Magnesium removal from brine water with low lithium grade using limestone, Rembang, Indonesia

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Abstract. Experiments have been carried out to remove magnesium ions from brine water using limestone, Rembang, Indonesia. The aim of the study was to produce brine water concentrates that were rich in lithium and did not contain magnesium elements. Brine water used has the following chemical composition: 74.67 ppm Li; 877.891 ppm Na; 1549.81 ppm K; 147.23 ppm Mg; 38.49 ppm Ca and others. The initial stages were 200 g of natural lime calcined at 900 °C for 3 hours using a furnace as a precipitation agent. It is then added to 1000 ml of brine water with a variation of 0.336 g, 1 g, 10 g, 20 g, 30 g, 40 g, 50 g by stirring for 3 hours at atmospheric pressure. The results showed that the magnesium removal from brine water began to be seen in the addition of roasted limestone of 1 g with the dominant phase as Mg₀.₀₃Ca₀.₉₇CO₃ in the precipitated residue. On the addition of 10 g and 20 g of roasted limestone into brine water, the percentage of magnesium removal was almost maximum of 98.8% and 99.8% with the precipitated residues as Mg(OH)₂ phases. This experiment was successful to remove magnesium from brine water so that the lithium concentration of brine water increased to 104.32 ppm Li and 105.86 ppm Li with the addition of roasted limestone of 10 g and 20 g, respectively. These results indicate that the use of roasted limestone to eliminate magnesium from brine water with low lithium grade is recommended.

1. Introduction
Lithium consumption in the world continues to increase every year along with the increasing use of lithium in various applications. This condition can be seen from the data that shows the lithium consumption level in 2016 is projected to be around 37,800 tons. Where this requirement increased from 33,300 tons in 2015. The following are distribution of marketing and lithium utilization in 2017 in a variety of applications including batteries (39%), ceramics and glass (30%), grease lubricants (8%), flux powder in casting and polymer production (5%), air treatment (3%), and other uses (10%) [1]. It is seen that the consumption of lithium for batteries has increased significantly along with the increasing need for electronic devices [2]. Based on market opportunities, lithium is the first rank in the metal needed (± 594x of total zinc requirements) and then followed by titanium (130x), coal (109x), bauxite (102x), uranium (91x), iron ore (41x), nickel (39x), copper (37x), and gold (18x) [3]. Currently, the availability of lithium in the world is not comparable to the consumption of lithium

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which is expected to increase continuously until 2025. Lithium resources in the world that have been identified in the United States, Argentina, Bolivia, Australia, Chile, China, and others.

Lithium reserves are shown as follows: The United States has a reserve of 6.9 million tons, Argentina and Bolivia are around 9 million tons, Australia is 2 million tons, Chile is more than 7.5 tons and China is about 2 million tons, Congo, Russia, and Serbia each has about 1 million tons, Brazil and Mexico each have around 200,000 tons, and Austria and Zimbabwe each have more than 100,000 tons [4]. On the other hand, the mapping of lithium resources in Indonesia is not yet known with certainty, so there needs to be an exploration to indicate the lithium deposits in Indonesia. In recent years, the LIPI Center for Metallurgy and Materials Research has tried to identify sources of lithium deposits based on Indonesia's geological structure which is rich in mineral resources. In decades, commercial lithium production still relies on sources of mineral ores such as spodumene, petalite, and lepidolite. In fact, extracting lithium from these sources is significantly more expensive than extracting lithium from brine containing lithium. The cost of extracting lithium from the rock is estimated to be twice that compared to producing from brine water. Though it is known that the potential of brine water as a raw material to produce lithium is very large [5].

As we know that besides lithium, there are other associated components of brine water such as magnesium, calcium, sodium, potassium, sulfate, boron and others. These components must be minimized in order to obtain a lithium-rich brine water concentrate that can be used to produce lithium carbonate. If this component is not removed, it will cause contaminants in the production process of lithium chemical compounds. Of the many constituent components contained in brine water, magnesium is one of the biggest challenges in processing brine water to produce high purity lithium carbonate. Magnesium removal is the initial step before extracting lithium from brine water. The success in eliminating magnesium from brine water with cheap and environmentally friendly technology will offset the production costs of lithium chemical compounds such as lithium carbonate from brine water.

Stephan Bogner (2017) [6] reported that MGX technology had successfully eliminated high magnesium levels (76,000 ppm) of lithium brine samples from a US site to undetectable levels (<1 ppm). This MGX technology uses a combination of nano-filtration and nano-flotation systems where it is sufficiently flexible and effective in providing continuously increasing solutions for lithium demand. Lalasari et al. (2017) [7] was able to precipitate magnesium from brine water by chemical precipitation techniques using NH₄OH chemical reagents. According to Kang & Yoon (2015) [8], magnesium can be removed by chemical precipitation using calcium hydroxide (Ca(OH)₂). Calcium hydroxide reacts with magnesium to form magnesium hydroxide (Mg(OH)₂) as a precipitate.

