

Breakthrough curves for adsorption and elution of rhenium in a column ion exchange system

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Abstract

Impure rhenium and molybdenum bearing solution was passed through a column of Varian strong base anionic resin for selective adsorption of rhenium and molybdenum ions from the solution. Elution of molybdenum and rhenium was carried out using 2 N NaOH and 0.2 N NH₄SCN, respectively. The effect of resin bed height on breakthrough time was investigated. Experimental and theoretical curves were compared with good agreement. The results showed that the behavior pattern of these curves was repeatable and almost constant.

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1. Introduction

The best sources of rhenium are molybdenite concentrate and flue dust from molybdenite roasters (Fisher and Meloche, 1952). The processing of these concentrates by pyrometallurgical and hydrometallurgical technology, then leads to rhenium recovery in the form of molybdic and perrhenic acid solutions (Kholmogorov et al., 1999). As the molybdenum concentration in these solutions is always high, small amounts of rhenium are separated from a relatively large amount of molybdenum. Some methods such as precipitation, chlorination (Snell et al., 1973), adsorption on activated carbon (Jabbarzadeh, 2001), solvent extraction (Hudson and Tyler, 1990) and ion exchange (Badami, 2004) are used for selective rhenium extraction from these

solutions. Atteberry and Boyd (1950), Huffman et al. (1951) and Kunin (1952) separated molybdenum and rhenium by using the anion exchange resin, Amberlite IR-4B. In these studies, the pH in the adsorption cycle was 4.8 and the pH in molybdenum elution was 8.35. Elution of molybdate and perrhenate were accomplished by using sodium hydroxide–boric acid buffer solutions and 5% sodium hydroxide solutions, respectively. Fisher and Meloche (1952) separated rhenium from molybdenum in the form of perrhenate by using Amberlite IRA-400 and used 2.5 N sodium hydroxide and 7 N hydrochloric acid solutions for removal of the

Table 1
Re and Mo concentrations in initial solutions A and B (mg/L)

Solution element (mg/L)	A	B
Re	71.3	304.7
Mo	4535	8198

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Table 2
Characteristics of Varian strong base anion exchange resin

Matrix	DVB content (%)	Standard form	Exchange capacity (eq/L)	Density (g/L)	Pores (%)	Maximum swelling (%)
Styrene-DVB	20	Cl ⁻	3.34	700	15	20

molybdate and perrhenate, respectively. To reduce the time needed for separation of molybdate, [Meloche and Preuss \(1954\)](#) suggested potassium oxalate and perrhenic acid for elution of molybdate and perrhenate ions, respectively. By using these agents the volume of eluting agents and time required were considerably reduced. [Shariat and Hassani \(1998\)](#) passed impure rhenium bearing solution through a column of strong anionic quaternary resin (Dow IRA 410) for selective adsorption of rhenium from the solution. Elution of the column was carried out with hydrochloric acid and the resultant product was perrhenic acid. In more recent work ([Kholmogorov et al., 1999](#)) rhenium concentration and molybdenum separation from sulfuric and nitric-sulfuric acid solutions were accomplished by using weak base anion exchangers. The anion exchangers AN-82-10P and AN-105-10P were reported to be the best for complete recovery of rhenium from nitric-sulfuric acid solutions and gave pure ammonium perrhenate salt products.

In a column process, the breakthrough takes place when the concentration of the counter ion in the effluent begin to increase predominantly until it finally reaches the same concentration as in the influent. After this point no more ion exchange takes place. The breakthrough point is considered as the time of completion of the adsorption cycle in industrial applications. In simple cases, analytical equations relating concentration and time are obtainable. Equilibrium and kinetic factors

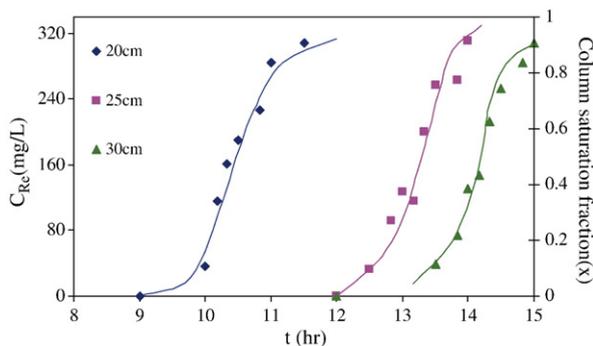


Fig. 1. Breakthrough curves and column saturation for Re adsorption at various bed heights.

