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THE EFFECT OF pH AND SODIUM SILICATE DOSAGE ON THE SEPARATION OF MAGNESIUM AND LITHIUM FROM ARTIFICIAL BRINE WATER USING CHEMICAL PRECIPITATION TECHNIQUES

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Abstract

This study aims to report the findings of an investigation into the separation of lithium and magnesium ions in the artificial brine water. The artificial brine water contains concentrations of magnesium, calcium, and lithium cations that closely resemble the concentrations seen in natural brine water sourced from Gunung Panjang using magnesium chloride, calcium chloride, and lithium chloride p.a. The objective of this experiment was to investigate the impact of pH and the addition of sodium silicate on the separation of magnesium and calcium ions from lithium ions in artificial brine water. The best outcomes were achieved when the pH of the brine water was set at 10, and sodium silicate was added in a stoichiometric ratio of 219%. These parameters led to a lithium content of 90.06%, magnesium removal of 70.32%, and a Mg/Li ratio of 6.29, indicating a substantial presence of magnesium ions precipitated as solids with pyroxene ($MgSiO_3$) phase. This research also succeeded in increasing the lithium content by 94.28% and reducing the Mg/Li ratio to 4.96 after the precipitated solids were subjected to a water-leaching process.

Keywords: *Separation, magnesium ion, lithium-ion, sodium silicate, artificial brine water*

1. INTRODUCTION

The development of lithium batteries is an attempt to mitigate the environmental consequences of greenhouse gas emissions resulting from the transportation industry [1]. Currently, lithium battery designed specifically for electric vehicles possesses a weight of 440 kg and a specific capacity of 182 Wh/kg. This battery is capable of storing 80 kWh of energy, enabling it to power a vehicle for a distance of 200 miles on a single charge [2]. Lithium production is predominantly sourced from Australia, accounting for 43.5%, Chile for 32.8%, Argentina for 12.8%, China for 7.0%, Zimbabwe for 2.3%, and other countries contributing 1.4% [3]. Research and development of lithium raw materials is expected to overcome reliance on battery raw materials sourced outside of Indonesia.

Lithium resources are derived from primary resources as well as from secondary materials [4]. Lithium is found in both the anode and cathode materials of the battery. Lithium titanate is among the materials utilized as an anode in lithium batteries [5]. The addition of lithium titanate and LIBOB (lithium bis-oxalate borate) has been found to enhance the ionic conductivity at the anode [6]. Lithium is also used as a cathode material for lithium-ion batteries, including lithium ferro phosphate, lithium manganese phosphate, and others [7].

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Several prior investigations have been conducted to extract lithium from saltwater sources utilizing various methodologies. These include an adsorption process using Skip Monoplus S-108 [8], NF membrane processes utilizing the aliphatic amine monomer membrane NF-90-2540 [9], solvent extraction processes using a synergistic combination of HBTA (benzoyl-tri-fluoro-acetone) and TOPO (tri-n-octyl phosphine oxide) [10] and precipitation processes utilizing chemical agents [11].

The precipitation procedure during the extraction of lithium involves the separation of lithium ions from magnesium and calcium ions by the utilization of a specific precipitating agent. The selected precipitant is a substance that possesses the ability to precipitate lithium ions while exhibiting no precipitation of magnesium and calcium ions or vice versa. Precipitation techniques are commonly employed for lithium extraction from saline water due to the simplicity of the equipment used and the cost-effectiveness of precipitating agent. The precipitants include aluminum-based materials [12], ammonium phosphate compounds [13], sulfuric acid precipitation [14], calcined limestone [15], oxalate salt compounds [16], calcium salt compounds [17], silicate salt compounds [18] and various other substances.