This study tried to remove magnesium from brine water by utilizing Indonesian mineral resources, namely limestone from Rembang. Limestone is pre-prepared and mixed into brine water. The expected goal is magnesium from brine water precipitated to form Mg(OH)₂ so that brine water is rich in lithium and free of magnesium.

2. Experimental
The materials used in the study were limestone from Rembang, Indonesia and Brine Water from Bogor, Indonesia. The research stages included the preparation of raw materials, magnesium removal processes, filtration, drying, and characterization as shown in Figure 1. The preparation stage of the raw material was 200 g of natural limestone to be burned at 900 °C for 3 hours using a muffle furnace to produce CaO compounds. The roasted limestone product was then characterized using X-Ray Diffraction (XRD) to investigate the formation of CaO as shown in Figure 2 and X-Ray fluorescence (XRF) to identify its chemical composition as shown in Table 1. In the preparation of the brine sample was carried out as follows: natural brine water was evaporated to around 40 % volume using a distillation apparatus equipped with a reflux condenser. The aim was to increase the lithium level from the brine water sample. The brine water samples from the evaporation were then characterized using inductively coupled plasma - optical emission spectrometry (ICP-OES) to determine its chemical composition as shown in Table 2.
**Figure 1.** The flow chart of research

**Table 1.** The chemical composition of roasted limestone (XRF analysis)

|       | Ca     | Mg     | K      | Si     | Others |
|-------|--------|--------|--------|--------|--------|
|       | 99.33% | 0.34%  | 0.04%  | 0.24%  | 0.05%  |

**Figure 2.** The XRD pattern of roasted limestone, Rembang
The second stage was magnesium removal from the brine water samples. The procedure was as follows: The roasted limestone (CaO) varied 0.336 g, 1 g, 2 g, 10 g, 20 g, 30 g, 40 g, 50 g was put into an Erlenmeyer containing 1000 ml samples of brine water. Then the stirring process is carried out for 3 hours at 1 atmospheric pressure. In this experiment, the use of 0.336 g roasted limestone is the minimum amount obtained through stoichiometric calculations. The third stage was the filtration and drying of samples. Filtration aims to separate lithium-rich brine filtrate and magnesium-rich residues. The residue was then dried in a muffle furnace at 110 °C for 2 hours. The last stage was characterization where the filtrate was analyzed using ICP-OES, while the residue was analyzed by Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS), XRD and XRF.

3. Results and Discussion

Based on Table 1, the composition of roasted limestone from Rembang was dominated by Ca compounds with levels of 70.22% with the most impurities being Mg (0.34%) and Si (0.24%). This impurity can affect the purity of the product resulted during the removal process of Mg. On the other hand, the XRD result in Figure 2 shows that the roasted limestone of Rembang was dominated by Ca(OH)$_2$, CaCO$_3$, and CaO compounds. The diffraction peaks which showed Ca(OH)$_2$ compounds were at the 2θ position of 18.228°, 36.939°, 47.547° with ICDD card no. 4-0733. In this experiment, Ca(OH)$_2$ and CaO compounds act as precipitate agents in the process of separating Mg elements from brine. Supposedly, in the roasting process at 900 °C, limestone (CaCO3) decomposes completely into CaO by releasing CO$_2$ gas. But in fact, the XRD characterization results show that there is still CaCO$_3$ which did not decompose completely into CaO. It also showed the existence of the Ca(OH)$_2$ phase in Figure 2. This Ca(OH)$_2$ compound was formed due to the hydration process of CaO with air containing H$_2$O.

In Table 2, it can be seen that the main components of brine water, Bogor after evaporation of 40 % volume are Na (877.891 ppm), K (1549.81 ppm), Mg (147.23 ppm), while the minor element is Li (74.67 ppm) and Ca (38.49 ppm). The Ca level in Brine shown in Table 2 was relatively low because, during partial evaporation, element Ca was partly precipitated to form CaCO$_3$. This result was consistent with the previous research conducted by Lalasari et al (2017) [7]. To be able to produce lithium-rich brine concentrate, it was necessary to remove the main element from brine, especially IIA class in a periodic system such as Mg. According to Stephan Bogner (2017) [6], the removal of Mg from lithium brine with traditional solar evaporation was less effective and not economical because Mg and Li have almost similar ionic properties so they were difficult to separate from each other. Magnesium separation from lithium brine needed to use other technologies. On this occasion will be explained in detail the results of research related to the Mg removal from brine water, Bogor using natural limestone, Rembang. Initial characterization will be carried out first on residual samples (precipitated products) using XRD, XRF and SEM-EDS analysis. Furthermore, characterization of brine filtrate samples using ICP-OES analysis to find out how much magnesium can be removed in lithium brine. The following was the amount of residue obtained after the addition of variously roasted limestone.

