

SOLVENT EXTRACTION OF RARE EARTH METAL BY A CONTINUOUS STIRRED VESSEL

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Abstract

The solvent extraction of neodymium, a rare earth metal, was studied with a continuous stirred vessel. One of the widely used extractants, 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (PC-88A), diluted with kerosene was selected as an extracting organic solvent. First, the extraction equilibrium of neodymium between aqueous and organic phases was measured in a batch-wise experimental run. The distribution ratio of the metal increased with pH and the relation between the distribution ratio and the conditions was investigated using ordinary slope analysis. In the second stage, the continuous operation of the extraction process was carried out in a laboratory scale standard type stirred vessel, with a 0.08m inner diameter, equipped with six flat blade turbine impeller and four baffles conducted under various operating conditions. The fractional yields of neodymium increased as pH, and flow rate ratio of solvent relative to feed increased. The state of liquid-liquid dispersion, which should affect the mass transfer, was also discussed in terms of the drop size and the holdup of the organic dispersed phase.

Keywords: Solvent extraction, Rare earth metal, Neodymium, Continuous operation, PC-88A.

1. Introduction

Rare earth metals are industrially useful and applied to advanced technologies in many fields. Since these metals are found in resource as a mixture, they should be separated into each other. This separation is difficult especially in the case between neighbouring elements in the periodic table, because they have the similar chemical

Nomenclatures

$C_{H^+,aq}$	Concentration of hydrogen ion in aqueous phase at equilibrium, kmol/m ³
$C_{M,aq,0}$	Concentration of hydrogen ion in aqueous raffinate, kmol/m ³
$C_{M,aq}$	Concentration of metal M in initial aqueous phase, kmol/m ³
$C_{M,aq}$	Concentration of metal M in aqueous feed, kmol/m ³
$C_{M,org}$	Concentration of metal M in aqueous phase at equilibrium, kmol/m ³
$C_{M,org,0}$	Concentration of metal M in aqueous raffinate, kmol/m ³
$C_{M,org}$	Concentration of metal M in initial organic phase, kmol/m ³
$C_{M,org}$	Concentration of metal M in organic solvent, kmol/m ³
$C_{(RH)2,org,0}$	Concentration of metal M in organic phase at equilibrium, kmol/m ³
$C_{(RH)2,org}$	Concentration of extractant RH as dimer in initial organic phase, kmol/m ³
$C_{(RH)2,org}$	Concentration of extractant RH as dimer in organic solvent, kmol/m ³
$C_{(RH)2,org}$	Concentration of extractant RH as dimer in organic phase at equilibrium, kmol/m ³
$C_{(RH)2,org}$	Concentration of extractant RH as dimer in organic extract, kmol/m ³
D	Drop diameter, m
D_M	Distribution ratio of metal M
d_{32}	Sauter mean diameter, m
E	Volume flow rate of organic extract, m ³ /h
E_0	Inlet volume flow rate of organic solvent, m ³ /h
$K_{ex,M}$	Reaction equilibrium constant of metal M
\bar{M}	Component M in organic phase
N	Stirring velocity, 1/h
pH	pH of aqueous phase
pH_0	pH of aqueous feed
R	Volume flow rate of aqueous raffinate, m ³ /h
R_0	Inlet volume flow rate of aqueous feed, m ³ /h
S	Volume flow rate of organic extract, m ³ /h
S_0	Inlet volume flow rate of organic solvent, m ³ /h
T	Temperature, K
T	Time, h
V_{aq}	Volume of aqueous phase, m ³
V_{org}	Volume of organic phase, m ³
X_M	Extraction rate of metal M, kmol/h
Y_M	Yield of component M

Greek Symbols

ϕ	Holdup of dispersed phase
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features due to the same electric configuration of outermost husks. Solvent extraction is presently one of the commercialized techniques for the separation,

and a number of fundamental studies of solvent extraction for rare earth metal separation have been conducted, in which the reaction equilibrium of respective rare earth metals with various kinds of extractants were mainly discussed [1-3]. For the practical use of this method on industrial scale, the multi-stage stirred vessel is commonly utilized as a contacting equipment. However, the studies of the extraction of rare earth metals using continuous stirred vessel have been conducted under only limited conditions, such as only limited metals species or low concentrations of metals and extractant [4, 5].

