Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

A Concept for the Estimation of HETS for Rare Earth Separations in Extraction Columns

B. Q. Liao[ab]; C. R. Wan[b]; J. Wang[c]
[a] Department of Chemical Engineering, Lakehead University, Thunder Bay, Ontario, Canada [b] Institute of Nuclear Energy Technology, Tsinghua University, Beijing, P.R. China [c] Research Institute of Rare Earths, Baotou Iron and Steel Group Company, Inner Mongolia, P.R. China

To cite this Article Liao, B. Q. , Wan, C. R. and Wang, J.(2004) 'A Concept for the Estimation of HETS for Rare Earth Separations in Extraction Columns', Separation Science and Technology, 39: 11, 2597 — 2607
To link to this Article: DOI: 10.1081/SS-200026716
URL: http://dx.doi.org/10.1081/SS-200026716

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 11, pp. 2597–2607, 2004

A Concept for the Estimation of HETS for Rare Earth Separations in Extraction Columns

B. Q. Liao,[1,2,*] C. R. Wan,[2] and J. Wang[3]

[1]Department of Chemical Engineering, Lakehead University,
Thunder Bay, Ontario, Canada
[2]Institute of Nuclear Energy Technology, Tsinghua University,
Beijing, P.R. China
[3]Research Institute of Rare Earths, Baotou Iron and Steel Group
Company, Inner Mongolia, P.R. China

ABSTRACT

An approach is proposed to estimate the height equivalent to a theoretical stage (HETS) for multicomponent rare earth separations in extraction columns. Based on the steady concentration profiles of rare earths in the two phases along the extraction column height and the separation factor, a graphical diagram is constructed to determine the number of theoretical stages. The ratio of the two component concentrations in the organic phase and the ratio of the two component concentrations in the aqueous

---

*Correspondence: B. Q. Liao, Department of Chemical Engineering, Lakehead University, 955 Oliver Road, Thunder Bay, Ontario, Canada P7B 5E1; Fax: (807) 343-8928; E-mail: baoqiang.liao@lakeheadu.ca.

DOI: 10.1081/SS-200026716
0149-6395 (Print); 1520-5754 (Online)
www.dekker.com

phase times the separation factor are plotted against the height of the column. Rectangular steps are drawn between these two lines to determine the number of theoretical stages and thus HETS. The average HETS for Nd/Pr separation was in the range of 0.86–1.06 m under tested conditions.

Key Words: Rare earths; Separation; Extraction column; Height equivalent to a theoretical stage; Separation factor; Concentration profiles; Equilibrium model.

INTRODUCTION

Nowadays individual rare earths (RE) in high purity are usually separated by countercurrent solvent extraction processes. Currently, there are a number of advanced solvent extraction processes, including the di(2-ethyl-hexyl) phosphoric acid (D_2EHPA)/$RE_2(SO_4)_3$, mono(2-ethyl-hexyl) 2-ethyl-hexyl phosphonate (HEH[EHP])/$RECl_3$, and naphnethic acid (HA)/$RECl_3$ systems,[1–3] used in the rare earth industry. However, mixer-settler is nearly the only type of extractor applied in the rare earth industry, due to its advantages of stagewise arrangement (easy to start up and stop), stable operation, and less sensitive to changes in feed and environmental conditions.[4] However, a long residence time, large solvent inventory, and poor sealing of the system are the main disadvantages of mixer-settlers.

Compared with mixer-settlers, extraction columns show significant advantages in the following aspects: space requirements are lower and the inventory of extractant per unit of throughput is also much less than in a mixer-settler. These advantages make extraction columns quite suitable for process control that needs a quick response to changes in operating and environmental conditions. Among the various types of extraction columns, reciprocating plate extraction column (RPC) is one type of continuous, differential extractor that has been widely used for extraction operations in different braches of industry.[5–7] A variety of extraction columns containing reciprocation parts of various shapes have been reported.[5–7] In 1959, Karr introduced an extraction column fitted with reciprocating plates having large-diameter holes (15 mm) and fractional free area (−60%).[8] This type of RPC has been widely applied in various industries, including environmental pollution control and petroleum processing, with a diameter of the column up to 1.52 m.[9] Until now, this type of extractor has been successfully used in hydrometallurgical processes for metal ions extraction and separations[10–12] and nuclear spent-fuel reprocessing[13] and showed good performance.

