



SELECTIVE RECOVERY OF LITHIUM FROM SEAWATER USING A NOVEL MnO_2 TYPE ADSORBENT III - BENCHMARK EVALUATION

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ABSTRACT

The granulation method of λ - MnO_2 adsorbent employing chitin-based binder, which has efficient selectivity towards lithium ion, has been developed. The granules of ca. 1 – 2 mm with high resistance to the column operation for seawater (pH = 8.1) can be achieved. The laboratory scale column separation with the granulated adsorbent shows that lithium ions from seawater can be selectively recovered against the majority of co-existing cations. In addition, the elution of Mn from the adsorbent can be prevented. The benchmark column separation plant with seawater intake 200 L/h has been built and the whole process was verified and evaluated. The composition analysis of dried precipitated salts showed ca. 35 % efficiency of lithium recovery in the benchmark plant. In order to enhance the lithium recovery efficiency the following recovery steps are expected when routine techniques are applied.

Keywords: Adsorption, Lithium recovery, Seawater, Manganese dioxide, Benchmark column separation plant

INTRODUCTION

Numerous fields of science and technology have recently shown interest in lithium. Nowadays, the demand for lithium has been dramatically

increasing, due to its wide range of applications as a raw material for large-capacity rechargeable batteries, light aircraft alloys, and future nuclear fusion fuel.

The total lithium land resources amount to 14 million tons [1]. Lithium is recovered from ores or brines [2], and mainly from minerals contained in granite pegmatites. Lithium-bearing granite pegmatites are found as dikes peripheral to granite intrusions, and are formed by crystallization of late stage residual fluids. Lithium occurs in a paragenetic range from early-stage minerals such as iron-rich spodumene through intermediate stages (spodumene, petalite, lepidolite and amblygonite) to low temperature hydrothermal alteration products such as eucryptite, bikitaite and cookeite. Lithium ores are concentrated to contain from 1-3 % to 4-6 % Li_2O by means of heavy media separation using dense and nonaqueous liquids, followed by froth flotation. Lithium extracted from spodumene entails an energy intensive chemical recovery process, which is more expensive than the recovery from brines. Because the production of lithium carbonate from spodumene is expensive, lithium carbonate production has mostly been shifted to the brine process. Subsurface brines have become to the dominant raw material for lithium production, owing to lower production costs as compared with the mining and processing costs of hard-rock ores. Lithium at relatively low concentration (< 100 ppm) is recovered by concentration and precipitation as Li_2NaPO_4 . The mixed phosphate is then converted to lithium carbonate as the final product. Brines containing more than 200 ppm Li and of low concentrations of alkaline earths, recover lithium by solar evaporation. Alkaline earths are then removed by precipitation. Lithium carbonate is precipitated by the addition of sodium carbonate to hot brine.

Although the amount of lithium in those resources is sufficient, alternative resources should be exploited to satisfy the increasing demand in near future. 230 billion tons of lithium in seawater is an immense source, though the lithium concentration in seawater is quite low (ca. 0.2 ppm). Even though there is no industrially applied technology to recover lithium from seawater, Japan and South Korea, suffering from lack of natural resources, have recently paid much attention to the selective isolation of lithium from seawater.

The selective recovery of lithium from seawater by co-precipitation, solvent extraction, and adsorption has been investigated. For the recovery of target ions from such dilute solutions the adsorption technique proved to be more suitable than any other.

A number of different adsorbents has been investigated for the selective lithium recovery from the fundamental point of view [3-6], and also for its recovery from seawater [7-11]. Among these adsorbents, the adsorbent based on manganese dioxides and its composites seems the most proper one, due to its high adsorption capacity in alkaline medium - pH of seawater is around 8.1 [12]. It also exhibits the specific selectivity towards

Li^+ in the presence of alkali and alkaline earth ions [4, 13]. The mechanism of Li^+ extraction/insertion has been extensively studied [5, 6].