In this work, we studied the continuous solvent extraction of rare earth metal using a standard type stirred vessel. Firstly the extraction equilibrium of neodymium, a model rare earth metal, between aqueous and organic phases was confirmed in a batch-wise run. In the second, the continuous extractions of neodymium with stirred vessel were carried out under various experimental conditions.

2. Experimental

2.1. Extraction equilibrium

The experimental conditions of extraction equilibrium are shown in Table 1. Neodymium chloride hexahydrate was used as a metal ion source. 2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) purchased from Daihatchi Chemical Industry, Japan, was used as an extractant, without further purification. This extractant was diluted by kerosene to be an organic solvent phase. Hydrochloric acid was used to adjust *pH* in the aqueous feed solution. All the chemicals except PC-88A were in analytical grade, purchased from Wako Pure Chemical Japan.

The specified amounts of feed and solvent phases in a flask of $5.0 \times 10^{-5} \text{ m}^3$ were shaken in a constant temperature bath at 298 K for 12 hours to be equilibrated and these liquid phases were separated by separating funnel. The metal concentrations and *pH* in the aqueous phases were determined by ICP-MS (ParkinElmer, ELAN DRC-e) and *pH* meter (Horiba, F-52), respectively. The metal and extractant concentrations in the organic phases were estimated by the material balance relationships with the concentration in the aqueous phase.

2.2. Continuous extraction with stirred vessel

The experimental conditions of the continuous extraction with stirred vessel are listed in Table 2. The material systems were the same as used in the extraction equilibrium measurements, except for trivalent iron chloride hexahydrate, which was used in some continuous runs.

An experimental apparatus of the continuous extraction operation is schematically shown in Fig. 1. A standard type stirred vessel of 0.08 m inner diameter and height with baffles was used as a contactor. A six flat blade turbine impeller of 0.05 m diameter was equipped at the center of the vessel. The stirred vessel was immersed in the constant temperature bath to keep the temperature of the liquids in the vessel constant. After the aqueous feed phase was provided to fill up the vessel, the supply of the organic solvent phase and the stirring were started to begin (*t* = 0) the continuous run with oil in water (O/W) type dispersion. While the feed and solvent phases

separately entered through the inlets at the bottom of the vessel, the raffinate and extract phases after the extraction were obtained together through the top outlet. The flow rates of the feed and solvent phases were monitored by rotameters, and adjusted to proper values by valves. The flow rates at exit were calculated from the volumes of the phases flowed out during specified time. The obtained raffinate solution was analyzed in the same way as used in the measurements of extraction equilibrium to determine the metal concentrations and pH.

The dispersion state in the stirred vessel, which should affect mass transfer, was also studied in terms of the drop size and the holdup of the dispersed phase. The drop diameter of the organic dispersed phase was measured as follows: a portion of O/W type liquid-liquid dispersion in the vessel was sampled during the run into an appropriate aqueous hydrophilic surfactant solution prepared in a pipette to avoid the coalescence of the organic phase drops; this surfactant solution containing the drops was microphotographed; and the numbers of the drops of the respective diameter ranges were counted from among the 200 ~ 300 drops on the photograph to estimate the mean diameter and the distribution [6]. At the end of the experimental run, the valves at the inlets of the vessel were closed simultaneously and the volumes of the liquid phases retained in the vessel were measured. From these volumes, the holdup of the dispersed phase, the volume ratio of dispersed phase relative to total liquid in the vessel, was determined.

Table 1. Experimental Conditions of Extraction in Batch-Wise System.

