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A Study on Recovery of Lithium from Geothermal Water and Study of Assal Geothermal Field

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ABSTRACT

Geothermal fluid is an important source of lithium (Li). Li is a metal increasingly demanded in the cell industry. The purpose of this project study is to learn basic chemistry on the recovery of lithium from geothermal water. There are several methods for recovery of Li such as separation: electrodialysis, solvent extraction, adsorption, and membrane filtration. In this study, we selected the adsorption method using λ-MnO2 (granuled) because it is the most economical and eco-friendly method. The conditions of the column experiments for recovery of lithium from Unzen geothermal water were fixed for bed volume 9.27g, Space velocity = 7.5 BV/h = 69.5 mL/h and flow rate = 1.0 mL/min.

The geothermal water sample content (mg/l). B-14.7; Na+- 2540; K +-259; NH4+-17 Ca2+- 194; Mg2+- 212; HCO3- -217; F- 0.5 Cl- - 4590; SO4- 379. Concentration of silicic acid in this sample is around 192 ppm.

Assal geothermal fields in Djibouti are significantly rich in mineral to be potentially economically viable. Concentration of Li is around 33 ppm. This can lead us to research for the extraction of lithium and rentable minerals. Some companies like Geo40 in New Zealand it is launched the extraction of lithium after having removed the silica.

1. INTRODUCTION

Lithium (Li), third chemical element in the periodic table and is an alkali metal in the same group as sodium, potassium, cesium and rubidium. It has the low density as 0.534. Li concentration in the earth's crust is very low with average of it is scanty (20 ppm) and in the oceans 0.17 mg /l.

Currently Li is considered to be one of the major element essential in the modern life of the 21st century because of its physical characteristics such as low weight, high voltage, high electrochemical equivalence and good conductivity (BARIŞ, 2015).These characteristics make Li as attractive raw material for rechargeable lithium ion battery (LIB) in the electric vehicle

2. THE USAGE VARIETY OF APPLICATIONS OF LITHIUM

The glass and ceramics industries are currently the largest consumers of Li, but the sector of rechargeable batteries continues to grow in recent years. Li is also used in several other areas such as lubricating greases, air treatment, polymer production, primary aluminum production, electric cars and others. Figure 1 shows the different sectors using Li.

The demand for Li is increasing very rapidly and production is increasing. This increase is explained by the growing development of electric cars to reduce CO2 and fight global warming. Li is placed among the green sources. Figure 2 shows the price evolution of one tone of Li2CO3 from 2002 to 2016.

The Li market is not in deficit (USGS). Current forecasts of Li demand and supply indicate that the market will be more than supplied in the coming years (Figure 3). The depletion of fossil fuels forces the constant search for new sources (Asdrúbal 2019).

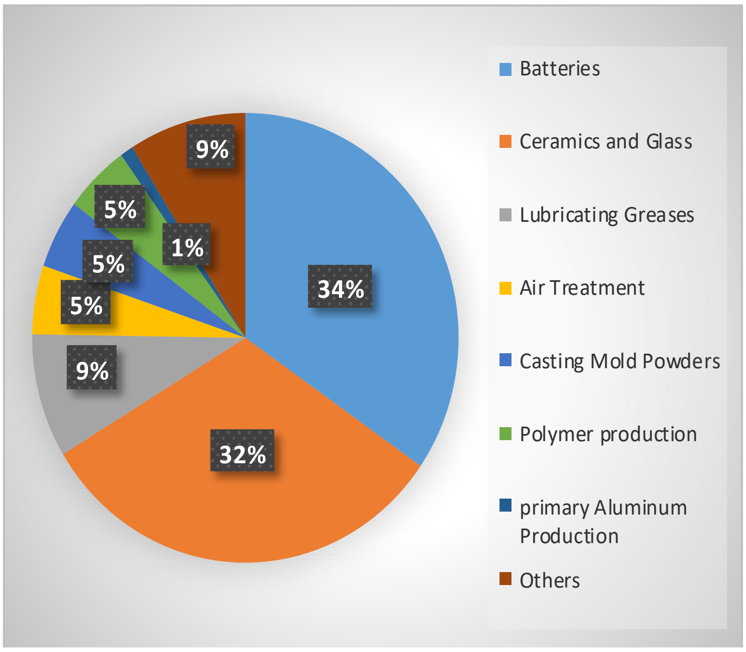

Figure 1 Distribution of used of Li.

