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The effective recovery of praseodymium from mixed rare earths via a hollow fiber supported liquid membrane and its mass transfer related

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ABSTRACT

The recovery of praseodymium from mixed rare earths via a hollow fiber supported liquid membrane (HFSLM) was examined. Bis(2,4,4-trimethylpentyl) phosphinic acid – known as Cyanex 272 – was used as an extractant carrier. The stripping solution was hydrochloric acid solution. The experiments examined in functions of the concentrations of the carrier in liquid membrane, the (initial) pH's of initial feed solution within the acidic-pH range, the concentrations of hydrochloric acid, the flow rates of feed and stripping solution, and the operation mode of runs through the hollow fiber module. In addition, the influence of circulation of the stripping solution at various numbers of runs through the HFSLM on the outlet concentration of praseodymium ions in the stripping solution was observed.

Mass transfer mechanism in the system was investigated. Extraction equilibrium constant (K_{ex}), distribution ratio (D), permeability (P) and mass transfer coefficients were determined. The aqueous-phase mass-transfer coefficient (k_i) and organic-phase mass-transfer coefficient (k_m) were reported to 0.0103 and 0.788 cm s^{-1}, respectively, in which k_m is much higher than the k_i. Thus it suggests the rate-controlling step is the diffusion of praseodymium ions through the film layer between the feed solution and the liquid membrane. Model prediction of the dimensionless concentrations and separation factors were also put on trial in this paper. The results showed promising agreement with the experimental data.

1. Introduction

Praseodymium (Pr) is one of elements recovered from mixed rare-earth (RE) metals. It is very useful despite of trace amount and is a composition in mischmetall, i.e. alloy [1]. Most of the praseodymium applications utilize its influence on light and its colour properties. It is used, along with other rare earths, in the core material for carbon arcs in film studio light, searchlights and floodlights. Praseodymium produces brilliant colours in glasses and ceramics. Yellow didymium glass, containing praseodymium, absorbs infrared heat radiation, and is therefore used in goggles to protect the eyes of welders and glass blowers. By courtesy of Rare Earth Research and Development Center, Office of Atoms for Peace, Bangkok, Thailand, source of praseodymium for study was supplied in nitrate solutions RE(NO_3)$_3$ – the digestion product of monazite ores processing. Separation of praseodymium RE metal and investigation on the mass transfer related is the objective of this study.

The selective separation of mixed rare-earth (RE) metals, including praseodymium, poses glaring challenge to the industry while, recently, numerous attempts has been made to develop efficient separation and concentration processes for RE metals which are in great demand owing to their unique physical and chemical properties best suited for the creation of advanced materials for high-technology devices. The technique of fractionation and ion exchange were originally used for the separation of RE metals; however, it complicated the industry with tedious effort and great time consuming particularly adjacent heavy rare earth. Solvent extraction subsequently became renowned as an effective technique for separating and concentrating on industrial scale. But it requires a large number of stages in a series of mixer-settlers to obtain high-purity products of RE metals since the chemical and physical properties of their adjacent elements bears very similar. Therefore alternative technique by the use of solvent extraction across hollow fiber supported liquid membrane (hereafter called HFSLM) to overcome those complications has been introduced. It combines many advantages over traditional solvent extraction as following [2,3]: (1) low capital and operating costs, (2) low energy consump-

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tion, (3) economic uses of expensive tailor-made extractants and solvents because only an extremely small amount of membrane liquid is required for filling the pores, (4) low maintenance costs due to fewer moving parts, and (5) and possibility of achieving high overall separation factor.

In the recent years, the separation of ions with very low concentration has been focused on liquid membrane (LM) techniques. Especially, the HFSLM is excellent to extract ions in the highly-diluted solution at part-per-trillion (ppt) concentration levels. LM's can carry out simultaneous extraction and stripping processes in the same stage, and benefits a non-equilibrium mass transfer and up-hill effect, where the solute can move from low- to high concentration solutions [4–7]. Main types of liquid membrane systems include emulsion liquid membrane (ELM) [8], supported liquid membrane (SLM) [9], bulk liquid membrane (BLM), flowing liquid membrane (FLM) [10] and electrostatic pseudo liquid membrane (EPLM) [5]. The liquid membrane acts as a solvent for a transported solute which is governed by the solubility in the liquid membrane. The most interesting case arises when this solubility is controlled by a chemical reaction between the transported solute and the extractant-carrier molecule to form a solute-carrier complex. This kind of transport is called "facilitated transport" or "carrier-mediated transport" [11]. The carrier-mediated transport through an organic membrane is used largely for the separation objectives [12,13]. The selectivity in this technique is controlled by both the extraction/back-extraction (stripping) equilibrium at the interfaces and the kinetics of the transported species under a non-equilibrium mass-transfer process [14]. Acidic ligands are frequently used as the extractant-carriers for separation of metal ions [15–18]. One of the most important advantages of such systems is the possibility to tune the selectivity and efficiency of the transport by controlling the (initial) pH of the aqueous feed phase and/or receiving phase or recovery phase (a stripping phase). It has been reported to satisfied separation of RE metals via HFSLM, for example, a selective separation of cerium(IV), tetravalent and trivalent lanthanide ions [19] and the separation of uranium ions from nitrate media [20]. For the latter case, the percent-ages of extraction and stripping were highly dependent on the concentration of HNO_3 in the feed solution and did not increase much because the permeabilities decreased due to membrane fouling concentration polarlization and the decrease in diffusivity of feed solution. In addition, Fontas et al. [21] reported that their HSLM system could be effectively used for the pre-concentration of Rh(III) from diluted solutions and thus the possibility to apply it in the analysis of this metal at low-level concentrations.

2. Theory

2.1. Liquid membrane mechanism

Cyanex 272 dissoved in organic solution as an extractant carrier was embedded in hydrophobic microporous as a part of liquid membrane in hollow fiber module. It played role as an accelerator for the transport of the specific component from the feed phase to the stripping phase. The extractant can be single or synergism with other extractant to enhance the separation. Liquid membrane blinded the phases between the feed and the stripping solutions which flowed counter-currently. The transport mechanism of Pr(III) ions through the liquid membrane is shown in Fig. 1.

