The Degree of Lithium (Li) Stability Compared To Calcium (Ca) and Magnesium (Mg) From Low Lithium Grade Brine Water with Addition of Limestone and Oxalic Acid

F. Firdiyono¹, Latifa Hanum Lalasari¹a, Ermiziar Tarmizi², Eko Sulistiyono¹, Lia Andriyah¹, Tri Arini¹, Nadia C. Natasha¹, Fariza E. Yunita
¹Research Center of Metallurgy and Materials, Indonesian Institute of Sciences, Kawasan PUSPIPTEK Gedung 470, Tangerang Selatan, 15314, Indonesia
²Department of Chemical Engineering, Institut Teknologi Indonesia, Jl Raya Puspiptek Serpong-Tangsel, Indonesia

E-mail: alati003@lipi.go.id; aifa_sari@yahoo.com

Abstract. The purpose of this study was to investigate whether lithium was precipitated along with the removal of Ca and Mg elements from brine water using limestone and oxalic acid. The first stage was Mg removal by adding CaO at room temperature for 3 hours. The second stage was the Ca removal by adding oxalic acid at a ratio of 2; 3; 4; 5; 10; 15; 20; 30; and 40 ml / 100 ml brine water and pH : 0, 1, and 4 at room temperature for 3 hours. The results showed the most optimal addition of CaO was 20 gr / 1 l of brine water with the Mg element can be removed above 99 %, while Li was only reduced by about 1 ppm, and the Ca content only increased by around 28 ppm. The use of oxalic acid will also reduce the amount of lithium besides the Ca removal in the form a precipitate of calcium oxalate. The use of oxalic acid at pH 0 and 4 would reduce the Li content more than at pH 1. At the use of oxalic acid up to 40 ml at pH 1, brine water still contained about 78% Li element.

1. Introduction

Bittern water is one of the sources of lithium raw material which is quite potential in addition to hot water and rock specimens. Bittern water is obtained from the evaporation of salt water in the production of salt from sea water or from the evaporation of spring water. In addition to consumption needs, the use of salt which is quite large is for industrial purposes. Indonesia with a large population, the need for salt for consumption will also be large. To meet the needs of salt, Indonesia can obtain it through the process of seawater desalination, because Indonesia is an archipelago with a sea area of two-thirds of its land area. The process of seawater desalination to obtain salt in very large quantities will produce a very abundant bittern water.

Until now the use of bittern water is still not optimal. Meanwhile on the other hand in bittern water contained lithium which has been concentrated. In bittern water there are still many impurities, such as Ca, Mg, K, B and others that must be removed. This bittern water when processed carefully will get lithium concentrate which is very useful in making lithium batteries. Chile, Bolivia, China are the main producers of lithium raw materials. The element of lithium can be found in seawater, spring water and spodumen rocks. In Indonesia supporting data regarding lithium raw material reserves do not yet exist, so an exploration phase is needed to determine the potential of these raw materials, while the exploration work itself requires a very large cost.
Lithium carbonate is the main ingredient in making lithium batteries. Lithium batteries are one source of electricity energy that is widely used for electric cars in the future. The advantages of lithium batteries include:

1. The battery can be recharged quickly
2. The electrical energy generated is quite large, etc.

In this paper we will discuss the process of eliminating the calcium element contained in a brine water solution, as a result of the process of eliminating the element magnesium in a solution carried out using lime. Ca elements that enter the solution will be eliminated again by using oxalic acid. On this occasion the characteristics of the lithium element will be investigated using lime and oxalic acid reagents when the process of removing Mg and Ca from low lithium lithium brine water is carried out.

2. Experimental
2.1. Materials
The raw material used in this experiment was the concentrate of the spring water evaporation process with an initial lithium content of 15-18 ppm. The chemical composition of brine water from the evaporation process was shown in Table 1. The limestone had undergone a roasting process at 900 °C was used as a stage 1 precipitation reagent which has a chemical composition as follows: 99.33% Ca, 0.34% Mg, 0.04% K, 0.24% Si and 0.05% others [1]. Oxalic acid and NaOH are pro-analyses with Merck specifications used as stage 2 precipitation reagents carried out controlling pH = 0, 1, 4.

| Al   | B      | Ca     | K      | Li      | Mg      |
|------|--------|--------|--------|---------|---------|
| 0.26 ppm | 353.32 ppm | 7672.48 ppm | 1975.56 ppm | 79.87 ppm | 1569.87 ppm |