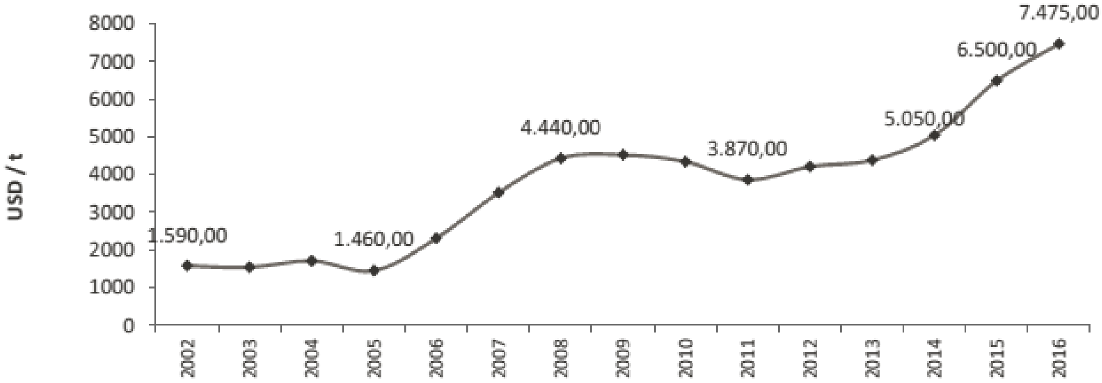

Figure 2: Annual price trend of Li2CO3 (USD Per ton).

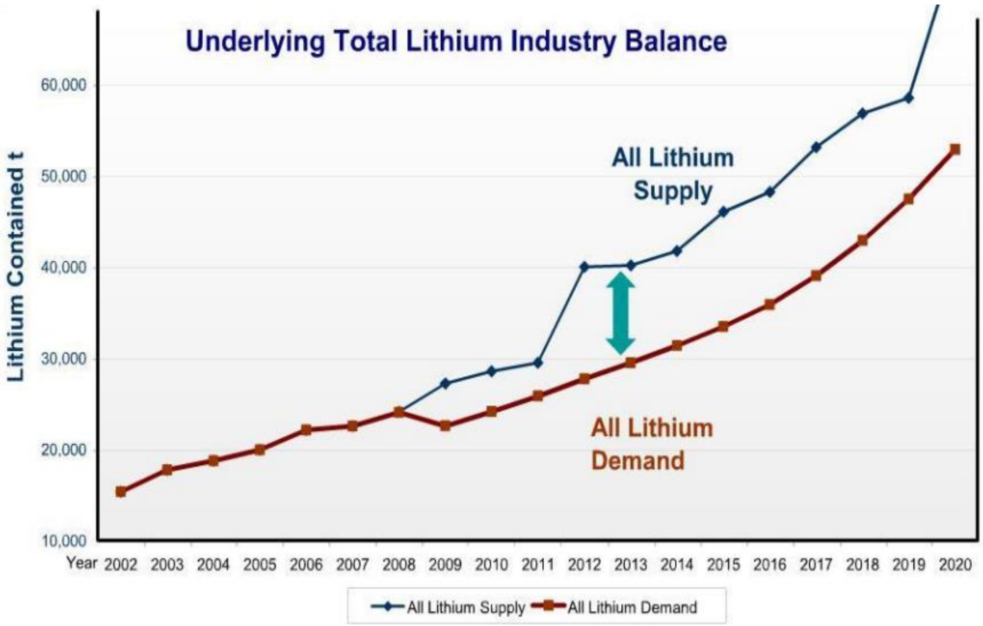

Figure 3: Total Demand and Supply of Li.

