

Article

Enhancing Salt Purification in Oli'o Village, East Nusa Tenggara: A Case Study on Optimizing Precipitating Agent Addition Methods and Salinity Levels

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Abstract. The East Nusa Tenggara province holds significant potential as a contributor to Indonesia's national salt production. However, salt production in this area often needs to meet quality standards due to the high presence of impurities, such as calcium, magnesium, and sulfate. The limitations in technology and salt purity in Indonesia necessitate the country to import high-quality salt. This research aims to develop and enhance the purity of NaCl in the salt production of Oli'o Village through the addition of chemical substances. The method employed to improve salt purity is the precipitation method, utilizing precipitants Na_2CO_3 , NaOH , and BaCl_2 to precipitate calcium, magnesium, and sulfate impurities. The primary research involved adding precipitants in a 1:1 stoichiometric ratio and stirring for 45 minutes. Experimental variables encompassed the method of precipitant addition and salinity levels (16, 20, 23, 25 °Be). The analysis of impurity concentrations before and after the addition of precipitants was conducted through complexometric titration for calcium and magnesium, argentometric titration for NaCl, and turbidimetry for sulfate. The research reveals that the direct addition of the three precipitants yields the best results. In terms of salinity variations, it is observed that salinity at 16 °Be provides the highest purity compared to other salinity levels. The increase in salinity enhances impurity concentrations, decreasing the impurity removal percentage's effectiveness.

Keywords: Precipitant addition, precipitation, purity, salinity, salt.

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1. Introduction

Indonesia, as an archipelagic nation, holds significant potential in salt production. The East Nusa Tenggara province has emerged as an auspicious location for high-quality salt production due to its prolonged dry season lasting for 9 to 10 months with minimal rainfall. However, despite this potential, Indonesia still imports salt to meet its domestic needs, especially for high purity salt. It is due to the fact that salt production has not yet been able to achieve industrial quality. According to data from the Central Statistics Agency (2024), Indonesia imports over 2.5 million tons of salt annually from 2017 to 2023, as observed in Fig. 1 [1]. This is due to the limited availability of locally produced salt that meets industrial quality standards. Indonesian National Standards stipulate that industrial salt must have high purity, with a minimum NaCl content of 98.5% [2]. With population growth and technological advancements, the demand for salt is expected to continue rising. However, local salt quality often fails to meet industrial standards due to its low NaCl content, posing a significant challenge in meeting salt needs independently.

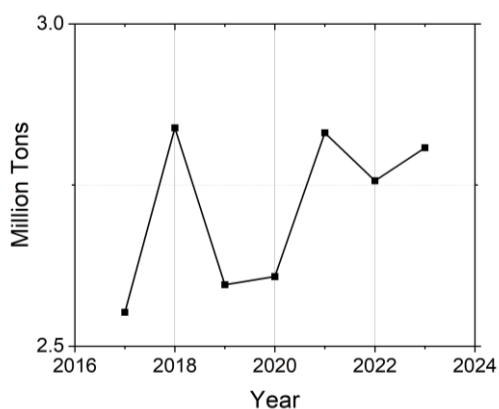


Fig. 1. Salt Import Data From 2017-2023 [1].

Salt, known as sodium chloride (NaCl), is an ionic compound with a 1:1 ratio of sodium ions to chloride ions [3]. In Indonesia, most salt production still employs conventional methods by evaporating seawater in evaporation ponds to increase its salinity with the assistance of solar energy [4]. The function of these evaporation ponds is to precipitate impurities present in seawater, such as calcium carbonate (CaCO_3) and gypsum [5]. However, this method is still too rudimentary to produce salt of the quality required by industrial standards.

The quality of salt is closely related to its NaCl content. The higher the NaCl content, the lower the impurities, making the salt purer. Common impurities found in salt solutions include magnesium chloride (MgCl_2), calcium carbonate (CaCO_3), magnesium sulfate (MgSO_4), and other compounds [6]. These contaminants must be kept within quality standards as they can cause serious issues, such as calcium ion (Ca^{2+}) impurities leading to calcium buildup in pipelines, which is difficult and costly to remove [7]. Additionally, these ions can be

harmful to human health if consumed in excess. Excess calcium ions can increase the risk of prostate cancer [8]. Meanwhile, although the kidneys can eliminate excess magnesium ions, continuous overconsumption can lead to diarrhea, nausea, and abdominal cramping [9]. Therefore, contaminants in this salt can be extremely dangerous for both human health and industrial processes.

Improving salt quality can be achieved through various methods, such as hydroextraction, recrystallization, or adding chemicals. Recrystallization is a purification method involving dissolving salt in hot water and then evaporating the solution to obtain purer salt. This process is influenced by temperature, time, and crystallization stages [10]. On the other hand, hydroextraction is a solid-liquid extraction process where salt is the solid phase. This purification process is influenced by salt size, solution concentration, and extraction time [11]. According to previous research, the purification process through recrystallization can produce salt with a NaCl content of 97.04% [10]. In contrast, the hydroextraction method yields a NaCl content of 99.34% [11]. Both methods can achieve high levels of purity. However, the drawback of the recrystallization process is its high energy requirement, while the hydroextraction method necessitates a saturated salt solution, which is difficult to obtain and high operational cost.

Another method to improve salt quality is by adding chemicals to seawater. The addition of NaOH can remove magnesium chloride (MgCl_2) and magnesium bromide (MgBr_2) impurities by forming precipitates of $\text{Mg}(\text{OH})_2$ [12]. Similarly, calcium ion (Ca^{2+}) impurities can be removed by adding Na_2CO_3 , forming precipitates of CaCO_3 [13], while sulfate ion (SO_4^{2-}) impurities can be precipitated as barium sulphate (BaSO_4) with the assistance of barium chloride (BaCl_2) [14]. The precipitation of all these impurities is based on their solubility and the use of chemicals such as Na_2CO_3 , NaOH, and BaCl_2 as precipitating agents is based on the theory of the similar ion effect, where all these precipitating agents contain Na^+ and Cl^- ions, which can increase the concentration of NaCl in seawater [15].