Materials	
Solute of aqueous phase	$\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$
Aqueous phase	Aqueous solution of HCl
Organic phase	Kerosene solution of PC-88A
Conditions	
Concentration of metal in aqueous phase, $C_{\text{M,aq},0}$ [kmol/m ³]	5.0×10^{-3}
Concentration of PC-88A in organic phase, $C_{(\text{RH})2,\text{org},0}$ [kmol/m ³]	0.25
Volume of aqueous phase, V_{aq} [m ³]	2.0×10^{-6}
Volume of organic phase, V_{org} [m ³]	2.0×10^{-6}
Temperature, T [K]	298
pH of aqueous feed, pH_0	0.2~3.0

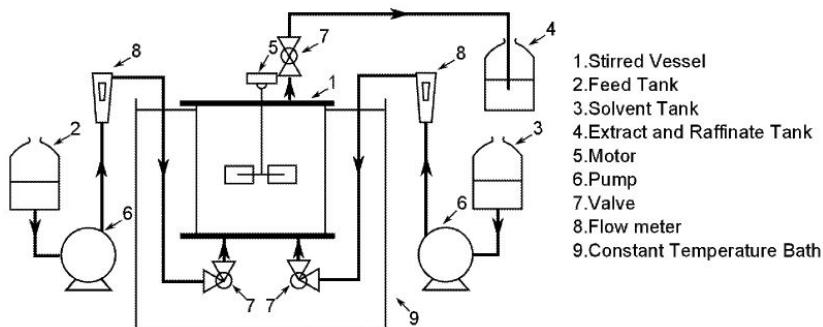


Fig. 1. Schematic Diagram of Stirred Vessel and Experimental System.

Table 2. Experimental Conditions of Extraction by a Continuous Stirred Vessel.

Materials	
Solute of aqueous phase	$\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
Aqueous feed	Aqueous solution of HCl
Organic solvent	Kerosene solution of PC-88A
Conditions	
Concentration of metal in aqueous feed, $C_{\text{M},\text{aq},0}$ [kmol/m ³]	5.0×10^{-3}
Concentration of PC-88A in organic solvent, $C_{(\text{RH})2,\text{org},0}$ [kmol/m ³]	0.25
Initial volume flow rate of aqueous feed, R_0 [m ³ /h]	$7.5 \times 10^{-3} \sim 1.3 \times 10^{-2}$
Initial volume flow rate of organic solvent, E_0 [m ³ /h]	3.0×10^{-3}
Stirring velocity, N [1/h]	$1.8 \times 10^4 \sim 4.1 \times 10^4$
Temperature, T [K]	298
pH of aqueous feed, pH_0	1.2~2.5

3. Results and Discussion

3.1. Extraction equilibrium

The distribution ratio, D_M , was defined as,

$$D_M = C_{\text{M},\text{org}} / C_{\text{M},\text{aq}} \quad (1)$$

with the concentration of metal in organic phase, $C_{\text{M},\text{org}}$ and that in aqueous phase, $C_{\text{M},\text{aq}}$ at equilibrium. The extraction reaction of trivalent lanthanides and iron ion with PC-88A is generally expressed as [1],



where M^{3+} and $(\text{RH})_2$ represent the metal ion and PC-88A dimer, respectively. The reaction equilibrium constant, $K_{\text{ex},\text{M}}$, is thus, described as,

$$K_{\text{ex},\text{M}} = (C_{\text{M},\text{org}} C_{\text{H}^+,\text{aq}}^3) / (C_{\text{M},\text{aq}} C_{\text{H}^+,\text{aq}}^3) = D_M C_{\text{H}^+,\text{aq}}^3 / C_{(\text{RH})2,\text{org}}^3 \quad (3)$$

where $C_{\text{H}^+,\text{aq}}$ is the concentration of hydrogen ion in aqueous phase, $C_{(\text{RH})2,\text{org}}$ is that of extractant dimer in organic phase at equilibrium. The arrangement of this equation leads to,

$$\log D_M = 3pH + \log K_{\text{ex},\text{M}} + 3\log C_{(\text{RH})2,\text{org}} \quad (4)$$

Figure 2 shows the effects of pH at equilibrium on $\log D_M$ in the case of Nd extraction. The D_{Nd} increased with an increase in pH in the case of $pH > 0.7$ and this could be expected from the relationship between $C_{\text{H}^+,\text{aq}}$ and D_M shown in Eq.(4), when the decrement of the free extractant was negligible, namely, $C_{(\text{RH})2,\text{org}} = C_{(\text{RH})2,\text{org},0}$, as the broken line in Fig. 2. Based on these results and Eq.(4), $K_{\text{ex},\text{M}}$ was 6.4×10^{-3} , which was almost the same as the previous results [2]. However, in the range of $pH < 0.7$, D_{Nd} decreased with increase of pH. This may resulted from the effects of solvation reaction with chloride ion [7].

