Solvent Extraction Separation of Co, Mn and Zn from leaching solution from Ni-Cd battery by Na-PC88A

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Abstract: Solvent extraction experiments for separation of impurities from Ni-rich solution were carried out for manufacturing of high purity Ni compounds from acid leaching solution of spent Ni-Cd secondary battery. Artificial and leaching solutions were used as aqueous phases and PC88A saponified by sodium in kerosene were used as organic phase. The extraction order is Zn>Mn>Co>Ni and extraction percentage of metal ions was increased with increase of the concentration of extractant, initial pH of aqueous phase and ratio of O/A. The separation of cobalt, zinc and manganese from nickel was effectively accomplished at the condition of extraction stage=1, O/A=1 and initial pH 5.0 with 1.0 mol/dm^3 PC88A saponified to 50% with NaOH.

1. Introduction

Ni-Cd rechargeable battery has been widely used for household electrical appliances and reserved power source in industry. This spent Ni-Cd battery was generally recycled by thermal process that was introduced to separate cadmium metal by distillation. The residue that is mainly composed of iron and nickel was used for the raw material of ferrite-nickel industry.

In our previous work [1-3], a simple hydrometallurgical process was developed to recover nickel as nickel sulfate from the spent Ni-Cd battery residue. In this process, impurities such as cobalt, zinc and manganese ions should be removed from acid leaching solution to manufacture high purity nickel sulfate. Ni-rich leaching solution removed Fe and Cs by precipitation contained 69g/l nickel, 8.65 g/l cobalt, 0.51g/l zinc and 6.9 g/l manganese, respectively.

Since the separation of cobalt from nickel is particularly difficult from weak sulfate solution for their similar chemical behaviors, solvent extraction has been effectively used in the separation of cobalt and nickel in aqueous solution [4]. Recently, PC88A, modified products of D$_2$EHPA, has been reported to be more effective in separating cobalt from nickel [5-9].

In this study, the extraction behavior of nickel, cobalt, zinc and manganese from artificial and leaching solution using PC88A saponified by sodium has been investigated to load cobalt, zinc and manganese ions into organic phase and to remain nickel ions in the aqueous phase. The effects on the saponified percentage of extractant, extractant concentration and the O/A ratio on extraction systems were also investigated, and the variation of the separation factor with extraction conditions were obtained.

2. Experimental

The chemical compositions of artificial and leaching solutions used in this test were shown in Table 1. The artificial solutions were made by dissolving salt sulfates in distilled water. The leaching solution was prepared after precipitation and removal of Fe and Cs from leaching solution of distillation residue that obtained from spent Ni-Cd secondary battery.

Table 1. Artificial and leaching solutions for solvent extraction.

Composition of aqueous solutions (g/dm^3)	Ni	Co	Mn	Zn
Artificial solutions	60	9.04	8.68	0.48
Leaching solutions	69.2	8.65	6.91	0.511

For pH adjustment, sulfuric acid and NaOH were used. PC88A from Daihachi was saponified by mixing with the calculated quantity of a concentrated NaOH solution was used as an extractant and kerosene from Kanto Chemical as a diluent.

Equal volumes of organic and aqueous solution containing metal ions were placed in a $0.1 dm^3$ separatory funnel and shaken for 10min. at 20℃ Experimental and standard conditions were shown in Table 2. The aqueous phase was separated after settling the mixture for 24 h. The concentrations of metal ions in the aqueous phase were measured by A.A.(Varian Techtron A.A.-1475). The pH of the aqueous phase was measured by a pH meter (Fisher Accumet pH Model 620).

Table 2. Experimental conditions and standard of solvent extraction.

