Reagents and Apparatus

PIA-8 was from Daihachi Chemical Industry Co. Ltd. (Osaka, Japan). No further purification was made before use. Purity was checked by a potentiometric two-phase titration. The purity obtained was 96.6%. Solvesso #150 (Sankyo Chemical Co. Ltd., Nagoya, Japan) was used as diluent. Standard stock solutions of La(III), Al(III), Co(II), and Ni(II) were prepared by dissolving $LaCl_3 \cdot 7H_2O$, $Al(NO_3) \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $NiCl_2 \cdot 6H_2O$, respectively. In the continuous countercurrent experiments, a simulated sample solution was made of the corresponding metal salts.

An Iwaki Model 2366 KM shaker was used to achieve the equilibration of two phases. A Toa Model HM-30S pH meter (TOA Electronic Co. Ltd., Tokyo, Japan) was used for pH measurements. The concentrations of metal ions were determined with a Seiko Model SPS-7000 (Seiko Electronic Co. Ltd., Tokyo, Japan) Plasma Spectrometer. A Countercurrent Multistage Model MX-4G Mixer-Settler (Tokyo Rikakikai Co. Ltd., Tokyo, Japan) was used for the multistage extraction and separation of lanthanum(III)), aluminum(III), cobalt(II), and nickel(II) in a simulated misch metal sample solution.

Measurement of Extraction Equilibrium

Aliquots (15.0 mL each) of the organic and aqueous phases were placed in a 50-mL separation funnel, after which the two phases were shaken on the mechanical shaker at 20 ± 0.1°C for 30 minutes and were allowed to stand for 10 minutes. The initial pH of the aqueous phase was adjusted by using sodium hydroxide and nitric acid. After phase separation, the pH value of the aqueous phase was measured with the pH meter. The concentration of a single metal ion in the aqueous phase was determined by titration with 1.00×10^{-2} mol/L EDTA using Xylenol Orange for lanthanum(III) and Cu-PAN for aluminum(III), cobalt(II), and nickel(II) as indicators. A mixture of two or more metal ions in the aqueous phase was analyzed by the plasma spectrometer. The concentration of metal ions in the organic phase was determined on the basis that the mass balance of the total concentration of metal ions in both aqueous and organic phases was constant. The distribution ratio (D) was calculated in the usual manner.

Continuous Countercurrent Multistage Extraction

The continuous countercurrent multistage extraction tests were carried out with the countercurrent multistage mixer-settler. The hard-glass mixer-settlers consisted of 282 mL mixers (69 mm × 68 mm × 60 mm) and 534 mL settlers (131 mm × 68 mm × 60 mm), and equipped with Teflon-molded shafts (8 mm diameter) and stirring propellers (30 mm diameter disk) which were directly driven by 15 W induction motors (500–1350 rpm). Both aqueous sample feed and extractant solution were pumped from their reservoirs with positive displacement pumps (flow rate 9–50 mL/min). The retention time of two phases in the mixer-settlers was adjusted by changing the flow rate. The extractant solution was imported from the fourth mixer-settler, and flowed off from the first mixer-settler, while the aqueous feed flowed in the opposite direction. Interstage transfer of the organic and aqueous phases after phase separation was made by gravity and suction force of a stirred dispersed phase. The aqueous sample and raffinate solutions obtained by extraction experiments were analyzed with the plasma spectrometer. The extracted organic phases were stripped by treatment with 2.0 mol/L sulfuric acid followed by analyzing the resulting aqueous samples with the plasma spectrometer. The extraction percentage was calculated in the usual manner.

RESULTS AND DISCUSSION

Extraction and Stripping Behavior

Extraction and stripping behaviors of lanthanum(III), aluminum(III), cobalt(II), and nickel(II) by 20% PIA-8 in Solvesso #150 have been investigated. Figure 1 shows the effect of pH on the distribution ratios (*D*) obtained for 0.01 mol/L metal ions in 1.0 mol/L sodium nitrate solution. As expected, lanthanum(III) and aluminum(III) could be extracted at relatively lower pH values than cobalt(II) and nickel(II); the pH values at 50% metal extraction efficiency ($pH_{0.5}$) decreased in the order nickel(II) > cobalt(II) > lanthanum(III) > aluminum(III). Plots of log *D* vs pH showed straight lines of slopes 2 and 3 that corresponded to the valencies of the metal ions. The organic phases which had previously extracted the metal chelates were treated with different concentrations of hydrochloric acid. Data shown in Fig. 2 indicate that the four metal chelates were stripped from the extracted organic solution. The HCl concentration at 50% stripping efficiency ($\log[HCl]_{0.5}$) increased in the order nickel(II) <

