Production and optimization of sea salt quality on the coast of Tomini Bay

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Abstract. Tomini Bay is a water area with an area of 59,500 km2. Especially for Gorontalo Province, it has a length of about 436.52 Km. Based on this data, the province of Gorontalo, especially the coast of Tomini Bay, has the potential to be the source of raw material for salt production. Generally, the salt production process goes through various stages of the processes, namely the first evaporation process, the second evaporation process, the concentration process, and the crystallization process. The objective of this research is to obtain pure salt that meets the Standards of SNI. The salt production method used are evaporation and purification with re-crystallization techniques by physical means (using hot water) and chemical methods by the addition of chemicals Ca(OH)2, NaOH, and Na2CO3. The results of this study showed that the obtained salt has NaCl content of 97.04%, Ca 0.55%, and Mg 0.28%. The obtained salt does not meet the salt requirements for SNI standards because there is still a large amount of Ca (SNI=0.10) and Mg (SNI=0.06). However, it meets the type of salt group, namely in category 1 with the best quality that meets the requirements for industrial materials and for consumption.

1. Introduction
Tomini Bay is a water area with an area of 59,500 km2. Especially for Gorontalo Province, it has a length of about 436.52 Km. Based on this data, Gorontalo province, especially the coast of Tomini Bay, has the potential as the raw material source for salt production, it's because the main source of raw material that's good for making salt is seawater. Generally, the salt production process goes through various stages of the processes namely, the first evaporation process, the second evaporation process, the concentration process, and the crystallization process. In the process of salt production, besides salt as the main product, the process also produces crystals of residual liquid called bittern. The quality of salt produced is influenced by the quality of seawater, the process and technology applied. Salt produced in Indonesia generally contains 85-90% of NaCl. This is still below the Indonesian National Standard (SNI) for sodium chloride salt content for human consumption, which is 94.7% (SNI 3556-2016) and 98.5% for industrial salt (SNI 0303-2012). Based on the quality of the salt produced and the salt requirements for human and industrial salt consumption, a process is required for the salt produced to meet the requirements. There are several methods to improve salt quality including physical and chemical methods, physical methods are methods to improve salt quality without the addition of chemicals such as hydro-extraction and evaporation (re-crystallization) methods [1], and chemical methods, which are methods to improve salt quality by the addition of chemicals such as sodium.
carbonate (Na$_2$CO$_3$), sodium hydroxide (NaOH), barium chloride (BaCl$_2$), calcium hydroxide (Ca(OH)$_2$), calcium chloride (CaCl$_2$), etc [2].

The hydro extraction process is the extraction process or separation of components in the solid phase by the liquid phase as a solvent. In this case, salt is the solid phase and the salt solution is the solvent. The performance of the hydro extraction process is influenced by the size of the salt, the concentration of the salt solution as a solvent, and the extraction time [3]. The process of re-crystallization is the process of improving the quality of salt by dissolving it into the water and then re-crystallizing it. The performance of the recrystallization process is affected by temperature, recrystallization time, and resistance to re-crystallization [4].

The application of the hydro-extraction method to improve the quality of salt can remove insoluble materials such as dust, soil, and sand as well as dissolved materials such as magnesium(Mg), calcium (Ca), and sulfate (SO$_4$), but it is difficult to remove impurities in the inner material of the salt because of its large diameter. The hydro extraction process is more effective if the salt size is very small but insoluble, the size of commercial salt found in the market is about 30-50 mesh. The re-crystallization process can remove dissolved materials such as magnesium, calcium, and others due to the formation of crystals, and leaving a small amount of liquid containing sulfate ions such as magnesium sulfate, this is because magnesium sulfate is difficult to form crystals. The standard concentration for consumption salt is 94.7% NaCl in minimum while for industrial salt is 98.5% NaCl, while the SO$_4$ is 0.2% in maximum, Mg 0.06%, Ca 0.1% and H$_2$O 3%.

One of the efforts that can be done to improve the salt quality is through the recrystallization process. Recrystallization is a method of purifying salt by dissolving salt into hot water and then evaporate the obtained solution. Before evaporating the salt solution it is necessary to add an impurity binder to the solution in order to separate the impurities from the salt. This is based on the study of Wisnu and Henry which states that to produce table salt which has NaCl levels above 95% can be done by washing [5].