Pr(III) ions in the produced RE nitrate, which served as a feed solution, presented in the ionic form of Pr^{3+} [22]. The Pr^{3+} ions reacted with the extractant (Cyanex 272 shown as HR) to form the complex species as shown in Eq. (1) [23]:

$$Pr^{3+} + 3HR \rightleftharpoons PrR_3 + 3H^+ \quad (1)$$

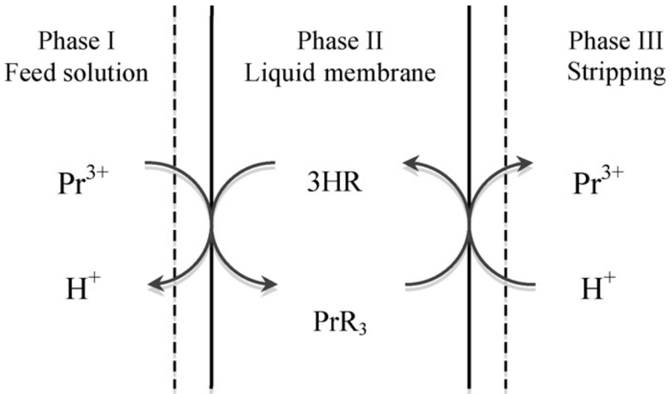

Fig. 1. Counter-transport scheme of Pr^{3+} extraction and stripping by Cyanex 272.

The praseodymium complex species diffused to the opposite side of the liquid membrane by the concentration gradient and reacted with the stripping solution HCl, to strip Pr^{3+} ions into the stripping phase as shown in Eq. (2), [23];

$$PrR_3 + 3H^+ \rightleftharpoons Pr^{3+} + 3HR \quad (2)$$

In this research, the extractability of praseodymium ions could be determined by the percentage of extraction:

$$\%\text{Extraction} = \frac{C_{f,in} - C_{f,out}}{C_{f,in}} \times 100 \quad (3)$$

and the percentage of recovery was calculated by:

$$\%\text{Striping} = \frac{C_{s,out}}{C_{f,in}} \times 100 \quad (4)$$

The selectivity was defined as:

$$S_i = \frac{C^i_{out,s}}{\sum_{i=1}^{n} C^i_{out,s}} \quad (5)$$

where $C_{f,in}$, $C_{f,out}$ is the inlet and outlet feed concentrations of component i (ppm); $C_{s,in}$, $C_{s,out}$ is the inlet and outlet stripping concentrations of component i (ppm).

The extraction equilibrium constant (K_{ex}) of Pr(III) ions extracted by Cyanex 272 in Eq. (1) was derived from the experimental data and calculated from the following equation:

$$K_{ex} = \frac{[PrR_3][H^+]^3}{[Pr^{3+}][HR]^3} \quad (6)$$

The distribution ratio for praseodymium was given by

$$D = \frac{[PrR_3]}{[Pr^{3+}]} \quad (7)$$

According to Eq. (6), the distribution ratio could then be derived to a function of the extraction equilibrium constant as follows:

$$D = \frac{K_{ex}[HR]^3}{[H^+]^3} \quad (8)$$

Regarding the permeability coefficient, it could be determined from the expression as proposed by Danesi [24] in Eq. (9).

$$-V_f \ln \frac{C_f}{C_{f,0}} = AP \frac{\beta}{\beta + 1} t \quad (9)$$

$$\beta = \frac{Q_f}{PL\varepsilon\pi N r_i} \quad (10)$$

where P is the permeability coefficient (cm s^{-1}), V_f is the volume of the feed (cm^3), $C_{f,0}$ is the praseodymium-ion concentration at time 0 (mol L^{-1}), C_f is the praseodymium-ion concentration at time t

Table 1
Compositions of the produced RE nitrate (pH 5.5).

Metal ion	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Yb
Concentration (ppm)	136.7	1218	158	230	1067	193	3	77	25	0.2

(mol L^{-1}), A is the effective area of the hollow fiber module (cm^2), t is the time (min), Q_f is the volumetric flow rate of feed solution (cm^3 s^{-1}), L is the length of the hollow fiber (cm), ε is the porosity of the hollow fiber (%), N is the numbers of hollow fibers in the module, r_i is the internal radius of the hollow fiber (cm).

$AP(\beta/\beta+1)$ is the slope of the plot between $-V_f \ln(C_f/C_{f,0})$ versus t in Eq. (9), and P can be obtained by Eq. (10). To determine mass-transfer coefficients for Pr(III) ions separation by HFSLM, the mass-transfer model and permeability coefficient (P) are employed. The permeability coefficient depends on mass-transfer resistance which is reciprocal to the mass-transfer coefficients as follows [25].

$$\frac{1}{P} = \frac{1}{k_i} + \frac{r_i}{r_{lm}}\frac{1}{P_m} + \frac{r_i}{r_0}\frac{1}{k_s} \tag{11}$$

where r_{lm} is the log-mean radius of the hollow fiber, r_0 is the external radius of the hollow fiber (cm), k_i is the aqueous mass transfer coefficient in tube side, k_s is the stripping mass-transfer coefficient in shell side, P_m is the membrane permeability coefficient.

The relation between P_m and the distribution ratio (D) is as follows [25]:

$$P_m = Dk_m \tag{12}$$

Combining Eqs. (7) and (12), thus

$$P_m = \frac{K_{ex}k_m[\mathrm{HR}]^3}{[\mathrm{H}^+]^3} \tag{13}$$

where k_m is the mass transfer coefficient of the membrane.

The value of liquid membrane permeability coefficient (P_m) from Eq. (13) is substituted into Eq. (11). Assuming that the stripping reaction is instantaneous and the contribution of the stripping phase is neglected, Eq. (11) becomes:

$$\frac{1}{P} = \frac{1}{k_i} + \frac{r_i}{r_{lm}}\frac{1}{K_{ex}k_m[\mathrm{HR}]^3/[\mathrm{H}^+]^3} \tag{14}$$

where k_i is the mass-transfer coefficient of feed solution.