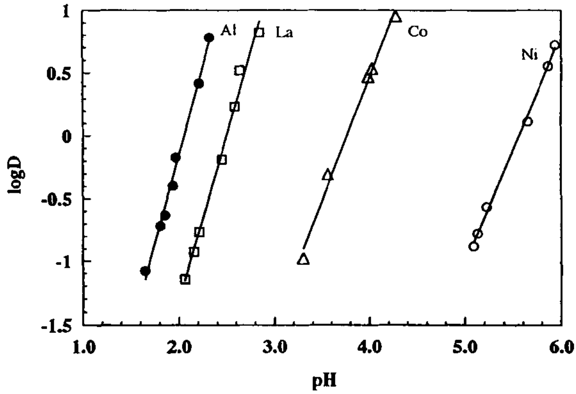

FIG. 1 Relationship between pH and distribution ratio (*D*) for metal ions. Organic phase: 20% PIA-8 solution in heptane. Aqueous phase: 0.01 mol/L metal ions in 1.0 mol/L sodium nitrate solution. Shaking time: 30 minutes at 1:1 phase ratio (O/A).

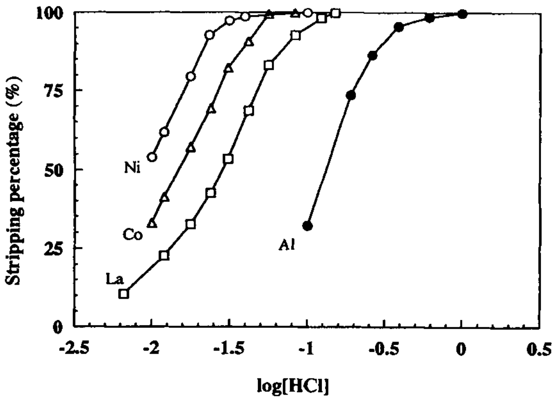

FIG. 2 Stripping curves of metal ions with hydrochloric acid. Organic phase: 20% PIA-8 solution in heptane preloaded with metal ions. Aqueous phase: hydrochloric acid of different concentrations. Shaking time: 30 minutes at 1:1 phase ratio.

cobalt(II) < lanthanum(III) < aluminum(III), the same as that of the extraction efficiency described above. The separation efficiency depends on the $\Delta pH_{0.5}$ (or $\Delta \log[HCl]_{0.5}$) value between the two metal ions. It is interesting to note from Figs. 1 and 2 that nickel(II) may be efficiently separated from cobalt(II) by extraction, and lanthanum(III) from aluminum(III) by stripping (backextraction) at appropriate acid concentrations, respectively.

Separation of Lanthanum(III), Aluminum(III), Cobalt(II), and Nickel(II) by 2.5 and 30% PIA-8 Solutions in Solvesso #150 with a Conventional Separator Funnel

Since PIA-8 has high selectivity as an extractant [12], we attempted the sequential separation of the four metal ions by extraction using 2.5% PIA-8 in Solvesso #150 as the diluent. The aqueous sample was a misch metal-simulated mixture of 31.9g/L lanthanum(III), 6.19g/L aluminum(III), 27.1g/L cobalt(II), and 40.4g/L nickel(II), and the extractant solution was preliminarily saponified to 50% by 14 mol/L sodium hydroxide solution. Figure 3 shows a typical separation profile plot of the extraction percentage as a function of the extraction stages. It was found that good separation among these metal ions could be achieved despite partial overlappings. Under the conditions used, a loss of 1% nickel(II) was observed due to coextraction of the 33rd successive extractions.