Previous studies have conducted the extraction of lithium from brine water using sodium silicate as a precipitating agent. The outcomes of these studies have demonstrated variability, which can be attributed to the specific conditions of the brine water source. These sources include Gunung Panjang brine water [19], brine water concentrate derived from salt pond waste in the form of bittern [20] seawater [21], and artificial brine water. In a study conducted by Ye Zhang [18], artificial brine water was utilized, which consisted of a combination of lithium chloride monohydrate, magnesium chloride hexahydrate, and sodium metasilicate nonahydrate. The experiments conducted by Hong Jun Yang [22] involved the utilization of synthetic materials obtained through the dissolution of lithium carbonate, calcium chloride, sodium hydroxide, and hydrochloric acid. Additionally, Hong Jun Yang [23] employed a combination of magnesium chloride and lithium chloride salt solutions, which were subsequently separated through a crystallization process to yield LiCl salt.

The present study investigated of the precipitation mechanism of magnesium from saline water using sodium silicate. The experimental procedure involved the utilization of synthetic materials that replicate the composition of Gunung Panjang's brine water comprising lithium chloride, magnesium chloride, and calcium chloride. The precipitation reactions that occur in the artificial solutions in this experiment [20], [24]:

$$4\ Na_2SiO_3 + 3\ MgCl_2 + 2\ HCl + m\ H_2O ======$$

$$Si_4Mg_3O_{11}.n\ H_2O + 8\ NaCl + (m-n+1)\ H_2O \ldots (1)$$

$$2\ CaCl_2 + Na_2SiO_3 + H_2O ==== 2\ CaO.SiO_2 + 2\ NaCl + 2\ HCl \ldots\ldots (2)$$

The expected outcome of this research is to determine the impact of pH on the efficacy of the lithium and magnesium ion separation procedure in brine water. In addition, the goal is to determine whether the performance of the lithium-ion and magnesium-ion separation process is impacted by the presence of anions in brine water other than chloride.

2. MATERIALS AND METHODS

2.1 Materials

In this experiment, the raw material used is artificial brine water containing a similar chemical composition (lithium, magnesium, and calcium) to the brine water sourced from Gunung Panjang. Gunung Panjang brine water originates from the hot springs located in the Ciseeng field geothermal area [25]. The Ciseeng geothermal fluids are derived from carbonate rocks and are characterized by the presence of a significant amount of travertine mineral [26].

Table 1. Results of ICP analysis in artificial and natural brine water

Element	**Artificial Brine water**	**Natural Brine Water**
Magnesium (Mg)	482.15	475.30
Lithium (Li)	25.28	22.06
Sodium (Na)	2,219	4,476
Potassium (K)	41.31	960.50
Calcium (Ca)	2,392	2,127
Boron (B)	0.001	95. 48
Mg/Li Ratio	19. 08	21.55

Artificial brine water was prepared by dissolving analytical chemicals sourced from Merck, such as Lithium Carbonate (Merck Catalog: 1.05680.0250), Magnesium Chloride Hexahydrate (Merck Catalog: 1.05833.100), and Calcium chloride dihydrate (Merck Catalog: 1.02382.1000) in 5 liters of distilled water. 1 M Sodium hydroxide solution (Merck Catalog: 1.06498.1000) and 1 M Hydrochloric acid solution pro analysis from Merck (Merck Catalog: 1.00317.2500) are added to adjust the pH of the artificial brine water solution.

The artificial brine water and Gunung Panjang brine water were analyzed using ICP-OES (inductively coupled plasma optical emission spectroscopy) Agilent 725. The chemical compositions of Gunung Panjang brine water and artificial brine water can be seen in Table 1. Sodium silicate was used as a precipitating agent in this experiment.

2.2 Methods

The experimental procedure started by mixing 500 milliliters of artificial brine water with a sodium silicate solution of predetermined concentration. Specifically, the concentrations used were 1.5, 3.0, 4.5, 6.0, 7.5, 9.0, and 10.5 g, which correspond to stoichiometric ratios of 31%, 63%, 94%, 125%, 156%, 188%, and 219%. This mixture was subjected to stirring for 5 minutes at room temperature, with a stirring speed of 300 rpm. The pH level of the mixture was carefully controlled and maintained at a predetermined value. Subsequently, the slurry underwent a process of liquid-solid separation.