Through the derivation steps by Dushu [26], Eqs. (15)–(17) can be simplified as:

$$\lambda_j = \frac{\gamma_f + \gamma_s}{1/K_{e1j} + 1/K_f + 1/K_s} \tag{15}$$

$$E_{sj} = \frac{\gamma_f}{\gamma_f + \gamma_s} - \frac{\gamma_s}{\gamma_f + \gamma_s}\exp(-\lambda_j \tau) \tag{16}$$

$$\alpha = \frac{1 - \exp(-\lambda_L \tau)}{1 - \exp(-\lambda_D \tau)} \tag{17}$$

where λ_j is the constant containing γ, A, and K_{e1j}; γ_f is the constant containing area, thickness and volume in tube; γ_s is the constant containing area, thickness and volume in shell; K_{e1j} is the equilibrium constant of the interfacial reaction in the feed phase; K_f is the dimensionless from of mass-transfer coefficient in feed boundary layer; K_s is the dimensionless from of mass-transfer coefficient in strip boundary layer; E_{sj} is the dimensionless concentration of ions in the strip phase; α is the separation factor; τ is the dimensionless form of time; subscript "L" is the Pr(III) ions; "D" is the mixed rare earth.

3. Experimental

3.1. The feed solutions and the reagents

The RE(OH)$_3$ from Rare Earth Research and Development Center, Office of Atom for Peace, Bangkok, Thailand was supplied as a raw material for the experiments.

The RE hydroxide was digested with nitric acid solution. Then, the RE oxide without cerium was obtained. After cerium removing, the colour changed from yellow to pale yellow shown in Table 1, analyzed by ICP.

In this work, nitrate solution from monazite processing was, again, obtained from the Rare Earth Research and Development Center, Office of Atoms Peace. Cyanex 272 extractant was supplied by Cytec Industries Inc. The extractants were diluted in kerosene supplied by the JPI grade from the PTT Public Co., Ltd. without further purification. The structures of the extractant were shown in Fig. 2. For liquid membrane, Cyanex 272 was used as an extraction, and hydrochloric acid was used as a stripping solution. The organic solution used as an extractant containing Cyanex 272 was circulated in both the tube and shell sides of hollow fiber for 40 min. Then, the experiment was commenced by feeding the feed solution in the tube side. Simultaneously, the stripping solution was pumped into the shell side counter-currently. Once-through-mode operation was used.

3.2. Apparatus

3.2.1. Hollow fiber supported liquid membrane (HFSLM)

The Liqui-Cel® Extra-Flow 2.5 × 8 Laboratory Liquid/Liquid Extraction System composed of two gear pumps, two variable speed controllers, two rotameters and four pressure gauges. The Liqui-Cel® Extra-Flow module offered by CELGARD LLC (Charlotte, NC; formerly Hoechst Celanese), was used as a support material. This module used Celgard® microporous polyethylene fibers woven into fabric and wrapped around a central tube feeder that supplies the shell-side fluid. Woven fabric allowed more uniform fiber spacing, which in turn leaded to higher mass-transfer coefficients than those obtained with individual fibers. The fibers were potted into

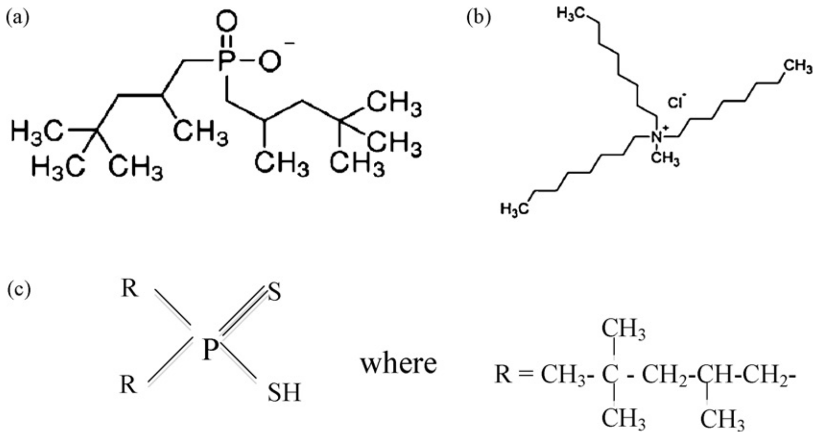

Fig. 2. The chemical structure of the extractants: (a) Cyanex 272 (b) Aliquat 336 and (c) Cyanex 301 [27].

