

Lithium extraction from brine water Tirtasanita Bogor, Indonesia by evaporation method

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Abstract. The objectives of this research are to characterize the chemical composition of brine water, Tirtasanita Bogor, Indonesia and investigate the influence of brine water vaporization ratio on lithium content and other chemical elements of brine water. The research method is brine water evaporated at boiling point using distillation equipment with various evaporation ratios up to 50 percent; 75 percent; 80 percent; 87.5 percent and 90 percent volume of brine water. The distillation process produces distillate and brine water liquid containing salt deposits. The brine water liquid from the evaporation process was then filtered to separate the filtrate of brine water and salt deposit. Distillate and filtrate of brine water were analysed by ICP-OES to know the chemical composition of both such as Li, K, Na, Ca, and Mg. The salt deposits were characterized by SEM-EDS. The experimental results show that the chemical compositions of brine water Tirtasanita Bogor, Indonesia are 17.27 ppm Li; 409.98 ppm K; 1929.87 ppm Na; 185.71 ppm Ca; 146.02 ppm Mg. From the result of SEM-EDS analysis shows that salt deposit has a spherical morphology with the dominant Ca content. This salt deposit is indicated as CaCO₃ compound.

1. Introduction

Lithium is the most abundant element to 25th in the earth's crust [1]. Several characteristics of this element are reactive, silvery white and easily oxidized while its cut surface is exposed to oxygen. Lithium is one of the most commonly used metals in the industry with a wide range of applications including batteries, lubricants and pharmaceutical products. For battery applications, Li-ions (LIBs) batteries perform better than nickel-cadmium batteries (NiCd) or nickel-metal hydride batteries (NiMH), such as lower energy density, lighter, high energy density, high working voltage, long cycle life, low self-discharge rate [2]. The existence of electric vehicles makes the utility of lithium – ion batteries increase and it makes the demand of lithium raise in the future [3]. Beside that, lithium is also used in glass and ceramic applications (30%), lubricating oil (11%), metallurgical industry (4%) and also chemicals/pharmaceuticals [4].

Lithium can be obtained from many resources which mainly from minerals contained in granite, pegmatite, or brine (brine) [5]. The production of lithium ore begins with lithium minerals (1899) in the United States [4]. The first lithium production of brine water in Lake Searles, the USA in 1936, brine water was exploited mainly in South America and China. The largest lithium producer in the world is Chile where lithium is extracted from salted brine water at Atacama Salt Flat.



Some newer installations (in 2013) are at various stages of exploration/operation for salt water sources: one in China, six in Argentina, three in Chile and one in Bolivia. Currently, 8% of lithium is obtained from the brine water of salt and marine lakes by sedimentation [1]. Indonesia has a lot of lithium resources from the potential of brine water that has not been fully utilized. Brine water is derived from sea water trapped in rocks in the earth due to geology events. The geological location will influence the chemical composition of the brine water [6]. Indonesia in the ring area of a fire has lithium reserves are not known clearly and surely until now.

There are many processes that can be used to extract the lithium from its resources such as roasting, evaporation, solvent extraction and adsorption [3]. The lithium extraction process from ore or mineral using roasting is followed by leaching process, while extraction from brine water includes evaporation, precipitation, adsorption and ion exchange [4]. Lithium extracted from lithium ores generally requires a chemical recovery process with intensive energy that is much more expensive than recovery from brine water. The contribution of brine water is almost twice that of minerals (Figure 1) [7]. Subsoil underground soil is now the most dominant source of raw material for lithium production because its production costs are much cheaper than the processing costs of lithium ores [8].

Currently, brine water is an important source of lithium carbonate in the world. One of many countries that has processed saltwater is Argentina. In 2015, Argentina has commercially produced lithium carbonate and lithium chloride from brine water [9]. Typically, brine water is saturated with salt, which contains of lithium, potassium, magnesium, sulphate, and borate. It is vary depending on the different location. To precipitate lithium as lithium carbonate, brine water should be concentrated to almost the concentration of saturated lithium chloride solution (6% Li^+) 99.5% of 99.99% [10]. Lithium carbonate products can now be produced using brine evaporation. The evaporation of brine followed by the deposition of K and Mg, then to purify the brine water, solvent extraction or ion exchange process to remove other impurities [11, 12].