Previous studies typically focused on purifying salt that had already been produced, using precipitating agents such as NaOH, Na_2CO_3 , and BaCl_2 during the final purification stage. Most studies only assessed the effects of precipitating agents on existing salt and did not consider the impact of seawater salinity during the production process. In contrast, this research used seawater directly in the salt production process and investigated how the addition of precipitating agents and variations in salinity affected the quality of the produced salt.

This research was focused on improving the quality of salt by adding chemicals as precipitants in Oli'o Village, Kupang ($10^\circ 04' 36''$ South Latitude and $123^\circ 46' 21''$ East Longitude). Previously, salt production in the village relied solely on conventional methods with

purification using recrystallization. However, the salt produced has a quality below 90%, far below the established standards, and requires a significant amount of energy while also generating air pollution in the process. So far, salt farmers in Oli'o Village had relied only on practical experience, not theoretical knowledge. Therefore, to implement a chemical precipitation method that was faster, more efficient, and environmentally friendly compared to recrystallization, a study on seawater samples in Oli'o Village was needed.

Table 1. Standard for Industrial Salt.

No	Parameter	Concentration (%)
1	NaCl	Min 98.5
2	SO ₄ ²⁻	Max 0.2
3	Mg ²⁺	Max 0.06
4	Ca ²⁺	Max 0.1
5	H ₂ O	Max 3

Specifically, this research investigated methods of precipitating agent addition and seawater salinity levels on the quality of the resulting salt, especially in reducing impurity levels of Ca²⁺, Mg²⁺, and SO₄²⁻ ions. It was hoped that the results of this research could optimize industrial processes and ensure salt production of high quality in accordance with national standards for the salt industry. Additionally, this research was also expected to make a significant economic contribution to the East Nusa Tenggara Islands, particularly Oli'o Village. The objective of this research is to meet national standards for the salt industry as listed in Table 1.

2. Research Methods

2.1. Materials

The primary material used for this research is seawater (5 ‰) from salt ponds, presented in Fig. 2 and Fig. 3, originating from Oli'o Village, Kupang. The precipitating agent used for purification is analytical grade chemicals with the brand Merck, including sodium carbonate (Na₂CO₃), sodium hydroxide (NaOH), and barium chloride (BaCl₂). The materials for analysis include analytical grade chemicals with the brand Merck, such as Ethylenediaminetetraacetic acid (EDTA), ammonium chloride (NH₄Cl), ammonia solution (25%), magnesium chloride hexahydrate (MgCl₂·6H₂O), Eriochrome black T, murexide, ethanol (95%), silver nitrate (AgNO₃), potassium chromate (K₂CrO₄), acetic acid (CH₃COOH 99%), and distilled water.

2.2. Research Procedure

In this study, seawater was heated using an electric stove to elevate its salinity to a specific ‰ level according to the research variations, namely 16, 20, 23, and 25. To increase the salinity of seawater, a temperature of 100 °C was used to evaporate the water. This range of salinity was chosen because the salt precipitation process is more efficient at these levels. If a

lower salinity, such as raw seawater with a salinity of around 3 ‰, were used, the salt concentration in the seawater would still be very low. This process would be highly inefficient, as a significantly larger volume of seawater would be required to produce the same amount of salt. If this range of salinity were altered, the purification process using precipitating agents would have different effects, especially if the salinity level were under 16 ‰.

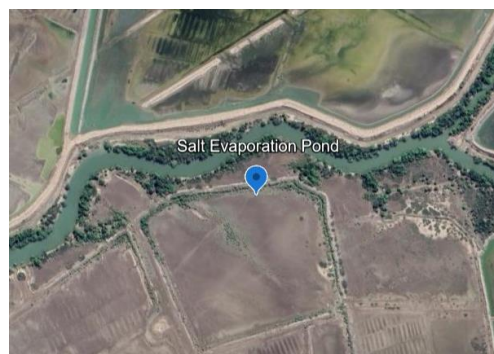


Fig. 2. Research Area Location.



Fig. 3. Sampling Area Location.

Once the desired salinity was reached, the seawater was then cooled to room temperature. Following the cooling process, an initial quantitative analysis of impurities, including ion Ca²⁺, Mg²⁺, SO₄²⁻, and NaCl, was conducted. Subsequently, a precipitating agent is added to the seawater to purify the salt through precipitation. The added precipitating agent maintains a stoichiometric ratio of 1:1 with the initial impurities and was stirred for 45 minutes at a speed of 400 rpm. The stirring time of 45 minutes was selected because under these conditions, optimum precipitation can be achieved, as demonstrated by previous research. The 1:1 ratio for precipitation was chosen to ensure that the precipitation reaction occurs optimally. Theoretically, this ratio is sufficient to bind the ions present without leaving excess precipitating agents, which could cause additional impurities. Using a 1:1 ratio also minimizes the excessive use of chemicals and reduces costs.

After that, a quantitative analysis of impurities (Ca²⁺, Mg²⁺, SO₄²⁻, and NaCl) in their liquid phase was carried out. The final step involved evaporating seawater from each concentration to form salt. Initially, the purified solution was heated until a salt precipitate formed. Then,

this salt precipitate was collected and heated in an oven until dry salt was obtained. The salt was heated in an oven at 105 °C to ensure all the water evaporated. This procedure can be seen in Fig. 4. These salts were analyzed using the same method to identify the content of ions Ca^{2+} , Mg^{2+} , SO_4^{2-} , and NaCl .