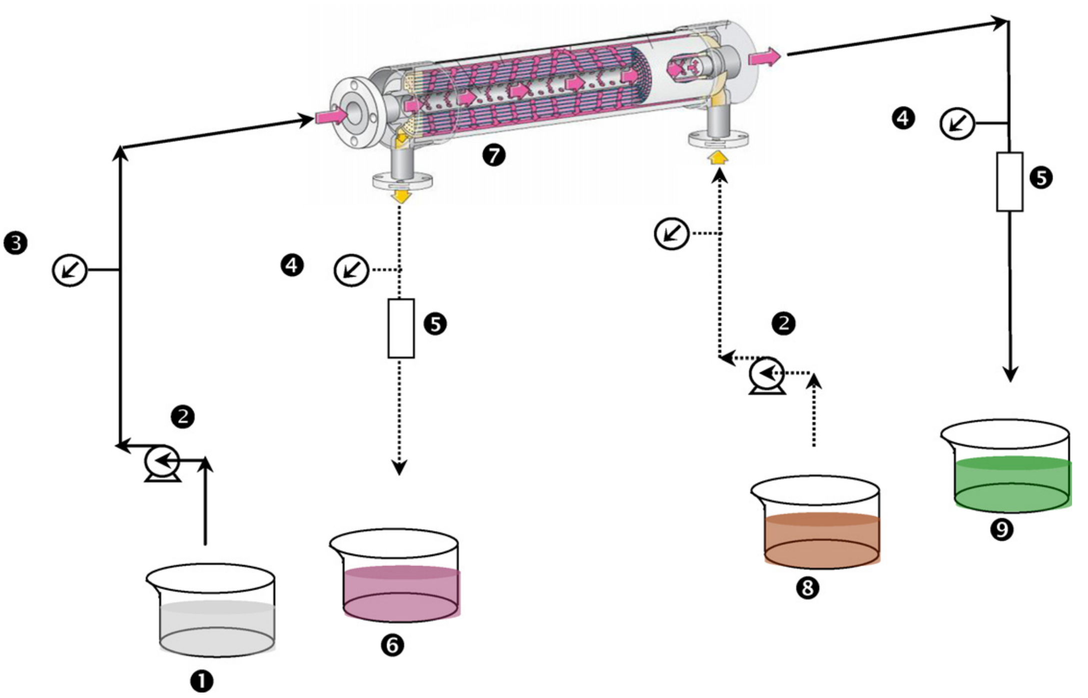

Fig. 3. Schematic counter-current flow diagram for one-through-mode operation in the hollow fiber supported liquid membrane (❶ inlet feed solution, ❷ gear pumps, ❸ inlet pressure gauges, ❹ outlet pressure gauges, ❺ outlet flow meters, ❻ outlet stripping solution, ❼ the hollow fiber module, ❽ inlet stripping reservoir, and ❾ outlet feed solution).

a solvent-resistant polyethylene tube sheet, and shell casing in polypropylene. The properties of hollow fiber module are shown in Table 2.

3.3. Procedures

The single-module operation is shown in Fig. 3. At first, the extractant was diluted in kerosene then circulated into tube and shell of HFSLM for 40 min to assure the extractant embedded in the micropores of hollow fiber. Thereafter, the feed solution was pumped into the tube side, meanwhile the stripping solution was counter-currently pumped into the shell side. The praseodymium ions from nitrate solution were moved across the liquid membrane to stripping phase and were collected in the stripping reservoir. The concentrations of praseodymium ions in sample from the feed and stripping solutions were analyzed by ICP to determine the percentages of extraction and stripping.

3.4. Analytical instrument

3.4.1. Inductively coupled plasma spectrometry (ICP)

ICP Spectrometer-model Stroflame-ICP M from Spectro Co. can detect the elements of concentrations higher than 1 ppm, in both acidic and basic states. The analyzing method comprises of:

(1) introducing 1 mL of sample into a volumetric flask of 10 mL
(2) adding use trip the volume to 10 mL by adding 1% (v/v) HNO_3, and
(3) analyzing the amount of praseodymium in this sample.

Table 2
The Properties of the hollow fiber module [28,29].

Property	Description
Material	Polypropylene
Fiber inside diameter (cm)	24.0×10^{-3}
Fiber outside diameter (cm)	30.0×10^{-3}
Pore size (μm)	0.03
Porosity (%)	30
Tortuosity	2.6
Active interfacial area (m^2)	1.4
Area per unit volume ($cm^2\ cm^{-3}$)	29.3
Module diameter (cm)	6.3
Module length (cm)	20.3
Number of fiber	10,000

4. Results and discussion

4.1. The effects of the (initial) pH of nitrate solution

$RE(OH)_3$ was added with HNO_3 to vary feed (initial) pH of 1, 3.5, 4.5, and 5.5 as shown in Fig. 4. It was observed that Ce and Nd were found very active for most the (initial) pH cases but not with (initial) pH of 5.5 since Ce and Nd (also the others RE metals) were observed with the passive profile which favors the selectivity of Pr. Fig. 5 exhibits the assay of RE nitrate solution at pH of 5.5 in more detail with particular note made for Ce that Ce is precipitated and drastically drop in profile by this (initial) pH. Interference to Pr selectivity was given less thus promoting the favor of using (initial) pH 5.5 for further study.

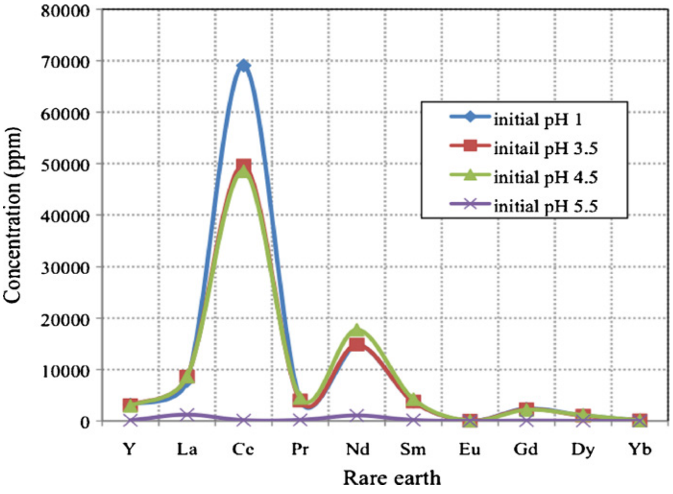

Fig. 4. The concentration of RE nitrate solution (ppm) by varying the pH.

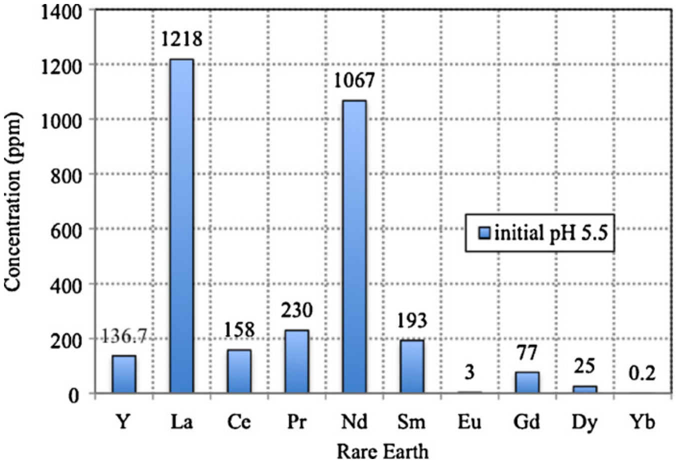

Fig. 5. The concentration of RE nitrate solution (ppm) at pH 5.5.

4.2. *The effects of the types of extractant on praseodymium*

Present in Fig. 6 for the experiment results on HFSLM system, the performance of each extractant in trial is exhibited. It is read that Aliquat 336 was the best yield of extraction but it was inferior to Cyanex 272 in term of recovery and Pr selectivity. Therefore Cyanex 272 became successful candidate extractant for further study considering to its ability as the best recovery bearing, the best selectivity and fairly good extraction.

