Separation of Magnesium and Lithium from Brine Water and Bittern Using Sodium Silicate Precipitation Agent

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Abstract: Potential natural resources of lithium in Indonesia from brine water and bittern generally have low lithium and high magnesium levels, which need to be separated before further extraction. This research investigates the separation process of magnesium from brine water and bittern using a sodium silicate solution. The experimental results showed that the magnesium precipitation efficiency using sodium silicate was better in brine water than in bittern. A separation selectivity ratio of magnesium to lithium (Mg/Li) below 1 was obtained in brine water of 0.59 and bittern of 0.11 with the addition of a 1.25 mole fraction of sodium silicate solution to magnesium ions. After the precipitation at optimum addition of sodium silicate and water leaching process using distilled water, lithium's recovery in the brine water and bittern filtrate was 84% and 35%, respectively. In brine water, water leaching increased lithium and magnesium ions in the filtrate. However, in bittern, the water leaching increased lithium recovery without dissolving magnesium ions into the filtrate. The precipitation products from the bittern were identified as complex lithium compounds in the forms of Li$_2$MgO$_2$SiL$_2$(MgSiO$_4$) and LiMg$_4$Na$_3$O$_9$Si$_{12}$ phases, while the precipitation products in brine water mostly had a phase of CaO·MgO·SiO$_2$ (Diopside) and LiCl.

Keywords: lithium resources; selectivity; diopside; magnesium silicate; water leaching

1. Introduction

The development of lithium batteries for electric vehicles shows a bright prospect for the future. It is related to the higher demand for environmentally friendly transportation technology. As the need for lithium batteries for electric vehicles grows, the consumption of lithium carbonate will increase. Lithium carbonate consumption in 2011 was mainly concentrated in ceramics and glass, with a percentage of 29%, and lithium batteries at 27% [1]. In 2015 the consumption of lithium carbonate shifted to 35% for lithium batteries [2]. World lithium production has increased by 6% annually from 2010 to 2017. In 2017, world lithium production was 43,000 metric tons, and it is predicted that in 2025 it will reach 95,000 metric tons [3].

The natural resources of lithium in the world come from two main sources: primary materials derived from natural resources and secondary materials derived from used battery waste and mining waste slag. Primary materials from natural resources come from extracting lithium from granitic rocks, spodumene, and lithium salts from brine water [4]. In 2018 the world’s lithium production was around 43,000 metric tons, of which 55% came from brine water. Some lithium carbonate producers from brine water are Chile (32.8%) and Argentina (12.8%), while lithium from rocks comes from Australia (43.5%) and Zimbabwe (2.3%) [5]. Australia dominated the world’s lithium production before 2015 with a capacity of 15.8 kt Li/Year from rock production. After 2015 Australia’s lithium production declined because it could not compete with lithium production from brine water from South America [6].

The main problem in producing lithium carbonate from brine water is the low content of lithium ions and high levels of magnesium ions. The magnesium and lithium ions in...
brine water are present in chloride, sulfate, or carbonate anions solutions. The separation process of magnesium ions and lithium ions in brine water is the key to successfully extracting lithium from brine water which is indicated by a small Mg/Li ratio. The smaller the ratio of Mg/Li in brine, the better the separation of Mg ions and Li ions so that brine water is free from Mg ions which can be used as raw material in the manufacture of high purity lithium carbonate [7]. Currently, the largest global lithium producer from brine water is in Atacama, Chile, with a magnesium ion level of 9600 ppm and lithium ion of 2100 ppm, with an Mg/Li ratio of 6.4 [8].

Various research activities have been carried out to separate magnesium and lithium from brine water to obtain brine water with a low magnesium content. The process of separating magnesium ions in brine water includes permeation using membrane [3], precipitation [7] and electrolysis [8]. The precipitation process is the simplest separation process because it does not require expensive chemicals or complicated equipment. Generally, the chemical reagents used for precipitation processes are based on aluminum [9,10], oxalic acid [11,12], ammonium phosphate [13], and sodium metasilicate [14]. Hai (2018) used sodium silicate to separate lithium and magnesium [15]. The process was carried out by reacting sodium silicate crystals with brine water vapor at a temperature of 180 °C. The precipitation product was hectorite, which can be directly applied as a lithium-based catalyst [15].