3. LITHIUM SOURCES

There are three main Li sources: ore, from brines (salt-lakes, geothermal fluids, groundwater etc.) and seawater. Li recycling is also a significant source

There are about 145 minerals containing Li, but few of them are marketable. Among them are spodumene, petalite (castorite), lepidolite, Hectorite and Jaderite. These last two minerals are of clay origins. Figure 4 shows the global distribution of Li sources (Xin Xu et al 2016).

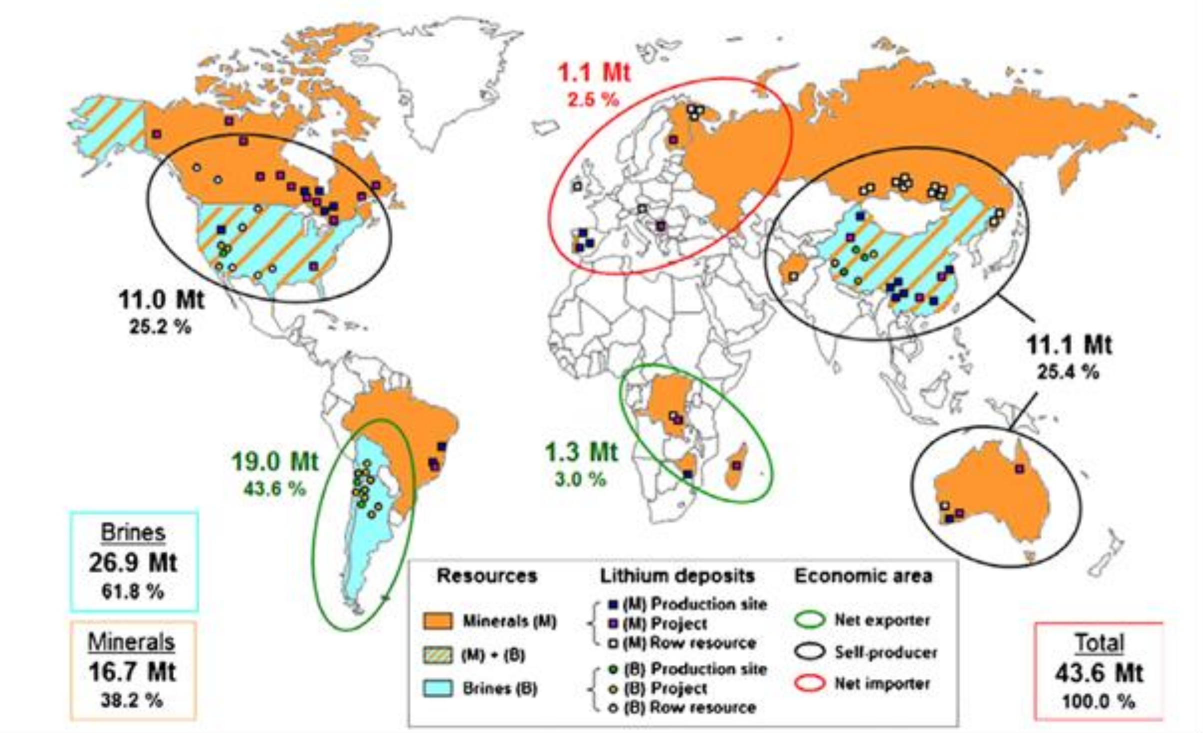

Figure 4: the global distribution of lithium sources.

Li concentration in geothermal water is about a hundred fold higher than that in seawater. But, the reasonable recovery technique of Li has not been developed. The purpose of this project study is to learn basic chemistry required to develop a new technique in future for recovery of Li from geothermal water.

4. EXPERIMENTAL

4.1 Materials

The geothermal water sample used in this report comes from Obama binary power plant located in Obama, Unzen, Nagasaki Prefecture, Japan. Led by Koyo Denki Co., Ltd. The properties of the geothermal water samples used are listed in Table 1.