4.3. *The effects of the extractant concentration*

The concentrations of Cyanex 272 were studied in the ranges of 5–15% (v/v). Praseodymium extraction increased with an increase in the extractant concentration, as shown in Fig. 7. The highest percentage of praseodymium extraction was obtained at the concentration of 10% (v/v) and it was recorded as the optimized concentration to use in further run.

However, in this work, the extractant concentration higher than 10% (v/v) showed no significant change in praseodymium extraction; attributed to the fact that, theoretically, the fluxes decreased at higher extractant concentrations because the viscosity of the film between the feed solution and the liquid membrane increased and obstructed the mass transfer.

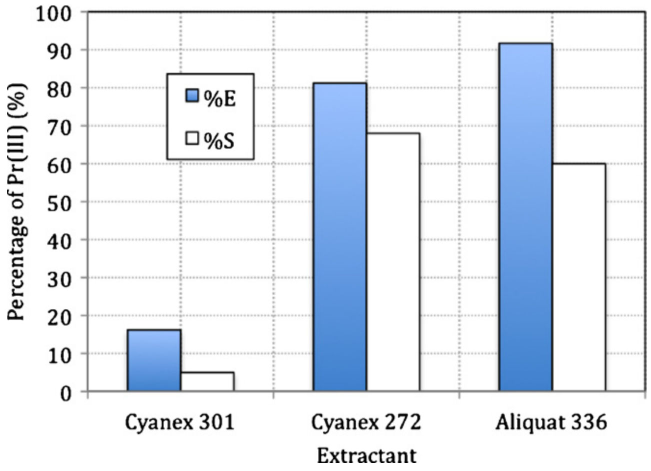

Fig. 6. The percentages of the extraction and stripping for praseodymium ions on extractant solution, $Q_f = Q_s = 100\,\text{ml min}^{-1}$.

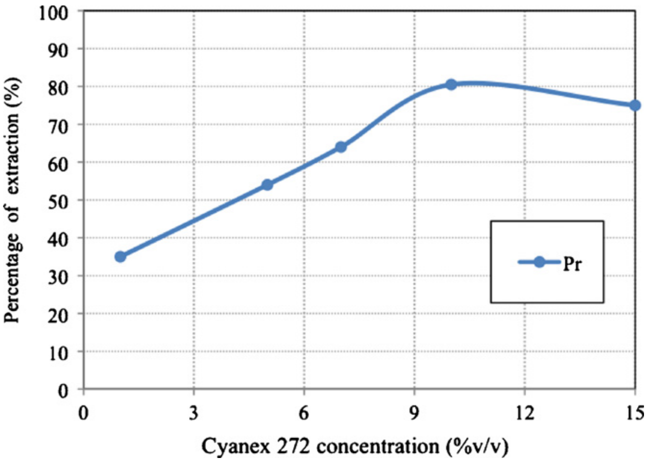

Fig. 7. The percentages of extraction against the Cyanex 272 concentrations: pH of feed solution = 5.5, stripping solution by using 0.6 M hydrochloric acid as stripping solution, $Q_f = Q_s = 100\,\text{ml min}^{-1}$.

4.4. *The effects of the stripping solution concentration*

The concentrations of stripping solution (HCl) were studied at 0.1–0.8 M. The progressive increase in the percentage of praseodymium stripping was found when the concentration of stripping solution increased. This indicated that HCl accelerated the extraction and stripping processes. From Figs. 7 and 8, for single-module operation, the highest praseodymium extraction and stripping of about 80% and 71%, respectively, were achieved respectively at the HCl concentration of 0.6 M. This (0.6 M) will be referred for the next study run in an attempt to establish the highest possible Pr recovery.

4.5. *The effects of the flow rates of feed and stripping solutions*

The percentage of extraction and stripping of praseodymium at different equal flow rates of feed and stripping solutions shown in Fig. 9. The results indicated that by using a single-module operation for 50 min at the flow rates of feed and stripping solutions of $100\,\text{ml min}^{-1}$, the highest percentages of praseodymium extraction and stripping of 80% and 71%, respectively, were obtained. However, the percentages of praseodymium extraction and stripping decreased with an increase of the flow rates of feed and strip-

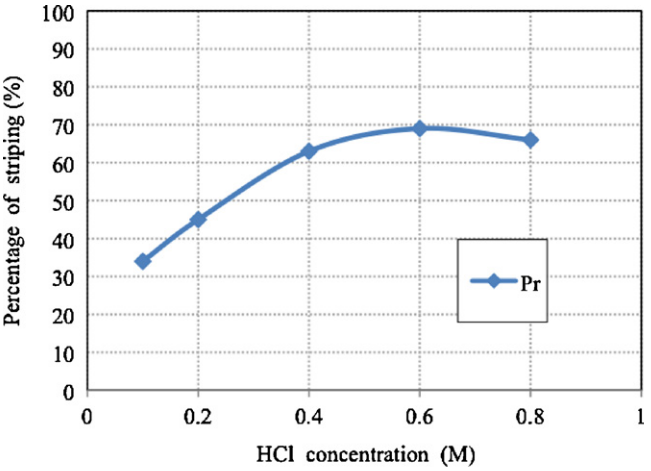

Fig. 8. The percentage of extraction against HCl concentration: Cyanex 272, 10% (v/v), pH of feed solution = 5.5, solution and $Q_f = Q_s = 100\,\text{ml min}^{-1}$.

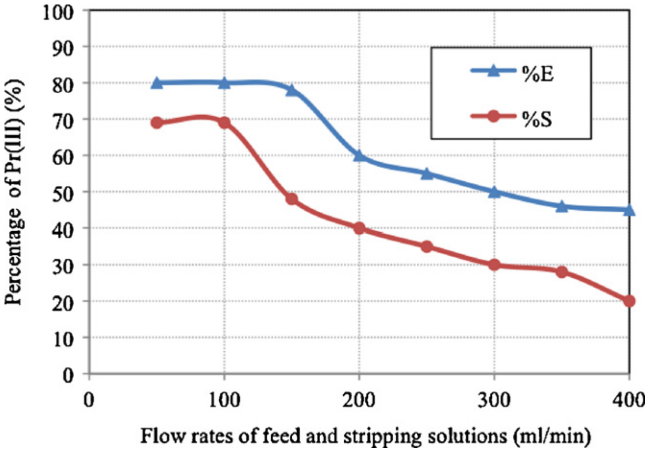

Fig. 9. The percentages of praseodymium ions extraction and stripping against flow rate of feed and stripping solutions: Cyanex 272 concentration, stripping solution [HCl] = 0.6 M and pH of feed solution = 5.5.

ping solutions due to resident time of solution in the hollow fiber module.

