Seventh Symposium on Salt, Vol. II 17–21 (1993)
Elsevier Science Publishers B.V., Amsterdam

Lithium Recovery from Seawater with Various Inorganic Ion Exchangers

Mitsuo Abe[1], Ramesh Chitrakar[2] and Masamichi Tsuji[1]

[1]*Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152, Japan*
[2]*Geological Survey of Nepal, Kathmandu, Nepal*

ABSTRACT

Antimonates of Sn (IV) and Ti (IV), λ- and cryptomelane-type MnO_2, hydrotalcite, hydrous oxides of Ti (IV) and Zr (IV), crystalline antimonic (V) acid ($Sb_2O_5{\cdot}4H_2O$), and α–Zr $(HPO_4)_2$ were studied for selective uptake of lithium from seawater by the batch and column methods and the extraction features were compared. Among these inorganic ion exchangers studied, metal antimonates exhibited the most effective uptake of Li^+ from seawater.

INTRODUCTION

At a lithium symposium, the demand for lithium was described for energy applications such as lithium battery and thermonuclear fusion reactors (Dang and Steinberg, 1978; Hartly et al., 1978). Several methods have been proposed for Li^+ recovery from seawater and brine (Vol'khin et al., 1973; Abe and Hayashi, 1983; Abe and Hayashi, 1984; Abe et al., 1986; Abe and Chitrakar, 1987) e.g. coprecipitation with insoluble compounds such as aluminate and aluminosilicate, ion exchange by inorganic ion-exchange materials, and so on. An ion-exchange method using a commercially available ion-exchange resin is not suitable because of very low selectivity for a small amount of lithium in a large quantity of alkali and alkaline earth metal ions. Tin (IV) antimonate (SnSbA) showed an unusual selectivity sequence for micro-amounts of alkali metal ions in the increasing order: $Na^+ < K^+ < Rb^+ < Cs^+ << Li^+$ (Abe and Hayashi, 1983; Abe and Hayashi, 1984; Abe et al., 1986). A similar selectivity sequence has been observed for λ–MnO_2 (Vol'khin et al., 1973; Ooi et al., 1986; Ooi et al., 1987a; Ooi et al., 1988; Ooi et al., 1989). Titanium (IV) antimonate (TiSbA) showed the selectivity sequence of the increasing order: Na^+ $K^+ < Rb^+ < Li^+ < Cs^+$ (Abe et al., 1985). These antimonates and λ–MnO_2 have been successfully applied to the extraction of Li^+ from seawater and hydrothermal water.

In the present study, a comparison was made on the separation of lithium from seawater with various inorganic ion exchangers by the batch and column methods.

EXPERIMENTAL

Preparation and characterization of exchangers

SnSbA (the mole ratio of Sb/Sn 1.8) (Abe and Hayashi, 1983), TiSbA (the mole ratio of Sb/Ti 0.64) (Abe et al., 1985), λ-MnO_2 (Hunter, 1981), cryptomelane-type MnO_2 (CRYMO) (Tsuji and Abe, 1984), $TiO_2{\cdot}nH_2O$ (Inoue and Tsuji, 1976) and crystalline antimonic acid (C-SbA) (Abe and Sudoh, 1980) were prepared as described. $ZrO_2{\cdot}nH_2O$ was prepared by hydrolysis of Zr(IV)-butoxide. The λ-MnO_2 prepared contained 0.17% Li or 0.25 meq/g. Hydrotalcite (KW300) and α-Zr$(HPO_4)_2$ (α-ZrP) were supplied by Mitsui Toatsu Kagaku Ltd. These materials were used in the Na^+ form. Exchangers with 100–200 mesh size were used throughout the experiments except for λ-MnO_2, KW300, and α-ZrP, which were in fine particles (> 400 mesh size).

The materials were characterized by powder X-ray diffraction (JEOL diffractometer, Model JDX-7E) using Ni-filtered Cu-Kα and thermal analyses (TG and DTA) with a Rigaku Denki thermoflex-type thermal analyzer.