The potential of natural lithium resources in Indonesia, which comes from brine water, has not yet been used commercially, even though Indonesia is located in the Ring of Fire zone [16]. In the Ring of the Fire zone, the geothermal sources’ intrusion process brings brine water into the earth’s surface in the form of hot mud sources [16]. One source of Indonesian brine water that has the potential to be developed is Bledug Kuwu which has a lithium content of 138.64 ppm and magnesium 690.62, with an Mg/Li ratio of 4.99 [12]. To extract lithium from Indonesian brine water, the brine water must undergo an evaporation process to increase the lithium content and the magnesium separation process.

In this study, magnesium and lithium were separated by precipitation of magnesium ions in brine water and bittern with sodium silicate solution. In the deposition process, a white precipitate of magnesium silicate is formed, which can be separated from the filtrate. The filtrate should be free of magnesium, and lithium not precipitated together with magnesium. The reaction of precipitation of magnesium ions with sodium silicate is as follows (Equation (1)) [17]:

\[
4 \text{Na}_2\text{SiO}_3 + 3 \text{MgCl}_2 + 2 \text{HCl} + m \text{H}_2\text{O} \rightarrow \text{Si}_4\text{Mg}_3\text{O}_{11} \cdot n \text{H}_2\text{O} + 8 \text{NaCl} + (m-n) \text{H}_2\text{O}
\] (1)

Generally, in brine water, besides magnesium, there is also an element of calcium that can react with sodium silicate to form calcium silicate deposits. The reaction for the formation of calcium silicate generally forms 2CaO·SiO₂, the reaction is shown as follows (Equation (2)) [18]:

\[
2 \text{CaCl}_2 + \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \rightarrow 2 \text{CaO} \cdot \text{SiO}_2 + 2 \text{NaCl} + 2 \text{HCl}
\] (2)

Several parameters need to be investigated regarding the effect of the evaporation process in separating magnesium from brine water to produce lithium-rich brine water. Therefore, in this study, we observed the performance of the magnesium ion precipitation process by sodium silicate to separate magnesium in brine water. Brine water in this study had different initial treatments, namely, brine water without the evaporation process and brine water concentrate (bittern) resulting from the evaporation process. Extraction of lithium from brine water commercially starts with increasing the concentration through evaporation by sunlight for 18–24 weeks. The result of the evaporation process in the form of brine water concentrate is then separated from the magnesium ions using a calcium carbonate precipitation process. Then the magnesium-free lithium concentrate is precipitated by the sodium carbonate precipitation process [19].
This study aims to investigate the precipitation of magnesium from brine water and bittern using sodium silicate as a precipitating agent with the presence of other ions. It also compares the selectivity of magnesium and lithium ions between brine water and bittern.

2. Materials and Method

2.1. Materials

Brine water was taken from Gunung Panjang (Ciseeng Geothermal Field) hot springs without further evaporation. In contrast, the bittern was a liquid by-product of the concentrated brine water (from the same source) through a two-stage evaporation process. It belongs to the geothermal bicarbonate group. Bicarbonate geothermal fluids are rich in calcium ions, forming thin calcium carbonate deposits known as Travertine [20].

The chemical composition of brine water and bittern is shown in Table 1.

Table 1. Chemical Composition of Raw Material of Brine Water and Bittern.

| Raw Material | Li (ppm) | Mg (ppm) | Na (ppm) | K (ppm) | Ca (ppm) | B (ppm) | Mg/Li |
|--------------|----------|----------|----------|---------|----------|---------|-------|
| Brine Water  | 22.06    | 475.30   | 4476     | 960.50  | 2127     | 95.48   | 21.55 |
| Bittern      | 1342     | 13,527   | 7574     | 28,816  | 24,222   | 2514    | 10.08 |

Previous geological research showed that the anion composition of bicarbonate and chloride was in the range of 903–1776 ppm and 219–208 ppm, respectively [20].