Because rare earth separations usually involve multicomponents, a challenge faced by the application of extraction columns is the determination of the height equivalent to a theoretical stage (HETS) for design, analysis, and scale-up of industrial-scale extraction columns. Conventionally, equilibrium distribution models of multicomponent systems have to be established, and computer modeling is used to calculate the required theoretical stage number for desired separation. Modeling results are then compared with the raffinate and organic phase outlet concentrations of the extraction column to find the equivalent theoretical stage number. This method needs extensively experimental studies to establish equilibrium distribution coefficient models, in which the equilibrium distribution coefficient changes significantly in terms of metal ion concentration, the relative quantity of rare earth elements in feed, and solution pH. In this communication, we propose a simple graphical method, based on steady concentration profiles and the separation factor, a relatively constant parameter, to determine the HETS for multicomponent rare earth separations in extraction columns.

EXPERIMENTAL SYSTEM

In this investigation, the extraction system was HEH[EHP]$-NH_3 \cdot H_2O-$HCl$-$(Nd, Pr, Ce, La). Extractant HEH[EHP] was ammoniated with a known amount of ammonia to control solution pH and the quantity of rare earth extracted. Element Nd was separated from others. Extraction equilibrium experiments were conducted in separatory funnels at the ambient temperature (21–23°C). Impacts of feed concentration and the relative amount of each component in feed on the separation factors and distribution coefficients were studied. The concentration of each rare earth element in the feed and raffinate, after extraction equilibrium and phase separation, was determined by an atom scan 2000 inductively coupled plasma (ICP) system. The concentration in organic phase is calculated from the difference between the initial and equilibrium aqueous phase concentrations.

Mass transfer experiments were conducted in a 37-mm inner diameter and 5.65-m-high RPC with 1.0 M HEH[EHP] (ammoniated percentage = 30%) in kerosene. A schematic diagram of the apparatus is shown in Fig. 1, and the constructional parameters are shown in Table 1. The two phases were pumped to the column by two calibrated diaphragm-metering pumps with the heavy aqueous (continuous) phase to the top and the organic dispersed phase to the bottom. The frequency of reciprocation could readily be adjusted from 0 up to a maximum of about 8 Hz by varying the speed of the motor. The amplitude of reciprocation could be adjusted by altering the position of the yoke at the top. Table 2 lists the operating and environmental conditions for mass transfer experiments.

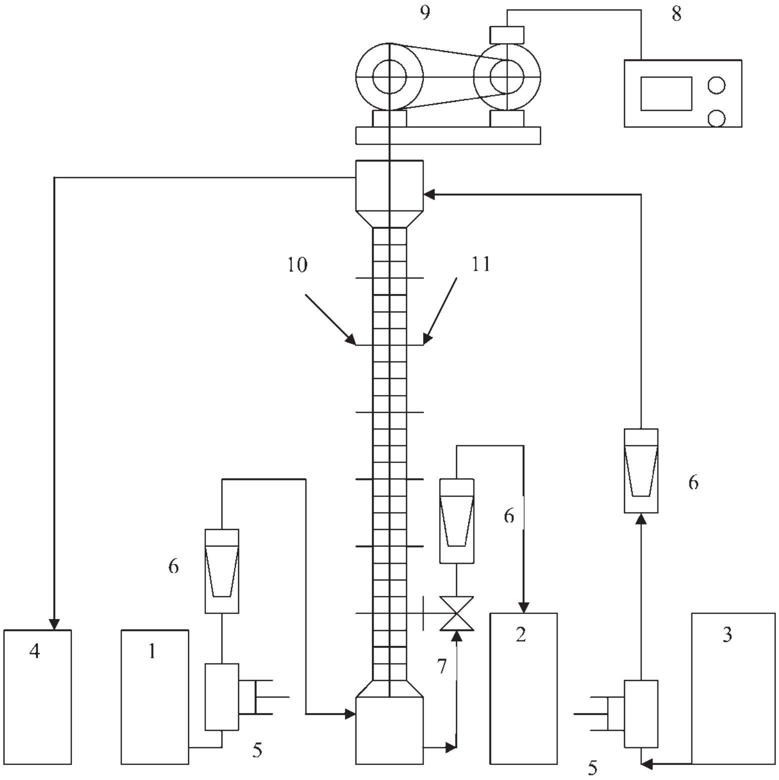

Figure 1. Schematic diagram of the reciprocating plate extraction column system. 1, organic feed tank; 2, raffinate tank; 3, aqueous feed tank; 4, organic extraction tank; 5, metering pump; 6, rotary flowmeter; 7, control value; 8, speed controller; 9, variable speed motor; 10, aqueous phase sample point; 11, organic phase sample point.