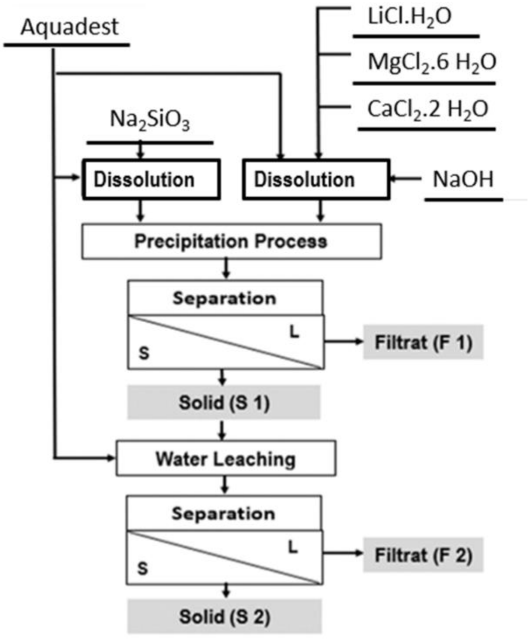

Figure 1. Flowchart of the experiment

The resulting filtrate (F1) was subjected to characterization using ICP (inductively coupled plasma optical emission spectroscopy) analysis. Afterward, the solid (S1) was leached with distilled water in order to extract the remaining lithium. The water leaching experiments were carried out using a 100 ml of distilled water for a duration of 30 minutes at room temperature and with a stirring speed of 300 rpm. Following the water-leaching procedure, the slurry underwent another liquid-solid separation. The resulting filtrate (F2) was subjected to characterization using ICP analysis, while the solid (S2) was then dried and characterized using XRD (X-ray diffraction), XRF (X-ray fluorescence), and SEM-EDS (scanning electron microscope-energy dispersive spectroscopy). The flowchart depicting the experimental procedure is presented in Fig. 1.

3. RESULT AND DISCUSSION

3.1 Precipitation Process with Sodium Silicate

The investigation focused on examining the impact of the ratio between sodium silicate and magnesium ion under varying pH conditions, namely pH levels of 2, 6, and 10. The findings are illustrated in Fig. 2. The data reveals a notable pattern, wherein at pH 10 the mass of the solid product experienced an increase more than 10 times, rising from 3.33 grams to 38.08 grams.

According to the data presented in Fig. 2, the addition of sodium silicate has significant effects on the formation of solid substances in contrast to the varying pH levels of the solution. The artificial brine water with an initial pH of 10 yielded the highest quantity of solids due to a higher tendency of magnesium ions to precipitate in alkaline conditions. Nevertheless, artificial solutions with a pH of 2 exhibited a greater degree of precipitation compared to the synthetic materials with a pH of 6.

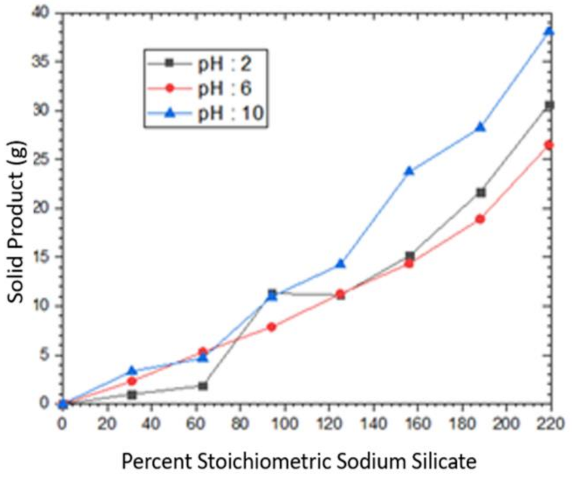

Figure 2. The effect of sodium silicate addition on the amounts of solid product at various pH

The objective of this process is to selectively separate lithium ions from magnesium ions. It is expected that lithium ions will be retained in the filtrate while magnesium ions will precipitate as solids. Figure 3 illustrates lithium co-precipitation that has occurred. The co-precipitation is considered unfavorable due to a reduction in lithium recovery. Figure 3 illustrates that the co-precipitation process of lithium ions by adding sodium silicate at a stoichiometric ratio of 219 are least apparent at a pH of 10, namely 9.94%, as compared to pH levels of 2 and 6. This means that the brine filtrate contains 90.06% lithium after the precipitation process at a pH of 10.