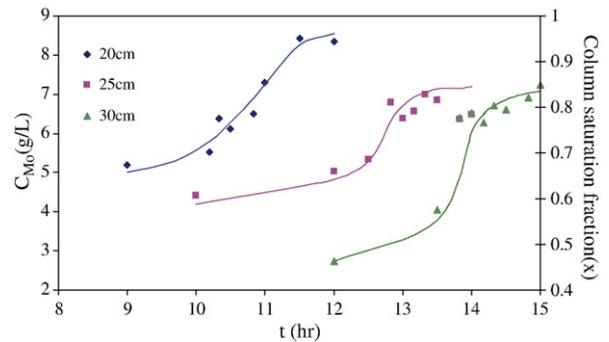


Fig. 2. Breakthrough curves and column saturation for Mo adsorption at various bed heights.

determine the shape of curves and the time scale. A summary of the simplest analytically derived breakthrough curve equations for conditions of no axial mixing, invariant rate coefficients (liquid film mass transfer coefficients and diffusion coefficients) and equilibrium data defined by α_B^A was introduced by [Slater \(1991\)](#).

Evidence on the rate controlling process is sought by examining the effects of liquid velocity and bed height. Simple analytical results have value in determining the rate controlling mechanisms in experimental work and in illustrating clearly the effects on plant performance of the major design variables. Batch experiments may be used for this purpose and the Helfferich's criterion should be used for guidance.

Literature lacks essential information on breakthrough curves of rhenium recovery from rhenium bearing leach solutions which come from copper production plants or spent catalysts. Significant amounts of these materials are created worldwide.

Determining that the equilibrium is favorable or unfavorable is the first purpose of this work. The data obtained for rhenium recovery from a molybdenite flue

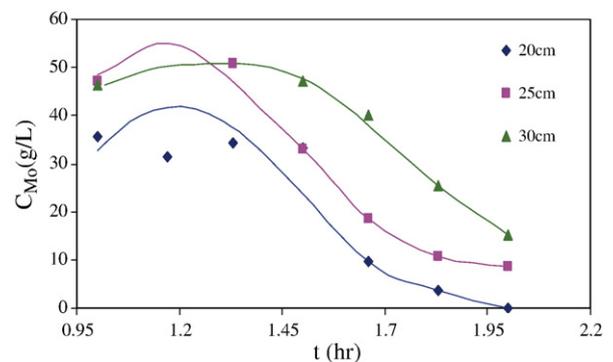


Fig. 3. Mo concentration in eluate solution vs. time at various bed heights.

Table 3
Rhenium and molybdenum concentrations (M) in rhenium eluate

Height (m) time(hr)	0.20			0.25			0.30		
	Re	Mo	SCN	Re	Mo	SCN	Re	Mo	SCN
1	0.06	0.139	0	0.07	0.125	0	0.07	0.111	0
1.17	0.06	0.139	0	0.06	0.139	0	---	---	---
1.33	0.05	0.13	0.02	---	---	---	---	---	---
1.5	0.06	0.126	0.014	0.04	0.087	0.073	0.06	0.134	0
1.66	0.04	0.092	0.068	0.035	0.082	0.083	0.045	0.105	0.05
1.88	0.006	0.014	0.18	0.02	0.05	0.13	0.016	0.033	0.15
2	0.0002	0.005	0.2	0.004	0.015	0.18	0.003	0.007	0.19

dust leach solution by an ion exchange column were formulated into appropriate equations for breakthrough curves and some column experiments were carried out to examine the column behavior with respect to parameters in the theoretical equations.

2. Experimental

Solutions A and B, which came from the leaching and purification processes of molybdenite roasted flue dusts were used in this study as initial solutions. Table 1 shows the molybdenum and rhenium contents of both solutions in the form of ReO_4^- and MoO_4^{2-} .