On this opportunity, we focused on characterizing the chemical compositions of brine water, Tirtasanita Bogor, Indonesia and investigating the influence of the brine water vaporization ratio on lithium content and other chemical elements of brine water.

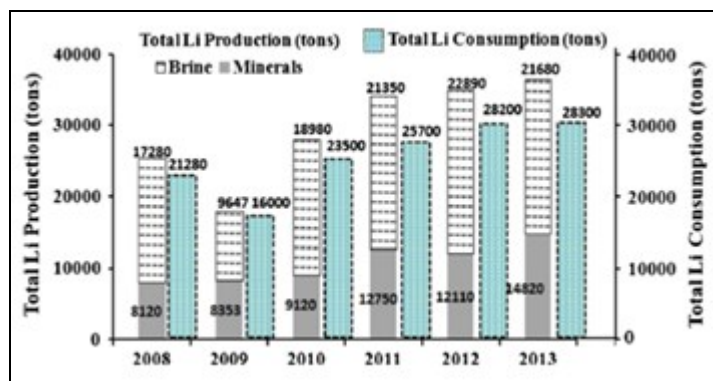


Figure 1. Lithium production (from mineral and salt water, data 2008-2013) [6].

2. Materials and methods

Brine water from Ciseeng, Bogor (Indonesia) was used in this research to extract the lithium. The coordinate of this place is -6.431355, 106.696434. The location where the brine water was taken can be seen in Figure 2.



Figure 2. Location of brine water from Ciseeng, Bogor (Indonesia).

The first step in this research was brine water filtered to remove the impurities. After that, brine water was heated with some variations of evaporated sample volume ratios that are 1: 2 (50%), 1: 4 (75%), 1: 5 (80%), 1: 8 (87.5%) and 1:10 (90%). The method which used in this research was the evaporated water at the boiling point using distillation equipment. This distillation process produces distillates and brine water liquid containing salt deposits. Then brine water liquid from the evaporation process filtered to separate the filtrate of brine water and salt deposit. Distillate and filtrate of brine water were analysed using inductively coupled plasma optical emission spectrometry (ICP - OES) to know the chemical composition in distillate and filtrate of brine water such as lithium (Li), potassium (K), sodium (Na), calcium (Ca), and magnesium (Mg). The salt deposits were characterized by scanning electron microscopy with energy dispersive spectroscopy (SEM - EDS) to determine the morphology of this sample and elements content that contained in the sample. The flowchart of experiment can be seen on Figure 3.

3. Results and discussion

The first investigation was carried out by analysis the raw material which was brine water from Ciseeng, Bogor (Indonesia). Table 1 is the result of the raw material sample using ICP analysis.

Table 1. The chemical composition of brine water Ciseeng, Bogor.

Element	Concentration (ppm)
Ca	185.706
K	409.981
Li	17.2717
Mg	146.019
Na	1929.87

Table 1 shows that the major elements contained in brine water, Ciseeng, Bogor include elements Ca, K, Li, Mg, Na with the largest concentration is Na elements. This is in accordance with the analysis conducted by G.C. Sembiring who said that Ciseeng brine springs and brine water type rich in sodium chloride (NaCl) [13]. From that analysis, can also be seen that the source of Ciseeng hot springs contain lithium element (17.2717 ppm). The brine water which has high enough concentration of lithium indicates that extraction process can be done. Unfortunately, the concentration of sodium (Na), potassium (K), magnesium (Mg) and calcium (Ca) are dominant in brine water as the impurities so that the impurities must be removed from brine water in order to extract the lithium. To determine the most influential variables, a series of experiments with results as shown in Table 2 and Table 3 are performed.