In our previous studies [11, 14, 15], we developed two types of novel $\lambda\text{-MnO}_2$ adsorbent prepared from spinel type lithium dimanganese tetraoxide – LiMn_2O_4 and $\text{Li}_{1.5}\text{Mn}_2\text{O}_4$. These adsorbents show the effective separation and recovery ability for Li^+ against a large amount of Na^+ (selectivity of $\text{Li}^+/\text{Na}^+ > 800$ in molar ratio). The chromatographic separation of Li^+ from artificial seawater can be carried out using the lab-scale experimental apparatus, and nearly 400 times concentration of Li^+ can be achieved, while most of Na^+ is remained in seawater.

In this study, using $\lambda\text{-MnO}_2$ prepared from $\text{Li}_{1.5}\text{Mn}_2\text{O}_4$, the benchmark column separation plant has been built up and has been operated under the seawater intake 200 L/h for 30 days and for 150 days, respectively, to verify the performance of large-scale selective lithium recovery as well as to evaluate the dried precipitated salt by evaporation crystallization.

EXPERIMENTAL

Preparation of granulated $\lambda\text{-MnO}_2$ adsorbent

A novel λ -type manganese dioxide adsorbent ($\lambda\text{-MnO}_2$) was prepared from spinel type lithium dimanganese tetraoxide – $\text{Li}_{1.5}\text{Mn}_2\text{O}_4$ as described in the previous papers [11, 14, 15].

The granulation of the adsorbent is performed by chitin-based binder (LiCl , chitin and N-methyl-2-pyrrolidinone) using High Speed Mixer (Fukae Powtec FS-GC-40JB). The SEM image of granulated adsorbent was prepared as 1-2 mm in diameter as shown in Fig. 1

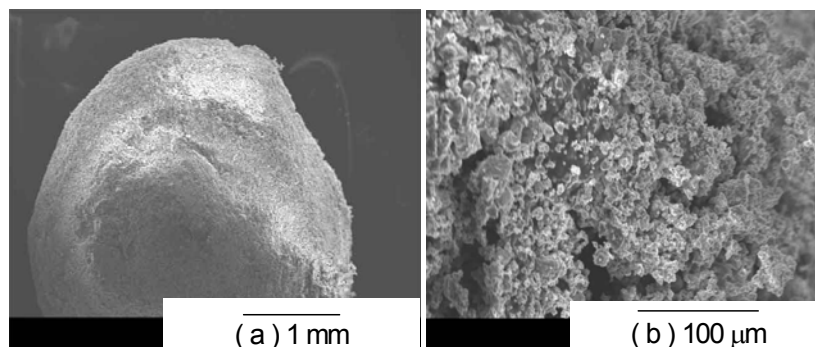


Fig. 1. SEM images of granulated adsorbent (a) 40 times, (b) 500 times.

Benchmark separation and concentration of lithium ions from seawater

A schematic diagram and pictures of a benchmark plant for lithium recovery are shown in Figs. 2 and 3, respectively. The plant consists of two

HCl storage tanks of 1000 L (front side), an evaporation crystallization unit (left side), and an adsorption column (right side).

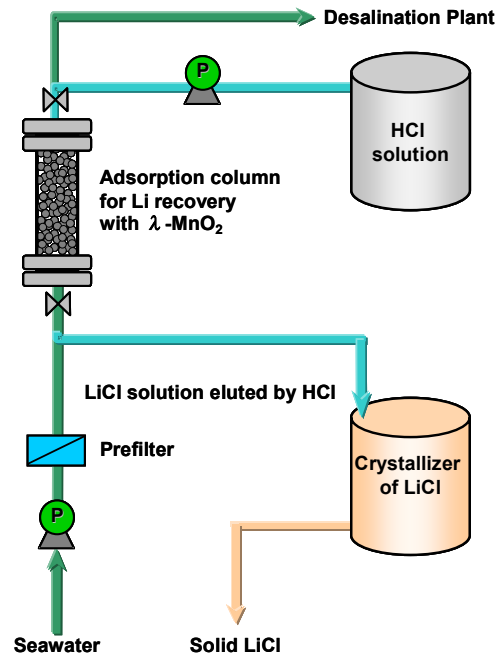


Fig. 2. Schematic flowsheet of the column apparatus setup.