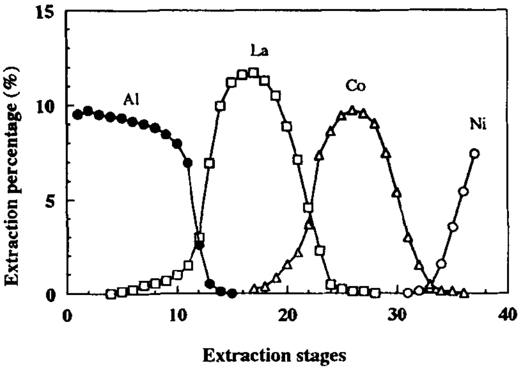

FIG. 3 Separation curves for La(III), Al(III), Co(II), and Ni(II). Organic phase: 2.5% PIA-8 solution in heptane. Aqueous phase: 31.9 g/L La(III), 6.19 g/L Al(III), 27.1 g/L Co(II), and 40.4 g/L Ni(II). Shaking time: 30 minutes at 1:1 phase ratio.

Sequential extractions of lanthanum(III), aluminum(III), cobalt(II), and nickel(II) were carried out with 30% PIA-8 in Solvesso #150, as shown in Table 1. In this case it can be seen that all metal ions except nickel(II) were completely removed by an extraction of six stages.

TABLE 1

Sequential Separation of Metal Ions from a Simulated Sample Solution[a]

	Initial aqueous phase (g/L)	Equilibrium organic phase (g/L)						Final aqueous phase (g/L)
		Ex_1	Ex_2	Ex_3	Ex_4	Ex_5	Ex_6	
La(III)	31.9	13.5	12.3	5.86	0.24	ND[b]	ND[b]	ND[b]
Al(III)	6.19	2.25	2.87	0.69	0.35	0.03	ND[b]	ND[b]
Co(II)	27.1	0.09	0.45	6.01	13.2	7.34	0.01	ND[b]
Ni(II)	40.4	ND[b]	ND[b]	ND[b]	ND[b]	5.01	15.3	20.1
pH	2.03	2.14	2.65	3.62	4.60	5.46	5.78	5.78

[a] Organic phase: 30% PIA-8 solution in Solvesso #150, which was preliminarily saponified to 50% by sodium hydroxide. Aqueous phase: a mischmetal-simulated sample solution. Shaking time: 10 minutes. Phase ratio: 1:1.

[b] Not detected. The concentration was less than the detection limit.

Separation of Lanthanum(III), Aluminum(III), Cobalt(II), and Nickel(II) by 10% PIA-8 Solution in Solvesso #150 with a Countercurrent Multistage Mixer-Settler

Based on the results described above, we used 10% PIA-8 in Solvesso #150 for the separation of lanthanum(III), aluminum(III), cobalt(II), and nickel(II) with the countercurrent multistage mixer-settler. Figure 4 shows the flow diagram for this study. The separation system consisted of ten

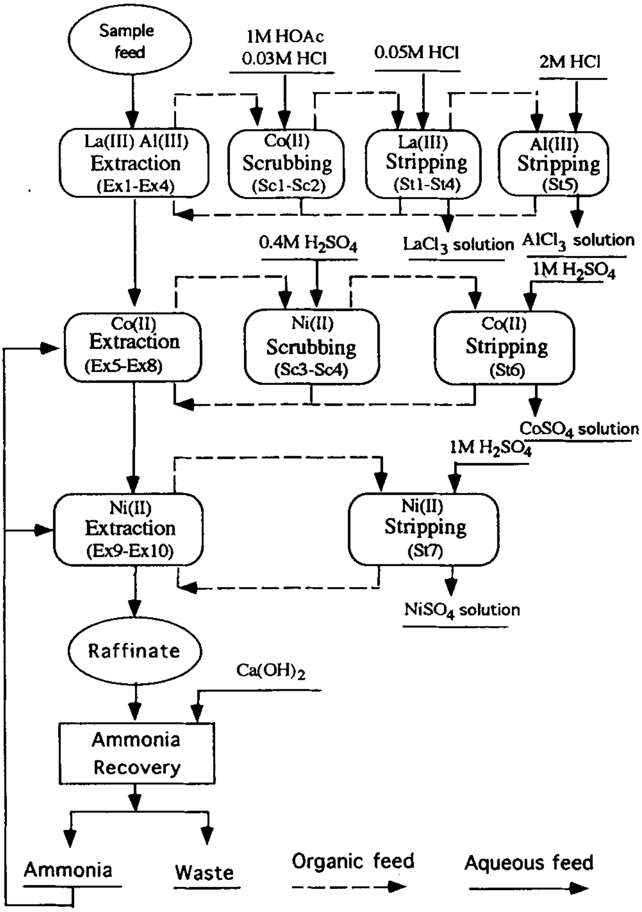

FIG. 4 Separation scheme of a continuous countercurrent multistage extraction for recovery and separation of La(III), Al(III), Co(III), and Ni(II) from misch metal.

