



Preliminary study on recovering lithium from high Mg^{2+}/Li^+ ratio brines by electrodialysis



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ARTICLE INFO

Article history:

Received 1 July 2016

Received in revised form 7 August 2016

Accepted 7 August 2016

Available online 9 August 2016

Keywords:

Recovering lithium

Electrodialysis (ED)

Brine

High Mg^{2+}/Li^+ ratio

ABSTRACT

An electrodialysis (ED) system equipped with monovalent selective permeability ion exchange membrane was used to investigate the separation of magnesium and lithium in salt lake brines. Some objective functions including separation coefficient of magnesium and lithium (F_{Mg-Li}), recovery ratio of lithium (R_{Li}) and current efficiency (η), were applied to explore the effect of the applied voltage, the linear flow velocities, the Mg^{2+}/Li^+ ratio and pH on the process of extracting lithium. The results showed that the increase of applied voltage could improve the separation coefficient and the recovery ratio of lithium, but energy consumption would also rise; with the increase of feed linear velocity, the separation coefficient had a rising trend, but too large linear velocity would lead to increasing energy consumption and reducing current efficiency. When the Mg^{2+}/Li^+ ratio was in the range of 5–92, ED technology showed higher separation efficiency. Linear flow velocities of concentrating and desalting compartments (1.9–7.6 cm/s) showed positive correlation with the migration of the ions. According to the comprehensive analysis of the experimental results, the optimal operation conditions of the ED device are as follows: the applied voltage (5 V), concentration of electrolyte solution (5 wt% Na_2SO_4) and the linear velocities of desalting/concentrating/electrolyte (6.2, 6.2 and 3.8 cm/s). When the brine with Mg^{2+}/Li^+ ratio of 60 was treated by the ED for 2 h under this condition, the separation coefficient was 12.48. And the recovery ratio of Li^+ , current efficiency and the Mg^{2+}/Li^+ ratio of concentrate was 72.46 wt%, 8.68 wt% and 7, respectively. The concentrate, which could be considered as a bittern with lower Mg^{2+}/Li^+ ratio (<8), will be easy to be treated in the subsequent process.

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1. Introduction

Lithium and its compounds have more extensive application for their special physical and chemical properties compared with other metal elements. They have been widely applied in lithium battery field which can be used in various communication equipment and environment-friendly vehicles, and a kind of fuel for fusion reactor [1–3]. With the rapid development of the world industry, the demands for lithium resources increase, and the consumption of lithium products in various areas grows continually and rapidly [4]. Therefore, only if some cost-effective technologies for lithium recovery were developed, could the scarce of lithium resources be relieved.

Lithium resources in salt lakes account for about 90% of total proven reserves of the onshore lithium resources in the world. These salt lakes are mainly distributed in Bolivia, Argentina, Chile, China and the United states [5]. The lithium concentration, magnesium concentration and Mg^{2+}/Li^+ ratio in some known brine deposits all over the world was listed in Table 1 [6,7]. Large-scale industrialized production of lithium mainly appeared in three lakes: Atacama (Chile), Hombre Muerto (Argentina) and Silver peak (U.S.) [8–10]. The precipitation method [9,11] has been developed to separate and recover lithium from above three salt lake brines with a low Mg^{2+}/Li^+ ratio (according to the suggestion of Yu et al. [7], the brine is low Mg^{2+}/Li^+ ratio when the mass value of Mg^{2+}/Li^+ ratio is below 8, others are high Mg^{2+}/Li^+ ratio). But the loss of some lithium salt makes it unsuitable for the majority of global salt lake brines which belong to the type of high magnesium and low lithium [12]. Other separation technologies such as solvent extraction [13–15], ion exchange [16], adsorption [17,18] and nanofiltration (NF) [19,20] have been developed to extract

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Table 1
Properties of some known brine deposits in the world [6,7].

Country	Deposit	Li ⁺ conc. (wt%)	Mg ²⁺ conc. (wt%)	Mg ²⁺ /Li ⁺ ratio
USA	Clayton Valley/Silver Peak	0.030	0.04	1.33
Argentina	Hombre Muerto	0.062	0.09	1.46
Argentina	Cauchari	0.062	0.18	2.84
Chile	Atacama	0.140	0.96	6.40
USA	Smackover	0.038	0.75	20.00
Bolivia	Uyuni	0.096	2.00	20.83
China	East Taijinar	0.085	2.99	35.20
China	West Taijinar	0.021	1.28	61.00
China	Da Qaidam	0.020	1.30	65.00
China	Yiliping	0.022	2.00	91.00
USA	Great Salt Lake	0.006	0.80	133.33

lithium from brine, but no effective method can be used to extract lithium effectively from high Mg²⁺/Li⁺ ratio salt lake brines [21]. Therefore, efficient methods for achieving higher extraction ratio of lithium from the high Mg²⁺/Li⁺ ratio brine are extremely desirable.