Table 1. Structural parameters of reciprocating extraction column.

Parameter	Value	Unit
Effective height of the column	5.65	m
Inner diameter	37	mm
Hole diameter of a perforated PVC plate	12	mm
Thickness of a perforated PVC plate	1.5	mm
Free cross-sectional area of a perforated PVC plate	58%	—
Interval between the adjacent perforated PVC plates	50	mm

Table 2. Operating conditions of RPC extraction experiments.

	HEH[EHP]		Velocity (cm/sec)				
Run no.	M	Ammoniated percentage (%)	Organic phase	Aqueous phase	Amplitude (cm)	Frequency (Hz)	Temperature (°C)
Extraction-run-1	1.0	30	0.240	0.061	1.30	7.17	21–23
Extraction-run-2	1.0	30	0.272	0.062	1.30	6.67	21–23

Eight sample points, including the extractant outlet and raffinate, for both the organic and the aqueous phase were designed to take samples along the extraction column height. Stainless steel hypodermic needles were inserted into the column through the nylon gaskets to withdraw aqueous phase. Organic phase was withdrawn through hypodermic needles using Telfon materials to capture organic liquid drops. The concentration of each rare earth element in the aqueous phase sample was directly analyzed by using an atom scan 2000 ICP. Rare earths elements in the organic phase sample were first stripped by using an HCl solution (6 N), and then the concentrations were analyzed by using an atom scan 2000 ICP.

RESULTS AND DISCUSSION

Equilibrium Model

Experimental results indicate that the equilibrium model of the four-component rare earth can be described by using the following set of equations,[1,2]

$$Y_{\mathrm{Nd}} + Y_{\mathrm{Pr}} + Y_{\mathrm{Ce}} + Y_{\mathrm{La}} = Y_{\mathrm{T}} \tag{1}$$

$$\alpha_{\mathrm{Nd/Pr}} = \frac{Y_{\mathrm{Nd}} X_{\mathrm{Pr}}}{(Y_{\mathrm{Pr}} X_{\mathrm{Nd}})} \tag{2}$$

$$\alpha_{\mathrm{Pr/Ce}} = \frac{Y_{\mathrm{Pr}} X_{\mathrm{Ce}}}{(Y_{\mathrm{Ce}} X_{\mathrm{Pr}})} \tag{3}$$

$$\alpha_{\mathrm{Ce/La}} = \frac{Y_{\mathrm{Ce}} X_{\mathrm{La}}}{(Y_{\mathrm{La}} X_{\mathrm{Ce}})} \tag{4}$$

where Y_i and X_i are the equilibrium organic and aqueous phase concentration of component i, respectively ($i =$ La, Ce, Pr, and Nd); $\alpha_{i/j}$ is the separation factor of component i to component j ($i =$ Nd, Pr, and Ce; $j =$ Pr, Ce, and La).

As shown in Fig. 2, the total concentration in the organic phase Y_{T} is constant when the quantity of ammonia in the organic phase is fixed and the equilibrium aqueous phase concentration is larger than 0.3 M. A total of 53 independent measurements indicated the separation factors are almost constant. The average separation factor values are $\alpha_{\mathrm{Nd/Pr}} = 1.6 \pm 0.1$, $\alpha_{\mathrm{Pr/Ce}} = 2.2 \pm 0.2$, and $\alpha_{\mathrm{Ce/La}} = 7 \pm 1$. The impact of changes in the relative quantity of Nd and Pr on $\alpha_{\mathrm{Nd/Pr}}$ is shown in Fig. 3. The linearity in Fig. 3 indicates that the separation factor $\alpha_{\mathrm{Nd/Pr}}$ is constant in terms of changes in the relative concentration of rare earth elements in feed.

According to Eqs. (1)–(4), the equilibrium organic phase concentration Y_i can be calculated from the known Y_{T}, $\alpha_{i/j}$, and X_i values.