The washing salt method requires clean salt solution to rinse the salt in order to separate impurities on the surface of the salt. However, this method itself cannot be used to obtain salt with higher purity, this is because this method can only remove impurities on the surface of the salt but can't remove impurities in the salt crystal lattice, thus it is necessary to purify it by crystallization [6]. The process "Na$_2$CO$_3$/NaOH or Na$_2$CO$_3$/Ca(OH)$_2$" is one of the most widely used processes to purify salt solutions that contain Ca$^{2+}$ and Mg$^{2+}$ impurities. In this process, the salt solution is mixed with alkaline metal carbonates such as Na$_2$CO$_3$ to form precipitation of CaCO$_3$. The CaCO$_3$ precipitate then separated from the solution. Then NaOH is added to the solution to form Mg(OH)$_2$. The Mg(OH)$_2$ precipitate is then separated from the solution by a filtration process. To remove the remaining sediment that is still dissolved in the filtrate, the filtrate is passed into the crystallizer. This process is not only used to purify salt solutions from impurities but can also be used to obtain pure sodium chloride salt [7].

The process of crystal formation can be carried out in three stages, namely (1) attainment of supersaturation, (2) formation of a crystal nucleus (nucleation), and (3) growth of crystal nuclei into crystals (crystal growth). Supersaturation is a condition in which the concentration of the solution is above its precipitant solubility value, or as a result of a chemical reaction between two homogeneous phases. The formation of a crystal nucleus occurs after the supersaturation condition is attained [8]. The recrystallization process is related to the precipitation reaction. A precipitate is a substance that separates from the solid phase and comes out into the solution. A precipitate is formed when the solution is too saturated with the related substance. The solubility of a precipitate is the molar concentration of the saturated solution. Solubility depends on temperature, pressure, the concentration of other substances contained in the solution, and the solvent composition [6]. Solids purification by recrystallization is based on differences in their solubility in a particular solvent or a mixture of solvents [9].

The following table 1 is the Indonesian National Standard (SNI 06-0303-1989) for industrial salt:
### Table 1. Indonesian National Standard (SNI 06-0303-1989) for industrial salt.

| Parameter | SNI (%) |
|-----------|---------|
| NaCl (db), min | 98.5 |
| H₂O | 3 |
| Ca (db), max | 0.10 |
| Mg (db), max | 0.06 |
| SO₄ (db), max | 0.20 |

Impurities in salt include compounds that are hygroscopic, namely MgCl₂, CaCl₂, MgSO₄, CaSO₄, and several substances that are reducing agents, namely Fe, Cu, Zn, and organic compounds [10]. In this process, the recrystallization is done by dissolving the salt in distilled water until a saturated salt solution is obtained. The saturated solution then reacted with chemicals, namely Ca(OH)₂ and Na₂CO₃ to form precipitation of CaCO₃ and Mg(OH)₂. The solution is then filtered and the obtained filtrate is evaporated to obtain NaCl crystals. The reaction is as follows:

\[
\begin{align*}
\text{MgSO}_4(\text{aq}) + \text{Ca(OH)}_2(\text{aq}) & \rightarrow \text{Mg(OH)}_2(s) + \text{CaSO}_4(\text{aq}) \\
\text{CaSO}_4(\text{aq}) + \text{Na}_2\text{CO}_3(\text{aq}) & \rightarrow \text{CaCO}_3(s) + \text{Na}_2\text{SO}_4(\text{aq}) \\
\text{MgCl}_2(\text{aq}) + \text{Ca(OH)}_2(\text{aq}) & \rightarrow \text{Mg(OH)}_2(s) + \text{CaCl}_2(\text{aq}) \\
\text{CaCl}_2(\text{aq}) + \text{Na}_2\text{CO}_3(\text{aq}) & \rightarrow \text{CaCO}_3(s) + 2\text{NaCl}(\text{aq})
\end{align*}
\]

Recrystallization is a technique for purifying a solid substance from a mixture of impurities by recrystallizing the substance after being dissolved with a suitable solvent (solvent). The basic principle used is the solubility difference. NaCl is the main component of table salt. The other components are impurities, usually the Ca²⁺, Mg²⁺, SO₄²⁻ ions. These impurities are bound to the solvent, thus they are suspended in the solution and can be separated by filtration.

Recrystallization is the most often used method to purify compounds in solid form. Recrystallization can also be applied in the process of refining salt. Salt recrystallization begins with dissolving the salt using hot water which is then filtered to separate impurities.

### 2. Methods

#### 2.1. Salt production by the evaporation of sea water

Prepare the seawater, and then measure the Be degree. Put the seawater into tubs with various heights (5; 7.5; and 10 cm from the bottom of the tub). Evaporate the seawater with sunlight until salt crystals are produced. Measure the rate of evaporation of seawater until salt forms. Perform the same treatment for different sea levels.