extraction stages, four scrubbing stages, and seven stripping stages. The main processes for separation are the coextraction of La(III) and Al(III) followed by selective stripping using different concentrations of hydrochloric acid, and the extraction of cobalt(II) from a mixture of nickel(II) and cobalt(II) using a nickel(II)-preloaded PIA-8 in Solvesso #150. The most suitable conditions for operation were chosen on the basis of the results obtained with a separator funnel (namely one stage), and the proposed separation scheme was then evaluated from the analytical results for the misch metal-simulated sample solution.

The pH of the aqueous phase was varied from 2.02 to 3.52 by adding acetate buffers in order to examine the coextraction efficiencies of lanthanum(III), aluminum(III), and cobalt(II). Table 2 lists the results for the extraction efficiency of the metal ions. At pH 3.52, excellent extraction efficiencies of lanthanum(III) (98.4%) and aluminum(III) (95.2%) were obtained, but a large amount of cobalt(II) (19.6%) was also extracted. Over 66.5% lanthanum(III) and 37.1% aluminum(III) were extracted at pH 2.02. A pH of 3.29 was therefore chosen as the most suitable value, in which case the extraction efficiencies of lanthanum(III) and aluminum(III) were 86.5 and 82.3% at one extraction stage, respectively.

The effect of the phase ratio on the extraction percentage of the metal ions was investigated at pH 3.29 using a separator funnel. Data shown in Table 3 indicate that the extraction efficiency increased with increasing phase ratios of O/A. In this study, an O/A phase ratio of 3:2 was chosen as being suitable for the coextraction of lanthanum(III) and aluminum(III).

TABLE 2

Effect of pH on Extraction Efficiencies of La(III), Al(III), Co(II), and Ni(II)

Aqueous phase pH[a]	Organic phase (g/L)				Extraction efficiency (%)		
	La(III)	Al(III)	Co(II)	Ni(II)	La(III)	Al(III)	Co(II)
2.02	2.12	0.23	0.017	ND[b]	66.5	37.1	0.63
2.95	2.39	0.42	0.051	ND[b]	74.9	67.7	1.88
3.12	2.51	0.48	0.12	ND[b]	78.7	77.4	4.43
3.29	2.56	0.51	0.14	ND[b]	80.6	82.3	5.17
3.52	3.14	0.59	0.53	ND[b]	98.4	95.2	19.6

[a] Aqueous phase: 3.19 g/L La(III), 0.62 g/L Al(III), 2.71 g/L Co(II), and 4.04 g/L Ni(II). Shaking time: 10 minutes. Phase ratio: 1:1. Organic phase: 10% PIA-8 solution in Solvesso #150.

[b] See Table 1.

TABLE 3
Effect of Phase Ratio (O/A) on Extraction Efficiencies of La(III), Al(III), Co(II), and Ni(II)[a]

Phase ratio (O/A)	Organic phase (g/L)				Extraction efficiency (%)		
	La(III)	Al(III)	Co(III)	Ni(III)	La(III)	Al(III)	Co(II)
1:1	2.56	0.51	0.14	ND[b]	80.6	82.3	5.17
3:2	2.10	0.39	0.18	ND[b]	98.7	94.4	9.96
2:1	1.58	0.30	0.65	ND[b]	99.1	96.8	32.2

[a] Same conditions as Table 2.
[b] See Table 1.

The stripping efficiency of lanthanum(III) and aluminum(III) was investigated by changing the concentration of hydrochloric acid from 0.05 to 0.24 mol/L at an O/A phase ratio of 2. As can be seen from Table 4, 88% of the extracted lanthanum(III) was stripped into 0.05 mol/L hydrochloric acid while the aluminum(III) remained in the organic phase. Therefore, the separation of these metals may be achieved through a stripping process of the loaded organic phase. The extracted aluminum(III) was quantitatively recovered by stripping with 2 mol/L hydrochloric acid.