By increasing the pH of the solution the rhenium distribution coefficient increases while that of the molybdenum decreases and the separation factor of rhenium ($\alpha_{\text{Mo}}^{\text{Re}}$) increases. So by increasing the pH of the solution, the ion exchanger separates rhenium from molybdenum more selectively. But by increasing the concentration of OH^- ions, the dynamic capacity of the ion exchanger decreases (Razavimanesh, 1999; Mahmudian, 2001). The optimal pH=10 because at this pH both the selectivity of resin and its dynamic capacity will be in the desired range. The strong base anion

exchange resin supplied by Varian had the properties listed in Table 2.

The ion exchange resin was purified according to the method discussed by Strathmann (2004). The resin was rinsed by triple distilled water and after drying, it was screened and classified to three groups according to particle size: >0.7 mm, 0.5–0.7 mm and <0.5 mm. In this study, the saturated Varian resin with the particle size 0.5–0.7 mm was used for the elution cycle. Preparation of the saturated resin is discussed by Mahmudian (2001). The column size was 1 cm × 40 cm.

In order to draw the breakthrough curves and compare them with the theoretical ones, fixed bed processes were used using the solution B. The flow rate of solution in the adsorption cycle was 375 mL/hr and 250 mL/hr in the elution cycles of molybdenum and rhenium using 2 N NaOH and 0.2 N NH_4SCN solutions, respectively. The study was carried out at three bed heights: 20, 25 and 30 cm. All concentration values were determined by ICP with Perkin-Elmer 2000. After every cycle, the column was washed with distilled water to remove entrained solution.

3. Results

Figs. 1 and 2 demonstrate the breakthrough curves and also column saturation fraction against time of rhenium and molybdenum at various bed heights for the adsorption cycle.

Fig. 3 represents the changes of molybdenum concentration in the eluate solution vs. time for various bed heights. The analyses of rhenium and molybdenum in the thiocyanate elution cycle are listed in Table 3. In

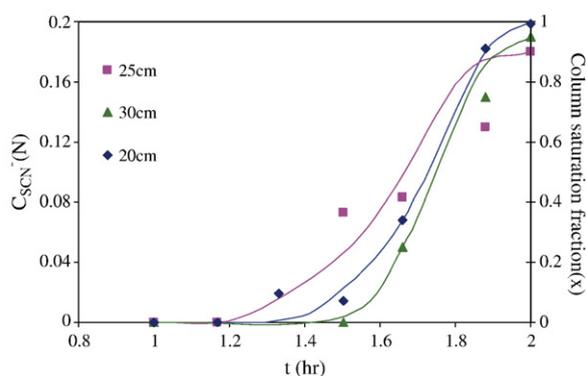


Fig. 4. Breakthrough and column saturation fraction vs. time fraction curves for adsorption of thiocyanate at various bed heights.

Table 4
Boundary layer thickness and solution flow rate in adsorption/elution

	U_L (m/hr)	δ (m)
Adsorption	3.95	4.12×10^{-5}
Elution	2.63	5.80×10^{-5}

Table 5

Calculated inter-diffusion coefficients (m²/s)

$\bar{D}_{\text{Re(VII)/Cl}^-}$	1.809×10^{-9}
$\bar{D}_{\text{Re(VII)/SCN}^-}$	1.48×10^{-9}

this table the concentration of thiocyanate in the eluate solution was calculated according to the concentrations of rhenium and molybdenum in the eluate solution by means of the Eq. (3-1).

$$C_{\text{SCN}^-} = 0.2 - C_{\text{Re}} - C_{\text{Mo}} \quad (3-1)$$

Fig. 4 demonstrates the concentration of thiocyanate in the eluate solution and column saturation against time at various bed heights.

4. Discussion

In order to calculate the thickness of the boundary layer, the flow rate of the solution should be determined:

$$L = A \cdot U_L \Rightarrow U_L = \frac{L}{A} \quad (4-1)$$

where A : column cross sectional area (m²); L : liquid flow rate (m³/s); U_L : liquid superficial velocity (m/s).