| Li    | Na       | K         | Ca    | Mg    |
|-------|----------|-----------|-------|-------|
| 74.67 ppm | 877.891 ppm | 1549.81 ppm | 38.49 ppm | 147.23 ppm |

Table 2. The chemical composition of brine water samples (ICP-OES analysis)
In Figure 3, it can be seen that the more roasted limestone was added to the brine water, the more obtained precipitate increases. This indicated that many associated components of brine water settled together with precipitate agents. Supposedly, the roasted limestone precipitated Mg ions into MgCO$_3$ or Mg(OH)$_2$ instead precipitating other compounds from brine water. Therefore it was necessary to optimize the use of precipitate agents such as a roasted limestone.

### 3.1 Structure, morphology and chemical composition of residues (precipitated products)

The following were the results of the characterization of the residue sample produced by chemical precipitation techniques using the addition of roasted limestone varied 0.336 gr, 1 gr, 10 gr, 20 gr, 30 gr, 40 gr, 50 gr into 1000 ml brine water. To find out the structure or phase formed from the residual sample, XRD analysis was carried out as shown in Figure 3.
Figure 4 clearly looked the phase changes shown in the precipitated residues after the roasted limestone addition (compared to Figure 2). At the addition of 0.336 g roasted limestone, the peaks that appeared on the residue have CaCO$_3$ and NaCl phases. The phase of MgCO$_3$ or Mg(OH)$_2$ had not been apparent in a residue. This indicated that the roasted limestone containing CaO and Ca(OH)$_2$ with an amount of 0.336 gr (according to stoichiometry) had not been able to remove some of the magnesium in brine water. In addition to 1 g of roasted limestone in the brine water, the reaction shifted to form Mg$_{0.03}$Ca$_{0.97}$CO$_3$ phase. This shows that adding 1 g of limestone can remove magnesium in brine water even though it was not perfect. If the amount of limestone burned was increased by about 10 g and above, then magnesium has undergone precipitation into the Mg(OH)$_2$ phase with excess Ca(OH)$_2$ phase in the residues. Precipitation reactions that may occur are as follows:

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

$$\text{Ca(OH)}_2 (\text{aq}) + \text{Mg}^{2+} (\text{aq}) \rightarrow \text{Mg(OH)}_2 (s) + \text{Ca}^{2+} (\text{aq}) \quad (2)$$

To better explain and know the chemical composition of the precipitated residue, it was necessary to do XRF analysis as shown in Table 3.

| Element | Roasted limestone (raw material) | Wt. % |
|---------|----------------------------------|-------|
|         | Roasted limestone addition       |       |
|         | 1 g                             | 2 g   | 10 g  | 20 g  |
| Na      | -                               | 34.88 | 41.09 | 10.1  | 15.3  |
| Mg      | 0.34                            | 21.13 | 28.94 | 27.24 | 11.06 |
| Si      | 0.24                            | 10.71 | 4.62  | 2.52  | 2.36  |
| S       | -                               | 0.01  | 0.01  | 0.04  | 0     |
| Cl      | -                               | 20.39 | 16.56 | 18.88 | 10.45 |
| K       | 0.04                            | 0.76  | 0.45  | 0.91  | 0.38  |
| Ca      | 99.33                           | 11.42 | 7.92  | 38.65 | 59.75 |

Based on Table 3, it can be seen that the addition of roasted limestone can remove magnesium in brine water. This was indicated by the percentage of Mg element in the residue at the addition of 1 g of roasted limestone which was increased to 21.13% from 0.34% Mg from the initial roasted limestone and the main element of the roasted limestone was Ca that became reduced from 99.33% to 11, 42%. The removal of Mg from brine water was seen to be great at the addition of roasted limestone of 2 g which was shown in percentages of Mg from the residue to increase to 28.94% and the element Ca reduced to 7.92%. This condition was satisfactory because of the possibility that Ca(OH)$_2$ from the roasted limestone reacts with Mg from brine water to form precipitate Mg$_{0.03}$Ca$_{0.97}$CO$_3$ or Mg(OH)$_2$. The Mg(OH)$_2$ phase was not apparent in the addition of 1 g and 2 g of limestone because of the possibility of having peaks with low relatively intensity, this was like the research conducted by Meshram (2014) [9]. Table 3 also showed that if the roasted limestone mass was increased to 10 g, the residue contains a high Ca element of about 38.65% and the Mg element of 27.24%. This result was in accordance with the XRD characterization shown in Figure 4 where the diffraction peaks were found on the addition of 10 g and 20 g of roasted limestone containing the dominant compound with Ca(OH)$_2$ phase, other than the expected Mg (OH)$_2$ phase. This showed that adding 10 g and 20 g of roasted limestone to brine water was excess.
Figure 5. The morphology of precipitated residues by addition roasted limestone (a) 0.336 g, (b) 1 g, (c) 10 g, (d) 20 g