Separation of cobalt(II) from nickel(II) was investigated using 10% PIA-8 in Solvesso #150. Although the separation factor ($\beta = D_1/D_2$) between cobalt(II) and nickel(II) was considerably large ($\beta_{Co/N} = 1{,}750$ at pH 4.67), it is very difficult to continuously adjust to a suitable pH by adding appropriate amounts of dilute acids or ammonia to the sample solution following

TABLE 4
Selective Stripping of La(III) from Loaded Organic Solution[a]

HCl (mol/L)	Phase ratio (O/A)	Aqueous phase (g/L)		Stripping efficiency (%)	
		La(III)	Al(III)	La(III)	Al(III)
0.05	2:1	2.78	ND[b]	88.0	—
0.12	2:1	2.96	0.18	93.7	28.1
0.24	2:1	3.05	0.29	96.5	45.2

[a] Loaded organic solution: 10% PIA-8 solution in Solvesso #150 which previously extracted 1.58 g/L La(III) and 0.32 g/L Al(III). The other conditions were the same as in Table 2.
[b] See Table 1.

the extraction of lanthanum(III) and aluminum(III). Therefore, we used a nickel(II)-preloaded PIA-8 in Solvesso #150 as the extraction solvent which was made by treating the ammonium salt solution of PIA-8 with 0.8 mol/L nickel(II) sulfate solution. The cobalt(II) in the misch metal-simulated solution was found to be separated by four multistage extractions using the extractant solution at an O/A phase ratio of 2:1.

The proposed method using a continuous countercurrent multistage extraction was applied to the recovery and separation of lanthanum(III), aluminum(III), cobalt(II), and nickel(II) from the misch metal-simulated sample solution. The operation conditions, given in Table 5, were chosen based on the results obtained. The ratio of organic and aqueous flow rates corresponded to the O/A ratio, and was set as large as possible in some processes. The retention times are expressed as the mixing times of both phases in the mixers, and the equilibrium pH values are the final pH of the effluents from the settlers at the stages. All operations were carried out at 20 ± 1°C. Table 6 summarizes the analytical results for the four metal ions in the aqueous and organic phases after the experiments. It can be seen that the extraction efficiencies of both lanthanum(III) and aluminum(III) were above 99.5% through four stages at an O/A phase ratio of 3:2. No extraction of nickel(II) was observed in these stages. The

TABLE 5

Operation Conditions for Separation of La(III), Al(III), Co(II), and Ni(II) by a Continuous Countercurrent Multistage Extraction

Operation conditions	Organic flow rate (mL/min)	Aqueous flow rate (mL/min)	Retention time (min)	pH
Extraction of La(III) and Al(III):				
Extraction (Ex_1–Ex_4)	20.7	12.9	8.38	3.20
Scrubbing (Sc_1–Sc_2)	44.1	12.9	4.94	2.56
Separation of La(III) and Al(III):				
Stripping (St_1–St_4)	20.7	12.9	8.38	1.81
Stripping (St_5)	20.7	12.9	8.38	<0.1
Separation of Co(II) and Ni(II):				
Preloading (P_1–P_2)	51.5	12.9	4.37	7.02
Preloading (P_3–P_4)	51.5	12.9	4.37	6.05
Extraction (Ex_5–Ex_8)	28.0	12.9	6.88	5.76
Scrubbing (Sc_3–Sc_4)	22.1	4.8	10.5	5.05
Stripping (St_6)	28.0	4.8	10.5	<0.1
Extraction (Ex_9–Ex_{10})	28.0	12.9	6.88	6.06
Stripping (St_7)	22.1	4.8	6.59	<0.1

TABLE 6
Results for Separation of La(III), Al(III), Co(II), and Ni(II) by a Continuous Countercurrent Multistage Extraction[a]