4.6. *The effects of the numbers of separation cycles*

The numbers of separation cycle were studied using the optimum conditions in a single-module operation to expect the highest possible separation and the least possible praseodymium concentration in the feed as well as to inspect the membrane stability. Fig. 10 shows that the percentages of praseodymium cumulative extraction and cumulative stripping were obtained at 6-cycle operation for 300 min. The cumulative extraction and stripping reached 91.7% and 78% respectively. The membrane stability was verified.

4.7. *The extraction equilibrium constant and distribution ratio*

The extraction equilibrium constant (K_{ex}) was calculated by the slope of the graph in Fig. 11 and found to be 1.98×10^{-1} $(\mathrm{L\,mol^{-1}})^4$. The distribution ratio (D) at the Cyanex 272 concentration of 1.0–10% (v/v) were calculated by Eqs. (6) and (7) as shown in Table 3. It was noted that the distribution ratio increased with the extractant concentration, agreed with the earlier report by Pancharoen et al. [30].

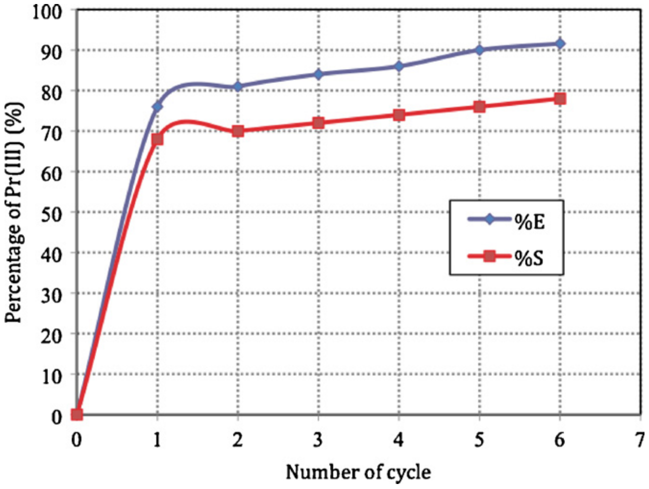

Fig. 10. The percentages of Pr(III) extraction and stripping against the numbers of separation cycle: Cyanex 272 (10% (v/v), stripping solution [HCl] = 0.6 M, pH of feed solution = 5.5 and $Q_f = Q_s = 100\,\mathrm{ml\,min^{-1}}$.

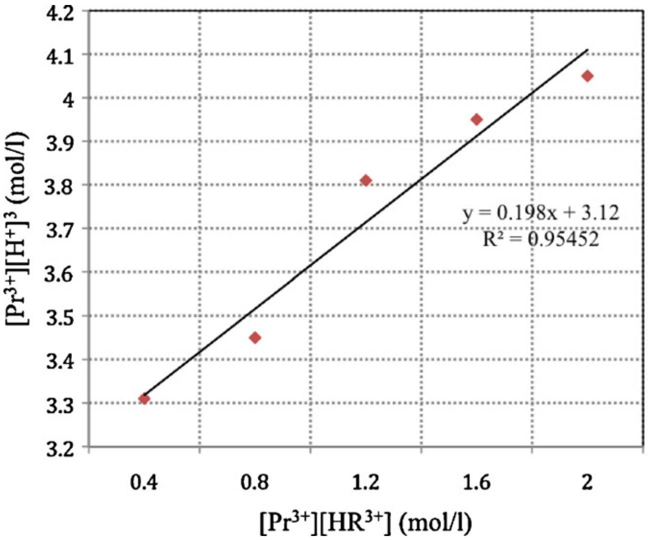

Fig. 11. Praseodymium extraction with Cyanex 272 as a function of equilibrium [Pr^{3+}][HR]^3.

Table 3
The distribution ratio (D) at the Cyanex 272 concentrations of 1.0–10.0% (v/v).

Cyanex 272% (v/v)	1.0	5.0	7.0	10.0
D ($\times 10^2$)	0.462	0.812	1.38	1.55

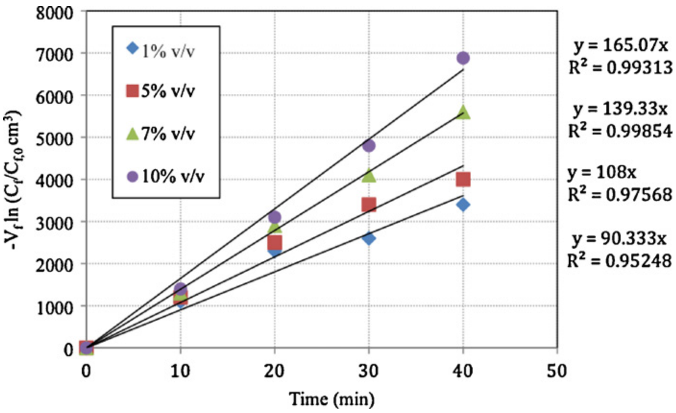

Fig. 12. Plot of $-V_f \ln(C_f/C_{f,0})$ of praseodymium ions in feed solution against time with different Cyanex 272 concentrations.

4.8. *The permeability coefficient*

The permeability coefficients for praseodymium separation at Cyanex 272 concentration of 1.0–10.0% (v/v) were calculated by the slope obtained in Fig. 12 as shown in Table 4. The results showed that the permeability coefficient increased with the extractant concentration–agreed with the earlier report by Pancharoen et al. [30].

4.9. *The mass-transfer coefficients*

The aqueous-phase mass-transfer coefficient (k_i) and organic-phase mass- transfer coefficient (k_m) were evaluated by Eq. (14).