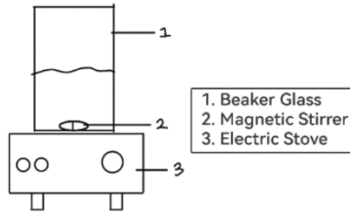


Fig. 4. Procedure for Salt Evaporation.

In addition to the salinity variations of 16, 20, 23, and 25 °Be, this study also includes variations in the methods of adding precipitating agents. Three methods of adding precipitating agents have been implemented, as follows:

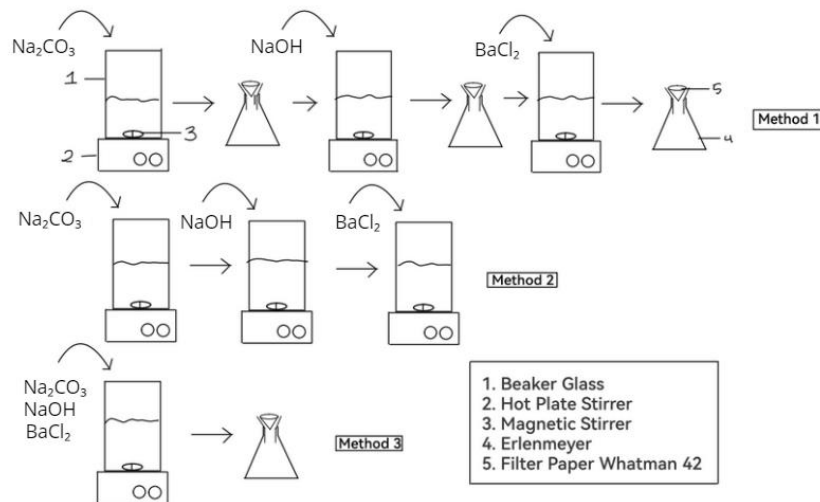


Fig. 5. Illustrations for The Three Methods.

2.3. Procedure for Seawater and Salt Sample Analysis

In this study, two main analytical methods were employed: titration and spectrophotometry, as shown in Fig. 6. A complexometric titration was performed to analyze impurities of Ca^{2+} and Mg^{2+} ions, using a 0.025 M EDTA solution. For this analysis, 1 mL of the sample was pipetted into an Erlenmeyer flask, followed by the addition of 10 mL of buffer solution, 49 mL of distilled water, and 2-3 drops of Eriochrome Black T (Ebt). The mixture was then titrated with 0.025 M EDTA until the indicator turned blue, with the volume of EDTA used being noted. This procedure was carried out in triplicate.

To further assess the sample, the total calcium ion content was determined by pipetting 1 mL of the sample into an Erlenmeyer flask, then adding 49 mL of distilled water and 1-2 mL of 1 N NaOH to adjust the pH to 12-

In the first method, chemical additions were done one at a time, with filtration after each addition. The sequence was as follows: Na_2CO_3 is added first, stirred for 45 minutes, and then filtered. Next, NaOH was added, stirred for 45 minutes, and filtered. Finally, BaCl_2 was added, stirred for 45 minutes, and filtered. After this process, the final solution was analyzed.

In the second method, chemical additions were still done one at a time, but without filtration between each addition. The process was as follows: Na_2CO_3 was added first and stirred for 45 minutes, followed by the addition of NaOH , which was stirred for 45 minutes, and finally, BaCl_2 was added and stirred for 45 minutes. After all three precipitating agents were added, the solution was filtered and analyzed.

In the third method, all precipitating agents (Na_2CO_3 , NaOH , and BaCl_2) were added simultaneously and stirred for 45 minutes. After the stirring process was complete, the solution was filtered and a final analysis was conducted. For a more detailed explanation, see the illustration in Fig. 5.

13. The mixture was allowed to stand for 5 minutes with occasional stirring, until no more $\text{Mg}(\text{OH})_2$ precipitate formed. Following this, 30-50 mg of murexide was added to the solution, which was then titrated with 0.025 M EDTA until the color changed from pink to purple. The volume of EDTA used was recorded.

For sulfate analysis, 50 mL of the sample was pipetted into a 250 mL Erlenmeyer flask, where 20 mL of buffer solution was introduced. The mixture was stirred at a constant speed for 60 seconds while 0.2 to 0.3 grams of BaCl_2 was added. After 5 minutes, the sample was measured using a spectrophotometer at a wavelength of 420 nm. This analysis was performed in triplicate.

Finally, total chloride ions were quantified through argentometric titration using a 0.1 M AgNO_3 solution. To analyze NaCl content, the seawater sample was filtered to remove any solids. Then, 1 mL of the sample was transferred into a 250 mL Erlenmeyer flask and

diluted with 59 mL of distilled water. Following this, 1 mL of 0.25 M K_2CrO_4 was added as an indicator, and the solution was titrated with 0.1 M $AgNO_3$ until an orange color appeared. The volume of 0.1 M $AgNO_3$ used was recorded, and the test was repeated three times for accuracy.

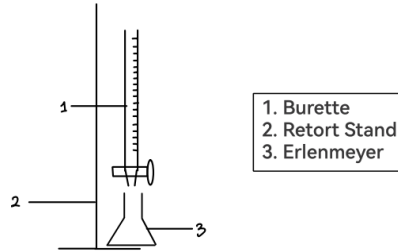


Fig. 6. Illustration of The Setup for Analysis Ca^{2+} , Mg^{2+} , and NaCl.