Conditions	Range	Standard conditions
Initial pH	4, 5, 6	5
Volume ratio of O/A	1, 2, 3, 4	1
Concentration of solvent (mol/dm³)	0.2, 0.4, 0.6, 0.8, 1.0	1.0
Saponified percent (%)	0, 10, 25, 50, 100	50

The concentrations of metal ions in the organic phase were calculated from mass balance. The extraction percentage a metal is defined as a ratio of the concentration of the metal in organic to that in the aqueous phase is represented by Eq. (1).

$$\text{Extrcation percentage} = \frac{\text{Concentration of metal in organic phase after extraction}}{\text{Concentration of metal in aqueous phase before extraction}} \times 100 \qquad (1)$$

The distribution coefficient of metal is defined as a ratio of the concentration of metal in organic phase to that of metal in the aqueous phase and is represented by Eq. (2)

$$D = \frac{(M)_o}{(M)_{aq}} \qquad (2)$$

The separation factor between the two metals was then calculated as the ratio of the distribution ratios of two metals. Thus, the separation factor, $\beta_{(Co-Ni)}$, $\beta_{(Zn-Ni)}$ and $\beta_{(Mn-Ni)}$ were determined using the distribution ratios of the relevant pairs of base metals.

3. Results and discussion

3.1 Effect on the saponified percentage of extractant

Extraction of Mn(II) and Co(II) ions by the acidic forms of extractant, D2EHPA, PC88A and Cyanex 223 was low[7] for which the sodium form of the extractant was used. In this experimental, extractions were carried out with NaOH and1.0 mol/dm³ PC88A in kerosene. Fig. 1 shows the extraction percentage of metal ions when the saponified percentage of extractant by NaOH changed from 0 to 100%. It is shown that the extraction percentage of Zn, Co, Mn and Ni increased with the saponified percentage of extractant and the extraction order is Zn>Mn>Co>Ni..In the case of extraction with non-saponified extractant, extraction percentage of zinc was 95% but other metals were not extracted. It is apparent from the results that the extractant without being saponified was not used for practical process because Zn ion was only extracted.
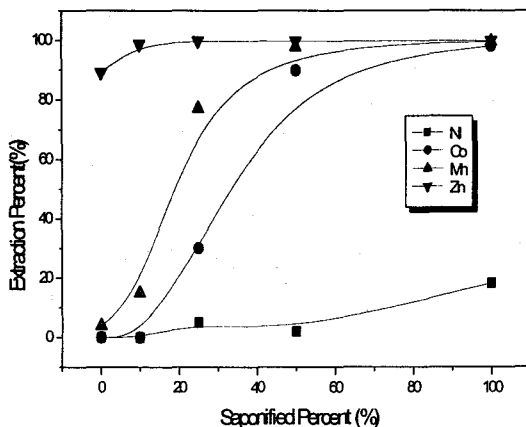
Fig. 1. Effect of saponified percentage (%) of PC88A on the extraction of metals at initial pH 5.0 at 1.0 mol/dm³ PC88A in kerosene.

The effect of the saponified percentage on the separation factor (β) is shown as Fig. 2. The separation factors (β) of Ni-Mn and Ni-Co increased with increased of the saponified percentage in the range of 0%-50% but the separation factor (β) of Ni-Zn decreased. When the saponified percentage of extractant was 100%, the separation factors (β) of Ni-Mn, Ni-Co and Ni-Zn decreased because 18 % of nickel was extracted into the organic phase. It is determined that the optimum condition of the saponified percentage is 50 %.
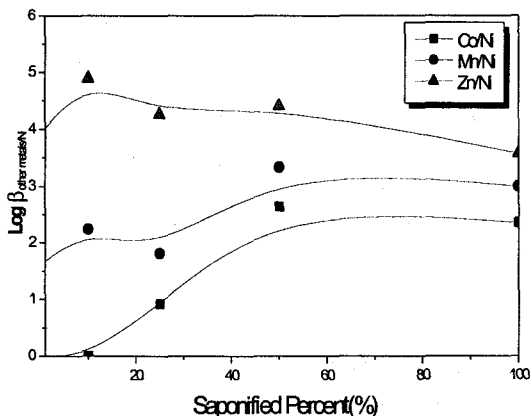

Fig. 2. Effect of saponified percentage (%) of PC88A on separation factor (β).