Bittern was produced with a two-stage evaporation process of the same brine water (see Figure 1). The first stage was the evaporation process using electric power by controlling the process temperature at 40 °C–50 °C. In this first stage, the brine water was evaporated by 97%. In the prism evaporator’s second stage of solar evaporation, 80% of water was removed. The final product of the prism house evaporator was bittern, NaCl s, and a small portion of MgCl₂ salt. Therefore, there was a decrease in the Mg/Li ratio from 21.55 to 10.08.

![Figure 1. Experimental flow diagram.](image-url)

As a precipitant, the sodium silicate solution in this study was prepared by dissolving 70 g of sodium silicate crystals (technical grade, 95%) per liter of water. The chemical composition of sodium silicate solution is shown in Table 2.
Table 2. Chemical Composition of the sodium silicate solution.

| Reagent     | Si   | Mg  | Na  | K   | Ca | B  |
|-------------|------|-----|-----|-----|----|----|
| Sodium Silicate | 16,731 | 18  | 25,695 | 189 | 27 | 8  |

The sodium silicate material was selected because it readily reacts with magnesium and calcium ions and does not react with lithium ions at low temperatures.

2.2. Method

Two experiments were carried out separately on brine and bittern since the concentration of Mg in brine and bittern was 475.30 ppm and 13,527 ppm, respectively. Both experiments were conducted at room temperature without heating and with a precipitation process time of 5 min, based on the previous study [14]. In this experiment, the main things observed were the percentage of lithium ions and magnesium ions still present in the filtrate and the Mg/Li ratio in the filtrate. The flow diagram of the experiment is shown in Figure 1.

Brine water without evaporation was added with sodium silicate with a varying mole ratio of sodium silicate to magnesium of 0.31, 0.63, 0.94, 1.25, 1.56, 1.88, and 2.19. The filtration process separated the filtrate (F1) and the precipitate (S1). Next, the solid precipitates (S1) were leached with distilled water at a volume of 200 mL for 30 min. In the case of bittern, the addition of sodium silicate was varied based on the mole ratio proportion to precipitate magnesium ion, which was 0.0, 0.62, 0.74, 0.87, 1.00, 1.11, and 1.24. For the comparison between bittern and brine water, the addition of sodium silicates was set up to a 1.25 mole ratio of sodium silicate to magnesium ion. The precipitation process time was set at 5 min at room temperature, with the stirring speed at 300 rpm.

A white precipitate of magnesium silicate (S1) was then separated from the filtrate (F1). The solid (S1) was then leached with distilled water with a solid/water ratio of about 1.5 for about 30 min to remove the lithium ions that may have occurred in the solid (S1). The filtrate (F2) was separated from the precipitate (S2) for further characterization. The process of leaching instead of washing was preferred in this observation because either magnesium or lithium ions might dissolve when the solid precipitates were mixed with distilled water.

2.3. Characterization

Chemical composition characterization of brine, bitterns, and filtrates (F1 and F2) was carried out using ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy, Agilent 725 ICP-OES) analysis equipment. In this study, the characterization was focused on lithium, magnesium ions, and other specified ions such as sodium, potassium, and calcium. The concentration ratio of ions in the filtrate and in raw materials was calculated and plotted. Effect of sodium silicate addition into brine water and bittern were measured and observed by the concentration ratio of magnesium and lithium ions \( \frac{C_i}{C_0} \) at a certain addition of sodium silicate \( (C_i) \) with the magnesium and lithium ions in raw material of brine water and bittern \( (C_0) \).