#### 2.2. Total solid analysis

Weigh an empty cup. Take 10 ml of the seawater sample and put it in an empty cup whose weight has been previously known. Evaporate the sample in an oven at 100°C until solid crystals are produced. Cool the salt crystals in a desiccator. Weigh out the salt crystals in a porcelain dish. Repeat the same procedure for different water types.

#### 2.3. Preparation of saturated salt solution

Prepare aquadest in beaker glass. Dry the commercial salt in the oven to remove water content from the salt. Weight about 180 grams of the salt. Dissolve the salt in 500 ml of distilled water until a saturated solution is obtained.
2.4. Crystallization procedure

2.4.1. Using hot water. Prepare the saturated salt solution to be crystallized. Add hot water with temperature variations of 30°C, 60°C, 90°C, and 120°C. Filter the treated solution then evaporate the filtrate in an oven until crystals form. Analyze the concentration of NaCl, Ca, and Mg. Calculate salt solids and salt depreciation.

2.4.2. Using chemicals. Prepare the saturated salt solution to be crystallized. Add Ca(OH)$_2$ and Na$_2$CO$_3$ reagent into the saturated salt solution, then stir until homogeneous. Filter the solution that has been chemically treated. Evaporate the filtrate in an oven until crystals form. Analyze the concentration of NaCl, Ca, and Mg. Calculates the number of salt solids and salt depreciation. With the following formula:

\[
x = \frac{M_2}{M_1} \times 100
\]

Salt Shrinkage = 1-x
Where:  
M1 = The sample period before crystallization  
M2 = sample mass after crystallization

3. Results and discussion

3.1. Sea water evaporation rate

In this study, the aim of this research is to determine the effect of various sea levels on the seawater evaporation rate. The process carried out was the evaporation of seawater at different heights with the help of heating. Evaporation under the sun can't be done due to conditions that were not possible or the rainy season. Observations were made every two (2) hours until crystals formed. The result can be seen in the following figure 1.

![Figure 1. Evaporation of Sea Water every two hours.](image)

Based on Figure 1, it can be seen that at a sea level of 5 cm, the time needed to obtain the salt crystals is 10 hours, at a height of 7.5 cm takes 14 hours and with a height of 10 cm takes 16 hours. From this data, it can be concluded that the average decrease in sea level is around 1-2 cm/2 hours, where the higher the altitude the longer it takes for the evaporation process to form salt crystals.

3.2. Salt recrystallization process

Recrystallization is the most often used method to purify compounds in solid form. Recrystallization can also be applied in the process of refining salt. Salt recrystallization begins with dissolving the salt...
using hot water which is then filtered to separate impurities. The results of recrystallization by using hot water can be seen in Figure 2.

![Figure 2. Hot water temperature variation to NaCl levels.](image)

Based on Figure 2, it can be seen that at the water temperature of 30°C the NaCl content is 74.82%, at the water temperature of 60°C the NaCl content is 79.50%, at the water temperature of 90°C the NaCl content is 84.18%, and at the water temperature of 120°C the NaCl content is 90.02%. Based on these data, it could be concluded that the NaCl content in salt increases as the water temperature used increased. The result of Ca and Mg content after recrystallization based on temperature variation can be seen in table 2 below.

| No | Component | Concentration (%) |
|----|-----------|-------------------|
| 1  | Ca        | 0.87              |
| 2  | Mg        | 2.74              |

Based on table 1 above, the obtained salt still contains a lot of Ca and Mg impurities. The SNI 06-0303-1989 standard for Ca and Mg ion is 0.1% and 0.06% respectively. To further purify the salt, the crystallization process is needed by using impurity binders, namely Ca(OH)$_2$ and Na$_2$CO$_3$.

In this recrystallization stage, impurities contained in the crystal will be released from the crystal due to salt dissolving. Furthermore, the recrystallization process has high selectivity, thus the amount of impurities remain in the resulting crystal is quite small.

In order to improve the quality of salt by using the recrystallization method, reagents are added to the saturated solution, namely Ca(OH)$_2$ and Na$_2$CO$_3$. The addition of these reagents is carried out to obtain salt that meets the requirements as an industrial raw material. This reagent serves to bind impurities in the form of Ca$^{2+}$ and Mg$^{2+}$ ions. These ions are the biggest impurities contained in seawater. The presence of these impurities causes the salt product obtained to have fairly low NaCl content.