Table 1: Reported physico-chemistry geothermal water samples (averaged concentration)

Parameters	Value	Cations	Concentration (mg/L)	Anions	Concentration (mg/L)
pH	8,53	Li^+	5.2	HCO3-	217
EC (mS/ cm)	1.475	Na^+	2540	F-	0.5
TDS (g/l)	-	K^+	259	Cl-	4590
Salinity	-	NH_4^+	17	NO3-	-
B(mg/L)	14.7	Ca^{2+}	194	SO4-	379
		Mg^{2+}	212		

The polymer iron sulfate solution of chemical formula FeSO4・7H2O of molar mass 278.01 g/mol was used to remove silicic acid before recovery experiment of lithium.

For Li extraction, λ-MnO2 was used as an adsorbent of Li. λ-MnO2 adsorbent in granulated form was produced and supplied from The University of Kitakyushu, Japan. The preparation procedure is the same as that mentioned in the literature. [Yoshizuka and Nalan Kabay 2018]. The properties of λ-MnO2 adsorbent are summarized in Table 2.

Table 2. Properties of λ-MnO_2 adsorbent.

Type	Spinel
Form	granulated
Specific surface area, m2/g	-*
Mean particle size, mm	1.0 –1.4
Total lithium capacity, mg Li/g	5.0

Other reagents used in this study were of analytical reagent grade. All of the solutions were prepared with ultrapure water.

4.2 Methods of the final column experiment for recovery of Li

4.2.1 Removal of silica acid

In this experiment, the volume of the samples to be analyzed is 10 L, 200 ml of polymer iron sulfate solution (! add concentration here) is required. Then mix 10 L geothermal water with 200 ml of polymer iron sulfate solution. The pH of the mixture drops around 1 to 2 so we control the pH, by adding 4 mol/L or 1 mol/L NaOH to bring the pH around 8 or 9. We leave 1h for the reagents to react well. A co-precipitation deposit of silica and iron hydroxide is obtained. Finally, the mixture is filtered using an qualitative filter paper (110mm Size). The resulting filtrate will be used for Li extraction.

4.2.2 Extraction of Li: adsorption by column experiment

Fill glass wool with 9.27 g of λ-Mno2 adsorbent then the column is treated with 1.0 Mol of hydrochloric acid for a period of 2 h. then washed for 1 h with deionized water. This is an ion exchange reaction (Yoshizuka 2018). As shown in the equation 1 Li +type λ-MnO2 is transformed to H+ type λ-MnO2. The exchange of ions occurs only between the lithium ion and the hydrogen ion.

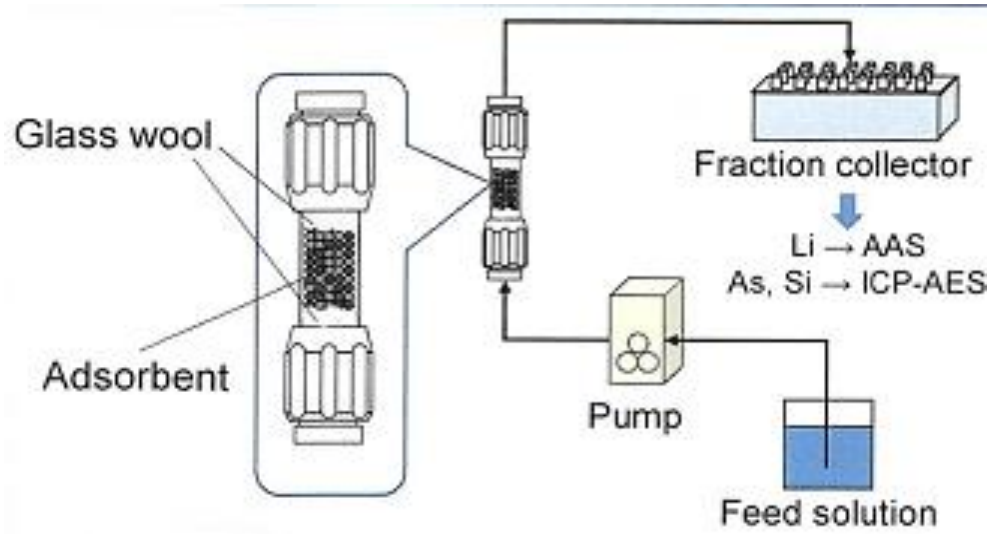

Figure 5: Schematic drawing of column experiment.