Table 2 shows the chemical composition of brine water distillate which analysed by ICP – OES. It appears that the lithium and other elements still exist in brine water when the brine water was evaporated at its boiling point. The highest content in distillate is K (0.80357 ppm) when the brine

water was evaporated at 87.5%. According to Table 2, the concentrations of lithium and other elements in distillate are below 1 ppm. This condition is quite satisfactory in the extracting of valuable elements of lithium from brine water, Tirtasanita Bogor which has a very small lithium content (17.27 ppm) compared to other countries such as Chile (1570 ppm), Bolivia (321 ppm), Argentina (20 – 760 ppm) [10, 14]. The mechanism is to form a lithium-rich brine water concentrate by increasing the evaporation ratio of the brine water sample at its boiling point.

Compared to distillate and liquid residue of brine water (Table 2 and Table 3), lithium content in distillate of brine water is lower than in liquid residue. It can be happened because lithium-valuable element content of brine water is virtually non-volatile along with H₂O at its boiling temperature although the evaporation ratio is raised to 90%. This evaporation process is relatively fast compared to traditional evaporation using sun light which takes relatively longer time. Another factor of great influence is the climate. Indonesia has a tropical season with high rainfall so to get lithium-rich brine water concentrates will be more difficult and longer. The results of ICP-OES analysis of brine water concentrate are shown in Table 3.

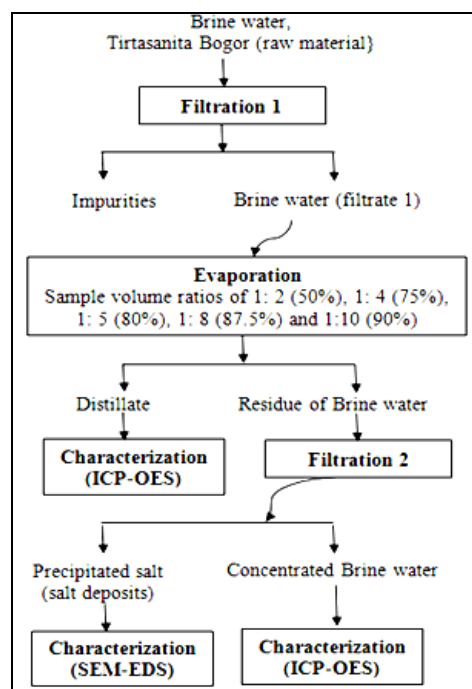


Figure 3. The flowchart of experiment.

Table 2. The results of ICP-OES analysis of brine water distillate.

Sample (Ratio volume)	Concentration (ppm)				
	Ca	K	Li	Mg	Na
50% (1:2)	0.418352	0.070373	0.018029	0.0312	0.337844
75% (1:4)	0.376558	0.106919	0.045491	0.024675	0.355945
87.5% (1:8)	0.2575	0.80357	0.036839	0.10572	0.4523
100% (1:10)	0.064298	0.271213	0.172305	0.374691	0.623371

Table 3. The results of ICP-OES analysis of residue of brine water (concentrated brine water).

Sample (Ratio volume)	Concentration (ppm)				
	Ca	K	Li	Mg	Na
Brine water	185.706	409.981	17.2717	146.019	1929.87
50% (1:2)	124.12	995.966	47.8852	192.946	4188.85
75% (1:4)	123.505	1902.63	104.941	198.39	3490.88
80% (1:5)	122.847	2244.77	119.859	196.912	2905.87
87.5% (1:8)	119.113	3413.26	196.012	201.868	2496.24
90% (1:10)	158.183	6690.19	213.246	194.657	2390.34

Table 3 shows that lithium content in residue of brine water raised from 17.2717 ppm to 213.246 ppm after evaporation at 90% evaporation ratio. It shows that higher lithium content up to 12 folds compared with brine water without evaporation. While other elements (Ca, Mg and Na) are not show a significant difference compared with brine water without evaporation. Calcium content in residue of brine water decreased from 185.706 ppm to 158.183 ppm. On the other hand, K, Mg and Na in residue of brine water increased from 409.981 ppm to 6690.19 ppm, 146.019 ppm to 194.657 and 1929.87 ppm to 2390.34 ppm.