2.2. Experimental procedure
Brine water used in this experiment was obtained from the evaporation of Tirta Sanita hot water, Ciseeng, Bogor. The removal of Mg element in the solution was done by adding CaO to brine water as previous research by Lalasari et. al (2019)[1]. The variations in the amount of CaO used in this process were: 0.1; 0.3; 0.5; 0.75; 1; 2; 5; 10; 20; 30; 40; and 50 g/1 l brine water. The process was carried out at room temperature with stirring time for 3 hours. The next step was the filtration process to separate the solids (residues) and their liquids (filtrates). To find out the shape of the crystals that occurred in the residue, the solids are heated at a temperature of 100 °C for 24 hours and then an XRD and SEM analysis was performed. The content of Mg, Ca, and Li in the filtrates were then analyzed using ICP-OES. After the content of the Mg, Ca, and Li elements in the filtrate was known, the process continues with the removal of Ca element. The elimination of Ca element was done by adding oxalic acid to the solution. The variations in the amount of oxalic acid used in the process were: 2; 3; 4; 5; 10; 15; 20; 30; and 40 ml / 100 ml sample water. The pH variations used in this process were 0, 1, and 4. The process was carried out at room temperature with a stirring time of 3 hours. This experiment will investigate how much of the lithium element settles with magnesium and calcium during the refining process of magnesium and calcium from brine water using reagents of limestone and oxalic acid. The flow diagram of the experiment was shown in Figure 1.
Chemical Precipitation (stage I)

(rasio mass CaO/Brine water (g/L) : 0.1; 0.3; 0.5; 0.75; 1; 2; 5; 10; 20; 30; 40; 50)

Filtration (Stage I)

Residue

The concentrated brine water

Limestone

Calcination at 900 °C for 6 hours

Characterization (ICP-OES)

Chemical Precipitation (Stage II)

Rasio volume oxalic acid/brine water : 2; 3; 4; 5; 10; 15; 20; 30; 40ml/100ml brine water at pH (0, 1, 4)

Filtration (Stage II)

Residue

Oxalic acid (H₂C₂O₄)

Characterization (ICP-OES)

Figure 1. The flow chart of research

3. Result and Discussion

The removal of magnesium element in brine water using limestone as precipitant reagent aims to bind Mg²⁺ elements from brine water so that Mg²⁺ settles. This experimental method is the same as that of Lalasari et al. (2019)[1]. However, the chemical composition of the brine water used is different, namely the Mg and Ca content in this experiment are greater as shown in Table 1. Addition of limestone to the solution will occur the deposition of Mg²⁺ in brine water as the following reaction [1]:

\[
\text{CaO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2(aq) \quad \text{........................... (1)}
\]

\[
\text{Ca(OH)}_2(aq) + \text{Mg}^{2+}(aq) \rightarrow \text{Mg(OH)}_2(S) + \text{Ca}^{2+}(aq) \quad \text{........................... (2)}
\]

The above reaction can take place well and spontaneously because the Ksp value of Mg(OH)_2 of 1.8 x 10^{-11} is very much smaller than the price of Ksp Ca(OH)_2 which is 6 x 10^{-6}. The results of these experiments can be seen in Figure 1.
Based on the picture above shows that the addition of CaO into the solution can reduce the Mg content. The use of CaO in the Mg removal process will also result in a reduction in the Li content and vice versa will result in the addition of the amount of Ca in the solution as well. The most optimal addition of CaO is 20 grams because in this addition the magnesium element can be removed as much as 99.45%, whereas Li is only reduced by about 1 ppm, and the Ca content in the solution will only increase by around 2807 ppm, from 7672 ppm to 10479 ppm. According to Lalasari et al (2019), the addition of CaO will cause the Mg$^{2+}$ ions to precipitate to form Mg(OH)$_2$ compounds such as reaction 2 and also precipitate together with Ca to form compounds (Mg$_{0.03}$Ca$_{0.97}$)(CO$_3$)$_2$. Formation of compound Mg$_{0.03}$Ca$_{0.97}$)(CO$_3$)$_2$ will be smaller with an increase in the use of CaO into brine water.