Seawater sample

An ocean seawater sample was collected in polyethylene bottles 1 km off the seashore of Takamatsu, Kagawa Prefecture, Japan. It was used after percolating through a membrane filter of 0.45 μm in diameter. Elemental analysis of seawater was carried out by flame photometry or atomic absorption spectrometry with a Varian spectrometer, Model AA1100. The Li and Na contents in seawater were found to be 0.17 mg/dm^3 and 9.80 g/dm^3, respectively, which were in good agreement with the literature (Abe and Hayashi, 1984).

Lithium extraction

The Li$^+$ uptake experiment from seawater by the batch method was carried out in the following conditions: 0.025 g of exchanger was equilibrated with 50 cm^3 or 500 cm^3 of seawater for 12 d at 30°C. After 12 d equilibration, the uptake of Li$^+$ from seawater on various exchangers was determined from the difference in the lithium concentration relative to the initial concentration of lithium in seawater. The distribution co-efficient (Kd) was calculated by using the equation:

$$K_d = \frac{\text{\% uptake}}{100\text{–\% uptake}} \times \frac{\text{volume of solution (cm}^3\text{)}}{\text{weight of exchanger (g)}} \qquad (1)$$

A very small column (2 x 0.2 cm I.D.) of exchangers was used in the column experiment. The flow rate was regulated by a high-pressure pump (Nihon Seimitsu Kagaku, Model NSP-800-5UDX). The effluents were collected using a drop-counting-type fraction collector (Ohtake Works, Model UM-200).

RESULTS AND DISCUSSION

Ion-exchange materials

The results by the powder X-ray diffraction, TG, and DTA showed good agreement with the literature data for each material.

Ion-exchange rate

In the ratio of a volume of seawater to weight of exchanger (R value) of 2 dm^3/g, a relatively fast equilibration was observed for KW300 and CRYMO (Fig. 1, left). A quantitative uptake was found in SnSbA and TiSbA, indicating the highly selective Li$^+$ exchange. The ion-exchange rate was compared among SnSbA, TiSbA and λ-MnO_2 in an R value of 20 cm^3/g (Fig. 1, right). TiSbA was equilibrated within 12 d, but the other two exchangers still showed an increase in uptake even after 12 d.

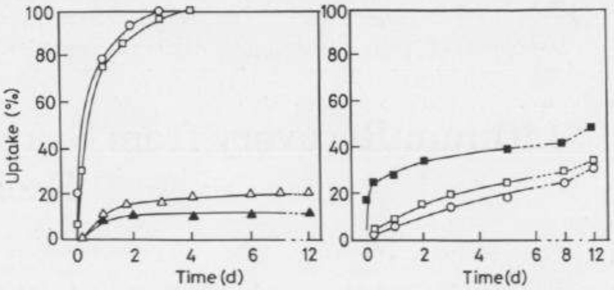

Fig. 1. Time dependence of Li$^+$ uptake from seawater on various inorganic ion exchangers. Total vol.: left, 50 cm^3; right, 500 cm^3. Exchanger: 0.025 g. Temp.: 30±0.5°C. Hollow circles: SnSbA; hollow squares: TiSbA; hollow triangles: KW300; filled triangles: CRYMO; filled squares: λ-MnO_2.

Lithium extraction by the batch method

Lithium uptakes from seawater after 12 d equilibration are compared in Table 1. There was a very low percentage of adsorption on the C-SbA, $TiO_2{\cdot}nH_2O$, $ZrO_2{\cdot}nH_2O$ and α-ZrP. These cannot be utilized for Li$^+$ recovery from seawater because of the low selectivity towards Li$^+$. Li$^+$ uptakes by CRYMO and KW300 were not enough for efficient recovery. λ-MnO_2, SnSbA and TiSbA showed a relatively high percentage of Li$^+$.

