Study of Sodium Chloride Production Using Gradual Evaporation of Seawater from Nggolonto Sea, East Nusa Tenggara

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ABSTRACT

Sea water as a raw material resources for the kitchen salt production contain not only sodium chloride (NaCl), but also other dissolved salts such as hygroscopic calcium and magnesium salts. The high content of other salts causes industrial sodium chloride has a low quality. This research aims were to find out the effect of seawater evaporation on NaCl content changes. The seawater obtained from Nggolonto, Nagekeo, East Nusa Tenggara, was used with an initial volume of 200 mL. Then it was concentrated in varying of final volume, i.e. 20, 23, 25, 27, and 29 mL. And the result, sodium chloride content was calculated based on the total chloride ion content, corrected toward the magnesium and calcium ions content, and the presence of sulphate anion. In addition, the chloride and magnesium also calcium ions content was analyzed volumetrically, while the sulphate anion was determined spectrophotometrically. The research result showed that NaCl content increase significantly up to 27 mL of final volume and was constantly afterward. Furthermore, the highest of NaCl content obtained from final volume of 29 mL was 96.01%. Nevertheless, comparing to the Indonesian National Standard (SNI) number 06-0303-1989, its content was still below the standard of 98.5%.

Keywords: NaCl, purification, salt production, precipitation of salt, sea water.

INTRODUCTION

Sea water is the main resources for producing NaCl salt [1]. Instead of NaCl, it also contains MgCl₂, CaCl₂, MgSO₄ and CaSO₄ [2], [3], [4]. Nevertheless, these salts obtained from crystallization process, are hygroscopic. Not only used as a food needs, it has also used for industrial purpose such as textile industry [5], chemical industry [6], alkaline-chlorine industry [7], pulp and paper industries, petrochemicals, and pharmacy [8], and snack industry [9]. In contrast for using in food needs, the NaCl salt quality for industrials requirement has to high purity up to 98.5% [10]. Unfortunately, NaCl salt obtained from conventional process has a low quality due to the presence of others salts contaminants [11]. A report has disclosed recently by applying of phytoplankton. This organism can be used to absorb the sun light and accelerate the evaporation process. Thus, enhance seawater salinity and produce high salt content. However, it has limitation due to availability and its handling [12]. Therefore, in order to improve the local sodium chloride quality to meet the industrial need, other techniques are required.
This research reports a gradual crystallisation or concentration of the seawater. Fundamentally, it could be done based on the difference of NaCl and others contaminant salts solubility. The solubility of CaCl₂, MgCl₂ and NaCl for every 100 mL were 174.0 g, 66.0 g and 38.1 g, respectively [14], [15]. In case of a solution containing those salts, and heated, the lowest solubility salt will be precipitated first. Hence, when the NaCl start to precipitate, as heating of sea water continued, most of CaCl₂ and MgCl₂ still remained in the solution as ions. Thus, this method is expected to be applied in order to produce high-purity industrial-grade NaCl salt. Moreover, the quantitative analysis of the precipitated NaCl was based on the chloride total ion, which was corrected to the calcium and magnesium ion concentration. It was also completed by determination of sulfate ion as for sodium correction. In addition, the first three ions was analysed volumetrically, whereas the sulphate ions concentration was measured spectrophotometrically [16].

EXPERIMENT

Chemicals and instrumentation

The main sample used in this experiment was sea water sample, taken from Nggolonio sea, sub-district of Aesesa, Nagekeo regency, Flores, East Nusa Tenggara. While the chemicals (pro analysis grade) were AgNO₃, K₂CrO₄, BaCl₂, HCl, EDTA, KCN, NaOH, CaCO₃, NaSO₄. The indicator used were Eriochrome Black T (EBT), murexide and methyl red. The instruments used were a UV-Vis Spectrophotometer- Shimadzu 1601.

Procedure of salt production

The sea water was taken of 10 meters off the coast [17]. It was then filtered to remove solid rough impurities and was placed into an airtight polyethylene bottle. Next, this filtered sea water was then filtered off using Whatman No. 41 filter paper to remove the smaller size of solid impurities. After that, the pre-treated sea water was used for the main experiment.