Fig. 3. Overview of the benchmark plant for selective lithium recovery.

Sixty kilograms of the granulated adsorbent intermediate ($\text{Li}_{1.5}\text{Mn}_2\text{O}_4$) were packed into the column shown in Fig. 3. The packed column was preliminarily treated with 100 L of 0.85 mol/L HCl for preparing λ - MnO_2 adsorbent by eluting Li^+ from $\text{Li}_{1.5}\text{Mn}_2\text{O}_4$. Eluted Li^+ was monitored by atomic absorption spectrophotometer (AAS, Shimadzu AA-6800) to confirm the generation of λ - MnO_2 .

Adsorption runs were carried out for 30 days and for 150 days, respectively. The adsorbent column was fed with pre-filtered seawater. The flow rate of seawater intake was set to 200 L/h. The effluent from the column was daily sampled to check the concentrations of Li^+ and Mn^{2+} by AAS and an induced coupled plasma atomic emission spectrometer (ICP-AES, Perkin-Elmer Optima 4300DV Cyclon), respectively. After adsorption stage, fresh water was used to wash out the seawater from the column. Elution was then performed with 0.85 mol/L HCl. The eluted solution was evaporated at 42 - 50 °C and dried *in vacuo*, to precipitate the metal salts as well as to distil HCl for recycling. The composition of the precipitated salts was determined with ICP-AES (alkali, and alkaline-earth metals, and Mn). Lithium ions concentration in intake seawater was also measured.

The benchmark plant for the selective lithium recovery from seawater was designed as a part of the Ocean Thermal Energy Conversion (OTEC), a system dealing with obtaining the alternative energy sources from seawater. The benchmark plant is also designed for using enriched deep ocean water for recovering various diluted elements. In this study, however, surface seawater pumped from the Imari Bay (Saga Prefecture, Japan) was used for the benchmark plant experiment.

RESULTS AND DISCUSSION

A number of lab-scale column tests have been performed to evaluate the proper operational conditions for the selective lithium recovery [14, 15, 16]. A thirty-days run was performed after lab-scale column tests to check the proper operational conditions in last year. The run was performed as a preliminary test and ca. 140 m³ of seawater passed through the adsorbent column. Figure 4 shows the breakthrough profile of Li^+ . Though Li^+ was gradually adsorbed in the column, the breakthrough was not achieved until the end of the run. The concentration of Na^+ could not be measured due to its quite high content in seawater. After elution of the column with 0.85 mol/L HCl, the eluted solution was evaporated with a crystallizer. 151.7 g of the dried precipitate salts was obtained. The composition of the dried salts was analyzed as summarized in Table 1. The precipitate salt contains several amounts of other alkali and alkaline-earth elements, which are highly concentrated in seawater and have hydrated ionic radius similar to that of lithium (0.78 Å). The total content of lithium during the run was 15.7 g in the form of LiCl. Since the concentration of Li^+ in Imari Bay is 0.15 ppm in average, 11 % of lithium recovery efficiency was obtained from 140 m³ of seawater.

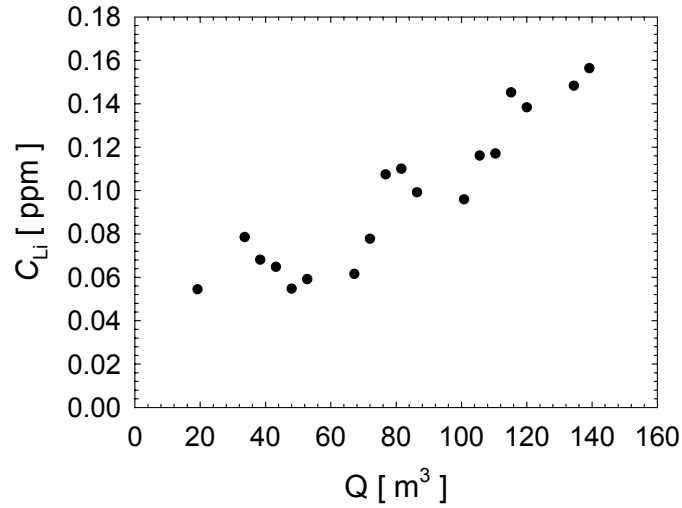


Fig. 4. Breakthrough profile of Li⁺ in 30 days run of benchmark plant.