		Aqueous phase (g/L)				Organic phase (g/L)			
	pH	La(III)	Al(III)	Co(II)	Ni(II)	La(III)	Al(III)	Co(II)	Ni(II)
Extraction of La(III) and Al(III):									
Ex$_1$	3.25	—	0.01	3.25	5.19	0.05	—	0.19	—
Ex$_2$	3.21	0.10	0.02	3.31	4.61	0.50	0.08	0.19	—
Ex$_3$	3.20	0.58	0.12	3.61	4.79	1.23	0.24	0.10	—
Ex$_4$	3.20	1.65	0.28	3.44	4.99	2.67	0.44	0.20	—
Sc$_1$	2.56	1.03	0.03	0.38	—	2.65	0.43	0.05	—
Sc$_2$	2.41	0.33	0.02	0.05	—	2.60	0.43	—	—
Separation of La(III) and Al(III):									
St$_1$	1.81	2.68	0.01	—	—	1.53	0.39	—	—
St$_2$	1.30	2.35	0.03	—	—	0.85	0.40	—	—
St$_3$	1.18	2.13	0.04	—	—	0.49	0.43	—	—
St$_4$	1.08	2.10	0.05	—	—	—	0.46	—	—
St$_5$	<0.1	0.01	0.76	—	—	—	—	—	—
Separation of Co(II) and Ni(II):									
Ex$_5$	5.76	—	—	—	18.0	—	—	0.59	1.02
Ex$_6$	5.28	—	—	1.08	6.69	—	—	1.30	0.85
Ex$_7$	5.24	—	—	1.50	3.06	—	—	1.31	0.34
Ex$_8$	5.16	—	—	2.77	4.88	—	—	1.32	0.16
Sc$_3$	5.23	—	—	0.45	1.03	—	—	1.31	0.05
Sc$_4$	5.15	—	—	0.52	1.12	—	—	1.30	—
St$_6$	<0.1	—	—	2.85	—	—	—	—	—
Ex$_9$	6.09	—	—	—	0.08	—	—	—	7.56
Ex$_{10}$	6.01	—	—	—	6.52	—	—	—	8.31
St$_7$	<0.1	—	—	—	17.5	—	—	—	—

[a] Simulated sample solution: 3.19 g/L La(III), 0.62 g/L Al(III), 2.71 g/L Co(II), and 4.04 g/L Ni(II).

recovery efficiency of lanthanum(III) was over 96% by stripping at four stages (St$_1$–St$_4$) following the two scrubbing stages (Sc$_1$–Sc$_2$). The coextracted cobalt(II) could be completely scrubbed off, and the stripping efficiency of extracted aluminum(III) was above 99% with 2 mol/L hydrochloric acid at only one stage (St$_5$). Through the above stages, the recovery efficiency of aluminum(III) reached 94%. After lanthanum(III) and aluminum(III) were separated, the pH value of the raffinate feed was adjusted to about 5 with sodium hydroxide solution. The countercurrent extraction was then carried out in four stages (Ex$_5$–Ex$_8$) by using the extractant solution preloaded with nickel(II). The coextracted nickel(II) was scrubbed off with 0.4 mol/L sulfuric acid in two stages (Sc_3–Sc_4) at an O/A ratio of 5:1. The scrubbing efficiency was 99% for nickel(II), and about 10% of the cobalt(II) was costripped through these stages. The extracted cobalt(II) was completely stripped with 1 mol/L sulfuric acid at an O/A ratio of 2:1. The recovery efficiency of cobalt(II) reached 84%. The nickel(II) in the sample feed was recovered using the preloaded extractant solution with a constant concentration of ammonia. With the extraction stages of Ex_9 and Ex_{10}, 17.5 g/L nickel(II) solution was obtained. The final raffinate was introduced to the recovery process of ammonia by the addition of limestone.

CONCLUSIONS

It was demonstrated that the recovery and separation of four metal ions from a misch metal-simulated sample solution containing 3.19 g/L lanthanum(III), 0.62 g/L aluminum(III), 2.71 g/L cobalt(II), and 4.04 g/L nickel(II) were possible by a continuous countercurrent multistage extraction using 10% PIA-8 in Solvesso #150. The analytical results obtained were satisfactory. The separation processes were optimized by conducting continuous countercurrent extraction experiments consisted of ten extraction stages, four scrubbing stages, and seven stripping stages. Lanthanum(III) and aluminum(III) were first separated from cobalt(II) and nickel(II) with the extractant solution. The coextracted cobalt(II) was scrubbed off with a mixed acid of 1 mol/L acetic acid and 0.03 mol/L hydrochloric acid in two stages. The extracted lanthanum(III) was selectively stripped into 0.05 mol/L hydrochloric acid in four stages. The aluminum(III) in the lanthum(III)-free organic phase was stripped into 2.0 mol/L hydrochloric acid. Cobalt(II) was separated from nickel(II) by using an extractant solution preloaded with ammonia and nickel(II) sulfate solution in each of two stages. The nickel(II) was recovered by extraction and stripping operations from the raffinate.

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