As an important membrane separation technology, ED has been used in many fields, especially in seawater and brackish water desalination and some certain separation fields [22–26]. ED gets more and more attention for water utilization and metal ions recovery. In the previous work, the lithium resource recovery from brine with the high Mg²⁺/Li⁺ ratio of 60 by using electrodialysis (ED) has been studied. However, the magnesium in the brine was precipitated by use of the lime and the Mg²⁺/Li⁺ ratio was decreased to 5 before extracting lithium [27]. Furthermore, Hoshino [28,29] developed a novel technology for recovering lithium from seawater by electrodialysis using ionic liquid membrane. The method involves an ionic-liquid-impregnated organic membrane, which only the Li⁺ ions in seawater and not the other ions, including Na⁺, Mg²⁺, Ca²⁺ and K⁺, permeate from the anode side to the cathode side in ED process. Then, the Li⁺ become concentrated on the cathode side and can be recovered. Extracting lithium from brine through combining electrodialysis (ED) with ion sieve adsorption method has been researched [30]. This method is a valuable technology which is relatively economical and environment-friendly, and it's also the key research direction in the future for extracting lithium from salt lake brines with high Mg²⁺/Li⁺ ratio.

As one of the technologies that give a possibility to separate monovalent ions from brine and seawater [31], ED equipped with monovalent selective ion exchange membranes was used to separate the magnesium and lithium from high Mg²⁺/Li⁺ ratio brine in this study. ED is a technique based on the transport of ions through selective membranes under an electrical field [32]. In the process of ion migration, the ion can pass through a membrane when it has opposite charge to fixed charge of membrane, otherwise the ion can't pass. So the ions concentration in concentrating compartment increases with the decline of the one in desalting compartment. So, concentrated solution and desalted liquid can be obtained. Then the separation and purification of certain ions can be achieved. Separation of sodium ions from trivalent chromium of tanning waste water by ED using monovalent cation selective membranes has been researched [33]. Moreover, monovalent selective ion exchange membranes usually have high selectivity towards lithium, but they were determined to have extremely low selectivity towards magnesium. So, it can decrease the ratio of magnesium and lithium in brine, and at the same time the lithium ions were concentrated in the concentrating compartment. This was also provided convenience for subsequent preparation of the lithium products. The applied voltage, linear velocity of

desalting and concentrating cells, Mg²⁺/Li⁺ ratio and pH value were investigated in this separation process of magnesium and lithium. The optimal operating conditions of ED were obtained through the analysis of separation coefficient, recovery ratio and current efficiency. Meanwhile, the specific energy consumption was also discussed.

2. Methods and materials

2.1. Experimental apparatus and membranes

The schematic diagram of ED process and migration of ions in membrane stack is depicted in Fig. 1. The experimental apparatus mainly consisted of dilute solution tank, concentrate solution tank, electrolyte solution tank, direct-current (DC) power unit, membrane stack and tube pump. The membrane stack was consisted of ten pairs (ACS and CIMS). The size of membrane was 300 mm × 100 mm, and its effective membrane area of each pair was 140.7 cm². The spacer thickness was 0.90 mm.

The internal structure of ED membrane stack is shown in Fig. 2. The stack is comprised of fixation plate, anode plate, cation exchange membrane, anion exchange membrane, concentrating cell spacer, and desalting cell spacer and cathode plate. Diagonal nets spacers are incorporated into the concentrating and desalting cells.

The ion exchange membranes used in this paper were manufactured by ASTOM company in Japan. Both of them belong to monovalent permselective ion exchange membranes. The performance parameters of those membranes were listed in Table 2.

2.2. Experimental procedure and analytical methods

The process of this experiment was conducted in batch mode at room temperature. The desalting compartment and concentrating compartment were filled with 2.5 L of artificial brine with high Mg²⁺/Li⁺ ratio (chlorine salt system) and 1.5 L of a certain concentration of sodium chloride solution, respectively. In addition, the electrolyte compartment was filled with 2.5 L of 5 wt% Na₂SO₄ solution. At the beginning of the experiment, the artificial brine, NaCl solution and Na₂SO₄ solution were put into the dilute solution tank, concentrate solution tank and electrolyte solution tank, respectively. Cathode compartment shared the same electrolyte solution tank with anode compartment, and the electrolyte solution was transported by the same pump. This technology made the lithium, which entered in the cathode compartment through the cathode membrane, return to the membrane stack through the anode membrane from anode compartment. So, the lithium loss could be reduced in the whole process. Then the booster pumps feed these solutions into the respective compartments. The linear flow velocity of the electrolyte compartment was 3.8 cm/s (flow rate 80 L/h) during the whole experiment. All experiments were run for 120 min, and samples were taken every 20 min. The concentration of Li⁺ was determined by AAS (Atomic Absorption Spectrometry), and Mg²⁺ and Cl⁻ were analyzed by EDTA titration method and “Silver Nitrate Titration” (ASTM D512-89 (1999) “Standard Test Methods for Chloride Ion in Water”), respectively. The amount of Na⁺ was calculated by charge balance method in the solution.

2.3. Data analysis

2.3.1. Separation coefficient of magnesium and lithium

The separation coefficient refers to the ratio of magnesium and lithium at time t over initial ratio of magnesium and lithium in the desalting compartment.

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