Extraction of magnesium from salt pond waste with low lithium grade using sodium silicate reagent

E Sulistiyono¹, S Harjanto¹ and L H Lalasari²

¹Departments of Metallurgical and Materials Engineering, Faculty of Engineering, Universitas Indonesia, Depok16424, Indonesia
²Research Center for Metallurgy and Material, Indonesian Institute of Science, Gedung 470, Puspiptek Serpong 15312, Tangerang Selatan, Indonesia

Email: sri.harjanto@ui.ac.id

Abstract. Nowadays, Indonesia’s salt production process has shifted from a traditional salt pond process to a salt pond with a geomembrane tarpaulin system. This system has the advantage of producing a faster salting process and a better salt quality as well as producing a thick yellow liquid waste known as bittern. The waste produced has not been fully utilized, even though the waste contains valuable elements, namely magnesium, lithium, and others. This paper investigates the potential utilization of bittern by extracting magnesium from by-product salt pond using sodium silicate reagent with various concentrations of 125–250 g/l. The bittern used in this experiment had the chemical composition as follows: 33,184 ppm magnesium (Mg), 23,787 ppm sodium (Na), 6.1 ppm lithium (Li), 5,491 ppm potassium (K), 617 ppm calcium (Ca), 152 ppm boron (B). The highest removal of magnesium ion by addition of sodium silicate of 250 g/l was about 96.2%. The results showed that the solid products were magnesium silicate precipitates without containing asbestos compounds. The magnesium silicate precipitate product can be applied as talc raw material for the pharmaceutical industry.

1. Introduction
Indonesia has a traditional salt-works location spread over 44 districts with the total salt production of 2,915,461.17 ton/year by 2016, which can be an abundant magnesium source [1]. Traditional salt production plants are man-made systems exploiting sea water for salt production by wind and solar evaporation [1]. Nowadays, Indonesia’s salt production process has shifted from a traditional salt pond process to a salt pond with a geomembrane tarpaulin system. This system has the advantage of producing a faster salting process and a better salt quality as well as producing a thick yellow liquid waste known as bittern. Integrating the "Pugar" and "MP3EI" policies, encouraging the industrialization of community salt is one of the solutions going forward by preparing Madura people's salt to become salt and salt derivatives of a quality that various industries can accept in the Surabaya, Gresik and Sidoarjo regions [2].

Bittern can be used as magnesium sources for magnesium carbonate hydrate products, mineral supplements for drink/food, struvite, supporting fertilizer and cooling system [1]. Sea-water is the main source for Mg(OH)₂ due to containing soluble salts of magnesium such as MgCl₂ and MgSO₄. The concentration of magnesium ion is about 1,272 ppm in sea water and about 30,000 ppm in the end bitterns of NaCl production units from sea-water [3].
Other potential elements, such as lithium in sea water, could be utilized more optimally if the magnesium element is extracted. As an illustration, the mass of the world's oceans is approximately 1.35 x 10^{12} metric ton, making vast amounts of theoretical resources seemingly available announce that more than 2,000,000 metric ton lithium is available from the seas. It is essentially making it an "unlimited" source given its geological abundance [4]. The average lithium concentration in the oceans has been estimated to 0.17 ppm with an Mg/Li ratio of about 7,000 [4]. With a high Mg/Li ratio, there has been no utilization of lithium from sea water for commercial purposes.

The separation process of magnesium from lithium in salt solutions included chemical precipitation processes, electrodialysis membrane, adsorption, and solvent extraction [5]. The separation process using chemical precipitation methods consists of two stages. The first is to carry out the precipitation process of elemental magnesium. The second is precipitating of elemental lithium, or it could be the precipitation of magnesium and lithium simultaneously by forming new complex compounds [6]. The precipitation method was employed by addition of aluminum-based [7], alkaline and alkaline salts [8], phosphate acid, and ammonium phosphate [9], oxalic acid with sodium carbonate [10], and sodium metasilicate [11].