Calcium precipitated easily because Ca has a very low solubility in water so that it removed first from brine water and its concentration decreased. Meanwhile, the concentration of magnesium (Mg), sodium (Na) and potassium (K) in residue of brine water increased because they have a higher solubility than Ca and caused, they do not evaporate with the distillate. The tendency of other elements such as Na, K, Ca and Mg can be seen in Figure 4.

Figure 4a shows that the concentrations of Li, Mg and K increase as the evaporation increases, this is because when the brine distillation process occurs, the lithium element does not evaporate with the distillate causing the Li content of the brine to increase after the evaporation process. Figure 4b shows that Li has the highest concentration between Ca and Mg when the brine water was evaporated at 90% where its concentration is more than 200 ppm. Among all elements, K increases significantly due to the evaporation process and becomes the element which has the highest concentration. Its concentration increased from < 1000 ppm into < 7000 ppm.

There is no significant effect on Mg concentration when the brine water was evaporated at 50%, 75%, 80%, 87.5% and 90% that is around 190 – 200 ppm. While the concentrations of Ca and Na were reduced due to precipitation processes. There are two kind of precipitates which possible to be formed such as sodium chloride (NaCl) and calcium sulphate (CaSO₄) [14].

Figure 5 shows that the evaporation ratio generates the increasing of precipitated salt. It causes by increasing evaporation ratio will decrease water content with constant solute and while the solute reaches its saturation point, it will be precipitated. So, it can be concluded that the higher evaporation ratio (%) of brine water will produce the higher precipitated salt (gram) but its concentration depends on the solubility and boiling point of element in water.