The long run was performed in the period from December 2004 till July 2005. 816 m³ of filtered seawater was pumped through the adsorption column with an average seawater intake of about 200 L/h. The Li⁺ concentration profile during the adsorption run is depicted in Fig.5.

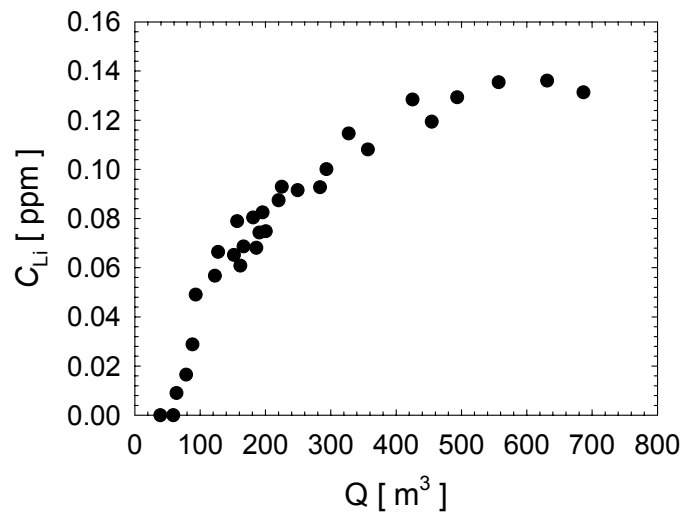


Fig. 5. Breakthrough profile of Li⁺ in 150 days run of benchmark plant.

The breakthrough was achieved after 600 m³ (3000 hours) of operation. The adsorbent was then washed with 1016 L of fresh water and eluted with 600 L of 0.85 mol/L HCl. The eluted solution was evaporated and dried *in vacuo* to obtain 791.4 g of the dried precipitate salt. The composition of the dried salt is also summarized in Table 1. The overall lithium content in the precipitate salt was 263.5 g as LiCl and 33.3% lithium recovery efficiency can be achieved. Furthermore, the concentration efficiencies of lithium from seawater are 3450 for the 30 days run and 11000 for the 150 days run, respectively.

Table 1. Metal composition of the dried precipitate salts

Element*	30 days run [wt%]	30 days run concentration efficiency	150 days run [wt%]	150 days run concentration efficiency	Contents in seawater [wt%]
LiCl	10.35	3450	33.3	11000	3.0×10^{-3}
NaCl	38.3	0.49	20.4	0.26	78.1
KCl	0.89	0.25	3.3	0.94	3.5
MgCl ₂	0.078	5.5×10^{-3}	8.2	0.57	14.3
CaCl ₂	36.9	11.3	13.4	4.11	3.26
MnCl ₂	5.3	-	19.4	-	-
SrCl ₂	8.2	205	2.0	50	4.0×10^{-2}

* calculated as metal chlorides existing in the precipitates

CONCLUSIONS

Selective lithium recovery from seawater is successfully verified on the benchmark plant scale after a lab-scale background. After the 150 days adsorption run, 791 g of the dried precipitate salt containing 264 g of LiCl was obtained from 816 m³ of seawater. However, the purities of LiCl in the precipitates are not satisfactorily high. The precipitate salts contain some other alkali and alkaline-earth elements appearing in seawater. In near future, we are planning further separation processes for LiCl purifying, such as solvent extraction and/or ion exchange.

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