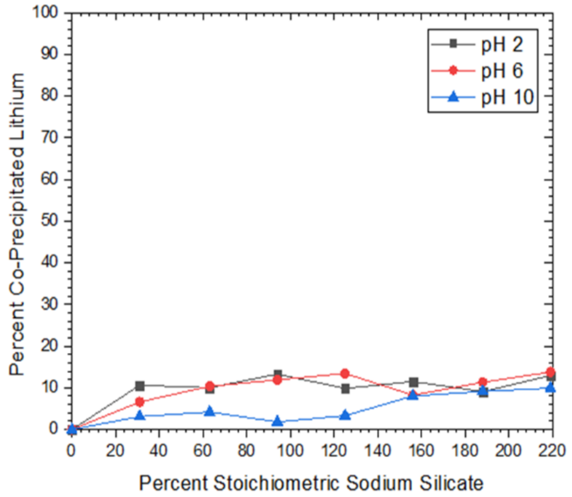

Figure 3. The effect of sodium silicate addition on the percentage of co-precipitated lithium in filtrate at various pH

In addition to the low co-precipitation of lithium, it is anticipated that a greater amount of magnesium will precipitate in this experiment. Figure 4 illustrates the percentage of magnesium ions precipitation. The data suggests that there was a positive correlation between the addition of sodium silicate and the precipitation of magnesium.

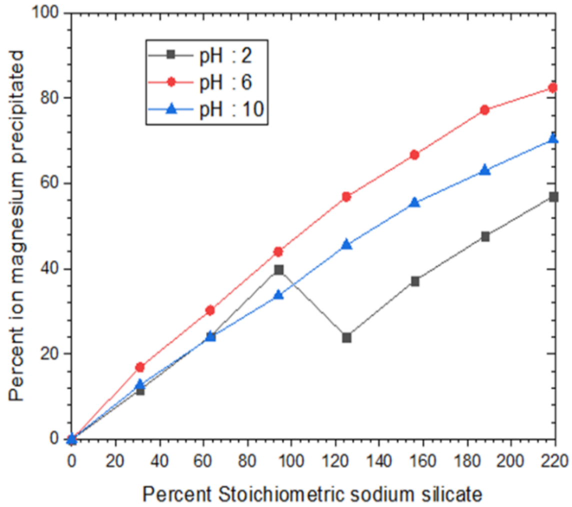

Figure 4. The effect of sodium silicate addition on the percentage of precipitated magnesium at various pH

Moreover, it is evident that the precipitation process of magnesium is most maximal at a sodium silicate stoichiometric ratio of 219. It is shown for the precipitation of magnesium amounted to 82.45% at a pH of 6 and 70.32% at a pH of 10. Brine water precipitation used sodium silicate at a ratio stoichiometry of 229 and pH of 10 are of concern in this study. This is because lithium ions are slightly precipitated together with magnesium ions as solids under these conditions.

The percentage of precipitated magnesium in this research still falls short of prior studies using natural brine water that achieved a magnesium precipitation rate of over 99% [19].

The other studies employing NaOH as a precipitating agent yields a precipitation efficiency of 80% for magnesium ions. The outcome of the precipitation process yields an amorphous solid consisting of the solid phases of magnesium hydroxide ($Mg(OH)_2$) and sodium chloride (NaCl) [28].