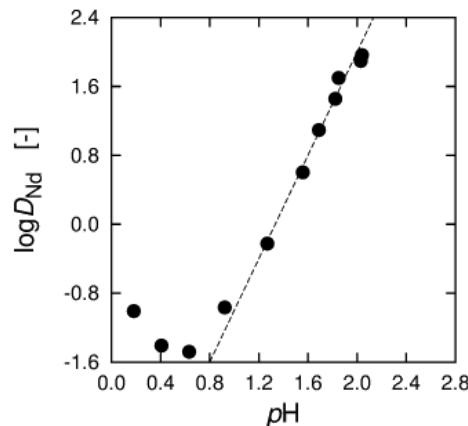


Fig. 2. Effects of pH on Distribution Ratio of Nd for Extraction Equilibrium.
 $C_{Nd,aq,0}: 5.0 \times 10^{-3} \text{ kmol/m}^3, C_{(RH)2,org,0}: 0.25 \text{ kmol/m}^3$.

3.2. Continuous extraction with stirred vessel

The fractional yield of metal M was defined as,

$$Y_M = E_0 C_{M,org} / R_0 C_{M,aq,0} \quad (5)$$

where R_0 , E_0 , $C_{M,org}$ and $C_{M,aq,0}$ mean the initial flow rates of the aqueous feed and organic solvent and the concentrations of metal in organic extract and aqueous feed respectively. The extraction rate of metal M was represented as,

$$X_M = EC_{M,org} - E_0 C_{M,org,0} \quad (6)$$

where E , and $C_{M,org,0}$ mean the flow rate of organic extract and concentration of metal in organic solvent.

In all runs, the feed aqueous and solvent organic phases could be contacted in the stirred vessel to stably form the O/W dispersions. The phase separation of the raffinate and extract phases was easily conducted, and any stable emulsion did not form in the vessel or settler.

Time courses of the pH and concentration of Nd in the aqueous raffinate, $C_{Nd,aq}$ are shown in Fig. 3. In this measurement, $C_{Nd,aq}$ and pH in the aqueous raffinate became constant after few minutes, and it was assumed that the system should attain the steady state after 10 minutes operation in this study. The volume flow rates of the inlet aqueous feed and organic solvent solutions, R_0 and E_0 , were approximately as same as those of the outlet aqueous raffinate and organic extract solutions, R and E , respectively. Therefore the changes in the volume flow rates of respective solutions could be negligible.

Figure 4 shows the drop size distributions of the organic dispersed phase in the systems with/without Fe ion in the feed aqueous phase at $N = 1.8 \times 10^4 \text{ h}^{-1}$. The maximum drop size was obtained in the range from 40 μm to 60 μm for both

solutions. The drop size distributions measured with the aqueous solution containing metal ion were approximately as same as those without metal ion, and the effects of the metal ion on the liquid-liquid dispersion was ignored in this study.