The solids obtained from the precipitation process (S1 and S2) were dried before they were characterized by X-ray diffraction (Benchtop X-ray Diffractometer). The amount of the solid was also measured. Semiquantitative analysis of the identified phase composition was measured using Match-3 software. The particle morphology and microstructure were observed using SEM-EDX (Scanning Electron Microscope—Energy Dispersive X-ray/Jeol JSM-639OA).
3. Results and Discussion

3.1. The Solid Products after Precipitation

Figure 2 shows the effect of sodium silicate addition on the precipitation products and the solid/liquid ratio of the bittern and brine. The precipitations products (S1) and solid/liquid ratio increase with increasing sodium silicate addition for bittern and brine. Bittern produces more solid precipitates and a higher solid/liquid ratio than brine because of its higher ions’ contents. About 65% of precipitate in bittern and a solid/liquid ratio of 2 were obtained by adding a 1.00 mole ratio of sodium silicate. Brine water gives 20% of precipitates and a solid/liquid ratio of 0.3 with 100% of sodium silicates.

3.2. The Separation of Magnesium and Lithium in Filtrate after the Precipitation Process

Figure 3 show that the water leaching process on solids (S1) resulting from the precipitation of magnesium from bittern and brine water by addition of sodium silicate. Figure 3a indicates that adding sodium silicate into bittern removes magnesium from the filtrate in higher amounts by the removal of some amount of lithium from the filtrate. It means that the separation of lithium from magnesium is unlikely to occur optimally in the bittern with the addition of sodium silicate. Adding a 1.25 mole ratio of sodium silicate into the bittern will remove magnesium from the filtrate and leave about 22% lithium (Figure 3a).

Figure 3. The concentration ratio of lithium and magnesium ions in the filtrate (S1) after precipitation by addition of sodium silicate in (a) bittern and (b) brine water.
On the other hand, adding at least a 1.25 mole ratio of sodium silicate to the brine removes the magnesium almost entirely from the filtrate. About 78% of lithium ion is still in the filtrate with the addition of a 1.25 mole ratio of sodium silicate into the brine. Adding more than 1 mole ratio of sodium silicate to the brine water will partly remove lithium ions from the filtrate as much as 84%. Further addition will remove slightly more lithium ions from the filtrate.

Through comparison, it can be seen that precipitation of magnesium ion from bittern and brine water by addition of sodium silicate differ. In the bittern, precipitation of magnesium ions is followed by the removal of lithium ions from the filtrate in higher amounts than in brine water with the same addition of sodium silicate. Lithium ions in bittern are likely trapped chemically to form complex substances with other elements such as magnesium and sodium as solid precipitates. The following section on solid precipitate characteristics will discuss it in more detail.

3.3. The Recovery of Lithium Ion from Solid Product by Water Leaching

Considering the lithium ion content, which is removed from the filtrate after the first stage separation or after the precipitation process, the following water leaching process was undertaken to retrieve lithium ions from the solid precipitates (S1) (see Figure 1).

Figure 4 show that the water leaching process on solids (S1) resulting from the precipitation process can increase the percentage of lithium ion retrieval into the filtrate. Accumulation of ion content after water leaching was calculated and compared in the Figures by the solid line and symbols. In general, water leaching of S1 from bittern gives additional lithium ion retrieval into the filtrate, about 13%. In other words, water leaching may dissolve lithium ions again into the filtrate from solid precipitate in the bittern (S1) at about 13% (see Figure 4a). The dissolution of magnesium ions after water leaching of solid precipitates is relatively low.

Table 3. Concentration distribution of magnesium and lithium ions after precipitation and water leaching.

| Stages          | Bittern (% | Brine Water (%) |
|-----------------|-----------|-----------------|
| Precipitation   | Fa        | 0.2             | 0.4             |
|                 | S1        | 99.8            | 78              |
| Water leaching  | Fa + F2   | 0.3             | 35              |
|                 | S1 + S2   | 99.7            | 65              |

