The Effect of Slow Evaporation on Ca, Na, K, and Mg Concentration in Natural Brine from Ciseeng, West Java

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Abstract. Indonesia’s location in the ring of fire gives Indonesia a lot of natural resources such as natural brine water from Ciseeng, West Java. Natural brine contains a lot of minerals such as Na, K, Ca, Mg. and could potentially be the source of those elements. One of the common process for recovering minerals in brine water is through solar evaporation process. This process is ineffective because the evaporation stops in the night time. The purposes of this study are to find another method for concentrating brine, characterize natural brine from Ciseeng, West Java, and investigate the effect of new evaporation method to the brine. In this work, the author conducted the evaporation using electric heater to keep the solution in the desired temperature coupled with blowers to blow air to the surface of the solution for 10 days. The volume of the system was maintained by making up the evaporated water with fresh brine. The results indicate that the evaporation can increase the Mg, Na, and K concentration up to 282%, 283%, and 207%, respectively, while the Ca concentration stays relatively constant compared to the fresh brine. The brine’s °Bé increase from 2.5 to 6. In the process, about 158% of Ca and 51% of Na were recovered as precipitate.

1. Introduction
Natural brine is a source of a lot of minerals such as sodium, potassium, calcium, and magnesium. Those minerals could be used for a lot of application. Sodium compound can be used as feedstock for chemical industry, potassium compound as fertilizer, calcium compound as building stones and cement, and magnesium as alloying agent. The concentration of those elements in the brine could vary depending on its source. Indonesia’s location in the ring of fire gives a lot of natural brine sources. One of unexploited natural brine in Indonesia is located in Ciseeng, West Java. The brine now used as public bathing area. People believes that the mineral content and its hot temperature could cure some of skin disease.
To harness the potential of minerals contained in the brine, some study has been conducted. The usual approach is using evaporation method to concentrate the brine up until certain degree of salinity. In the process of concentrating the brine, calcium, sodium and some magnesium are recovered as precipitate. Turk[1], Balarew[2], and Nie[3] study the evaporation of brine using solar evaporation, but using solar energy to evaporate the brine is ineffective because the evaporation is stopped during the night and also during rainy season, thus an alternative for this method need to be studied. The concentrated brine is then processed by precipitation[4–7], ion-exchange[8], or solvent extraction[9] to recover other precious minerals such as magnesium and lithium.

This study will conduct preliminary research of brine evaporation using electric heater in a semi-pilot plant scale. Brine will be evaporated for 10 days and concentrated brine and precipitate will be analyzed. The purpose of this study is to characterize the effect of evaporation to the mineral’s concentration and to the precipitated mineral. The concentrated brine from this study will be used as raw material to extract the remaining minerals using another method in the next work.

2. Materials and Methods
Preliminary research was carried out to see the effect of evaporation to the concentration of minerals in the natural brine. The evaporation apparatus consists of electric heater to keep the temperature of brine in the desired temperature and blowers to blow air to the surface of brine. The composition of brine from Ciseeng was analyzed using ISP-OES to determine the chemical composition. The results are listed in Table 1.

| Component | Concentration (ppm) |
|-----------|---------------------|
| Sodium    | 6194.99             |
| Potassium | 483.54              |
| Calcium   | 763.33              |
| Magnesium | 427.23              |

The experiment consists of a loop which was circulated in 3 open vessels. 1st vessel equipped with air blower and rack of thin sheet of plastic on which the brine will flow through, 2nd vessel contain electric heater to keep the temperature of brine around 40°C, and 3rd vessel contain electric heater also set up at 40°C and air blower. Fresh brine was introduced to the system until all 3 vessels are filled.
After the vessels are filled, a pump was used to circulate the brine from 1st, 2nd, 3rd, and back to 1st vessel again. Fresh brine was added for making up the evaporated water every day. Brine was sampled each day from 1st and 2nd vessel and filtered using Whatman paper no. 42 and then analyzed using ICP-OES to determine its chemical composition. Salt precipitated in the vessels were then characterized using SEM, XRF, and XRD to determine its morphology, dry basis chemical composition, and phase. The flowsheet of experiment is shown in Figure 2.

Baume degree (°Bé) was used to see the density of the processed brine. °Bé have been used by traditional salt farmer to know when they should harvest their salt. °Bé correlation to specific gravity (s.g.) at temperature of 60°F can be seen in equation (1)

\[
s.g. = \frac{145}{(145 - °Bé)}
\]

(1)

3. Result and Discussion

The experiment was conducted for 10 days straight. The average temperature of the system is 40.4°C and 61.33% of brine is evaporated. Figure 3 shows the chemical composition of Ca, K, Mg, and Na. It can be seen that the concentration of Ca is relative constant while the concentration of K, Mg, and Na is increasing in the same pattern throughout the experiment. The concentration of Mg, Na, and K increase for 282%, 283%, and 207%, respectively. This result is in line with previous study for seawater evaporation. Study by Abdeel-Aal, et al [10] stated that Ca will precipitate first in the form of CaCO₃, followed by CaSO₄, NaCl and MgSO₄, respectively [10].

But the result is slightly different from that previous study. Ca already precipitate at °Bé 2.5 (can be seen from the relatively constant value of Ca concentration from day 1 to day 3 of experiment), while those study stated that Ca will start to precipitate at °Bé > 3. Figure 4 shows the °Bé value throughout the experiment. This is possible because the brine from Ciseeng contain a lot more Ca (763.33 ppm) compared to the Ca concentration in sea water (416 ppm) [11]. This high concentration of Ca makes brine already saturated with Ca and start precipitating earlier. 61.18% of Ca was precipitated, calculated using mass balance.