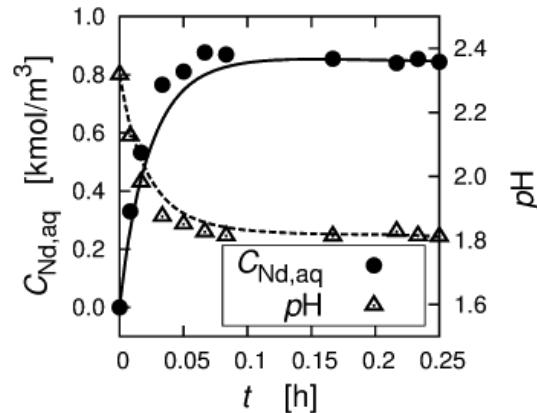


Fig. 3. Time Course of pH and Nd Concentration in Aqueous Raffinate.
 $N: 1.8 \times 10^4 \text{ 1/hr}$, $C_{\text{Nd,aq},0}: 5.0 \times 10^{-3} \text{ kmol/m}^3$, $C_{(\text{RH})2,\text{org},0}: 0.25 \text{ kmol/m}^3$,
 $R_0: 9.0 \times 10^{-3} \text{ m}^3/\text{h}$, $E_0: 3.0 \times 10^{-3} \text{ m}^3/\text{h}$, $pH_0: 3.32$.

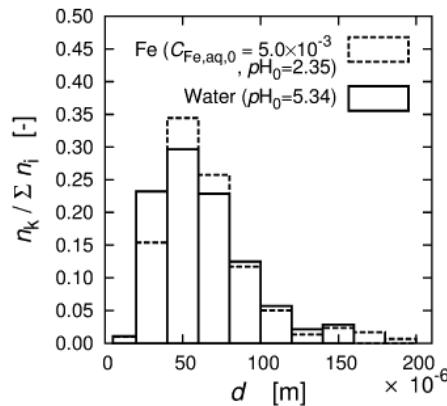


Fig. 4. Drop Size Distributions of Organic Dispersed Phase in Vessel. $N: 1.8 \times 10^4 \text{ 1/hr}$, $C_{(\text{RH})2,\text{org},0}: 0.25 \text{ kmol/m}^3$, $R_0: 9.0 \times 10^{-3} \text{ m}^3/\text{h}$, $E_0: 3.0 \times 10^{-3} \text{ m}^3/\text{h}$.

Table 3 shows the sauter mean diameter, d_{32} , and holdup of the dispersed phase, Φ , measured with the aqueous phase without metal ion. The d_{32} decreased, and Φ increased as N increased. The ratio of E relative to the outlet flow rate of total solution, $R+E$, was fixed at 0.25, and Φ attained this value at $N = 3.5 \times 10^4 \text{ h}^{-1}$. In the range of $N < 2.4 \times 10^4 \text{ h}^{-1}$, Φ was smaller than the ratio of 0.25. That is to say, the volume fraction of dispersed phase was different with location in the vessel, so that the perfect mixing might not be achieved in the vessel in this range.

Figure 5 shows the effects of aqueous feed flow rate on the fractional yield, Y_M , and extraction rate, X_M of Nd at the fixed organic solvent flow rate of $E_0=3.0\times10^{-3} \text{ m}^3/\text{h}$ where pH_0 in the feed solution and N were fixed as 2.59 and $1.8\times10^4 \text{ h}^{-1}$, respectively. The Y_{Nd} increased with the decrease of R_0 , because the residence time of aqueous solution in the stirred vessel increased with the decrease of R_0 , while the X_{Nd} decreased with the decrease of R_0 because the difference of metal concentrations between two phases, which is the driving force of extraction reaction, decreased with increase of residence time of aqueous solution in the stirred vessel. Figure 6 shows the effects of pH_0 in the aqueous feed solution on Y_{Nd} and X_{Nd} , in which N , R_0 and E_0 were fixed as $1.8\times10^4 \text{ h}^{-1}$, $9.0\times10^{-3} \text{ m}^3/\text{h}$ and $3.0\times10^{-3} \text{ m}^3/\text{h}$, respectively. The Y_{Nd} increased as pH_0 increased, because pH should largely affect D_{Nd} , as shown by Eq. (2) and in Fig. 2. According to Eq. (2), Y_{Nd} should be affected by pH_0 and $C_{\text{org},(\text{RH})2}$. The stirring velocity and solvent/feed flow ratio were also expected to have an influence on the extraction rate. Then for the further study, the effects of these experimental parameters on the extraction would be investigated. Then to understand the effects of the operating conditions on the extraction rate, other experimental parameters, such as the extractant concentration, ratio of the feed and organic solvent flow rates, and so on, should be studied to evaluate the extraction efficiency with the stirred vessel and to develop the rare earth metal extraction process.