3.2 Effect of extractant concentration

The effect of the extractant concentration was investigated by varying the concentration of 50 % Na-PC88A from 0.2 to 1.0 mol/dm³ in initial pH of 5.0. The extraction percentage of metal ions and separation factor were shown in Fig. 3 and 4.

The extraction percentage of Zn was 99% over the whole range and those of Co and Mn increased with the increase of 50 % Na-PC88A concentration but the extraction percentage of nickel was not increased. When the concentration of 50 % Na-PC88A was 0.2, there is not enough extractant to extract the impurities such as cobalt and manganese. When the concentration of 50 % Na-PC88A was 1.0, all the impurities, as well as nickel (2%) were

extracted into the organic phase. Therefore, in the case of 1.0 mol/dm^3 50 % Na-PC88A, the separation factors were found to be low.
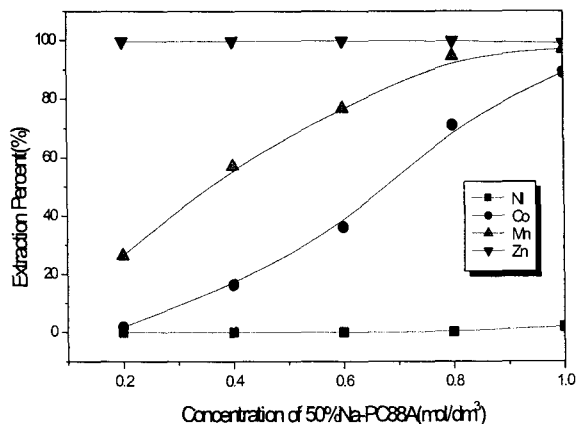

Fig. 3. Effect of Na-PC88A concentration on extraction of metal at initial pH 5 (50% Na-PC88A).

In Fig. 4, the separation factors increased with 50 % Na-PC88A concentration but decreased 1.0 mol/dm^3 50 % Na-PC88A because the extraction percentage of nickel was slightly increased. Although the separation factors at 1.0 mol/dm^3 50 % Na-PC88A decreased, the extraction at the condition of 1.0 mol/dm^3 50 % Na-PC88A seems to be better than others because most of impurities in aqueous solution were removed.
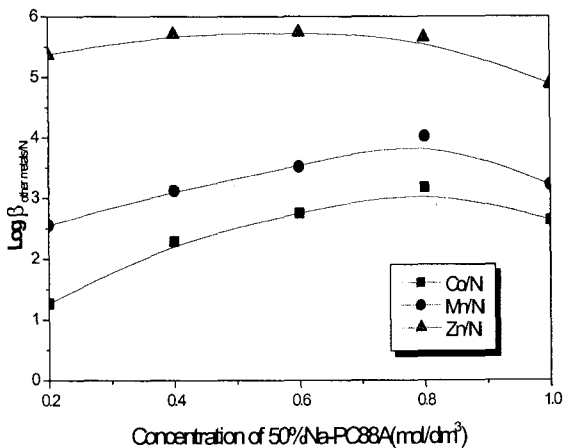