3.4. Mg/Li Ratio in Filtrate after Precipitation and Water Leaching

From the Mg/Li ratio analysis, it can be seen that this precipitation has separated magnesium ions from lithium ions. Figure 5a shows that with the addition of sodium silicate concentration of 49.6% stoichiometry into bittern, there is a slight increase in the Mg/Li ratio, followed by a decrease in the Mg/Li ratio along with the addition of sodium silicate. The increase in the Mg/Li ratio is because, at the 49.6% stoichiometric position, with the addition of sodium silicate, there is a decrease in magnesium ion levels in the filtrate, which is greater than the decrease in lithium ion levels. The addition of 49.6% mole of sodium silicate to the bittern (Figure 3a) reduced lithium concentration in the filtrate by 34.68% to 65.32%, and magnesium was only reduced by 19.75% to 80.25%.

Figure 5. Comparison of Mg/Li ratio in the filtrate (F1) after precipitation process and accumulation after water leaching in the filtrate (F2) of (a) bittern and (b) brine.

In brine water (Figure 4b), water leaching increases lithium ion yield with an accumulation of about 6%. Water leaching gives higher lithium ion retrieval from the solid precipitated by higher sodium silicate addition. Even the accumulation of lithium ions in the filtrate from brine water (Figure 4b) is still lower than in the filtrate from bittern (Figure 4a). However, water leaching also dissolves magnesium ions again from the solid precipitates into the filtrate.

The distribution of magnesium and lithium ion concentration in the filtrates (F1) and cumulative concentration after water leaching (F1 and F2) for additional sodium silicate at a mole ratio of 1.25 is listed in Table 3. It summarizes the effect of water leaching on magnesium ion and lithium ion dissolution.
Table 3. Concentration distribution of magnesium and lithium ions after precipitation and water leaching.

| Stages             | Bittern (%) | Brine Water (%) |
|--------------------|-------------|-----------------|
|                    | Mg$^{2+}$  | Li$^+$          | Mg$^{2+}$  | Li$^+$          |
| Precipitation      |             |                 |             |                 |
| [F1]               | 0.2         | 22              | 0.4         | 78              |
| [S1]               | 99.8        | 78              | 99.6        | 22              |
| Water leaching     |             |                 |             |                 |
| (accumulation)     | [F1] + [F2] | 0.3             | 35          | 17              | 84              |
|                    | [S1] + [S2] | 99.7            | 65          | 83              | 16              |

3.4. Mg/Li Ratio in Filtrate after Precipitation and Water Leaching

From the Mg/Li ratio analysis, it can be seen that this precipitation has separated magnesium ions from lithium ions. Figure 5a shows that with the addition of sodium silicate concentration of 49.6% stoichiometry into bittern, there is a slight increase in the Mg/Li ratio, followed by a decrease in the Mg/Li ratio along with the addition of sodium silicate. The increase in the Mg/Li ratio is because, at the 49.6% stoichiometric position, with the addition of sodium silicate, there is a decrease in magnesium ion levels in the filtrate, which is greater than the decrease in lithium ion levels. The addition of 49.6% mole of sodium silicate to the bittern (Figure 3a) reduced lithium concentration in the filtrate by 34.68% to 65.32%, and magnesium was only reduced by 19.75% to 80.25%.

![Figure 5. Comparison of Mg/Li ratio in the filtrate (F1) after precipitation process and accumulation after water leaching in the filtrate (F2) of (a) bittern and (b) brine.](image)

The precipitation process of bittern (Figure 5a) showed a decrease in the Mg/Li ratio from 10.08 to 0.11 by adding 1.25 sodium silicate. In addition, the water leaching process of the precipitate solid (S2) from bittern decreases the Mg/Li ratio. The water leaching process may dissolve lithium from the solid precipitate S2 to the filtrate. Thus, it reduces the Mg/Li ratio in the filtrate accumulated with water leaching.

In the case of brine water (Figure 5b), Mg/Li ratio accumulated with water leaching is higher than without water leaching. It means that in brine water, the water leaching process dissolves a higher amount of magnesium ions than lithium ions.