In the low R value of 2 dm^3/g, Li$^+$ in seawater quantitatively adsorbed by λ-MnO_2, SnSbA and TiSbA with a high Kd value of >2 x 10^5. When the R value increased to 20 dm^3/g, the Kd value for Li$^+$ decreased to $1.9_6 \times 10^4$, $8.5_3 \times 10^3$ and $1.0_9 \times 10^4$ on λ-MnO_2, TiSbA and SnSbA, respectively. The amount of Li$^+$ adsorbed was in the order: TiSbA (0.146 meq/g) < SnSbA (0.173 meq/g) < λ-MnO_2 (0.242 meq/g). In the large R value of 20 dm^3/g, a larger uptake (0.417 meq/g) for Li$^+$ was reported on a mixed (λ + γ)–MnO_2 by Ooi et al. (1986). Almost the same uptake (0.425 meq Li$^+$/g) was described by the same authors in the different ratio of volume to weight (40 dm^3/g). The uptakes appear saturated in the R value larger than 20 dm^3/g.

Recovery of lithium by the column method

In chromatographic separations, the simplest procedure is the frontal chromatography, which consists of a continuous charge of the feed solution containing the components to be separated on the column. This type of process can be effectively applied for the removal of minor components if they are more selectively adsorbed than the bulk components in the solution. A given volume of seawater was charged continuously at the top of the column containing a known weight of the exchanger at 1 cm^3/min or 2

TABLE 1

Selective uptake of Li^+ from seawater on various inorganic ion exchangers

Exchanger	Chemical composition	Vol/Wt ratio (dm^3/g)	Added Li^+ (meq/g)	Li^+ uptake		K_d (cm^3/g)
				(%)	(μeq/g)	
C-SbA	$Sb_2O_5 \cdot 4H_2O$	2.0	0.0490	<1	<0.5	<20
HZDO	$ZrO_2 \cdot 1.7H_2O$	2.0	0.0490	<1	<0.5	<20
Am-HTDO	$TiO_2 \cdot 2H_2O$	2.0	0.0490	<1	<0.5	<20
α-ZrP	$Zr(HPO_4)_2 \cdot 2H_2O$	2.0	0.0490	<1	<0.5	<20
CRYMO	$MnO_2 \cdot 0.3H_2O$	2.0	0.0490	11.1	5	249
KW300	$2.5MgO \cdot Al_2O_3 \cdot nH_2O$	2.0	0.0490	22.4	11	577
KW300*	"	0.333	0.00816	70.2	5.7	778
λMnO_2	$MnO_2 \cdot 0.1H_2O$	2.0	0.0490	>99	49	$>2 \times 10^5$
λMnO_2	"	20	0.490	49.5	242	$1.9_6 \times 10^4$
$(\lambda + \gamma)$-MnO_2**	$MnO_2 \cdot 0.18H_2O$	20	0.490	85	417	$1.1_5 \times 10^5$
$(\lambda \times \gamma)$-MnO_2**	"	40	0.980	43.3	425	$3.0_5 \times 10^4$
TiSbA	$3.1TiO_2 \cdot Sb_2O_5 \cdot 4.9H_2O$	2.0	0.0490	>99	49	$>2 \times 10^5$
TiSbA	"	20	0.490	29.9	146	$8.5_3 \times 10^3$
SnSbA	$1.1SnO_2 \cdot Sb_2O_5 \cdot 4.9H_2O$	2.0	0.0490	>99	49	$>2 \times 10^5$
SnSbA	"	20	0.490	35.3	173	$1.0_9 \times 10^4$

*Baba et al. (1984) for Li^+-enriched simulated seawater.
**Ooi et al. (1987b).

cm^3/min at 30°C (Fig. 2, left). The Li^+ was detected in the earlier stage of charge on SnSbA or TiSbA column compared to λ-MnO_2 column at both flow rates. A coarse particle size of SnSbA or TiSbA (100–200 mesh size) was responsible for the slower uptake than λ—MnO_2 (>400 mesh size). The concentration of Li^+ did not reach that of the feed solution even after 800 cm^3 of seawater was percolated. A similar breakthrough curve was observed in the repeated experiment with the flow rate of 1 cm^3/min.

The column was thoroughly washed with water and the elution was carried out with 1 M or 5 M HNO_3 solution (Fig. 2, right). The column used for the elution was that corresponding to the breakthrough curve of the flow rate 1 cm^3/min denoted by the hollow triangle in Fig. 2, left. The adsorbed Li^+ by the column was quantitatively eluted with a relatively long tailing along with other metal ions.