$$Li_{1.5}Mn_2O_4 + 1.5H^+ \rightarrow H_{1.5}Mn_2O_4 + 1.5Li^+ \quad (1)$$

The adsorption of Li was carried out from 0 L of geothermal water for 6 days and 21 hours (143.8 hours), and then washed 1 L of deionized water, and finally eluted 1.2 L of 1 mol/L HCl. Take 0.6 L of eluent obtained after elution and start the evaporation step. During evaporation, the temperature is adjusted around 90 oC, to obtain 1 mL concentrated liquid, and then dried to obtain the precipitate powder.

5. RESULTS AND DISCUSSIONS

5.1. Batch experiments

5.1.1. Determination of silicic acid concentration

Adsorption of Li to λ-MnO2 is strongly prevented. Therefore, silicic acid should be removed from geothermal water. First, silicic acid concentration was determined by spectrophotometry and inductively coupled plasma atomic emission spectrometry (ICP-AES). The former is for monosilicic acid concentration and the latter is for total silicic acid concentration. The monosilicic acid concentration was 182 ~ 188 ppm (SiO2) and the total silicic acid was 192 ppm (SiO2), suggesting that silicic acid existed mainly as monosilicic acid in the geothermal water sample.

5.1.2. Removal of silicic acid from geothermal water

In this study, in order to remove silicic acid from geothermal water, the coprecipitation method with ferric hydroxide (Fe(OH)3) was used. It is well known that silicic acid can be adsorbed on Fe(OH)3 above pH 8. As a source of Fe(OH)3, a commercial iron sulfate polymer solution (Nittetsu Kogyo) was used. One to five cm3 of the iron sulfate polymer solution was added into 100 cm3 geothermal water and the pH was adjusted above 9 because of enough growth of Fe(OH)3 colloid particles. The pH was checked using a pH paper. After the filtration of the suspended solution with 0.45 µm membrane filter, silicic acid concentration in filtrate was determined by ICP-AES. Figure 6 shows the effect of volume of the iron sulfate polymer solution added on removal of silicic acid. The total silicic acid concentration decreased from 254 ppm to 6 ppm. Coprecipitation of silicic acid with Fe(OH)3 is based on the formation of a Fe-O-Si(OH)3 bond.

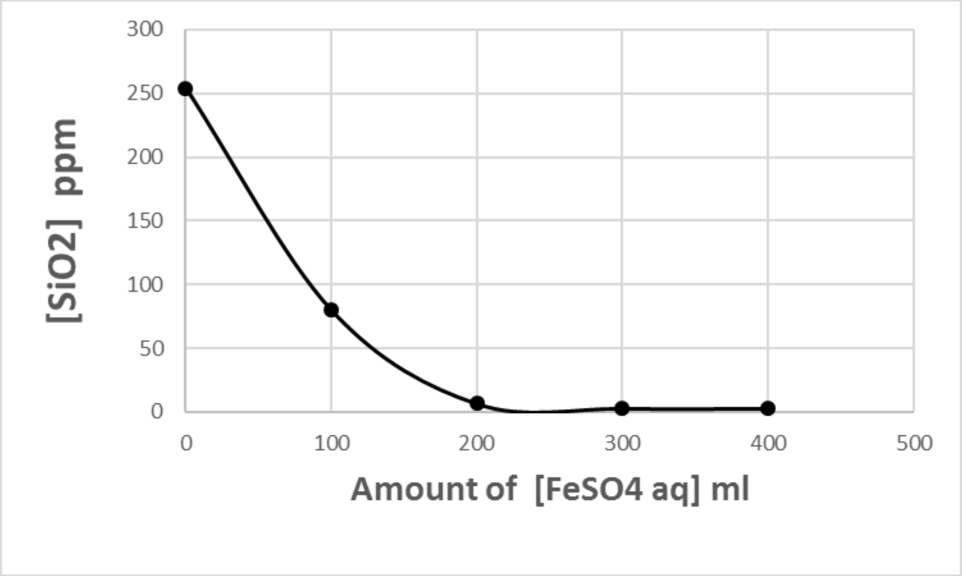

Figure 6: Effect of volume of iron sulfate polymer solution (coagulant) added to 10 L of geothermal water on removal of silicic acid.