3. Results and Discussion

3.1. Characteristics of Seawater in Oli'o Village, Kupang City

The characterization of seawater varies across different regions despite its apparent uniformity. The composition of seawater can change depending on environmental conditions such as proximity to industrial discharge points, sea level, seawater temperature, ocean currents, algal growth, and various other parameters [16]. Therefore, an initial analysis of seawater characteristics is conducted to understand the specific composition of each location. This analysis is essential to determine the most effective purification methods and ensure the final product quality meets industrial standards. To calculate the ions present in seawater, calculations were performed according to the Eq. (1) – Eq. (4) below.

$$[Ca^{2+}] = \frac{1,000 \times V_{EDTA} \times [EDTA] \times (AW_{Ca^{2+}})}{V_{sample}} \quad (1)$$

$$[Mg^{2+}] = \frac{1,000 \times V_{EDTA} \times [EDTA] \times (AW_{Mg^{2+}})}{V_{sample}} \quad (2)$$

$$[NaCl] = \frac{1,000 \times V_{AgNO_3} \times [AgNO_3] \times (MW_{NaCl})}{V_{sample}} \quad (3)$$

$$[SO_4^{2-}] = \frac{\text{Absorbance}}{\text{Standard curve constant}} \times \text{Dilution} \quad (4)$$

where

- V = Volume (ml)
- [EDTA] = EDTA concentration (M)
- AW = Atomic weight (g/mol)
- [$AgNO_3$] = $AgNO_3$ concentration (M)
- MW = Molecular weight (g/mol)
- Standard curve constant = 0.0045

Table 2. Seawater Characterization.

Component	Concentration (mg/L)	%w/v
Ca^{2+}	696.5 ± 58.3	2.72
Mg^{2+}	$1,648.5 \pm 108,2$	6.45
SO_4^{2-}	$2,888.9 \pm 251.5$	11.31
Cl^-	$20,336.0 \pm 386,1$	79.53

From Table 2, the initial characteristics of seawater in the village of Oli'o show a high level of impurities and a NaCl percentage below 80%. Therefore, to increase the salt content, a purification process involving additional chemicals is necessary. This process aims not only to remove other impurities but also to add sodium (Na^+) and chloride (Cl^-) ions to the seawater. Thus, the chemicals used are Na_2CO_3 , $NaOH$, and $BaCl_2$, which can add these ions. Additionally, sulfate ions are the largest impurities compared to others. Previous research has shown that excessive consumption of sulfate by the human body can cause several health issues, such as diarrhea, dehydration, and gastrointestinal disorders [17]. Therefore, special attention is needed to address these sulfate ions.

To ensure further verification, the salt commonly produced by salt farmers in this village also underwent analysis. The analysis results yielded the composition of salt as listed in Table 3.

Table 3. Salt Characterization in Oli'o Village.

Component	%w/w
Ca^{2+}	$0.150 \pm 0,07$
Mg^{2+}	0.970 ± 0.205
SO_4^{2-}	1.344 ± 0.726
NaCl	88.110 ± 2.154
Other	9.430

From the table, it can be inferred that the primary composition of salt, namely NaCl, still exhibits low quality with a salt purity (NaCl) of only 88.11%. Additionally, although the salt produced from seawater contains impurities such as Ca^{2+} , Mg^{2+} , and SO_4^{2-} , which are relatively small in quantity, these impurities still exceed the industry standards listed in Table 1. The salt produced by these salt farmers also contains 9.43% of unknown compounds. These unknown compounds could be caused by two factors: insoluble solids and minerals other than Ca^{2+} , Mg^{2+} , SO_4^{2-} , and NaCl ions. The presence of insoluble solids can be attributed to contamination during the production process, such as dust or sand. Furthermore, insoluble solids can also originate from minerals such as calcium carbonate ($CaCO_3$) or magnesium hydroxide ($Mg(OH)_2$) that form and do not fully dissolve.

3.2. The Influence of Precipitating Agent Addition Methods

In the research concerning the impact of precipitating agent addition methods, the sample salinity is set at 16 ‰. Once reaching 16 ‰, the sample

undergoes the initial analysis phase, where the analysis result is presented in Table 4. The analysis is conducted on its liquid phase, yielding %w/v for Ca^{2+} , Mg^{2+} , SO_4^{2-} , and Cl^- ions. Since the analysis is focused on the liquid phase, the obtained percentage results are assumed to only encompass the presence of Ca^{2+} , Mg^{2+} , SO_4^{2-} , and Cl^- ions in seawater.

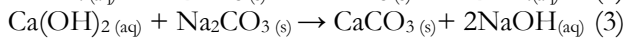
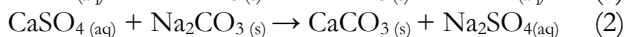
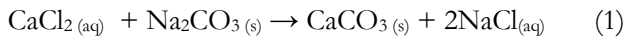
Table 4. Results of Initial Analysis of 16 °Be Seawater.

Component	Concentration (mg/L)	%w/v
Ca^{2+}	1,155.778 ± 89.090	0.61
Mg^{2+}	7,051.884 ± 40.913	3.73
SO_4^{2-}	8,777.778 ± 145.185	4.64
NaCl	171,990.0 ± 3583.3	91.01

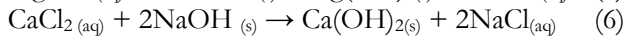
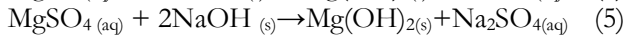
This initial analysis is carried out to determine the amount of precipitating agent to be added. The added precipitating agent was stoichiometrically 1:1 with the impurities obtained from Table 4.

After determining the amount of precipitating agent to be added, the purification process was carried out according to the variations previously described. The reactions that occurred for each addition of precipitating agents are shown in the following reaction equations (Eq. (1)-(7)) [15]:

Addition of Na_2CO_3



Addition of NaOH



Addition of BaCl_2



From the three methods, a comparison was conducted for each of their final results. Each method yields different final values, as evident in Table 5.

Table 5. The Final Comparison Results of the 3 Methods in the Liquid Phase.