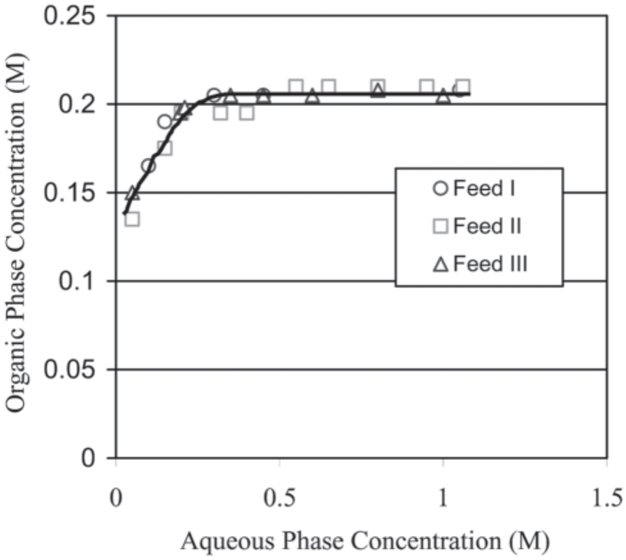

Figure 2. Impact of aqueous feed composition and concentration of rare earth in organic phase. Feed I—La_2O_3: 6.71%, CeO_2; 2.61%, Pr_6O_{11}: 3.58%, Nd_2O_3: 87.1%; Feed II—La_2O_3: 31.09%, CeO_2: 48.0%, Pr_6O_{11}: 5.53%, Nd_2O_3: 15.38%; Feed III—La_2O_3: 51.53%, CeO_2: 30.21%, Pr_6O_{11}: 9.42%, Nd_2O_3: 8.4%.

Methodology for Estimating the HETS

Based on the definition of separation factor, $\alpha_{\mathrm{Nd/Pr}}$, and rearranging Eq. (2), the following relationship is obtained,

$$\left(\frac{Y_{\mathrm{Nd}}}{Y_{\mathrm{Pr}}}\right) = \alpha_{\mathrm{Nd/Pr}}\left(\frac{X_{\mathrm{Nd}}}{X_{\mathrm{Pr}}}\right) \tag{5}$$

This is the basis for the estimation of the HETS. It is established on the fact that separation factor can be considered a constant. For an equivalent theoretical stage, the ratio of Y_{Nd} to Y_{Pr} in the organic phase (location 1) should be equal to the ratio of X_{Nd} to X_{Pr} in the aqueous phase (location 2) times the separation factor $\alpha_{\mathrm{Nd/Pr}}$. The difference in height between location 1 and location 2 is the HETS. If the concentration profiles of Nd and Pr components in both the aqueous and the organic phase are known, a plot of $Y_{\mathrm{Nd}}/Y_{\mathrm{Pr}}$ and $\alpha_{\mathrm{Nd/Pr}}(X_{\mathrm{Nd}}/X_{\mathrm{Pr}})$ against the height of the extraction column will yield two curves, as shown in Figs. 4 and 5, where the abscissa represents the height of the extraction column, and the ordinate expresses the values of $Y_{\mathrm{Nd}}/Y_{\mathrm{Pr}}$ and $\alpha_{\mathrm{Nd/Pr}}(X_{\mathrm{Nd}}/X_{\mathrm{Pr}})$. Starting from the value of $\alpha_{\mathrm{Nd/Pr}}(X_{\mathrm{Nd}}/X_{\mathrm{Pr}})$ with X_{Nd} and X_{Pr}

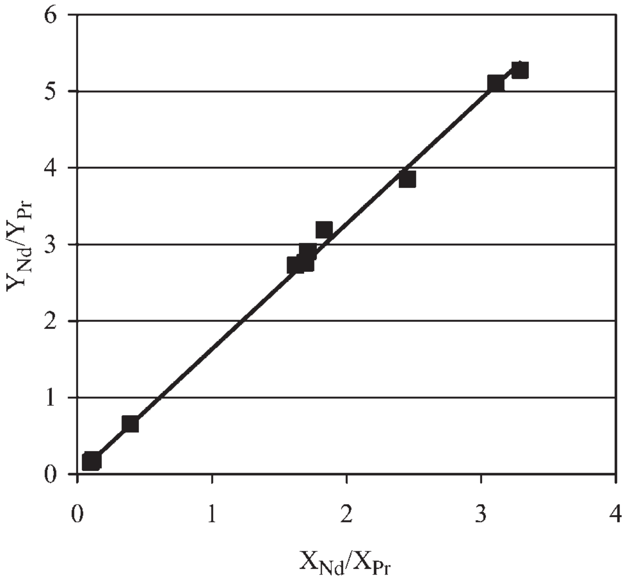

Figure 3. Impact of the relative concentration of rare earth elements in aqueous feed on the separation factor, $\alpha_{Nd/Pr}$ (total initial concentration of rare earth: 0.6–1.2 M).

in the raffinate (point A), draw a line parallel to the abscissa and intersect with the Y_{Nd}/Y_{Pr} line at point B. The distance between points A and B is the HETS for the first stage. Then rectangular steps are drawn between these two lines to obtain the number of equivalent theoretical stages. The average HETS is calculated by using the effective height of the extraction column divided by the determined number of equivalent theoretical stages. This simple method provides significant advantages over the computer calculation, because the HETS of each theoretical stage is visual.