5.1.2. Determination of Li in geothermal water

The concentration of Li, which is a target element, was measured by ICP-AES. Averagely, it was 4.16 ppm. In addition, the Li concentration after removal of silicic acid from geothermal water was also measured. No loss of Li was confirmed by the coprecipitation of silicic acid with Fe(OH)3, described above.

5.1.3 Preparation H+ type λ-MnO2

λ-MnO2, which was supplied from Professor Yoshizuka, was Li+ typeλ-MnO2 because of unstability of H+ type λ-MnO2. According to his paper, the H+ type λ-MnO2 should be prepared from the Li+ type λ-MnO2 immediately before adsorption experiment of Li. Therefore, desorption behavior of Li+ from the Li+ type λ-MnO2 was examined to accurately determine the preparation condition of the H+ type λ-MnO2 from Li+ type λ-MnO2. According to a literature, one gram of the Li+ type λ-MnO2 was added in 100 cm3 of 1 mol dm-3 HCl. Figure 7 shows the desorption behavior of Li+ from the Li+ type λ-MnO2. After 10 min, most of the Li+ desorbed from the Li+ type λ-MnO2. The reaction can be represented as follows. This is the ion exchange reaction between Li+ and H+.

$$3\mathrm{Li}_{1.33}\mathrm{Mn}^{4+}_{1.67}\mathrm{O}_4 + \mathrm{H}^+ \rightarrow 3\mathrm{H}_{1.33}\mathrm{Mn}^{4+}_{1.67}\mathrm{O}_4 + 4\mathrm{Li}^+ \tag{2}$$

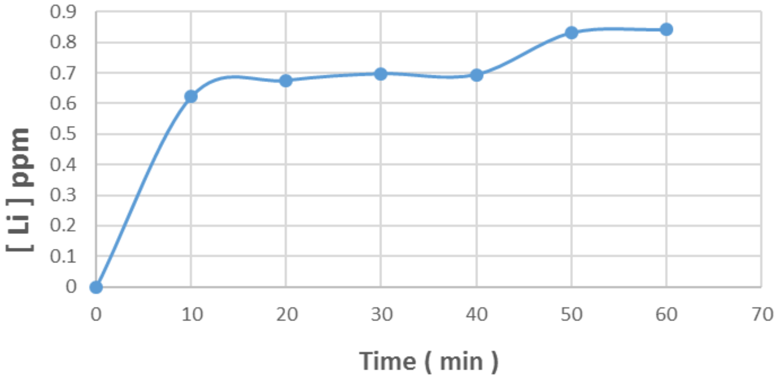

Figure 7: Variation of Li concentration with time.

5.1.4. Adsorption behavior of Li+ by the H+ type λ-MnO2

Using the H+ type λ-MnO2 prepared, adsorption experiment of Li+ was carried out. One gram of the H+ type λ-MnO2 was introduced in the LiCl solution whose pH was about 10. According to Yonezu et al., the exchange rate of H+ to Li+ relatively faster in alkaline condition than in acidic condition. It can be deduced that OH- ion in bulk solution may pull H+ in the H+ type λ-MnO2 to form H2O. Li+ may transfer from the bulk solution to the empty site in the H+ type λ-MnO2. Figure 8 shows the adsorption behavior of Li+ by the H+ type λ-MnO2 under alkaline condition. Until 20 min, most of the Li+ was effectively adsorbed.