Component	%w/v	%w/v	%w/v
	Method 1	Method 2	Method 3
Ca^{2+}	0.050	0.050	0.010
Mg^{2+}	0.540	0.590	0.110
SO_4^{2-}	0.810	0.020	0.004
NaCl	98.610	99.340	99.870

Table 5 indicates that Method 3 shows a more significant decrease in the values of Ca^{2+} , Mg^{2+} , and SO_4^{2-} ions compared to the other two methods. Method 3 involves the direct mixing of the three precipitating agents. Therefore, by simultaneously mixing, this method can potentially trigger more complex reactions compared to the other methods used.

Figure 7 illustrates the significant differences in results for Method 3, where it can eliminate a considerable number of impurities, specifically Ca^{2+} , Mg^{2+} , and SO_4^{2-} ion. The percentage of removal in Method 3 almost reaches 100%, which is significantly higher than that of the other two methods. From this graph, it can be concluded that the direct mixing of the three precipitating agents does not cause side effects but still effectively functions individually to reduce impurity levels.

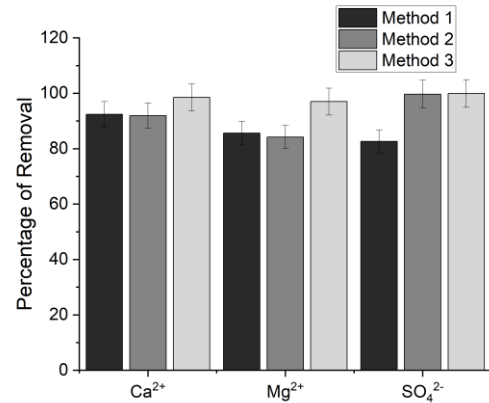
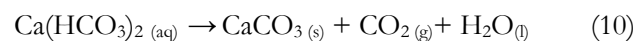
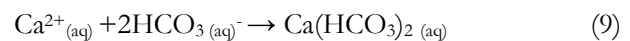


Fig. 7. Results of the Percentage of Impurities Removal.

The observed phenomenon in Fig. 7 indicates that the reduction percentage of Ca^{2+} ions in Method 3 reaches 98%. This drastic decrease may be attributed to the highly alkaline conditions resulting from adding NaOH. With the addition of a strong base, the solution of seawater pH can reach the range of 12-14, significantly higher than the addition of Na_2CO_3 , which is a weak base. At pH 13.4, almost all carbonate ions are in the form of CO_3^{2-} , while at pH 9, bicarbonate ions (HCO_3^-) still dominate, with an $\text{HCO}_3^-/\text{CO}_3^{2-}$ ratio of about 10:1 [18]. The experimental conditions referenced in the citation involve mixing CaCl_2 and NaHCO_3 at a temperature of 0 °C with pH variations 9 and 13.4. Therefore, the addition of NaOH as a strong base in Method 3 makes the CO_3^{2-} ion dominant, and the reactions that occur can be outlined as follows [19]:



Meanwhile, in the presence of bicarbonate ions, the reaction that occurs is:



From the two reactions above, it can be concluded that to form solid CaCO_3 , only one molecule of carbonate ion (CO_3^{2-}) is sufficient, while bicarbonate ion (HCO_3^-) requires two molecules. Therefore, with an increase in the number of CO_3^{2-} ions at high pH in the solution, more CaCO_3 precipitates are produced. This provides a logical explanation for why Method 3, with the high pH resulting from adding NaOH, shows a significant decrease in Ca^{2+} ion levels compared to

Methods 1 and 2. In methods 1 and 2, Na_2CO_3 is added first, and the resulting pH ranges between 11 and 12. However, in method 3, all chemicals are added simultaneously, and it raises the pH to around 13 to 14. Thus, the significant increase in pH due to the addition of NaOH in Method 3 can be considered a key factor that leads to high efficiency in reducing Ca^{2+} ion levels.

In addition to the greater reduction in Ca^{2+} ion levels in Method 3, there is a significant increase in the percentage reduction of Mg^{2+} ions, reaching the highest value of 96% in this method, as seen in Fig. 7. This substantial increase may be attributed to the dominance of CO_3^{2-} ions in the solution. Previous research indicates the formation of $\text{CaMg}(\text{CO}_3)_2$ precipitates when Na_2CO_3 precipitating agents are added to seawater, which can be identified through XRD [20].

To verify whether dolomite has indeed formed, this study conducted XRD (X-Ray Diffraction) analysis on the precipitate formed after the purification process. Prior to the analysis, the precipitate was dried first. The X-ray diffraction measurements in Fig. 8 confirm that the sample contains deposits such as CaCO_3 , $\text{Mg}(\text{OH})_2$, BaSO_4 , NaCl, and dolomite. Therefore, the formation of dolomite becomes a crucial factor in this seawater purification process. Dolomite precipitated spontaneously if the mixed solution contains magnesium, calcium, and carbonate ions in a ratio of 1:1:2 [21]. As explained earlier, the high pH resulting from simultaneous addition in Method 3 makes carbonate ions more dominant. This high carbonate alkalinity facilitates faster dolomite formation [22]. Hence, the reduction in Mg^{2+} ion levels in Method 3 can be more significant than other methods because it can form $\text{Mg}(\text{OH})_2$ and $\text{CaMg}(\text{CO}_3)_2$ precipitates.