The enrichment factor f defined by the following equation was determined by using the eluted amounts of Li^+ and Na^+:

$$f = \frac{Li^+/Na^+ \text{ mole ratio in exchanger}}{Li^+/Na^+ \text{ mole ratio in seawater}} \qquad (2)$$

High f values ($>10^4$) were observed on λ-MnO_2, SnSbA and TiSbA exchangers (Table 2); i.e. Li^+ in seawater can be concentrated to more than 10^4 by using one of these inorganic ion exchangers. λ-MnO_2 showed the highest f value of 2.7×10^5 of these three exchangers in the present experimental conditions.

The largest recovery of Li^+ from percolated seawater was found on SnSbA (84% in the case of 1 cm^3/min for the flow rate of feed) and the lowest recovery was found on λ-MnO_2 (67% in the case of the same flow rate). The Li^+ recovery decreased on SnSbA and λ-MnO_2 when the flow rate of feed increased to 2 cm^3/min, but approximately the same recovery of Li^+ was found on the TiSbA on the two different flow rates.

CONCLUSIONS

The extraction of Li^+ from seawater was successfully performed with extremely high f values in column operation with λ-MnO_2, SnSbA and TiSbA among the various inorganic ion exchangers studied. The apparent density of these antimonates is larger by approximately three times than λ-MnO_2. It implies that the use of antimonate exchangers will be more advantageous than the other inorganic ion exchangers studied in the present work for Li^+ recovery from seawater.

TABLE 2

Recovery of Li^+ by the column method

Exchanger	Flow rate (cm^3/min)	Vol. of seawater (cm^3)	Weight of exchanger (g)	Vol./weight ratio (dm^3/g)	Percolated Li^+ (meq/g)	Eluted Li^+ (meq/g)	Eluted Na^+ (meq/g)	Recovery of Li^+ (%)	Enrichment factor f
SnSbA	1	750	0.25	3.0	0.0735	0.062	0.072	84	$1.4_9 \times 10^4$
	2	784	0.25	3.1	0.0760	0.047	0.072	62	$1.1_3 \times 10^4$
TiSbA	1	740	0.10	7.4	0.181	0.142	0.026	78	$9.4_9 \times 10^4$
	2	800	0.10	8.0	0.196	0.143	0.026	73	$9.5_6 \times 10^4$
λ-MnO_2	1	820	0.065	12.6	0.308	0.207	0.013	67	$2.7_7 \times 10^5$
	2	770	0.070	11	0.269	0.155	0.013	58	$2.0_7 \times 10^5$

f: Enrichment factor defined by equation (2). Temperature of the column: 30±0.5°C.

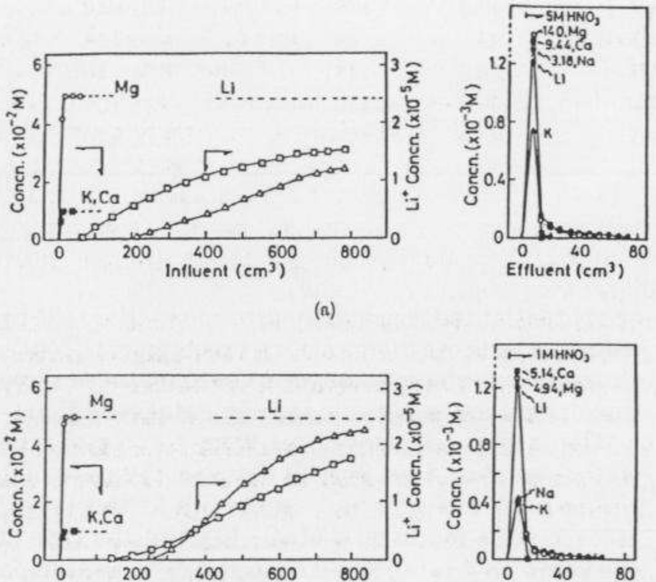

Fig. 2. Selective uptake of Li (left) from seawater and their elution curves (right) on SnSbA (a), TiSbA (b), and λ-MnO_2 (c). Column, 2 x 0.2 cm I.D. Temp., 30±0.5°C. Flow rate: hollow triangles, 1.0 cm^3/min; hollow squares, 2.0 cm^3/min for breakthrough of Li+ and 0.3 cm^3/min for elution.