U_L values for the absorption and elution cycles were calculated using Eq. (4-1) and are listed in Table 4. The thickness of boundary layer is determined by using Eq. (4-2) (Campbell, 1992).

$$\delta = 0.05d \left(\frac{\rho d U_L}{\mu} \right)^{-0.84} \quad (4-2)$$

where d : average resin particle diameter (m)=0.6 mm; δ : liquid film thickness (m); h : bed height (m); ρ : liquid density=1040 kg/m³; μ : liquid viscosity=0.001 kg/m.s

To determine the rate controlling step, Helfferich number (Slater, 1991) must be calculated.

$$\text{He} = (0.167 + 0.0064 \alpha_B^A) \frac{\delta Q \bar{D}}{0.015 D C_0 d} \quad (4-3)$$

where D : diffusivity in solution (m²/s); \bar{D} : diffusivity in resin (m²/s); Q : total resin capacity (m³ of resin beads) (keq/m³).

Table 6

Helfferich value for rhenium adsorption and elution cycles

Adsorption	7522
Elution	15.1

Table 7

Breakthrough curves, differential systems, liquid film rate control (Slater, 1991)

Constant pattern: ion B in feed solution

(a) Irreversible equilibrium $\alpha_B^A=0$ Ruthven (1984)

$$x_B = \exp(-N_L) \quad 0 \leq N_L \tau \leq 1$$

Drew, in Klotz (1946)

$$x_B = \exp[N_L(\tau-1)-1] \quad \text{for } 1 < N_L \tau < 1 + N_L$$

(b) Favorable equilibrium $0 < \alpha_B^A < 1$ Glueckauf (1955)For $\gamma = Q(1-e)/C_0$

$$V = V_{\text{bed}}(\gamma + e) \{1 - (\gamma + e)^2 (1/N_L) [(\alpha_B^A / (1 - \alpha_B^A))$$

$$\ln(1-x_B) - \ln(x_B) / (1 - \alpha_B^A) - 1]\} \quad \text{Michaels (1952)}$$

$$N_L(\tau_1 - \tau_2) = [1 / (1 - \alpha_B^A)] \ln \{x_1(1-x_2) / x_2(1-x_1)\} - \ln \{(1-x_2) / (1-x_1)\}$$

(c) Linear equilibrium $\alpha_B^A=1$

Hougen and Marshall (1947), Perry and Chilton (1973), Hiester and Vermeulen (1952), Vermeulen (1958), Ruthven (1984)

$$x_B \approx 0.5 \operatorname{erfc} \left[(7/8) N_L^{0.5} - (7/8) (N_L \tau)^{0.5} \right]$$

error < 0.6% for $N_L > 2$

Proportionate pattern; ion B in feed solution

(d) Unfavorable equilibrium $\alpha_B^A > 1$

Walter (1945); local equilibrium

$$x_B = \left\{ \alpha_B^A - (\alpha_B^A / \tau)^{0.5} \right\} / (\alpha_B^A - 1)$$

Notes: $N_L = K_L a Z / U_L$ $\tau = (L - e V_{\text{bed}}) C_0 / Q V_{\text{bed}} (1 - e)$.

For determining Helfferich number, α (separation factor) and the diffusivity (\bar{D}) in resin and inter-diffusion coefficient (\bar{D}_{AB}) must be calculated.

Diffusion coefficients in solution are (David, 2000-2001):

$$D_{\text{Cl}^-} = 2.03 \times 10^{-9} \text{ m}^2/\text{s} \quad (4-4)$$

$$D_{\text{ReO}_4^-} = 1.46 \times 10^{-9} \text{ m}^2/\text{s} \quad (4-5)$$

$$D_{\text{SCN}^-} = 1.758 \times 10^{-9} \text{ m}^2/\text{s} \quad (4-6)$$

and

$$\bar{D}_{AB} = \frac{\bar{D}_A \bar{D}_B (z_A^2 \bar{C}_A + z_B^2 \bar{C}_B)}{z_A^2 \bar{C}_A \bar{D}_A + z_B^2 \bar{C}_B \bar{D}_B} \quad (4-7)$$

Since all anions have a single electrical charge, molar concentrations can be replaced with ionic fraction. So:

$$\bar{D}_{AB} = \frac{\bar{D}_A \bar{D}_B (x_A + x_B)}{x_A \bar{D}_A + x_B \bar{D}_B} \quad (4-8)$$

Table 8
Mass transfer coefficients in the liquid film (m/s)

Adsorption	4.71×10^{-5}
Elution	4.68×10^{-5}

but $x_A + x_B = 1$ so

$$\bar{D}_{AB} = \frac{\bar{D}_A \bar{D}_B}{x_A \bar{D}_A + x_B \bar{D}_B} \quad (4 - 9)$$

where A & B are Cl^- & ReO_4^- for adsorption and ReO_4^- & SCN^- for elution cycles.