A lower Mg/Li ratio in the filtrate solution (F1) indicates a more effective separation between magnesium ions and lithium ions. The findings are illustrated in Fig. 5. The observed trend indicates a decrease in the Mg/Li ratio in the filtrate solution (F1) with the addition of sodium silicate. Specifically, the Mg/Li ratio fell from 19.08 to 10.40, 4.32, and 6.29 for pH values of 2, 6, and 10, respectively. Nevertheless, it is worth noting that the minimum observed Mg/Li ratio in the filtrate solution (F1) was found to be 4.32, which is comparatively higher than the Mg/Li ratio achieved in previous research utilizing natural brine water, where the ratio in the filtrate solution (F1) was reported to be 0.103 [19].

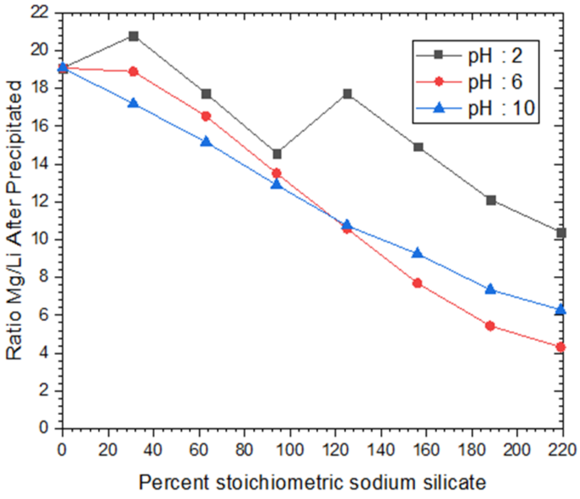

Figure 5. The effect of sodium silicate addition on the Mg/Li ratio in the filtrate at various pH

3.2 Water Leaching Process

This phenomenon occurs due to the presence of more complex anions in natural brine water, including sulfate (SO_4^{2-}), nitrate (NO_3^-), and bicarbonate (HCO_3^-) anions while artificial materials exclusively consist of chloride ions (Cl). Therefore, further research needs to be carried out to reduce the Mg/Li ratio in the brine filtrate to below 1 so that could be used as raw material for producing lithium carbonate.

Following the precipitation procedure, the solid substance (S1) underwent water leaching in order to extract the remaining lithium contained in the solids. Afterwards, the slurry underwent a liquid-solid separation. The filtrate obtained (F2) was analyzed using ICP-OES analysis. The percentage of lithium recovery from the initial residue (S1) can be determined by equation (3), and the outcomes are visually presented in Fig. 6.

$$R = \frac{X\,.\,100\%}{Y} \qquad (3)$$

R = Percentage of lithium recovery

X = lithium mass in water leaching filtrate (F2)

Y = lithium mass in the first residue (S1)

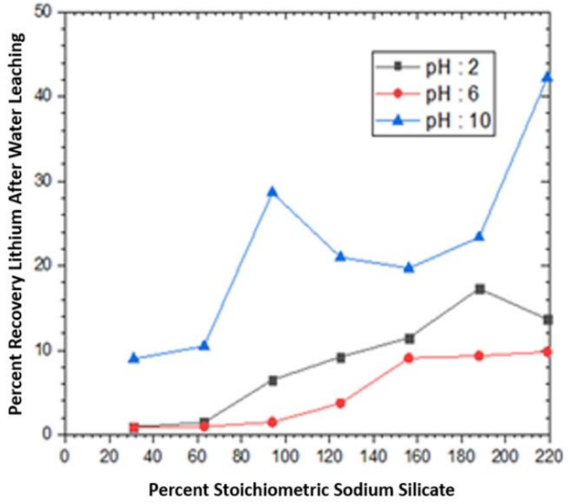

Figure 6. The effect of sodium silicate addition on the lithium recovery after water leaching at various pH