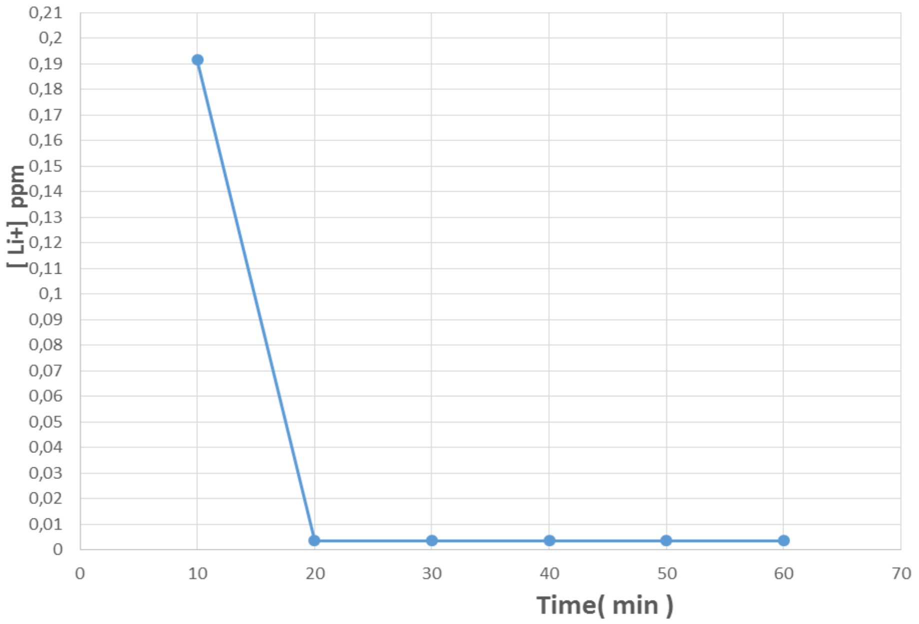

Figure 8: Variation of Li concentration with time.

5.2. Column experiment for a practical recovery of Li

Using H+ type λ-MnO2 as an adsorbent of Li+, adsorption experiment of Li+ in geothermal water which most of silicic acid was removed was performed by column method. In this column experiment, the operating conditions are regulated as follows. The bed volume was 9.27 mL, the flow rate was of the order 1 .0 ml / min., space velocity 7.50 B.V. (Bed Volume)/h and the pH is 9.47. Figure 9 shows the pH variation and Li concentration as a function of B.V. The permeate pH increases and the Li adsorption is almost zero. This explains that the totality of Li contained in the geothermal fluid is adsorbed.

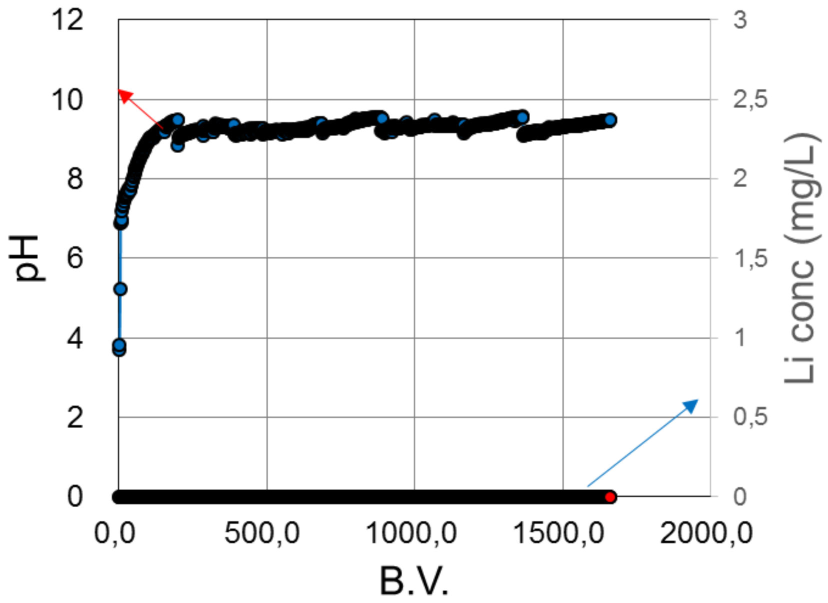

Figure 9: Effect of Li adsorption by λ-MnO2.