For both adsorption and elution cycles the value of x_A varies from 1 to 0 (e.g. in elution the concentration of SCN^- decreases as it replaces ReO_4^- ions) and for each x_A an inter-diffusion coefficient was calculated. Finally, the average inter-diffusion coefficient was reported for each cycle (Table 5).

The effective diffusivity in resin for the adsorption and elution cycles are 5.1×10^{-12} (Razavimanesh, 1999) and 7.27×10^{-16} m²/s (Mahmudian, 2001), respectively and $\alpha_{Re}^{Cl} = 0.034$ (Meloche and Preuss, 1954). So, for the rhenium elution cycle:

$$\alpha_{SCN}^{Re} = (\alpha_{Re}^{SCN})^{-1} = 0.0227 \quad (4 - 10)$$

By substitution of \bar{D} and α values in the Eq. (4-3), the Helfferich number was calculated and is reported in Table 6.

Helfferich number for both the adsorption and elution cycles is greater than 1 so according to Slater (1991) the diffusion in the liquid film is the rate controlling step. Because of this fact and because the separation factor $0 < \alpha < 1$ for both cycles, Glueckauf equation from Table 7 is suggested for anticipation of breakthrough curves. In that equation, the terms x : equivalent fraction in solution, V_{bed} : resin bed volume including voids, V : liquid volume at specific time, N_L : number of liquid film transfer units, e : resin bed voidage and γ : solution activity coefficient are present. Accord-

Table 9
 N_L and γ values

	Bed height (cm)	N_L	γ
Adsorption	20	84.1	6733
	25	105.3	6733
	30	126.2	6733
Elution	20	108.6	14.2
	25	135.8	14.2
	30	163.0	14.2

Table 10
Rhenium absorption and elution breakthrough relationships, and breakthrough times (for $x=0.05$) obtained at various bed heights

	Bed height (cm)	Breakthrough relationship	$T_{Breakthrough}$ Calc. (hr)	$T_{Breakthrough}$ expt.(hr)
Rhenium absorption	20	$t = 36278.3 - 55.8 \ln(1-x) + 1641.3 \ln x$	8.7	10.2
	25	$t = 39681.67 - 56.04 \ln(1-x) + 1648.25 \ln x$	11	12.5
	30	$t = 52706.87 - 56.04 \ln(1-x) + 1648.26 \ln x$	13.3	13.5
Rhenium elution	20	$t = 3752.9 - 0.776 \ln(1-x) + 34.24 \ln x$	1	1.5
	25	$t = 4677.96 - 0.775 \ln(1-x) + 34.215 \ln x$	1.27	1.5
	30	$t = 5612.73 - 0.7766 \ln(1-x) + 34.24 \ln x$	1.52	1.66

ing to relation $V=L.t$, where L is liquid flow rate, the parameter t can be used instead of V in the Glueckauf equation.

To calculate mass transfer coefficient in liquid film,if

$$1 < \frac{\rho d U_L}{\mu e} < 1000 \quad (4 - 11)$$

then (Slater, 1991):

$$K_L = 1.15 \left(\frac{\rho d}{\mu e} \right)^{0.5} \left(\frac{U_L}{e} \right)^{0.5} \left(\frac{\mu}{\rho D} \right)^{-0.67} \quad (4 - 12)$$

K_L values are listed in Table 8.

To calculate a :

$$a = 6(1-e)/d = 6(1-0.15)/0.6 \times 10^{-3} = 8500 \quad (4 - 13)$$

where a : surface area per unit volume of equipment (m³/m²).

By using the calculations of Table 7, N_L and γ were calculated and are listed in Table 9. By substituting the calculated values in equations, a breakthrough equation is obtained for any height of bed at adsorption and elution cycles. These equations are presented in Table 10. The resin volume, which is considered in the equations for adsorption cycle as the bed volume, is 0.1 total volume of the bed. By assuming a value for an empirical factor x in the equations, the breakthrough time is calculated.