ACKNOWLEDGMENT

A part of this research was financially supported by The Salt Science Research Foundation under Grant No. 8902.

REFERENCES

Abe, M. and Sudoh, K., 1980. Ion-exchange equilibria of transition metals and hydrogen Ions on crystalline antimonic (V) Acid. J. Inorg. Nucl. Chem., 42: 1051–1055.

Abe, M. and Hayashi, K., 1983. Selectivities of alkali metal ions on tin (IV) antimonate cation exchanger prepared at different conditions. Solvent Extr. Ion Exch., 1: 97–112.

Abe, M. and Hayashi, K., 1984. Selective separation of lithium from seawater by tin (IV) antimonate cation exchanger. Hydrometallurgy, 12: 83–93.

Abe, M. and Chitrakar, R., 1987. Recovery of lithium from seawater by tin (IV) antimonate cation exchanger. Hydrometallurgy, 19: 117–128.

Abe, M., Chitrakar, R., and Hayashi, K., 1986. Selective Separation of Lithium from Seawater and Hydrothermal Water by Titanium (IV) or Tin (IV) Antimonate Cation Exchanger. In: C.J. King and J.D. Navratil (Editors), Chemical Separation, Vol. 1. Principles, Litervan Literature, Denver, pp. 187–201.

Abe, M., Chitrakar, R., Tsuji, M. and Fukumoto, K., 1985. Synthesis of titanium (IV) antimonates and their ion exchange properties for alkali and alkaline earth metal ions. Solvent Extr. Ion Exch., 3: 149–172.

Baba, Y., Inoue, K., Goto, A. and Nakamori, I., 1984. The adsorption mechanism of lithium from sea water. Bull. Soc. Seawater Sci. Jpn., 38: 137–141 (in Japanese with English abstract).

Dang, V.D. and Steinberg, M., 1978. Preliminary design and analysis of recovery of lithium from brine with the use of a selective extractant. Energy, 3: 325–336.

Hartly, J.N., Gore, B.F. and Young, J.R., 1978. Potential lithium requirements for fusion power plants. Energy, 3: 337–346.

Hunter, J.C., 1981. Preparation of a new crystal form of manganese dioxide: λ-MnO_2. J. Solid State Chem., 39: 142–147.

Inoue, Y. and Tsuji, M., 1976. Hydrous titanium oxide ion exchanger: method of synthesis and some properties. J. Nucl. Sci. Technol., 13: 85–91.

Ooi, K., Miyai, Y. and Katoh, S., 1986. Recovery of lithium from seawater by manganese oxide adsorbent. Sep. Sci. Technol., 21: 755–766.

Ooi, K., Miyai, Y. and Katoh, S., 1987a. Ion-exchange properties of ion-sieve-type manganese oxides prepared by using different kinds of introducing ions. Sep. Sci. Technol., 22: 1779–1789.

Ooi, K., Miyai, Y. and Katoh, S., 1987b. Lithium-ion sieve property of λ-type manganese oxide. Solvent Extr. Ion Exch., 5: 561–572.

Ooi, K., Miyai, Y. and Katoh, S., 1988. Recovery of lithium from seawater using a new type of ion-sieve adsorbent based on $MgMn_2O_4$. Sep. Sci. Technol., 23: 179–191.

Ooi, K., Miyai, Y., Katoh, S. and Abe, M., 1989. Recovery of lithium from sea water. Bull. Soc. Seawater Sci. Jpn., 42: 219–227.

Tsuji, M. and Abe, M., 1984. Synthesis of cryptomelane-type hydrous manganese dioxide as an ion-exchange material and their ion-exchange selectivities towards alkali and alkaline earth metal ions. Solvent Extr. Ion Exch., 2: 253–274.

Vol'khin, V.V., Leont'eva, G.V. and Onorin, S.A., 1973. Synthesis, structure and properties of ion-sieve cation exchanger ISM-1. Neorg. Mater., 9: 1041–1046 (in Russian).