Table 4
The permeability coefficient (P) at the Cyanex 272 concentrations of 1.0–10.0% (v/v).

Cyanex 272% (v/v)	1.0	5.0	7.0	10.0
P ($\times 10^2\,\mathrm{cm\,s^{-1}}$)	2.699	3.812	5.189	7.751

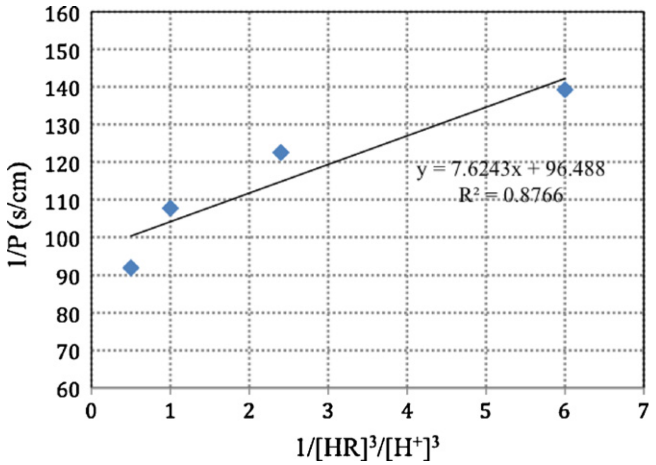

Fig. 13. Plot of $1/P$ as a function of $1/([HR]^3/[H^+]^3)$.

The plot of $1/P$ as a function of $1/([HR]^3/[H^+]^3)$ against Cyanex 272 concentration was shown in Fig. 13. The slope and the ordinate were $(r_i/r_{lm})(1/K_{ex}k_m)$ and $1/k_i$, respectively. Thus, k_i and k_m were 0.0103 and 0.788 cm s^{-1}, respectively.

As a result, the membrane mass-transfer coefficient (k_m) was greater than the aqueous phase implying that the rate-controlling step was the diffusion of praseodymium ions through the film layer between the feed solution and the liquid membrane.

4.10. The dimensionless concentration in the feed phase and strip phase

The equilibrium constant and the forward ions selective reaction rate constants of both ions were determined by equilibrium and kinetic agreed with the results stated earlier by Picdering and Chaudhuri [31].

The model prediction of the dimensionless concentrations were taken in both the feed and the stripping phases. The validity of Eq. (16) was conducted against the experimental data. By using those previous-defined parameters, the computational results represented by dot line in Fig. 14 were in good agreement with the experimental data. Therefore, it could be concluded that Eq. (16) could very well simulated the dimensionless concentrations.

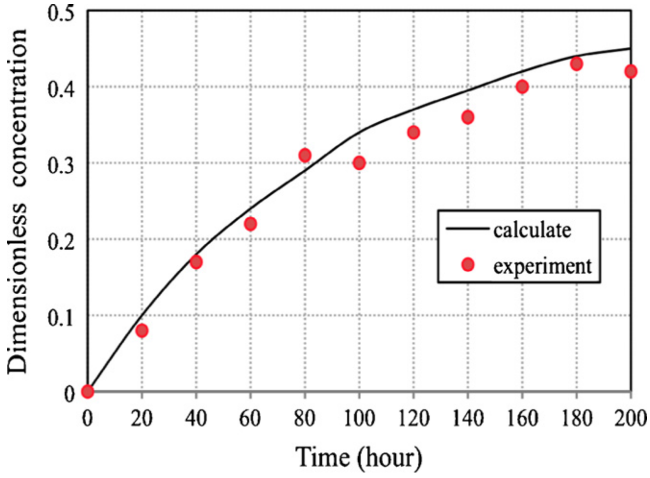

Fig. 14. The model prediction dimensionless concentration of praseodymium ions vs the experimental data dimensionless concentration of praseodymium ions in the stripping phase (E_{sPr}); solid line: results computed by Eqs. (16) of E_{sPr}.

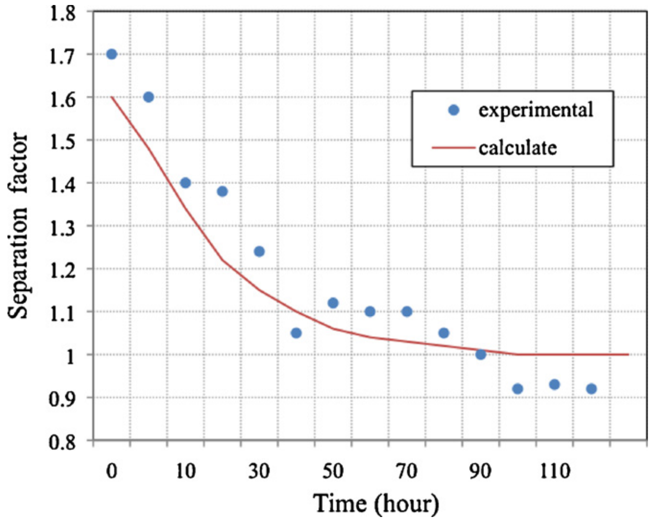

Fig. 15. The model prediction of separation factor versus. the experimental result experimental data of separation factor; solid line: results computed by Eqs. (17).

It is observed that the dimensionless concentrations changed rapidly in the first few hours of operation and then slowly progressed to reach equilibrium. The equilibrium dimensionless concentration, E_{sPr}, at equilibrium was read to about 0.5. This should probably be contributed from the solvent system of the strip phase was same as that of the feed phase. Accordingly, for this study system, Eq. (16) could be derived to Eq. (18) as below.

$$E_{sPr} = 0.5 - 0.5\,\exp(-3.17 \times 10^{-6} t) \qquad (18)$$

4.11. Experimental data and model prediction of separation factor

The separation factor of the praseodymium ions separation process was showed in Fig. 15. The computational results were shown by the solid line which was in good agreement with the experimental data. Therefore, it could be concluded that Eq. (17) simulated the dimensionless concentrations well.