The data shown in Fig. 6 demonstrates that the water leaching process is able to recover lithium ions contained in the first residue (S1). Nevertheless, it has been shown that magnesium ions are also simultaneously extracted during this process. The percentage of lithium recovery exhibited fluctuation during water leaching at pH 10 due to the alkaline nature of the solution. At pH 10, the stability of lithium ion bonds becomes unstable, resulting in enhanced solubility of lithium in water with a lithium recovery of 42.23%. After the recovery of lithium from precipitated solids, the total mass of lithium contained in the filtrate at pH 10 was 94.28% as shown in Fig. 7. The formula for calculating the total lithium content in the filtrate after the precipitation and water leaching processes are as follows.

$$Lf = \frac{Lf1 + (Lp \times R)}{L} \times 100\,\% \qquad (4)$$

L_F = the total mass of lithium contained in the brine filtrate after the precipitation and water leaching

L_{F1} = lithium mass in the brine filtrate after precipitation

L_p = lithium mass in the solids

L = lithium mass in initial artificial brine water

R = recovery of lithium after water leaching (%)

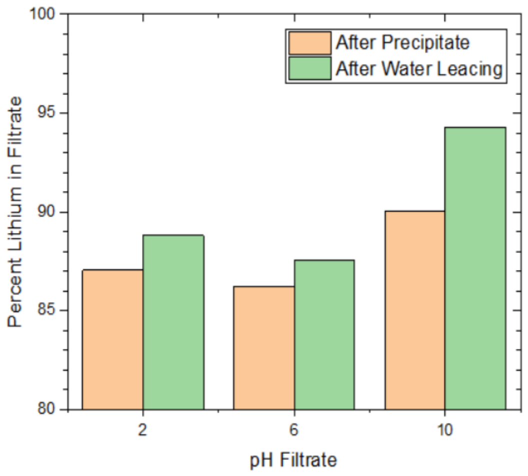

Figure 7. The effect of pH on the percentage of lithium in the brine filtrate after the precipitation and water leaching processes

Figure 8 illustrates the ratio of Mg/Li in filtrate brine after water-leaching process.

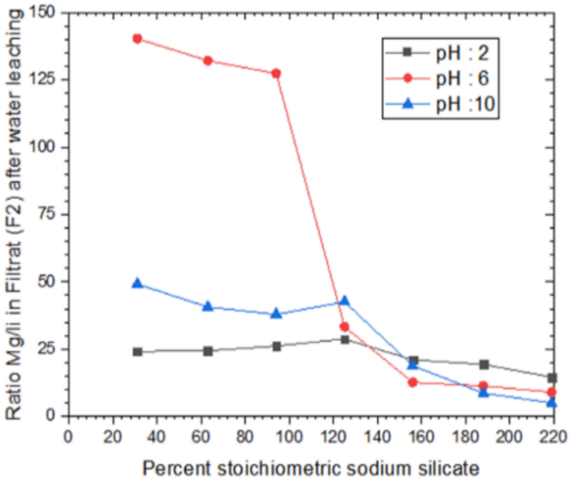

Figure 8. The effect of sodium silicate addition on the Mg/Li ratio in the filtrate after water leaching at various pH

The concentration of co-extracted magnesium ions is significantly higher than that of lithium ions so that the smallest Mg/Li ratio is obtained at about 4.96 at a stoichiometric ratio of 219% and a pH of 10. This observation indicates that the water-leaching method at atmospheric conditions and room temperature is still not effective in the recovery of lithium that is trapped inside the first solids. Efforts to increase the separation of lithium and magnesium ions using the water leaching method may be done by enhancing the leaching temperature to 50 ºC and leaching times. The water leaching process could also carried out using an autoclave reactor or adding ultrasonic radiation to recovery lithium trapped in the solids.

3.3 Solid (S2) Characterization

The solid product was characterized by XRD to determine the crystalline composition. The solid which characterized are solid from the water leaching process with the previous precipitation process at pH value of 10 and using an addition of 220% stoichiometric ratio between sodium silicate and magnesium ions.