The extraction of magnesium from bittern water, a by-product of salt ponds, aims to obtain valuable magnesium silicate elements. Magnesium silicate in the form of precipitates is a soft and neutral white crystallite that is used as a synthetic talc material. The synthesis talc starts with forming a precipitate obtained from the mixture between a solution of sodium metasilicate and magnesium chloride with a Mg/Si identical to that of talc [12]. The precipitation reaction is equation (1), with m and n as whole integers:

\[
4 ( \text{Na}_2\text{SiO}_3) + 3 ( \text{MgCl}_2) + 2 \text{HCl} + m \text{H}_2\text{O} \rightarrow \text{Si}_4\text{Mg}_{10}\text{O}_{11} \cdot n \text{H}_2\text{O} + 8 \text{NaCl} + (m-n+1) \text{H}_2\text{O} \tag{1}
\]

The mineral talc has the formula Mg_3Si_2O_5(OH)_2 and theoretical chemical composition, expressed as oxides, of 31.7% by weight (wt) magnesium oxide (MgO), 63.5% silicon dioxide (SiO_2), and 4.8% water (H_2O) [13]. Typical cosmetic talcs have average particle sizes ranging between 4 µm and 15 µm [13]. Talc is a white powder, odorless, stable, and insoluble in water or alcohol [13]. Therefore, natural talc minerals are abandoned in the industrial market and replaced with synthetic minerals with homogeneous composition and grain size [13]. Other applications of talc minerals besides for pharmaceutical and cosmetic needs [13] are ceramic material [14], paper making [15], and a potentiometric sensor for hydrogen ion [16].

Unlike magnesium, which can precipitate into magnesium silicate, lithium compounds cannot react with sodium silicate solution to form lithium silicate. The formation of lithium silicate may occur at elevated temperatures by solid-state reaction. The products may be lithium metasilicate (Li_2SiO_3) and lithium orthosilicate (Li_2SiO_4). It depends on the temperature and the mole ratio of silica and lithium carbonate [17]. In addition to the solid-state process at high temperatures, lithium silicate could be made by a sol-gel process at a low temperature of 70 °C. The Sol-gel process was carried out by mixing the silica solution with LiOH solution or with lithium methoxide (CH_3OLi) to form lithium metasilicate (Li_2SiO_3) and lithium orthosilicate (Li_2SiO_4) deposits [18].

In this paper, the study aims to extract magnesium from bittern with low lithium grade at room temperature by adding sodium silicate. The bittern is reacted with a sodium silicate solution to form a white precipitate of magnesium silicate. The bittern filtrate from the chemical precipitation process is expected to contain low magnesium because almost all of the magnesium is extracted. While the lithium element is maintained in the filtrate, it caused a decrease in the Mg/Li ratio. Further, the bittern filtrate may be used as raw material to manufacture lithium chemical compounds such as lithium carbonate for lithium battery applications.
2. Methodology
In this study, the material used is a bittern, a by-product from salt processing with a geomembrane tarpaulin system in district Lamongan, East Java, Indonesia. The chemical composition of bitterns which was characterized by using ICP, are listed in table 1.

Table 1. Chemical composition of bittern raw material.

| Element | Mg  | Na  | Li   | K    | Ca  | B   | Ratio Mg/Li |
|---------|-----|-----|------|------|-----|-----|-------------|
| Concentration (ppm) | 33,184 | 23,787 | 6.10 | 5,491 | 152 | 5,442 |

In table 1, it can be seen that the raw material used for bittern contains 33184 ppm magnesium and lithium, 6.10 ppm. Compared to sea water, which contains a lithium of about 0.17 ppm, there is an increase in lithium levels by 36 times. Table 1 shows that the Mg / Li ratio is about 5.442, so it requires many chemical reagents that impact high operating costs to extract lithium from bittern. Therefore, the first step was to take magnesium from the bittern to utilize magnesium from the bittern as an economically valuable magnesium-based product.

2.1. Experimental procedure
In this experiment, 200 ml of the bittern was added with sodium silicate, which varied at 50 g, 60 g, 70 g, 80 g, 90 g, and 100 g. The bittern contains magnesium with a concentration of 33.184 ppm or 33.184 g/l as shown in table 1. Based on stoichiometric calculations, to precipitate magnesium from the bittern requires 168.68 g sodium silicate per liter of the bittern.

The 400 ml of sodium silicate solution in various concentrations, such as 125 g/l, 150 g/l, 175 g/l, 200 g/l, 225 g/l, and 250 g/l were prepared. At first, the sodium silicate solution was cooled to room temperature. Then it was reacted with 200 ml bittern for 2 hours at a stirring speed of 300 rpm in atmospheric pressure. The results of the precipitation process were filtrated to get bitten filtrate, and the solids precipitate. In each precipitation experiment, the filtrate volume and the amount of solids precipitates were also measured. The solid deposits or precipitates were then washed with 1,000 ml aquadest for 30 minutes. The washed solids were dried for 24 hours at a temperature of 110 °C before further characterization.