Figure 5 showed that precipitated residues in various precipitation agents (roasted limestone) had varying morphology such as cubic, nearly round, and irregular at 1000x magnification. The cubic shape was indicated as NaCl. The round shape was indicated as CaCO$_3$. The shape of the needle and discs were indicated as Mg(OH)$_2$ [10]. In Figure 5a, the morphology of the particles was dominated by a cubic, irregular round shape, and agglomeration. This showed that precipitated particles at the roasted limestone addition of 0.336 g were more dominant in containing NaCl and CaCO$_3$. The results of this analysis were in accordance with the XRD characterization shown in Figure 4. The addition of 1 g of roasted limestone (Figure 5b) showed that particle morphology was predominantly resembling sponges with a fairly heterogeneous form including round, thin needles, cubic and irregular shapes that tend to agglomerate. This explained that the particles in this precipitated residue contained several compounds including MgCO$_3$, CaCO$_3$, Mg(OH)$_2$, NaCl. Whereas, in addition to 10 g and 20 g roasted limestone (Figure 5c and Figure 5d), the morphology of the particles became large grains. The large particles were formed because mutually agglomerating particles form large chunks with a thin needle above the chunk. The morphology shown in this residue was dominated by Ca(OH)$_2$ and Mg(OH)$_2$. 
3.2 The chemical composition of brine filtrate samples
To investigate the effect of adding roasted limestone to the removal of magnesium and other associated elements in brine water, the filtrate sample was characterized using ICP-OES as shown in Table 4.

Table 4. The chemical composition of brine filtrate samples in various roasted limestone addition

| Elements | Brine Water concentrate (ppm) | Filtrate concentration (ppm) in various addition roasted limestone (ppm) |
|----------|-----------------------------|---------------------------------------------------------------------|
|          |                             | 10 g       | 20 g       | 30 g       | 40 g       |
| Li       | 74.67                       | 104.32     | 105.858    | 93.2973    | 88.9843    |
| Na       | 877.891                     | 737.309    | 771.395    | 815.548    | 902.229    |
| K        | 1549.81                     | 1987.07    | 2025.75    | 1827.78    | 1777.99    |
| Mg       | 147.23                      | 1.7412     | 0.278966   | 0.04782    | 0.035921   |
| Ca       | 38.49                       | 32.8911    | 33.074     | 33.6691    | 33.8250    |

Table 4 showed that the addition of roasted limestone to brine water can remove magnesium from brine water. The removal of magnesium was quite successful at the addition of roasted limestone 10 g where the magnesium content of brine water was reduced from 147.23 ppm to 1.7412 ppm. The same conditions occurred with the addition of 20 g, 30 g, and 40 g of roasted limestone wherein the brine filtrate contained magnesium at 0.279 ppm, 0.048 ppm, and 0.036 ppm respectively. This showed that the magnesium removal in the addition of 10 g of roasted limestone and above was very significant. The elimination of magnesium elements from brine water also caused an increase in the levels of other elements such as lithium and potassium from brine water. This was indeed expected to produce lithium-rich brine concentrates. From the previous characterization, it was explained that magnesium was detected in the residue with the addition of 1 g of roasted limestone. This indicated that the removal of magnesium from brine water also occurred with the addition of 1 g roasted limestone and above. Therefore, it was necessary to further characterize brine filtrate in the next study. It aimed to produce the optimum conditions for adding roasted limestone to brine water so that obtained lithium-rich brine concentrate and free of magnesium.

4. Conclusion
Limestone burned at 900 ºC for 3 hours was used as a precipitation agent containing several compounds including CaO, Ca(OH)₂ and CaCO₃ phases. The magnesium removal from brine water was detected at the roasted lime addition of 1 g which shown from XRD analysis on the precipitated residue indicating the dominant phase as Mg₀.₀₃Ca₀.₉₇CO₃. While the addition of 10 g and 20 g of roasted lime, the dominant phase was Mg(OH)₂ and Ca(OH)₂. The apparent morphology of precipitated residues was fairly heterogeneous forms including round, thin needles, cubic and irregular shapes that tend to agglomerate. The result of XRF analysis also showed that the magnesium content in the residue increased to 21.13%, 28.94% and 27.24% in roasted limestone addition to 1 g, 2 g, and 10 g compared to the magnesium content of the initial burnt limestone was 0.34%. The results of ICP-OES analysis on brine filtrate samples also showed that the roasted limestone as a precipitation agent was quite successful in removing magnesium from brine water up to 0.2-0.03 ppm and able to increase lithium levels from brine water so that this method is suitable to be applied to produce lithium-rich brine.

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