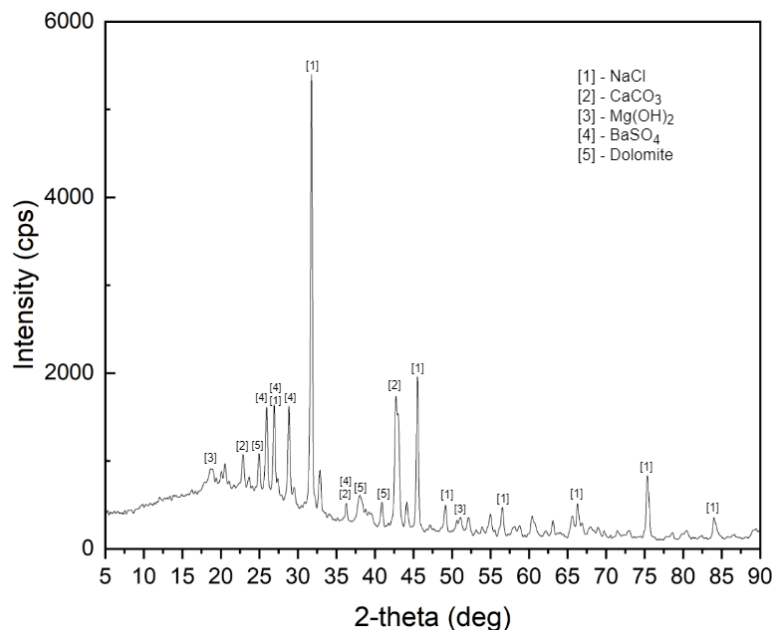


Fig. 8. XRD pattern of the precipitate formed after the addition of the three precipitating agents.

Finally, regarding the percentage reduction of sulfate ions, there is a tendency almost similar to Method 2, as depicted in Fig. 7. The contributing factors can also be considered akin to Method 2 due to the elevated pH conditions. In Method 3, the simultaneous addition of BaCl_2 to seawater with NaOH causes the solution's pH to become basic. At high pH, especially above 10, the presence of hydroxyl ions (OH^-) restricts the movement of water around OH^- ions. Consequently, water becomes more mobile around Ba^{2+} and SO_4^{2-} ions. This enhances the likelihood that barium ions would easily bind to the surface of BaSO_4 and form the first nuclei. As a result, a significant increase in the rate of 2D nucleation can be observed under high pH conditions [23]. Therefore, more BaSO_4 precipitates are formed due to the high nucleation rate. However, the rapid nucleation rate formation leads to small particle sizes.

After comparing all the tested methods, it can be concluded that Method 3 is the best choice for salt

purification based on the experimental data of percent of removal of impurities that can be eliminated. Furthermore, it can be seen from Fig. 9 that the purity of NaCl salt achieved by Method 3 is the highest, exceeding 99.5%. Not only does Method 3 yield high purity, but it also has the advantage of using direct mixing of the three precipitating agents, making it highly practical for implementation in real-life situations due to its simple yet effective process in reducing impurity levels. For Method 1, which involves filtration, there is a drawback as it is difficult to filter, especially since precipitate particles like $\text{Mg}(\text{OH})_2$ and BaSO_4 often pass through filter paper. Therefore, Method 3 is chosen as the primary method for addressing salinity variation.

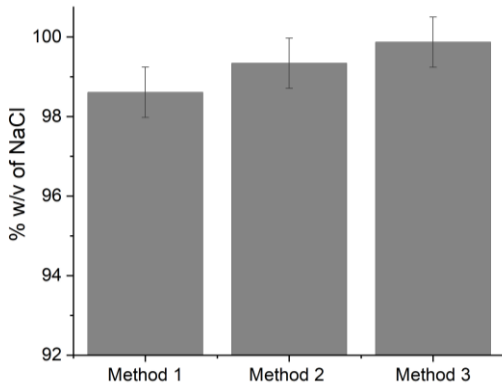


Fig. 9. The Purity of Salt in the Three Methods.

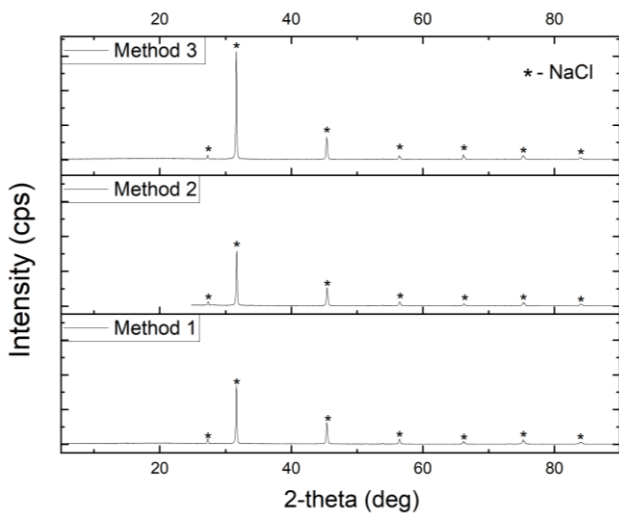


Fig. 10. XRD Comparison of Salt Samples Three Methods.