Experimental values of breakthrough time are presented beside the theoretically calculated times using empirical factor $x=0.05$. It can be seen that these times are very close to each other, so these equations are suitable for the anticipation of breakthrough behavior. Figs. 5 and 6 show experimental breakthrough curves for adsorption and elution cycles, together with the calculated empirical curves.

It can be seen that there is a greater difference between experimental and calculated predicted values in the elution cycle than in the adsorption cycle. One reason for this error arises from the calculation of thiocyanate concentration in the eluate solution according to the concentrations of rhenium and molybdenum. It was assumed that molybdenum and other ions were removed by the NaOH solution before the elution of rhenium— but in reality the ion exchanger was not free from these ions, so their elution magnifies the error.

According to Figs. 2 and 3, by the repeating of the same procedure for molybdenum adsorption and elution (which has been done for rhenium), the mathematically calculated breakthrough curves can be established and compared with the experimental ones.

5. Summary

Impure rhenium and molybdenum bearing solutions were passed through a column of Varian strong base anionic resin and selective separation of rhenium and

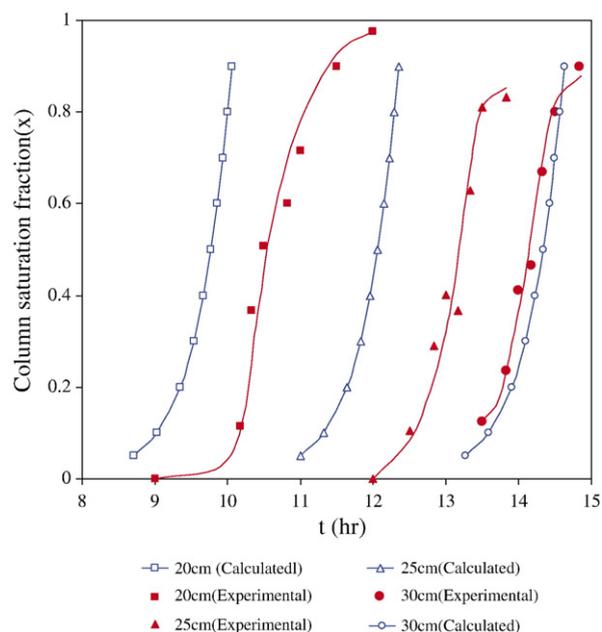


Fig. 5. Calculated and experimental breakthrough curves of Re adsorption at various bed heights.

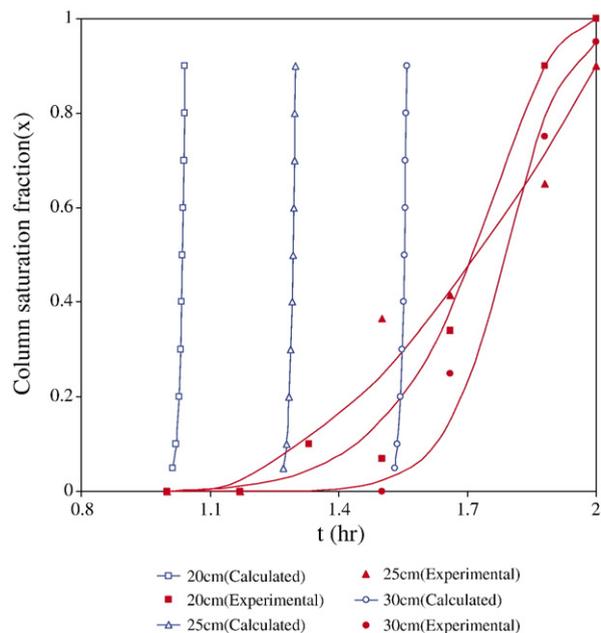


Fig. 6. Calculated and experimental breakthrough curves of Re elution at various bed heights.

molybdenum ions from the solution was successfully done. Batch experiments showed that the equilibrium in both adsorption and elution was favorable. At the specific condition that column experiments was performed, the rate controlling mechanism was the diffusion in the liquid film which was determined by calculating the Helfferich's number. Empirical mathematical equations can be established that predict breakthrough curves.