As a result of the precipitation process of Mg(OH)$_2$ by using CaO, the amount of Ca elements in the solution would also increase. The removal of Ca$^{2+}$ from the solution was done by adding oxalic acid to the solution, so that calcium oxalate deposits are formed as follows:

\[ \text{H}_2\text{C}_2\text{O}_4\text{(aq)} + \text{Ca}^{2+}\text{(aq)} \rightarrow \text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O(aq)} \]  

\[ \text{(3)} \]

The above reaction can take place well because the Ksp value of CaC$_2$O$_4$ of $1.9 \times 10^{-9}$ is slightly smaller than the price of Ksp Ca(OH)$_2$ which is $6 \times 10^{-6}$. Experiments of precipitation of Ca elements using 1 N oxalic acid were carried out with variations in the amount of oxalate from 2 ml to 40 ml at pH from 0 to 4. According to Dong Jung Kang (2015) [2], the optimal pH of oxalic acid to react with Ca$^{2+}$ ions was at pH 0-1, whereas at pH 4 is expected that oxalic acid will bind Mg$^{2+}$ ions to magnesium oxalate.
Figure 3. Effect of pH and addition of oxalic acid on Ca content in solution.

Figure 4. Effect of pH and addition of oxalic acid on Li content in solution.

Figure 3 shows the same tendency in the process of removing Ca elements using oxalic acid. Increased use of the amount of oxalic acid will result in a reduction in the amount of Ca in the solution. The experiment did not show a very significant difference in removal of the Ca element between pH 0, 1 and 4. In the use of oxalic acid up to 40 ml, the dissolution would still contain about 40% Ca element. Figure 4 shows that the use of oxalic acid will also reduce the amount of lithium in solution. The use of oxalic acid at pH 0 and 4 will reduce the amount of element Li in the solution more than at pH 1. At the use of oxalic acid up to 40 ml with pH 1, the dissolution will still contain about 78% Li element. Sulistiyono et al (2018) [3] explained that the chemical precipitation process of brine water using oxalic acid caused the lithium elements to settle together with Ca and Al to form Al$_{1.19}$Ca$_1$Li$_{0.81}$ compounds. This causes the Li content in the brine water to decrease.
Figure 5. XRD pattern of Ca residues with oxalic acid

The picture above shows the XRD pattern of the residue that is formed when the solution is added 15 ml of 1 N oxalic acid at pH 0, 1, and 4. From the picture is clear that oxalic acid will bind Ca\(^{2+}\) ions and form precipitating CaC\(_2\)O\(_4\) compounds. Precipitation of Ca element with oxalic acid was apparently not affected by the acidity degree of the solution. CaC\(_2\)O\(_4\) compounds that are formed will precipitate at pH 0, 1 and at pH 4.

Figure 6. The morphology of residue from the addition of oxalic acid to solution

The picture above shows the results of SEM analysis on the residue resulting from the addition of 15 ml of 1N H\(_2\)C\(_2\)O\(_4\) (pH 0; pH 1; and pH 4) with a magnification of 1000x. That indicates that the residue is dominated by CaC\(_2\)O\(_4\) which has a monoclinic and perismatic crystal system. Figure 5a does not provide a significant change in shape with Figure 5b, which means the addition of pH 0 and pH 1 does not provide a significant morphological change in residue. The residual morphology at pH-4 appears to be irregular which is thought to have other elements besides Ca in the residue.

The above experimental results show that oxalic acid can bind the Ca element into Ca oxalate, but the use of oxalate still leaves the Ca element in a large enough solution. In the use of oxalic acid up to 40 ml with pH 1, 2, and 4 then the dissolution will still contain about 40% Ca element.
4. Conclusions
CaO reagent is an effective material to eliminate magnesium in the brine water solution, but excessive use of CaO in the Mg removal process will also cause a reduction in Li content and vice versa resulting in an increase in the amount of Ca in the solution. The most optimal addition of CaO is 20 g/l of brine water with magnesium element can be removed as much as 99.45%. Li is only reduced by about 1 ppm. Precipitation of Ca with oxalic acid is not affected by the acidity of the solution. CaC2O4 compounds that are formed will precipitate both at pH 0, 1 and at pH 4. The use of aksalat acid will also reduce the amount of lithium in solution. The use of oxalic acid at pH 0 and 4 will reduce the amount of Li element in the solution more than at pH 1. The remaining element Li in the solution is still around 78% on the use of oxalic acid 40 ml / 100 ml brine at pH 1.

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