3.5. The Calcium Ion in Filtrate after Precipitation Process

Calcium is another earth alkaline impurity in the bittern and brine water. Its behavior is essential since its content is very high in bittern and brine water. Figure 6a shows that adding sodium silicate decreases calcium ions in the filtrate from only 29% to 71%. With the addition of the water leaching process, the accumulated calcium ion decreases to only 18%, leaving 82% in the filtrate. Removing calcium from the bittern by sodium silicate

![Figure 6. Comparison of Mg/Li ratio in the filtrate (F1) after precipitation process and accumulation after water leaching in the filtrate (F2) of (a) bittern and (b) brine.](image)
precipitation is very difficult; its concentration in the bittern can only be reduced by about 30% (70% is still in the filtrate) with the addition of a 1.25 mole fraction of sodium silicate.

![Figure 6](image1.png)

**Figure 6.** Comparison of concentration ratio in the filtrate (F1) after precipitation process (dashed line) and water leaching filtrate (F2) (solid line) of (a) bittern and (b) brine.

On the other hand, the sodium silicate precipitation process in brine water (Figure 6b) removes calcium ions up to 99%, from 2127 ppm to 4 ppm, by adding a 1.25 mole fraction of sodium silicate. With a low level of calcium ions, travertine (CaCO₃) gel formation can be avoided.

### 3.6. Concentration of Other Elements in the Filtrate after Precipitation

Figure 7 shows the comparison of ions elements recovery in the filtrate at the maximum removal of magnesium ion in bittern and brine water with the addition of a 1.25 mole ratio of sodium silicate with magnesium. The accumulation of lithium in brine water obtained recovery reached 78% compared with in bittern which was only 22%. Separating magnesium in brine water and bittern showed very low results: bittern had 0.2% remaining, and brine water had 0.36% magnesium remaining in the filtrate (F1) (Figure 7).

![Figure 7](image2.png)

**Figure 7.** Comparison of concentration ratio of elements in the filtrate (F1) after precipitation process and water leaching filtrate (F2) on the optimum addition of sodium silicate of 1.25 mole ratio.

It can be seen that in bittern, there is still 82% of the calcium element in the filtrate, while in brine water, there is only 2.05% of the calcium element (Figure 7). Sodium in processed bittern and brine water has a recovery above 100%. In bittern, sodium recovery
reached 114.7, and brine water was higher at 143.8% (Figure 7). This is because the reagent for the precipitation process is sodium silicate which contains sodium easily soluble in water. The potassium ions impurity in bittern is lower than in brine water, which is 11.65% for the bittern, and in brine is 71.11% (Figure 7). The concentration of the boron element in brine water is reduced by 84.63% to 15.37% (Figure 7).

3.7. Solid Product of the Precipitation Process

The solid product to be characterized comes from the precipitation process with the most optimal results from the concentrated sample of brine water and brine water without the process of concentration, i.e., sodium silicate addition by more than 1.25 mole fraction. Phase identification of the diffraction peaks of the solid precipitates from bittern and brine water is shown in Figure 8 and tabulated in Table 4.