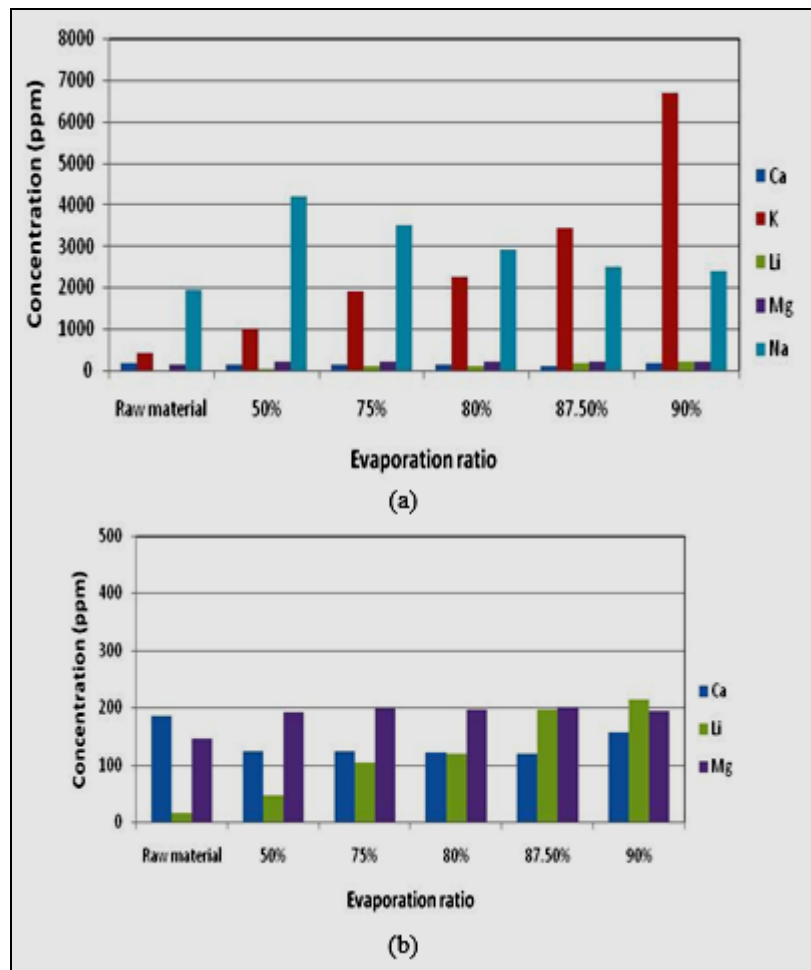


Figure 4. The effect of evaporation ratio on the element content of residue of brine water (concentrated brine water). a) Concentration of Ca, K, Li, Mg and Na after evaporation process; b) Comparison of Ca, Li and Mg content after evaporation process.

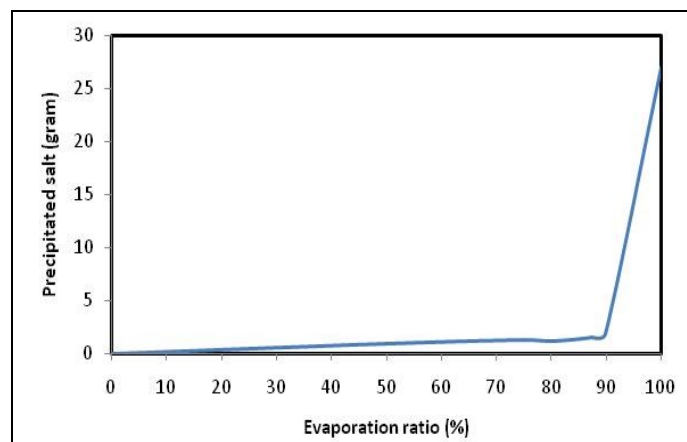


Figure 5. The effect of evaporation ratio (%) on the precipitated salt (gram).

Table 4 shows the EDS of precipitate which produced from brine water that has been evaporated with different volume ratio. From the table, the most visible elements in that precipitate are O, Na, Mg, Al, Cl, K, and Ca. The highest element which produced from this process is Ca (52.28 % mass) while the lowest element is Al (0.09 % mass). The concentrations of Mg increase from 0.65 % mass into 0.73 % mass as the evaporation increases, while the Ca concentration decreases from 52.28 % mass into 43.56 % mass as evaporation increases but the concentration of K and Na increases from 0.50 % mass, 0.65 % mass into 0.51 % mass and 0.77 % mass when the brine water was evaporated at 75% but it decreases into 0.47 % mass and 0.49 % mass when the brine water was evaporated at 80%. The concentrations of Al are not change significantly from 0.09 % mass to 0.1 % mass when it was evaporated at 50%, 75% and 80%.

Table 4. Semi-quantitative SEM-EDS analysis of brine water (residue) from Ciseeng, Bogor.

Element	% mass		
	Volume ratio 50% (1:2)	Volume ratio 75% (1:4)	Volume ratio 80% (1:5)
O	44.98	46.28	48.70
Na	0.60	0.77	0.49
Mg	0.65	0.68	0.73
Al	0.09	0.10	0.09
Si	-	-	0.53
S	0.04	-	-
Cl	0.86	2.00	1.31
K	0.50	0.51	0.47
Ca	52.28	47.30	43.56
Fe	-	0.01	-
Cu	-	2.35	4.11

Figure 6 shows the SEM image after evaporation with a volume ratio of 50%, 75%, 80% and 87.5% with 500 times magnification. From the obtained SEM image, it looks dominant calcium element with rhombohedral or cubic morphology. Figure 6b shows that the particle size of calcium element is the finest among the others while Figure 6c shows that the particle size of calcium element is the biggest. Nevertheless, this particle has the uniform distribution and size particles on each condition. Comparing with Figure 6, the pictures below (Figure 7) show the SEM image with 1000 times magnification. These pictures confirm that when brine water was evaporated at 75% (Figure 7b) produce the finest calcium element among the other evaporation processes. In addition, in Figure 7b also appears that more precipitate produced when the evaporation process at 75% was done on brine water if compared with others. On the other hand, Figure 7c also confirms that when brine water was evaporated at 80% produce the biggest calcium element among the other evaporation processes.