Table 3. Effects of Stirring Velocity on Sauter Mean Diameters and Holdups of Dispersed Phase. $C_{\text{org},(\text{RH})2,0}$: 0.25 kmol/m³, R_0 : $9.0\times10^{-3} \text{ m}^3/\text{h}$, E_0 : $3.0\times10^{-3} \text{ m}^3/\text{h}$, pH : 5.34.

$N\times10^{-4} \text{ [1/h]}$	1.8	2.4	3.2
$d_{32}\times10^6 \text{ [m]}$	89.3	88.0	86.7
$\Phi \text{ [-]}$	0.09	0.14	0.25

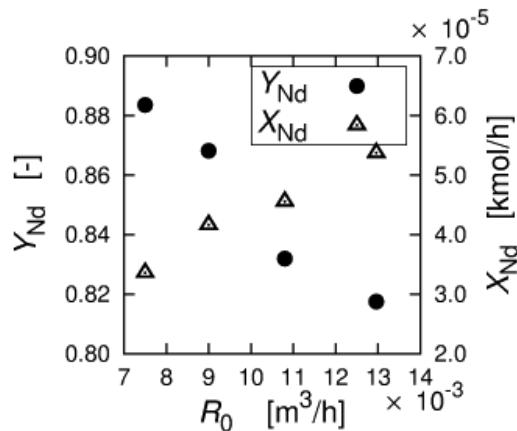


Fig. 5. Effects of R_0 on Yield and Extract Rate of Nd, Y_{Nd} and X_{Nd} .
 N : $1.8\times10^4 \text{ 1/hr}$, $C_{\text{Nd,aq},0}$: $5.0\times10^{-3} \text{ kmol/m}^3$, $C_{(\text{RH})2,\text{org},0}$: 0.25 kmol/m³, E_0 : $3.0\times10^{-3} \text{ m}^3/\text{h}$, pH_0 : 2.59.

In order to understand further the effects of the operating conditions on the extraction rate, other experimental parameters, such as the extractant concentration, ratio of the feed and organic solvent flow rates, and so on, should be studied to evaluate the extraction efficiency with the stirred vessel and to combine the mass transfer rate equation with equilibrium relationships, for the improvement of the rare earth metal extraction process.

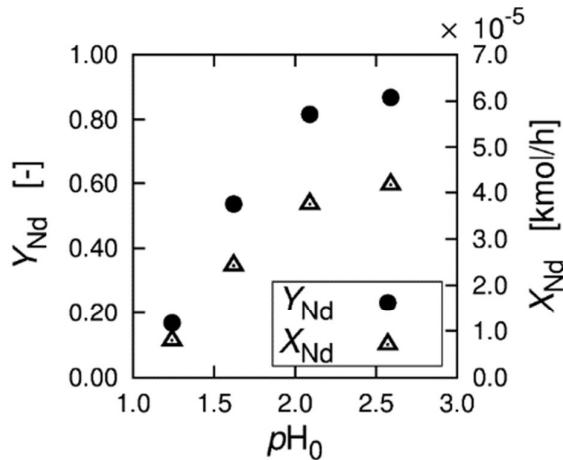


Fig. 6. Effects of pH_0 on Yield and Extract Rate of Nd, Y_{Nd} and X_{Nd} .
 $N: 1.8 \times 10^4$ 1/hr, $C_{Nd,aq,0}: 5.0 \times 10^{-3}$ kmol/m³, $C_{(RH)2,org,0}: 0.25$ kmol/m³,
 $R_0: 9.0 \times 10^{-3}$ m³/h, $E_0: 3.0 \times 10^{-3}$ m³/h.

4. Conclusions

It was confirmed that the distribution ratio of neodymium increased as pH increased and the extraction reaction of neodymium was almost same as reported in the previous study. In the cases of the extraction with a stirred vessel, the continuous operation could be successfully conducted to attain the steady state, and the metal ion could be extracted. The fractional yield of the metal ion increased as the flow rate of and pH in the feed phase decreased.

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