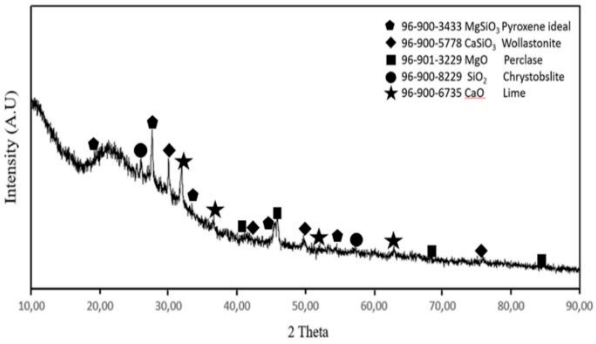

Figure 8. Results of XRD characterization of solids resulting from the optimum precipitation process at pH 10 and the addition of 220% stoichiometric sodium silicate

From the results of the XRD (X-ray diffraction) characterization in Fig. 8, it can be seen that the peaks formed are associated with amorphous compounds.

Table 3. Phase of solid resulting from the optimum precipitation process at pH 10 and the addition of 220% stoichiometric sodium silicate

Phase Solid		wt.%
96-900-3433 $MgSiO_3$	Pyroxene ideal	51.2
96-900-5778 $CaSiO_3$	Wollastonite	19.5
96-901-3229 MgO	Perclase	17.1
96-900-8229 SiO_2	Chrystobslite	7.1
96-900-6735 CaO	Lime	5.1

There are wide peaks in the range 2 theta: 10° - 90° which resembled an amorphous pattern were silica precipitates resulting from the sodium silicate precipitation process with hydrochloric acid [27]. Unlike the experiments using sodium silicate and hydrochloric acid, peaks were formed in the experiments using artificial materials. The peak is at degree 2 theta, namely 23.95°, 24.18°, 26.00°, 27.60°, 30.01°, 31.90°, and 45.00°. Based on the peak data, the analysis obtained the composition of the phases present in the solid as can be seen in Table 3.

Table 3 reveals that the solid (S2) is mostly composed of pyroxene ($MgSiO_3$) phases, accounting for 51.2% of the composition, followed by wollastonite ($CaSiO_3$) at 19.5%. This observation suggests that the sodium silicate has effectively precipitated magnesium and calcium ions present in the artificial brine water. Nevertheless, there are the presence of Perclase (MgO) accounts for approximately 17.1% of the composition and lime (CaO) comprises around 5.1%. The high solubility of MgO and CaO contributed to this result. A Chrystobslite phase containing 7.1% by weight was observed, indicating that certain sodium silicates did not undergo reactions with magnesium and calcium ions. Instead, these silicates formed silica gel, which subsequently transformed into a silica phase upon drying.

Table 4. The chemical composition of precipitated solids by XRF analysis

Element	% wt
Silica (Si)	32.87
Calsium (Ca)	11.79
Magnesium (Mg)	6.65
Chloride (Cl)	0.43
Aluminum (Al)	0.47
Phosphor (P)	0.16
Oxygen (O)	47.34
Other	0.29

The chemical compositions of solid (S2) were analyzed and displayed in Table 4. The analysis indicated that the predominant constituents of solid (S2) are Silica (Si) comprising 32.87%, Calcium (Ca) comprising 11.79%, Magnesium (Mg) comprising 6.65%, and Oxygen (O) comprising 47.34%. These results obtained from XRF (X-ray fluorescence) analysis confirm the earlier XRD findings, which identified these elements as the primary constituents of the phases observed.

4. CONCLUSION

It can be inferred that the utilization of sodium silicate in the precipitation process enables the effective separation of lithium ions from magnesium ions. The experimental findings demonstrate that the precipitation of magnesium is significantly influenced by several parameters, including the quantity of sodium silicate added and the pH level. The best parameters for the precipitation process using sodium silicate to separate lithium ions from magnesium ions have been found as follows: (i) the addition of sodium silicate 219% stoichiometric magnesium ion and (ii) pH level of 10 with precipitation of magnesium amounted to 70.32%, a Mg/Li ratio of 4.96 and a lithium content of 94.28% in the brine filtrate.

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