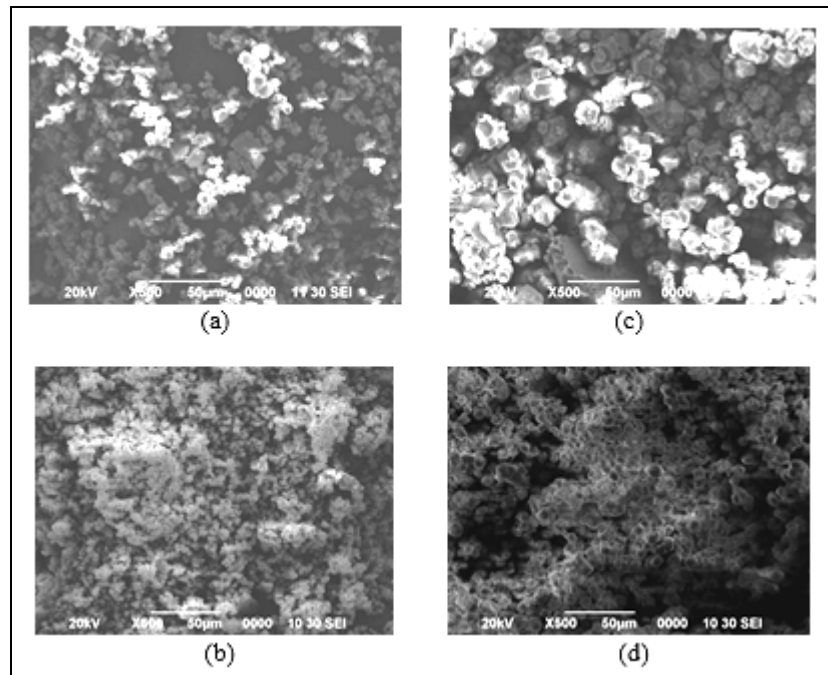


Figure 6. SEM image of recovery lithium by evaporation method with 500x magnification (a) volume ratio of 50% (1:2); (b) 75% (1:4) volume ratio; (c) 80% (1:5) volume ratio; (d) 87.5% volume ratio (1:8).

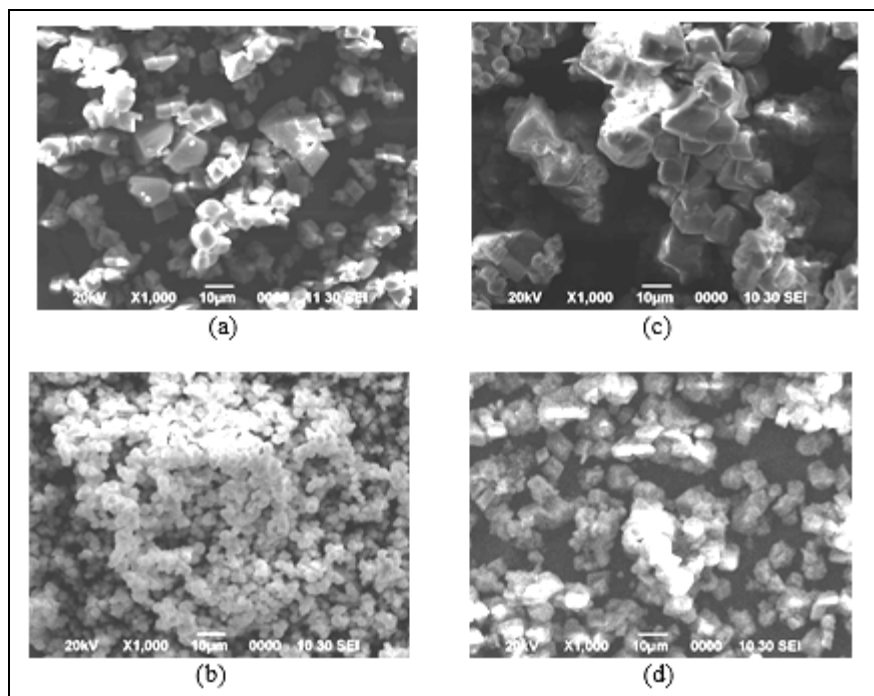
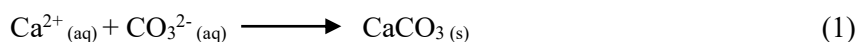