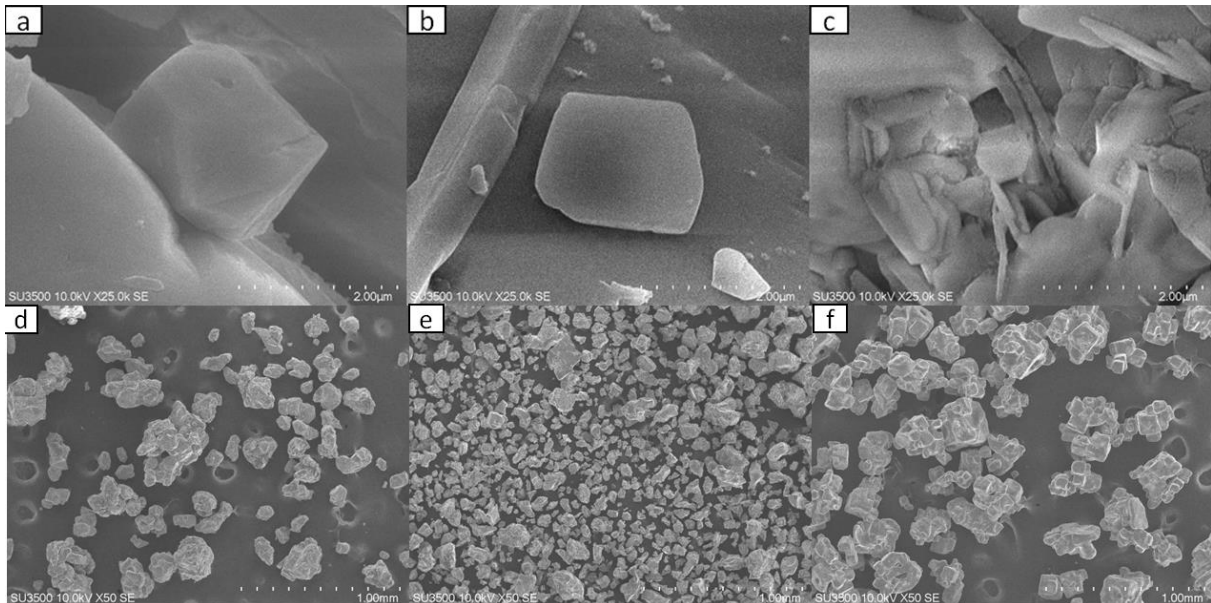


Fig 11. Scanning Electron Microscope (SEM) Results of Salt Samples for Three Methods: (a) Method 1 25,000x magnification; (b) Method 2 25,000x magnification; (c) Method 3 25,000x magnification; (d) Method 1 50x magnification; (e) Method 2 50x magnification; (f) Method 3 50x magnification.

In this study, to compare with conventional methods, analysis was also conducted using XRD and SEM instruments, as shown in Fig. 10 and Fig. 11. The XRD results indicate that the consistent peak positions across the three methods suggest the formation of the same crystal phase, NaCl. The findings of this study align with the reference data from JCPDS 78-0751, where NaCl has peaks at 27.42° , 31.76° , 45.54° , 56.59° , 66.37° , 73.23° , and 84.19° [24]. This confirms that each method successfully produced high-purity NaCl, with no impurities detected in the salt.

Based on the SEM results, it can be observed that the NaCl crystals produced from Method 1, Method 2, and Method 3 have a similar structure, which is cubic. This structure is consistent with the characteristics of pure NaCl. At 50x magnification, Method 3 shows a clearer crystal shape. Although the cubic form is not distinctly visible in Method 1 and Method 2 at low magnification (50x), at higher magnification (25,000x), the cubic shape of NaCl can be clearly seen in both methods. This indicates that even though the crystals appear less defined at low magnification, the cubic NaCl structure remains consistently formed across all methods.

3.3. The Influence of Salinity

Before adding precipitating agents, an initial analysis was conducted for each salinity level (16, 20, 23, 25 °Be) to determine the required amount of precipitating agent. The results of this initial analysis are presented in Table 6.

From the initial analysis results, each component shows its own tendency with respect to salinity increase. For the Ca^{2+} ion, it is observed that as salinity increases, the concentration of Ca^{2+} ion decreases. For instance, at a salinity of 16 °Be, the Ca^{2+} ion concentration is 0.61% w/v, which decreases to 0.10% w/v at a salinity of 25 °Be. This decrease is attributed to the phenomenon of seawater evaporation, where the content in seawater increases with rising salinity. This increased concentration can lead to seawater becoming saturated with calcium carbonate. When this saturation level is reached, calcium ions form calcium carbonate precipitates. This finding aligns with the theory that aragonite and calcite are the first precipitates formed during seawater evaporation [25]. Both compounds are forms of CaCO_3 but have different crystal structures and solubilities.

In addition to the Ca^{2+} ion, other impurity ions such as magnesium and sulfate increase with salinity. This increase is due to the decrease in water volume during the evaporation process, ultimately raising the impurity ion concentration. Looking at the impurity percentage, it is evident that at a salinity of 16 °Be, the magnesium ion content is only 3.73%, while at a salinity of 25 °Be, it increases to 3.97%. A similar phenomenon also occurs with sulfate ions, with a percentage of 4.64% at a salinity of 16 °Be increasing to 4.85% at a salinity of 25 °Be.

Table 6 and Fig. 12 illustrate the influence of salinity on impurity ions in seawater. Based on the graph, it can be concluded that a salinity condition of 16 °Be is optimal for adding precipitants, as almost all impurity removal percentages approach 100%. Figure 12 also shows that, especially for the Mg^{2+} ion impurity, the reduction percentage remains nearly constant at all salinity levels. From these results, it can be inferred that the increase in salinity does not significantly affect the percentage reduction of magnesium when precipitants are added with a stoichiometric ratio of 1:1.

For the Ca^{2+} ion, although the removal percentage does not differ significantly between salinities of 20 °Be and 23 °Be, but at 25 °Be, the reduction percentage for Ca ions drastically drops to only 61%. The likely cause is the high concentration of Mg ions at 25 °Be. This is due to the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ions ratio significantly impacting the rate of calcite (CaCO_3) formation. The higher presence of Mg^{2+} ions in the solution causes uneven incorporation of Mg^{2+} ions onto the calcite crystal surface, resulting in a lower rate of calcite formation compared to the original crystal formation rate [26]. Therefore, even though the stirring process lasts for 45 minutes, complete precipitation may not occur due to its slow formation rate.

Table 6. The Percentage Results Before and After Purification in the Liquid Phase.