2.2. Characterization
The chemical composition of solid magnesium silicate was measured by using XRF (X-Ray Fluorescence, Bruker S 2 Puma). The chemical substances analysis was conducted by using XRD (X-Ray Diffraction, Bentchop X-Ray Diffractometer). The particles’ morphology and microstructure were observed by using SEM-EDX (Scanning Electron Microscope – Energy Dispersive X-Ray / Jeol JSM-6390A). The samples’ chemical composition was characterized by using ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy, Agilent 725 ICP-OES) analysis.

3. Result and discussion
The precipitation experiments have been carried out with various concentrations of sodium silicate solution of 400 ml mixed into 200 ml bittern. In this experiment, the solid and bittern filtrate was separated by a vacuum filtering process.

Table 2. Solid deposit and filtrate in precipitation process.

| No | Sample              | Sodium silicate concentration (g/l) |
|----|---------------------|------------------------------------|
|    |                     | 125  | 150  | 175  | 200  | 225  | 250  |
| 1  | Residual filtrate (ml) | 300  | 271  | 231  | 208  | 213  | 178  |
| 2  | Solid mass (g)       | 60.54| 54.88| 79.69| 111.17| 110.34| 130.62|
Table 2 shows the amount of solid deposit and filtrate which were produced after precipitation process by addition of sodium silicates. The addition of sodium silicate in high concentrations increases the amount of solids precipitate obtained.

3.1. Bittern filtrate
The results of ICP-OES analysis on the bittern filtrate after the precipitation process using a sodium silicate solution at various concentrations could be seen in Table 3 as follows. The elements concentration of Sodium (Na), Potassium (K), Calcium (Ca), and Boron (B) are not affected by sodium silicate addition in the filtrate.

Table 3. The chemical composition of bittern filtrate after the precipitation.

| Sodium Silicate Concentration (g/litre) | Concentration (ppm) | Ratio |
|----------------------------------------|---------------------|-------|
|                                        | Mg  | Na  | Li  | K  | Ca  | B   | Mg/Li |
| 125                                    | 10,629 | 1,793 | 0.854 | 3,334 | 60.57 | 15.12 | 12,443 |
| 150                                    | 8,927  | 2,351 | 0.432 | 3,579 | 36.11 | 11.61 | 20,659 |
| 175                                    | 6,115  | 2,835 | 0.579 | 3,588 | 27.73 | 11.45 | 10,561 |
| 200                                    | 3,760  | 3,026 | 0.0626 | 3,272 | 25.09 | 11.33 | 60,064 |
| 225                                    | 2,529  | 3,026 | 0.251 | 2,948 | 16.65 | 9.11  | 10,091 |
| 250                                    | 1,418  | 3,307 | 1.373 | 3,009 | 13.07 | 10.53 | 1,033  |

The magnesium and lithium ions removal can be calculated considering the filtrate volume in table 2 after sodium silicate addition that are shown in equation (2).

Ion Removal (%) = \[
\frac{[V_R \cdot C_R - V_F \cdot C_f]}{V_R \cdot C_R} \cdot 100\% \tag{2}
\]

Information:
Ion removal: Ion removal from filtrate (percent)
\(V_R\): Volume from row materials (200 ml)
\(C_R\): Concentration element from row materials (table 1)
\(V_F\): Volume filtrate after precipitation (table 3)
\(C_f\): Concentration filtrate after precipitation (table 3)

Figure 1 shows that the magnesium and lithium ions were removed from the bittern filtrate and precipitated with sodium silicate addition. More than 80% of lithium-ion is removed from filtrate with sodium silicate addition in the concentration range of 125 – 250 g/l. The figure shows that magnesium ions are removed from filtrate and precipitated up to 96.2% by adding 250 g/l sodium silicate. Potential Mg-Li separation may occur with the addition of more than 230 g/l sodium silicate. The addition of 250 g/l sodium silicate gives lithium-ion content of 1.373 ppm, while the Mg/Li ratio is 1,033.
3.2. Precipitate characteristics

3.2.1. The chemical composition of the solid product. Characterization of the solid products, mainly in the form of magnesium silicate product, carried out using XRF and the sodium silicate can be seen in Table 4.

| Compounds                  | Concentration (% wt) |
|----------------------------|----------------------|
|                            | MgO  | Na$_2$O | SiO$_2$ | P$_2$O$_5$ | CaO  | Fe$_2$O$_3$ | SO$_3$ | Cl$_2$   |
| Magnesium silicate product | 12.377 | nd$^a$ | 70.903  | 0.673    | 0.303 | 0.13       | 4.258  | 8.635    |
| Sodium silicate raw material | nd$^a$ | 27.147 | 71.74   | 0.466    | 0.257 | 0.079      | nd$^a$ | 0.199    |

$^a$ nd: no detected

It seems that the magnesium silicate precipitates still have high sulfur and chloride impurities. This impurity is due to sulfur and chloride compounds from the raw material of salt pond waste in sulfate and chloride-based salt compounds. Therefore, the magnesium silicate precipitate's washing process needs to be repeated to obtain better purity quality.