References

- Atteberry, R.W., Boyd, G.E., 1950. Separation of seventh group anions by ion exchange chromatography. *J. Am. Chem. Soc.* 72, 4805–4806.
- Badami, E., 2004. Extraction of Rhenium Salts from Aqueous Solutions Containing Perrhenate, Thiocyanate and Chloride by Ion Exchange. M. Sc. Thesis, Sharif University of Technology, Iran.
- Campbell, J.M., 1992. Gas Conditioning and Processing. The Equipment Modules, Campbell Petroleum Series, vol. 2.
- David, R.L., 2000–2001. Handbook of Chemistry and Physics. CRC Press.
- Fisher, S.A., Meloche, V.W., 1952. Ion exchange separation of rhenium from molybdenum. *Anal. Chem.* 24 (7), 1100–1106.
- Glueckauf, E., 1955. Ion Exchange and its Applications. SCI Symposium. Society of Chemical Industry, London, 34–36.
- Hiester, N.K., Vermeulen, T., 1952. Saturation performance of ion exchange adsorption columns. *Chem. Eng. Prog.* 48, 505–516.
- Hougen, O.A., Marshall, W.R., 1974. Adsorption from a fluid stream flowing through a stationary granular bed. *Chem. Eng. Prog.* 43, 197–208.
- Hudson, M.J., Tyler, D.J., 1990. Extraction of perrhenate anion using goethite surface modified with hydrophobic quaternary amines. *Hydrometallurgy* 24 (1), 111–125.

- Huffman, E.H., Iddings, G.M., Lilly, R.C., 1951. Anion exchange of zirconium, hafnium, niobium and tantalum in hydrochloric acid solutions. *J. Am. Chem. Soc.* 73, 4474–4475.
- Jabbarzadeh, S., 2001. Separation of Rhenium and Molybdenum from the Leach Solutions from the Molybdenite Roasters' Flue Dusts by Adsorption on the Activated Carbon: Kinetics and Thermodynamics. M. Sc. Thesis, Sharif University of Technology, Iran.
- Kholmogorov, A.G., Kononova, O.N., Kachin, S.V., Ilyichev, S.N., Kryuchkov, V.V., Kalyakina, O.P., Pashkov, G.L., 1999. Ion exchange recovery and concentration of rhenium from salt solutions. *Hydrometallurgy* 51, 19–35.
- Klotz, I.M., 1946. The adsorption wave. *Chem. Rev.* 39, 241–268.
- Kunin, R., 1952. Ion exchange. *Anal. Chem.* 24, 64–66.
- Mahmudian, A., 2001. Kinetics and Thermodynamics of Continuous Adsorption and Desorption of Rhenium from Leaching Solutions of Molybdenite Roasting by Ion Exchange. M. Sc. Thesis, Sharif University of Technology, Iran.
- Meloche, V.W., Preuss, A.F., 1954. Analytical separation of rhenium and molybdenum by ion exchange. *Anal. Chem.* 26 (12), 1911–1914.
- Michaels, A.S., 1952. Simplified method of interpreting kinetic data in fixed bed ion exchange. *Ind. Eng. Chem.* 44 (8), 1922–1930.
- Perry, R.H., Chilton, C.H. (Eds.), 1973. *Chemical Engineers' Handbook*, 5th edition. McGraw Hill, New York. Chapter 16.
- Razavimanesh, A., 1999. Kinetics and Thermodynamics of Ion Exchange Separation of Metals from Solutions. M. Sc. Thesis, Sharif University of Technology, Iran.
- Ruthven, D.M., 1984. *Principles of Adsorption and Adsorption Processes*. Wiley Interscience, New York.
- Shariat, M.H., Hassani, M., 1998. Rhenium recovery from Sarcheshmeh molybdenite concentrate. *J. Mater. Process. Technol.* 74, 243–250.
- Slater, M.J., 1991. *Principles of Ion Exchange Technology*. Butterworth-Heimann Ltd.
- Snell, F.D., Hilton, C.L., Etre, L.S., 1973. *Encyclopedia of Industrial Chemical Analysis*, vol. 17. Interscience Publishers.
- Strathmann, H., 2004. Ion exchange membrane separation processes. *Membrane Science and Technology Series*, vol. 9. Elsevier, Amsterdam.
- Vermeulen, T., 1958. *Advances in Chemical Engineering*, vol. 2. Academic Press, New York.
- Walter, J.E., 1945. Multiple adsorption from solutions. *J. Chem. Phys.* 13, 229–234.