Figure 7. SEM image of recovery lithium by evaporation method with 1000x magnification (a) volume ratio of 50% (1:2); (b) 75% (1:4) volume ratio; (c) 80% (1:5) volume ratio; (d) 87.5% volume ratio (1:8).

This salt deposit is indicated as a CaCO_3 compound as the result of previous research by Lalasari *et al.* in Figure 8. The reaction of partial evaporation is as follows:



That reaction shows that evaporation process causing the calcium ion (Ca^{2+}) will react with carbonate ion (CO_3^{2-}) in brine water to form calcium carbonate (CaCO_3) as precipitate. Calcium carbonate (CaCO_3) or known as calcite easy to form as precipitate because it has a very low solubility in water (15 mg/L at 25°C). Its solubility will increase if the temperature of water decreases. This reaction also confirms that calcium element which dominant in that precipitate is calcium carbonate (CaCO_3).

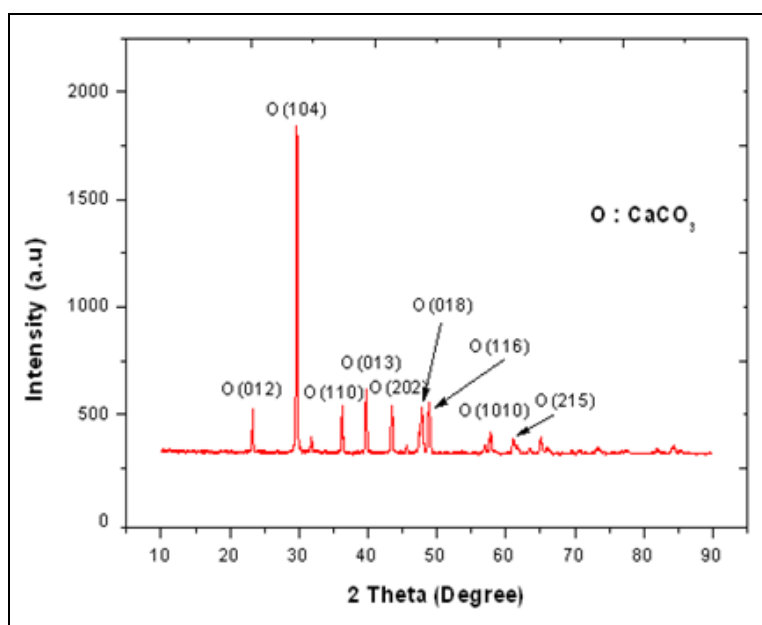


Figure 8. The XRD pattern of precipitated salt [15].

This analysis tells that brine water in Ciseeng has a potential to be a lithium resources and the evaporation process can be used as primary treatment to extract the lithium from brine water. Furthermore, the lithium extraction as raw material for battery applications must be studied.

4. Conclusions

The concentrations of Li, Mg, Na, and K increase as the increases of evaporation ratio, while the concentration of Ca decreases as the increases of evaporation ratio. The brine water evaporation process can increase the lithium content up to 12 folds at the evaporation ratio of 90% compared with brine water without evaporation. The lithium concentration increased from 17.2717 ppm to 213.246 ppm. The SEM-EDS analysis and XRD pattern show that precipitated salt has rhombohedral or cubic and spherical morphology with dominant Ca content. This precipitated salt is indicated as a CaCO_3 compound.

5. References

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