Fig. 4. Effect of 50 % Na-PC88A concentration on separation factor (β) at initial pH 5.
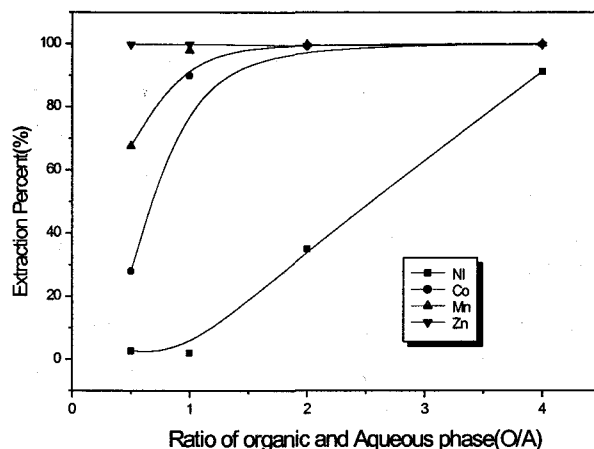
Fig. 5. Effect of O/A ratio on the extraction of metals at initial pH 5.0 and 1.0 mol/dm^3 50% Na- PC88A in kerosene.
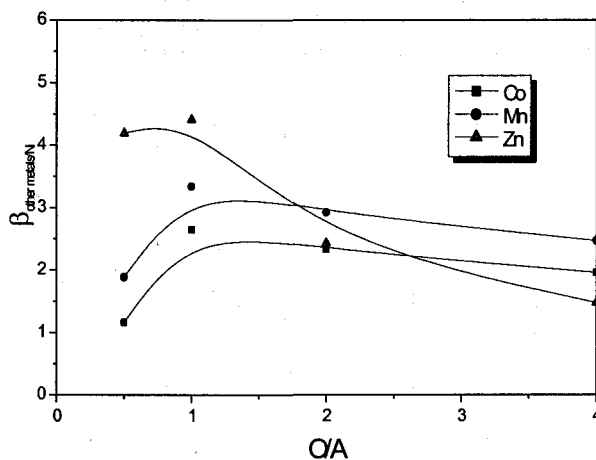

Fig. 6. Effect of O/A ratio on separation factor (β) at initial pH 5.0and 1.0 mol/dm^3 50% Na-PC88A in kerosene.

3.4 Applicability for practical leaching solution

To test the applicability for leaching solution from distillation residue of Ni-Cd spent battery, the solvent extraction experiments have been carried out at the condition of 1.0 mol/dm^3 50 % Na-PC88A, O/A=1 and initial pH 5.3(not controlling of pH). The extraction percentage of metal ions and separation factor were shown in Table 3 and 4.

In this experiment, 95%, 98%, 99% and 11% of Co, Mn, Zn and Ni were extracted into the organic phase. In Table 4, the separation factors ($\beta_{(Co-Nl)}$, $\beta_{(Zn-Nl)}$ and $\beta_{(Mn-Nl)}$) were higher than those of artificial solution at standard experimental conditions. Nickel (11%) in organic phase may be recovered by scrubbing. It is known that solvent extraction by Na-PC88A have a good effect on the separation of Co, Mn and Zn from Ni-rich leaching solution in these experimental conditions.

Table 3. Change of metal ion concentration and extraction percentage of various metals after solvent extraction of Ni-Cd spent battery leaching solution.

Compositions (g/dm^3)	Ni	Co	Mn	Zn
Before solvent extraction	69.2	8.65	6.91	0.44
After solvent extraction	61.3	0.4	0.11	0.001
Extraction percentage (%)	11.4	95.4	98.4	99.2

Table 4. Separation factors (β) of Co, Mn and Zn against Ni after solvent extraction of Ni-Cd spent battery leaching solution.

Base metals	Co/Ni	Mn/Ni	Zn/Ni
Log (Separation factors (Log (β))	3.13	3.68	5.12

4. Conclusions

The following conclusions could be drawn from the solvent extraction experiment for separation of Co, Mn and Zn from Ni-rich leaching solution by Na-PC88A.

(1) The extraction order of metal ions is Zn>Mn>Co>Ni.
(2) Extraction of metal ions was increased with increase of the concentration of extractant, initial pH of aqueous phase and ratio of O/A.
(3) 95% Co, 98% Mn and 99% Zn separations were achieved in one stage with 1.0 mol/dm^3 Na-PC88A saponified to 50% at initial pH 5.3 and O/A ratio of 1.

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