The HETS for Pr–Nd Separation

Based on the methodology proposed above, the Y_{Nd}/Y_{Pr} and $\alpha_{Nd/Pr}(X_{Nd}/X_{Pr})$ values from the steady concentration profiles along the height of the column are plotted in Figs. 4 and 5. The theoretical stage number is 6.6 and 5.4, respectively. Consequently, the average HETS is 0.86 and 1.06 m, respectively. On the other hand, as shown in Table 3, the individual HETS is in the range from 0.65 to 1.0 m and 0.7 to 1.3 m, from Figs. 4 and 5, respectively. The difference in HETS of each stage might indicate the change in mass transfer

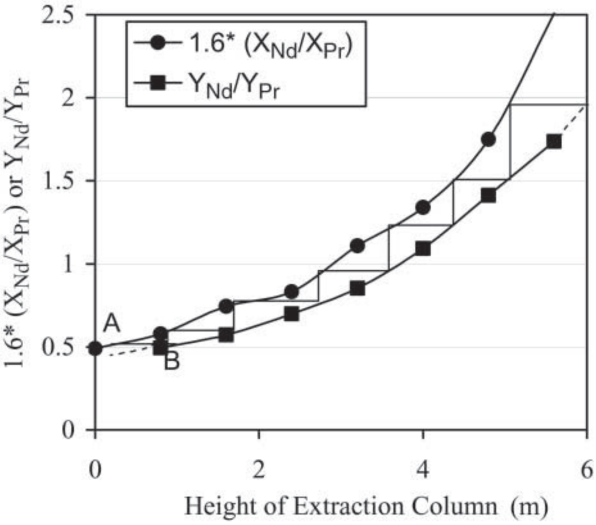

Figure 4. A plot of $Y_{\mathrm{Nd}}/Y_{\mathrm{Pr}}$ vs. $\alpha_{\mathrm{Nd/Pr}}(X_{\mathrm{Nd}}/X_{\mathrm{Pr}})$ for the estimation of the critical HETS-run-1 (aqueous feed concentration (g/L)—La: 41.40, Ce: 79.29, Pr: 9.92, Nd: 15.26; raffinate concentration (g/L)—La: 36.28, Ce: 38.98, Pr: 1.22, Nd: 0.37).

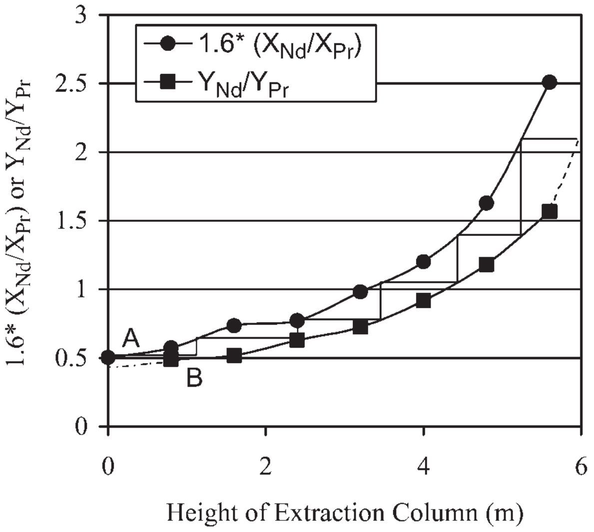

Figure 5. A plot of $Y_{\mathrm{Nd}}/Y_{\mathrm{Pr}}$ vs. $\alpha_{\mathrm{Nd/Pr}}(X_{\mathrm{Nd}}/X_{\mathrm{Pr}})$ for the estimation of the critical HETS-run-2 (aqueous feed concentration (g/L)—La: 41.40, Ce: 79.29, Pr: 9.92, Nd: 15.26; raffinate concentration (g/L)—La: 32.08, Ce: 35.37, Pr: 0.39, Nd: 0.12).