In this system, the separation factor was highest at an initial stage, declined rapidly in next few hours and reached unity at equilibrium stage. With the limit approach, Eq. (17) can be reduced to Eq. (19) and later to Eq. (20) given that the solvent system of the feed solution was similar to that of the strip solution ($\gamma_f = \gamma_s$) [32].

$$\lim_{\tau\to 0}\alpha = \frac{\lambda_{Pr}}{\lambda_{Ln}} \qquad (19)$$

$$\lim_{\tau\to 0}\alpha = \frac{(1/K_{e1Ln}) + (1/K_f) + (1/K_s)}{(1/K_{e1Pr}) + (1/K_f) + (1/K_s)} \qquad (20)$$

5. Conclusion

Progressive research helps separate praseodymium ion form mixed rare earths ($RE(NO_3)$). The optimum values of the parameters were applied to the mixed rare earths ($RE(NO_3)$) to attain high percentages of praseodymium ions extraction and stripping with those used by Cyanex 272, which is a basic extractant. In this work, for 300 min at 6-cycle operation via HFSLM system, the praseodymium percentages of cumulative extraction and cumulative stripping were 91.7% and 78%, respectively, from (initial) pH of feed solution of 5.5, 10% (v/v) Cyanex 272, 0.6 M HCl, and 100 mL min^{-1} of feed and stripping solutions. The concentration of praseodymium ions remaining in the feed meets the discharge permit issued by Rare Earth Research and Development Center, Office of Atom for Peace, Bangkok Thailand. The mass-transfer coefficients of the aqueous phase (k_i) and organic phase (k_m) were 0.0103 and 0.788 cm s^{-1}, respectively. Therefore, the rate-controlling step was the diffusion of praseodymium ions through the film layer between the feed solution and liquid membrane.

By this study, it demonstrates that Praseodymium ions could be selectively extracted from mixed RE by solvent extraction in HFSLM, particularly under room temperature, unlike other techniques which require high temperature to operate. This is one of great benefits offered by HFLSM extraction.

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References

[1] P. Enghag, Encyclopedia of the Elements: Technical Data-History Processing-Applications, John Wiley & Sons Inc, 2004.
[2] L.L. Tavlarides, J.H. Bae, C.K. Lee, Science and Technology 22 (2) (1987) 581–617.
[3] B. Suanmamuang, S. Laoharochanapan, Office of Atoms for Peace, Thailand Institute of Nuclear Technology, Bangkok, Thailand, 2002.
[4] T. Franken, Membrane Technology 85 (5) (1997) 6–10.
[5] GuF Z.M., Membrane Science and Technology 23 (4) (2003) 214–223.
[6] A.M. Sastre, A. Kumar, J.P. Shukla, R.K. Singh, Separation and Purification Methods 27 (2) (1998) 213–298.
[7] W.D. Zhang, A. Li, Z.Q. Ren, Chinese Journal of Chemical Engineering 20 (2006) 843–846.
[8] N.N. Li, U.S. Patent 3,410,794 (1968).
[9] R. Bloch, A. Finkelstein, I and EC Process Design Development 6 (2) (1967) 231–237.
[10] M. Teramoto, H. Matsuyama, T. Yamashiro, S. Okamoto, Journal of Membrane Science 45 (1–2) (1989) 115–136.
[11] L. Boyadzhiev, Z. Lazarova, in: R.D. Noble, S.A. Stern (Eds.), Membrane Separation Technology: Principles and Applications, Elsevier Science, 1994.
[12] T. Araki, H. Tsukube (Eds.), Liquid Membrane, Chemical Applications, CRC Press, Boca Raton, FL, 1990.
[13] R.D. Noble, J.D. Way (Eds.), Liquid Membrane: Theory and Applications, ACS Press, Washington, 1987.
[14] X.J. Yang, A.G. Fane, Separation Science and Technology 34 (9) (1999) 1873–1890.
[15] M.R. Yaftian Corresponding Author Contact Information, A.A. Zamani, S. Rostamnia, Separation and Purification Technology 49 (2006) 71–75.
[16] R.S. Juang, Journal of Membrane Science 85 (2) (1993) 157–168.
[17] H. Kondo, M. Nishida, I. Yoshida, Analytical Sciences 18 (2) (2002) 113–118.
[18] Y. Yamini, M. Chaloosi, H. Ebrahimzadeh, Talanta 56 (4) (2002) 797–803.
[19] P. Ramakul, W. Pattaweekongka, U. Pancharoen, Journal of the Chinese Institute of Chemical Engineers 36 (5) (2005) 1–7.
[20] U. Pancharoen, P. Ramakul, W. Patthaveekongka, Journal of Industrial and Engineering Chemistry 11 (6) (2005) 926–931.
[21] C. Fontas, C. Palet, V. Salvado, M. Hidalgo, Journal of Membrane Science 178 (1–2) (2002) 131–139.
[22] K. Changkrueng, Master Thesis, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, 2006.
[23] Y. Xiong, D. Wu, D. Li, Hydrometallurgy 82 (2006) 184–189.
[24] Y. Li, C.M. Turck, J.K. Teumer, E. Stavnezer, Unique sequence, ski, in Sloan-Kettering avian retroviruses with properties of a new cell-derived oncogene, Journal of Virology 57 (1986) 1065–1072.
[25] N.S. Rathore, J.V. Sonawane, Anilkumar, A.K. Venugopalan, R.K. Singh, D.D. Bajpal, ShuklaF J.P., Journal of Membrance Science 189 (2001) 119–128.
[26] H. Dushu, K. Huang, S. Chen, S. Liu, J Yu, Journal of Separation Science and Technology 43 (2008) 259–272.
[27] http://www.cytec.com. Jan. 3 2010/.
[28] http://www.liqui-cel.com. Jan. 1 2010/.
[29] I. Kasemsestha, U. Pancharoen, Journal of Metals Materials and Minerals 8 (2) (1999) 15–24.
[30] U. Pancharoen, S. Somboonpanya, S. Chaturabul, A.W. Lothongkum, Journal of Alloys and Compounds 489 (2010) 72–79.
[31] P.J. Pickering, J.B. Chaudhuri, Chemical Engineering Science 52 (3) (1996) 377–386.
[32] J.D. Clarka, B. Hana, A.S. Bhownb, S.R. Wickramasinghea, Separation and Purification Technology 42 (3) (2005) 201–211.