The sea water initial volume used was 200 mL. It was then placed into a beaker glass and heated at 80° C until the final volume was obtained. The variations of final volume were 20, 23, 25, 27, and 29 mL. Afterward, it was cooled for about 30 minutes in a desiccator until the temperature of 42°C was reached. The warm concentrated solution was then filtered off using Whatman No. 41 filter paper. Next, the precipitated salt was dried in an oven at 105°C for 40 minutes, and finally it was cooled down and weighed. The heating, cooling, and weighing procedures were repeated until constant weight was achieved. The dried of a precipitated salt was then kept in a bottle for quantitative analysis.

Procedure for salt analysis

The total chloride ion was analysed argentometrically using 0.1 M AgNO₃, whereas calcium and magnesium ion was analysed by complexometry method using 0.0141 M of EDTA solution. The sulfate anion was analysed as BaSO₄ dispersion, observed using UV-vis spectrophotometry.

XRF analysis

The X-ray fluorescene analysis was undertaken using PANalytical type Minipal 4.0. Sample of salt used were solid.
RESULT AND DISCUSSION

The pre-treated sea water sample was analysed first to determine the contents of calcium and magnesium ion, also the NaCl. The results of pre-treated sea water content are presented in Table 1.

| Chemical composition | Concentration (%-w) | Sea water | Solid salt | Salt reference* |
|----------------------|---------------------|-----------|------------|-----------------|
| Ca^{2+}              | 3.24                | 1.30      | 0.10       |
| Mg^{2+}              | 1.10                | 0.80      | 0.06       |
| NaCl                 | 3.91                | 96.1      | 98.5       |

*The value recorded based on Indonesian National Standard (SNI) number 06-0303-1989

Table 1 showed that the NaCl content in sea water was very low, due to the high-water content. Therefore, in order to reduce the water content as a solvent, the thermal evaporation has to be done. However, the high concentration of calcium and magnesium ion as the contaminant, will reduce the purity of NaCl salt since both salts enable to precipitate, either as chloride or sulphate salts. In fact, the sea water component was very complex, however, except calcium and magnesium, others salts were negligible. Therefore, NaCl purification of sea water in this research was only based and focused on those three salts.

As mentioned above, the difference solubility of main salts could be used as a primary property for component separation [15]. All of the solid produced from variations of final volume was white crystal. The result of quantitative analysis i.e. total chloride ion, calcium and magnesium ions, also sulfate ions was observed as curve in Figure 1 to Figure 4.

![Figure 1. Total Chloride Ions at Final Volume Variation](image-url)

The total chloride ions (Figure 1) show that at the beginning it tends constant, however, it was then decline significantly afterwards. It could be expected that after sodium chloride has been precipitated, mainly up to the final volume of 27 mL, the sulphate ions, either as a sodium and magnesium, were also precipitated. Therefore, the concentration of total chloride was...
decreasing at the final volume of lower than 27 mL. It could be showed at Figure 2, the sulfate ions concentrations were increasing with the lower final volume at the longer concentrating.

![Figure 2. Sulfate Concentration at Final Volume Variation](image)

Salt precipitation occurs when its concentration exceeds the solubility at certain temperature. Moreover, the precipitation took placed rapidly from a supersaturated solution. Therefore, the important factor that have a role against precipitation were salt concentration and temperature. In order to control salt concentration, which correlated with solubility, water removal up to the final volume desired, was done at 80°C. It was then cooled until 42°C. In fact, the precipitation occurred at this condition, salt solubility as a reference was used at the same temperature. [12]. The solubility of several salts in water at 42°C is presented in Table 2.

| Entry | Salts      | Solubility (g/100 mL) |
|-------|------------|-----------------------|
| 1.    | NaCl       | 36.66                 |
| 2.    | Na₂SO₄     | 43.08                 |
| 3.    | MgSO₄      | 46.67                 |
| 4.    | MgCl₂      | 59.31                 |
| 5.    | CaCl₂      | 116.51                |

Based on Table 2, NaCl has the lowest solubility, hence it precipitates first, then was followed by sulfate salts, both sodium and magnesium. Afterward, the two last salts, especially calcium chloride will precipitate when less water remained. Therefore, in this research, quantitative analysis of NaCl was corrected against sulfate ions, then further modified by calculating calcium and magnesium of the chloride salts. The result of calcium and magnesium salts concentration, which has been corrected toward magnesium sulphate, is presented by Figure 3.
In contrary to total chloride curve, the concentration profile for calcium and magnesium increase as the final volume decreasing. Consequently, as a longer concentrating was conducted, the contaminant i.e. magnesium and calcium salts increase. Thus, it results in a lower purity of NaCl. The NaCl produced, corrected to others salts as contaminants, has an identical profile to the total chloride, as shown at Figure 4.