Table 3. Mass transfer results of RPC extraction experiments.

Theoretical stage no.	HETS (m)	
	Extraction-run-1	Extraction-run-2
1	0.80	1.10
2	0.80	1.30
3	1.0	1.00
4	0.85	0.90
5	0.78	0.80
6	0.65	0.70
7	0.90	—
Average value of HETS for the whole column (m)	0.86	1.06

rates in different sections of the column. Compared with the average HETS value (1.06 m) in Fig. 5, the lower average value of HETS (0.86 m) in Fig. 4 was due to a higher mass transfer rate caused by a higher vibration frequency.

CONCLUSIONS

Multicomponent rare earths (Nd, Pr, Ce, and La) extraction equilibrium data were obtained by using ammoniated HEH[EHP] (kerosene) as extractant. After a critical aqueous concentration (0.3 M), the total concentration of rare earths in the organic phase is relatively constant with respect to the concentration and composition of rare earth in aqueous phase under tested conditions. The separation factor is almost constant ($\alpha_{Nd/Pr} = 1.6 \pm 0.1$) under tested conditions.

Multicomponent rare earth separation was performed in RPCs under different testing conditions. Steady concentration profiles were measured to estimate the HETS. A graphical approach is proposed to estimate the HETS based on concentration profiles and the critical separation factor. The average HETS value is in the range from 0.86 to 1.06 m for Nd/Pr separation under tested conditions.

ACKNOWLEDGMENTS

Financial support from the Ministry of Metallurgical Industry and Baotou Rare Earths and Iron & Steel Company, P.R. China, are highly appreciated.

REFERENCES

1. Jia, J.T.; Wu, S.; Zhang, Y.W.; Liao, C.S.; Yan, C.H.; Xu, G.X. Application of the concepts of neural network and tree structure in rare earth separations. Chinese Sci. Bull. **2001**, *46* (9), 744–746.
2. Yan, C.H.; Liao, C.S.; Jia, J.T.; Wu, S.; Li, G.B. Comparison of the economical and technical indices on rare earth separation processes of ion-adsorptive deposit by solvent extraction. China Rare Earth J. (Chinese) **1999**, *17* (3), 256–262.
3. van Deventer, J.S.J.; Aldrich, C. Application of neural nets to solvent extraction systems. ISEC **1996**, *1*, 831–836.
4. Wichterlova, J.; Rod, V. Dynamic behavior of the mixer-settler cascade-extractive separation of the rare earths. Chem. Eng. Sci. **1999**, *54* (18), 4041–4051.
5. Lo, T.C.; Prochazka, J. Reciprocating-plate extraction column. In *Handbook of Solvent Extraction*; Lo, T.C., Baird, M.H.I., Hanson, C., Eds.; John Wiley & Sons: New York, 1983, 373–390.
6. Lo, T.C.; Baird, M.H.I.; Rao, N.V.R. The reciprocating column-development and applications. Chem. Eng. Commun. **1992**, *116*, 67–88.
7. Lo, T.C.; Baird, M.H.I. Liquid–liquid extraction. In *Encyclopedia of Separation Technology*; Ruthven, D.M., Ed.; John Wiley & Sons: New York, 1997; Vol. 1, 760–790.
8. Karr, A.E. Performance of a reciprocating plate column. AICHE J. **1959**, *5*, 446–453.
9. Karr, A.E.; Ramanujam, S. Scaleup and performance of 5 ft, (1.52 m) diameter reciprocating plate extraction column. Solv. Extr. Ion Exch. **1988**, *6* (2), 221–231.
10. Sharma, R.N.; Baird, M.H.I. Solvent extraction of copper in a reciprocating plate column. Can. J. Chem. Eng. **1978**, *56*, 310–315.
11. Landau, J.; Dim, A.; Houlihan, R. Reciprocating-plate extraction column for hydrometallurgical applications. Metall. Trans. **1973**, *4* (12), 2827–2832.
12. Koshimura, H. *Separation and Extraction of Copper from Ammonia Solution with the Reciprocating-Plate Column*, Research Report; Tokyo Metropolitan Industrial Technology Center, 1987; No. 16, 107–112.
13. Ya Galkin, B.; Yegorov, N.N. Performance of a reciprocating plate extraction column for nuclear spent-fuel processing. ISEC **1988**, *2* (4), 217–220.