3.2.2. The precipitate phase. Figure 2 shows the XRD pattern of the sodium silicate used in experiment (a) and solid product of precipitation reaction (b). The sodium silicate raw material peaks are shown at 16.8°, 24.9°, 29.4°, 34.8°, 37.1°, 48.0°, 52.0°, and 65.69° (figure 2(a)). However, there are other four quartz peaks at 22.7°, 26.7°, 45.5°, and 49.5°, indicating that sodium silicate raw material contains free silica compounds. This XRD analysis results were similar to previous studies that also used crystalline sodium silicate raw material [19]. The presence of quartz (SiO$_2$) compounds that were insoluble in water caused difficulties in the dissolving of crystalline sodium silicate reagent in the water.
3.2.2. The morphology and microstructure of solid product. Figure 3 shows the morphology of the washed and dried solid precipitates products (a) and commercial magnesium silicate or talc available in the market (b). The morphology of the magnesium silicate crystals that are soft and not sharp like needles is the ultimate goal of making synthetic magnesium silicate. Needle-shaped morphology indicates the presence of compounds such as asbestos that are harmful to health. Free-asbestos magnesium silicate has potential application as talc raw materials since it is safer from a health perspective. Figure 3(b) shows that the morphology of commercial magnesium silicate or talc with needles-like or thread-like granules, which are the characteristic of asbestos minerals [22]. The magnesium silicate precipitate with low crystallinity was advantageous because it can be easily formed into nanoparticles magnesium silicates compound using ultrasonic [23].
Figure 3. The morphology of samples: (a) solid product (this study); (b) commercial talc.

The morphology of synthetic talc from bittern (figure 3(a)) appeared coarser and dispersed with fine particles than the commercial talc (figure 3(b)). Both of the particle shapes are granules. According to the previous research, to change the rough-looking talc morphology, it is necessary to modify the surface using phthalimide material. One of the surface modifications using Phthalimide material could change the grain structure, physical and optical properties [24].

Figure 4 shows the chemical composition area map of the samples using SEM-EDX. The quantitative chemical composition is listed in table 5. The commercial talc sample contains calcium, which was not identified in the precipitate samples. However, the solid precipitate sample contains sodium and potassium, which are typical ions from sea salts.

Figure 4. Mapping SEM-EDX: (a) magnesium silicate precipitate; (b) commercial talc.

Table 5. The chemical composition of mapping area by SEM-EDX.

| Mapping area | C   | O   | Na  | Mg  | Si  | K   | C   | O   | Mg  | Si  | Ca   |
|--------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|
| 001          | 16.32 | 40.14 | 4.89 | 12.05 | 25.70 | 0.90 | 13.55 | 45.59 | 0.07 | 0.28 | 40.51 |
| 002          | 25.67 | 42.93 | 1.86 | 9.46  | 19.76 | 0.32 | 19.27 | 43.99 | 0.11 | 0.00 | 36.63 |
| 003          | 33.77 | 35.62 | 3.16 | 7.76  | 19.06 | 0.62 | 31.46 | 40.17 | 0.08 | 0.05 | 28.24 |
Based on table 5, the mapping analysis results with SEM-EDX showed that the magnesium silicate residue of this study was different from the talc composition in the market. The granules resulted from the precipitation process were dominated by silica (SiO₂), magnesium silica (MgSiO₃), and residual sodium silica (Na₂SiO₃). It was observed a relatively high carbon content indicating the presence of magnesium carbonate compounds. Talc, which is available in the market, is dominated by calcium carbonate (CaCO₃). It was characterized by high levels of calcium, oxygen, and carbon. Very low magnesium and silica levels indicated few magnesium and calcium silicate compounds in commercial talc.

4. Conclusion
This research successfully extracted magnesium from bittern using sodium silicate into a magnesium silicate, a valuable product as a raw material for commercial talc. The result of this study shows that potential magnesium-lithium ion separation from the filtrate to obtain a solid magnesium silicate was by adding more than 230 g/l of sodium silicate solution. Compared to commercial talc on the market, magnesium silicate precipitate was free of asbestos that does not contain calcium elements. The experimental results also showed that the Mg/Li ratio reduced from 5,442 to 1,033 in the bittern filtrate.

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