Figure 2. Schematic diagram of experiment.
Figure 3. Concentration of Ca, K, Mg, and Na in the system for 10 days.

Figure 4. $^6$Bé changes during experiment.

The results of this research compared to other research can be seen in table 2. Natasha et. al.[12], and Lalasari et. al[13] did the evaporation on brine from ciseeng site B while this experiment used brine from ciseeng site A, the maps of ciseeng site A and site B can be seen in Figure 5. The distance from those two brine sources were only around 300 m but the composition is different. Brine from site B has higher Ca, Na, and Mg content compare to brine from site A. Those two other experiments were conducted in a lab scale apparatus while this experiment was conducted in a pilot plant scale. The results from this study are different when compared to the other study. Ca concentration seems to stayed constant and Na and Mg concentration were increased while study by Natasha et. al.[12] saw a decrease in Ca and Na concentration. These could happen because of the differences in the starting concentration of Ca and Na and also the differences in the evaporation treatment. This experiment was conducted semi-batch system while the other experiments were conducted in the batch system. Fresh brine was introduced every day and the evaporation happened in lower temperature (average 40.4°C). These lower temperature means that the solubility of CaCO$_3$ were higher[14] compared to the higher temperature evaporation in those
other experiment. The rise of Na and Mg concentration is still in line with theory that Na and Mg was not supposed to precipitate under °Bé 25 and 30, respectively[2,10].

Table 2. Results comparison with other researches.

| Raw Material          | Water evaporated | Concentration (ppm) | Before Evaporation | After Evaporation |
|-----------------------|------------------|---------------------|-------------------|------------------|
|                       |                  | Ca  | Na  | Mg   | Ca  | Na  | Mg   |
| This research         | Brine from Ciseeng Site A | 61% | 763 | 6159 | 472.23 | 772.24 | 12851 | 1211.1 |
| Natasha et. al. [12]  | Brine from Ciseeng Site B | 50% | 2010 | 27050 | - | 170.06 | 4188.85 | - |
| Lalasari et. al.[13]  | Brine from Ciseeng Site B | 80% | 2940 | 28870 | 9170 | 53020 | 9500 | 2100 |

Figure 5. Map of brine source location Site A and Site B.

3.1. SEM Analysis

SEM Analysis was performed to see the morphology of the precipitate from the evaporation process, the results can be seen in figure 6. It can be seen that the precipitation product has various particle size and crystal. This could happen because small amount of sodium chloride was co-precipitated alongside calcium carbonate as the main product and supported by EDX quantitative analysis results of the sample (table 3) which shows that sodium was also co-precipitated.
### Table 3. EDX quantitative analysis of SEM sample

| Component | Mass (%) |
|-----------|----------|
| Ca        | 38.14    |
| O         | 38.02    |
| C         | 13.14    |
| Cl        | 3.89     |
| Na        | 3.02     |
| Si        | 2.01     |
| Al        | 0.69     |
| K         | 0.61     |
| Mg        | 0.49     |

**Figure 6.** Morphology of precipitated salts at (a) 1000x and (b) 2000x magnification

3.2. **XRF and XRD Analysis**

Table 4 show XRF analysis result of precipitated salts. XRF analysis was conducted using Bruker S2 Puma and was able to see the concentration of element starting from sodium. It can be seen that calcium are the main constituent of the salts followed by strontium, sodium. This co-precipitation of sodium and magnesium was not expected since based on previous study [2,10] sodium and magnesium would not precipitate until $^\circ\text{Be}$ value reached around 25 and 30, respectively. This co-precipitation could happen because some of the brine might be evaporated on the wall of the evaporation apparatus, Figure 7, and reached high $^\circ\text{Be}$ value, thus sodium and magnesium were precipitated. Extremely similar chemical properties between strontium and calcium [15] made the co-precipitation of strontium is possible. XRD pattern was analyzed using High Score Plus Software. Figure 8 show XRD analysis result of precipitated salts. Phases of calcium carbonate (CaCO$_3$) and sodium chloride (NaCl) are present in the result. This result confirms SEM and XRF analysis that calcium carbonate was the main phase while sodium chloride was the minor.
Table 4. Chemical composition of precipitated salts.

| Component | Mass (%) |
|-----------|----------|
| Ca        | 85.94    |
| Sr        | 3.63     |
| Cl        | 2.93     |
| Na        | 2.12     |
| Si        | 1.59     |
| Fe        | 1.17     |
| Mg        | 1.12     |
| Others    | 1.5      |

Figure 7. Salts precipitated at the lips and side surface of evaporation tank.

Figure 8. XRD pattern of precipitated salts.
4. Conclusion
Based on preliminary research of evaporation-precipitation of brine from Ciseeng, heating the brine at average temperature of 40.4°C could increase the °Be values up until 6. The concentration of Mg, Na, and K increase for 282%, 283%, and 207%, respectively, while the concentration of Ca stays relatively the same. In the process, 61.18% of Ca was precipitated and only small amount of Mg and Na were precipitated. Mg and Na precipitation was possible due to the evaporation on the lips of evaporation tank. The concentration of Mg, Na, and K increase for 282%, 283%, and 207%, respectively. The main constituent of the salt precipitated are Ca (60.31%) and Sr (2.33%). Sr was co-precipitated because of extremely similar chemical properties with calcium.

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