At the beginning, when the final volume was 29 and 27 mL, NaCl purity as well as its concentration was unchanged. However, it was decrease significantly afterward. Comparing to the total chloride, it can be seen that NaCl concentration was decline faster than that of total chloride. Concerning to the rate of precipitation, the concentration can be calculated using curve of salts concentration for each final volume (Figure 5).
In addition, based on the linear trend line of NaCl and chloride curve, slope was indicating the rate of precipitation. Therefore, precipitation rate of NaCl was about three times higher than that of chloride’s. On the other hand, comparing to sulphate and calcium also magnesium, precipitation rate of NaCl was highly faster as determined from Figure 6.

Furthermore, according to the rate precipitation, Table 3 was data compilation to compare each profile of curve. Rate of precipitation express the change of concentration per unit volume. It was then represented in equation profiles as described.

Based on data resulted, it shown that precipitation rate of NaCl was highly faster than calcium and magnesium, either as chloride or sulfate salts. According to salts solubility, it seems that precipitation rate of sulfate salt, mainly came from sodium salt than others. Due to
the reducing of final volume, the low NaCl concentration was obtained. Thus, it was in accordance with the increasing of calcium and magnesium salts precipitated, being a contaminant [18], [14].

Table 3. Profiles of Salt Precipitation Rate

| Salts       | Equation            | Precipitation rate (%)/mL |
|-------------|---------------------|---------------------------|
| NaCl        | $y = 7.1034x -100.66$ | 8.490                     |
| Total chloride | $y = 2.4524x + 12.260$ | 2.452                     |
| Sulfate     | $y = -0.668x + 29.467$ | 0.668                     |
| Ca, Mg      | $y = -0.795x + 29.228$ | 0.795                     |

Moreover, up to the final volume of 29 mL and 27 mL, the precipitated obtained were high sufficient of NaCl concentration. It was a similar concentration of 96.01% and 94.08%, respectively. Even though it was lower than SNI standard i.e. 98.5%, however, the final volume of 29mL was the optimum condition which produced the highest purity of NaCl. The NaCl crystal salt produced was shown in Figure 7. In this condition, both of calcium and magnesium, either as chloride and sulphate salts, largely was ionic molecules that remained in the solution.

Figure 7. The sodium chloride produced (Final volume of 29 mL)

In addition, the composition of salt produced at optimum condition, i.e. the final volume of 29 mL has been determined using XRF. The result was shown at Table 4.
Table 4. The elemental analysis of salt produced at the final volume of 29 mL using XRF

| No | Elements detected in salt | Weight percentage (%) |
|----|--------------------------|-----------------------|
| 1. | Fosfor (P)               | 0.10                  |
| 2. | Sulfure (S)              | 0.30                  |
| 3. | Chlorine (Cl)            | 92.35                 |
| 4. | Potassium (K)            | 0.27                  |
| 5. | Calcium (Ca)             | 3.16                  |
| 6. | Iron (Fe)                | 0.06                  |
| 7. | Copper (Cu)              | 0.04                  |
| 8. | Magnesium (Mg)           | 3.61                  |
| 9. | Molibdhenum (Mo)         | 3.1                   |
| 10.| Bromide (Br)             | 0.01                  |
| 11.| Niodium (Nd)             | 0.50                  |

It can be showed that the NaCl content based on chloride ion was 92.35% and was lower than volumetric determination. Thus, it was in accordance with others ions that undetermined by volumetric analysis.

CONCLUSION

The concentration technique through sea water heating, which based on the salt’s solubility, can improve NaCl salt purity. The longer the concentration or the lower the final volume, it produced lower NaCl purity. The best condition was reached at the final volume of 29 mL even though its purity was still lower than SNI’s standard.

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