The NaCl, Ca, Mg content in the salt sample obtained from the recrystallization process can be known from the analysis result. NaCl levels were analyzed using the argentometric titration method, while Ca and Mg levels were analyzed using AAS.

This recrystallization process is expected to reduce and eliminate impurities in the salt sample. Most of the impurities in the sample are Ca and Mg compounds and physical impurities in the form of sludge trapped in salt crystals. The salt impurities in the form of sludge cause the salt to appear brown. The Ca and Mg impurities make the salt taste more bitter [10]. After the recrystallization, the obtained
salt was appear whiter in color and cleaner than before. The following is the result of reagent variations and the percentage of NaCl levels:

![Figure 3. Variation of reagent volume against NaCl Levels.](image)

Based on Figure 3, it could be seen that in the recrystallization stage the addition of reagents with 15%, the impurity content can be further reduced to small enough value, thus salt with greater NaCl content is obtained.

This research was carried out by adding 15% w of Na$_2$CO$_3$ solution into NaCl solution where the volume was varied. After the addition of Na$_2$CO$_3$, the solution was allowed to react for 45 minutes to form CaCO$_3$ and MgCO$_3$ precipitates, after that, the Ca(OH)$_2$ solution was added and the solution was allowed to react. The addition of 15% w of Na$_2$CO$_3$ was aimed to remove Ca$^{2+}$ impurities as CaCO$_3$ and Mg$^{2+}$ as MgCO$_3$. The addition of Ca(OH)$_2$ solution can also increase the removal of Mg$^{2+}$ impurities to form Mg(OH)$_2$ precipitate. The result on the salt purification process for variations in the addition of the volume of 15% w of Na$_2$CO$_3$ per 10 mL of the salt solution is shown in the following table 3:

| No | Component | Concentration (%) |
|----|-----------|-------------------|
| 1  | NaCl      | 97.04             |
| 2  | Ca        | 0.55              |
| 3  | Mg        | 0.28              |

From the analysis of table 3 above, the addition of 2.5 mL of Na$_2$CO$_3$ solution shows that the content of NaCl is 97.04%, Ca 0.55%, and Mg 0.28%. The obtained results did not meet the SNI standards due to the large content of Ca and Mg. However, the obtained salt has entered the K-1 type of salt, which is the best quality that meets the requirements for industrial materials and for consumption with the following composition: NaCl: 97.46%, CaCl$_2$: 0.723%, CaSO$_4$: 0.409%, MgSO$_4$: 0.04%, H$_2$O: 0.63%, Impurities: 0.65%.

4. Conclusion

Based on the analysis result of the research that has been carried out, the following conclusions can be drawn:

- Preparation of high purity salt can be done by heating either with the help of sunlight or by using fuel. The refining process can be continued with crystallization by using chemicals.
The results of salt recrystallization obtained are 97% NaCl, 0.55% Ca and 0.28% Mg. The obtained salt does not meet the salt requirements for SNI standards due to the high content of Ca and Mg. However, it is sufficient for industrial raw materials as well as for consumption.

References

[1] M G R 2000 Sodium chloride: Crystallization (Academic Press)
[2] Rahman A, Islam A and Farrukh M A 2010 Preparation of analytical grade sodium chloride from khewra rock salt World Appl. Sci. J. 9
[3] Langer H and Offermann H 1982 On the solubility of sodium chloride in water J. Cryst. Growth 60 389–92
[4] Turk L J 1970 Evaporation of brine: a field study on the Bonneville Salt Flats, Utah Water Resour. Res. 6 1209–15
[5] Wisnu B and Kusumayanti H 2006 Perbaikan proses iodisasi garam dengan sistem injeksi di Kabupaten Pati Gema Teknol. 15 78–80
[6] Schimdt J-H, Meirhofer W and Schwaiger H 2009 Process Optimization of Brine Purification and Evaporation for Combined Crystallization of NaCl and Na2SO4 by Means of Mechanical Vapour Recompression 9th Int. Symp. Salt.
[7] Lesdantina D 2009 Pemurnian Nacl Dengan Menggunakan Natrium Karbonat
[8] Paryanto I 2000 Pengaruh Penambahan Garam Halus pada Proses Kristalisasi Garam Farmasetis J. Sains dan Teknol. Indones. V2 9
[9] Anwar C, Bambang P, Harno D P and Titik D W 1994 Pengantar Praktikum Kimia Organik Univ. Gajah Mada, Yogyakarta
[10] Saksono N 2002 Studi pengaruh proses pencucian garam terhadap komposisi dan stabilitas yodium garam konsumsi Makara J. Technol. 6 146706