**Figure 8.** The XRD pattern of the solid product after the precipitation process from bittern and brine water.

**Table 4.** Phase and Semiquantitative composition of the solid product of brine water after the precipitation process.

| Phase                        | Solid Precipitates of (wt.%) |
|------------------------------|------------------------------|
| Diopside (CaMgO₆Si₂)        | 42.7                         | 60.4                         |
| Li₂MgO₃SiL₂(MgSiO₄)         | 10.0                         | 4.1                          |
| LiMg₂Na₂O₈Si₃₂              | 4.2                          | -                            |
| Titanite (CaSi₂O₅)          | 18.7                         | 12.3                         |
| Halite (NaCl)               | 8.7                          | 9.9                          |
| Lithium Chloride (LiCl)     | -                            | 8.4                          |
| Forsterite (Mg₂SiO₄)        | 2.3                          | 5.0                          |
| Cristobalite (SiO₂)         | 13.5                         | -                            |
As shown in Figure 8, the solid precipitate phase was dominated by Diopside complex compounds in both raw materials (brine water and bittern). Diopside compounds are compounds consisting of calcium and magnesium silicates with the chemical formula CaOSiO$_2$·MgOSiO$_2$. These complex compounds, under wet conditions, form a SiO$_2$ network. The network can bind Li$^+$, Na$^+$, and K$^+$ ions. Based on the previous study, this free-SiO$_2$ gel has adsorption power, with the size of Li$^+ > $Na$^+ > $K$^+$ [21]. In the sodium silicate precipitation process with bittern, lithium bonds were found to form complex compounds, namely Li$_2$Mg$_2$SiLi$_2$(MgSiO$_4$) and LiMg$_3$Na$_3$O$_9$Si$_{12}$ compounds. Table 4 lists the solid precipitates phase and their semiquantitative amount.

Lithium cannot be extracted from either of these compounds by water leaching; thus, much lithium that enters the solid cannot be recovered. These complex bonds can be made for catalyst raw materials by being processed into hectorite compounds [22]. In the sodium silicate precipitation process with brine water, fewer complex compounds were produced, namely only Li$_2$Mg$_2$SiLi$_2$(MgSiO$_4$) in the amount of 4.1%. Most of the lithium involved in the precipitation process in brine water is lithium chloride (LiCl) at 8.4%, so the lithium that has settled on the solids resulting from brine water precipitation is recovered more easily by the washing process.

Regarding the presence of SiO$_2$ in the solid precipitates, there is a possibility of multiple reactions in the formation of calcium silicate to 2CaO·SiO$_2$, 3CaO·SiO$_2$, 4CaO·SiO$_2$ compounds and others [18]. Moreover, it is possible to form free SiO$_2$ gel or silica precipitates, where this silica gel or silica precipitate plays a role in the binding process of lithium ions in the filtrate. The formation of free silica can be seen from the number of Si elements larger than Mg and Ca elements in the solid mapping results. The solid resulting from the sodium silicate precipitation in the bittern has a more complex bond, making lithium more easily precipitated. These complex bonds tend to be more easily formed between magnesium and lithium ions than calcium ions with lithium. Therefore, the solids resulting from the sodium silicate precipitation process in bittern tend to form complex bonds more easily.

Figure 9 shows the morphology of bittern (Figure 9a) and brine water (Figure 9b) solid precipitates. The solid precipitate of the bittern (Figure 9a) shows a relatively bigger size with irregular lumps indicating the presence of a gel. Meanwhile, in the brine water deposit (Figure 9b), the grain size is smaller and regular, indicating the absence of gel clumps. There is no needle-like structure observed in the particles.

![Figure 9. The Morphology of the solid product after the precipitation process (S1) (a) bittern and (b) brine water.](image_url)

4. Conclusions

The recovery of lithium in the precipitation process in brine water reaches 78–80%, while in bittern, it is 20–35% with the addition of 1.25 mol of sodium silicate. The addition of a 1.25 mole ratio of sodium silicate with magnesium effectively reduced the magnesium ion concentration in the filtrate by more than 95% in bittern and brine water. In addition, the Mg/Li ion ratio was reduced from 10.08 to 0.11 in bittern and from 21.55 to 0.64 in brine filtrate. The water leaching process on wet solids from bittern and brine water can increase
lithium recovery in the filtrate. However, water leaching may dissolve magnesium again from solid precipitate into the filtrate without reducing the selectivity of the filtrate product. The precipitation process using bittern produced more complex lithium compounds with the phases of \( \text{Li}_2\text{Mg}_4\text{Si}_4\text{O}_{12} (\text{MgSi}_4\text{O}_6) \) and \( \text{LiMg}_4\text{Na}_3\text{O}_3\text{SiO}_{12} \), while the precipitation products from brine water mostly contain \( \text{CaOMgOSi}_2\text{O}_3 \) (Diopside) and \( \text{LiCl} \).

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