Component	16 °Be (%w/v)	20 °Be (%w/v)	23 °Be (%w/v)	25 °Be (%w/v)
Ca^{2+}	0.610	0.370	0.190	0.100
Mg^{2+}	3.730	3.750	3.840	3.970
SO_4^{2-}	4.640	4.760	4.670	4.850
NaCl	91.010	91.120	91.300	91.080
After the addition of precipitating agents				
Ca^{2+}	0.010	0.020	0.040	0.050
Mg^{2+}	0.110	0.120	0.070	0.270
SO_4^{2-}	0.0040	0.950	0.740	1.960
NaCl	99.870	98.910	99.160	97.720

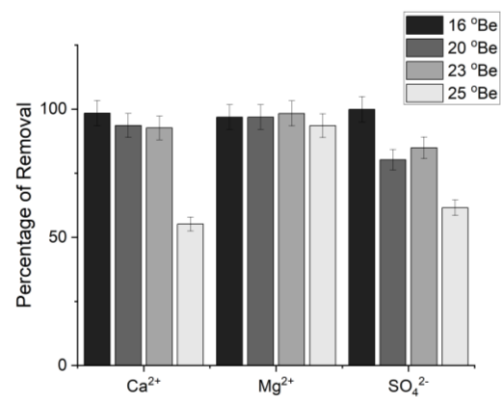


Fig. 12. Results of the Percentage of Removal for Each Salinity Level.

Finally, there is a significant difference in sulfate ion concentration with increasing salinity, as seen in Fig. 13. When salinity increases from 16 °Be, there is a trend of decreasing removal percentage. This decrease may be caused by the increase in magnesium ion (Mg^{2+}) concentration, which slows down the reaction rate at high magnesium concentrations. Support for this has been found in the study by Karaman, stating that an increase in Mg^{2+} concentration can lead to a decrease in the constant reaction rate [27]. Therefore, in this experiment, with a deposition duration of 45 minutes, not all BaSO_4 crystals may have formed due to the influence of high Mg^{2+} concentration.

An increase in salinity can be another potentially influential factor, especially due to the increased concentration of sodium chloride (NaCl) in seawater. The higher the concentration of NaCl , the greater the ionic strength in the solution, which plays a crucial role in the barium sulfate (BaSO_4) precipitation process. Thus, an increase in sodium and chloride ion concentrations in seawater can enhance BaSO_4 solubility due to the higher ionic strength [28].

According to research, a high concentration of NaCl can lead to an increase in the induction period. This increase in the induction period may occur because Na^+ ions are incorporated into the crystal lattice of BaSO_4 ,

which can result in a decrease in nucleation rate. This decrease in nucleation rate can slow down the formation of BaSO₄ precipitates, leading to a lower sulfate removal percentage tendency with increasing salinity [29]. However, in the data for salinities of 20 °Be and 23 °Be, anomalies or results inconsistent with the previous explanation are observed, possibly due to inconsistencies in the deposition duration during the experiment.

Considering all the information outlined above, the optimal salinity for precipitant addition is 16 °Be. By evaluating impurity ion concentrations, this salinity produces the best performance as the concentrations of ions such as Ca²⁺, Mg²⁺, and SO₄²⁻ are still within moderately low levels. Therefore, a more effective reduction in impurity ion concentrations can be achieved compared to other salinities. Furthermore, at a salinity of 16 °Be, it produces the highest NaCl content exceeding 99.5 %w/v in its liquid phase compared to other salinities, and there is a tendency that the higher the salinity, the lower the purity of NaCl, as seen from Fig. 13.

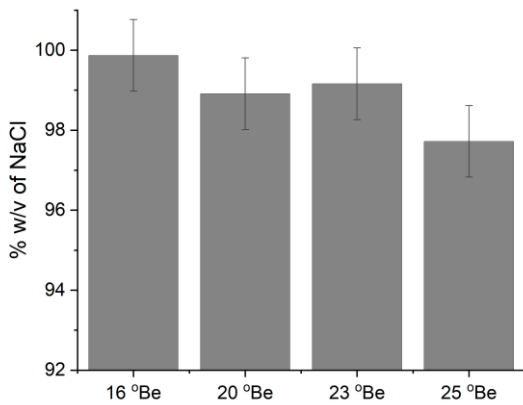


Fig. 13. The Salt Purity at Each Salinity Level.

3.4. Salt Analysis

To align with industry quality standards, which are expressed as weight/weight percentages, this experiment was analyzed the salt solids using the same method. Since the best result was achieved at 16 °Be with Method 3, the same seawater was evaporated to produce salt solids, which were then be analyzed to yield data as shown in Table 7.

Table 7. The Results of Salt Analysis in the Solid Phase.

Component	%w/w
Ca ²⁺	0.086 ± 0.056
Mg ²⁺	0.086 ± 0.041
SO ₄ ²⁻	0.210 ± 0,015
NaCl	99.548 ± 3.343

When compared to the quality standards as shown in Table 1, the best salt from this experiment already meets the purity requirement for NaCl content. However, regarding impurity levels such as Ca²⁺ ions, it already meets the standard as it is below 0.1%, but for Mg²⁺ ions, it slightly exceeds the standard, which should be

maximum 0.06%. As for sulfate content, it reaches the maximum value of the standard, which is 0.2%.

The results obtained in this study are quite comparable to those from previous research by Djaeni, where a salt purity of 99.57% was achieved [15]. In the current study, the purity reached 99.548% These findings confirm that the purification process using chemical agents effectively produces a high level of salt purity, exceeding 99%. However, this purity is strongly influenced by the method used, operational conditions during purification, and the type of precipitating agents employed.

4. Conclusions

Based on the research, the third method, involving the direct and simultaneous addition of precipitant materials, emerged as the most optimal among the three tested. This approach provided the best quality with no side effects and offered ease of application in salt production, as it eliminated the need for filtration unlike the first method. Furthermore, the study revealed that an optimal salinity level of 16 °Be was crucial for effective impurity reduction. Higher salinity levels were found to reduce the effectiveness of impurity removal. To ensure practical applicability and address potential issues, this method should be tested on an industrial scale or in larger salt ponds, confirming its consistency and suitability for community use.

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