Figure 10 shows elution curve by 1 mol/L HCl. Between B.V.= 5 and B.V. = 13, Li concentration was observed. This interval was chosen to evaporate and dry to obtain the LiCl powder.

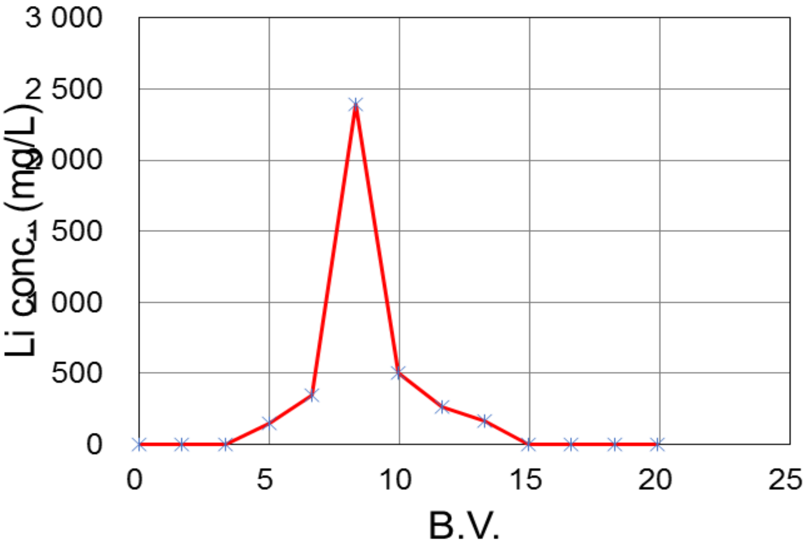

Figure 10: Column elution curve.

After adsorption operation of Li+, 1 mol dm-3 HCl was introduced in to the colume. Figure 9 shows the elution curve of Li+ from the column after adsorption experiment. As shown in the batch experiments, Li+ desorb in bulk solution by the exchange reaction between H+ in the bulk solution and Li+ in the Li+ type λ-MnO2. From the elution curve, Li+ can be recovered efficiently from geothermal water.

6. PERSPECTIVES IN ASSAL GEOTHERMAL WELL

In the 1980s geothermal exploration wells (Assal 3 to Assal 6) were drilled in the Assal rift zone in the Republic of Djibouti. During the Assal 3 production test, sulfide-scaling deposit is observed. these are scaling sphalerite and galena. Likewise, analyzes of geothermal reservoir fluids also show the presence of Lithium; some wells have a lithium content of 33 ppm. the silica scaling remains very strong in all Assal 3 to Assal 6 wells.

Not far from the geothermal drilling well is the big dirty lake: Lake Assal. We now know that the brines of the large salt lakes (salars) are the resources for exploiting lithium. it accounts for almost half of the world's current lithium production, and 75% of the world's estimated lithium reserves.

A study of salar fluids from Lake Assal would be encouraging in the search for lithium in the Republic of Djibouti.

Table 3: geothermal water composition (mg/kg) Assal 3, Assal 4 , Assal 5 and Assal 6.

	A3	A6	A4	A5	Lake Asal
pH	4.9	4.8	5.0	5.0	7.1
Na	37 452	39 839	13 000	42 000	101 200
K	7273	6250	500	6000	5161
Ca	23 928	20 630	400	8532	2677
Mg	37	34	1500	700	12,500
Cl	106 000	103 000	20 000	52 000	199 155
SO_4	32	12	2500	447	4320
SiO_2	520	550	900		
HCO_3	66	76	102	38	184
Li	31	17	33		6
F	7	4			
NH_3	9.1	9.3			
Zn*	3.1	5.6			
Pb*	3.4	5.2			
Fe*	6.7	4.4			

7. CONCLUSION

- Removal of silicic acid is a crucial step before recovery of Lithium.
- Adsorption column experiment by λ-MnO2 is one of the most economical Li separation methods and its efficacies of 96%. We can be concluded that: granule λ-MnO2 can be used successfully for recovery of Li from geothermal brines.
- Assal geothermal fields are significantly rich in mineral to be potentially economically viable

7. ACKNOWLEDGMENTS

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