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Original paper

IMPROVING PUBLIC SALT QUALITY BY CHEMICAL TREATMENT

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ABSTRACT

The public salt produced by salt farmers in Juwana, Pat,i Central Java, Indonesia with the NaCl content of about 92.86% (dry base) is still below the standard quality of industrial salt (98.5% of dry base). Improving public salt quality has become an important topic of discussion. This research look into the influences of chemical compound, namely sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) *and barium chloride* ($BaCl_2$) *to reduce pollutant ion* ($Ca^{2+,}$ Mg^{2+} *and* SO_4^{2-}) *in order to increase the percentage of NaCl content in public salt. The purification process was carried out in three series mixer. In this investigation, 100 ml of public salt solution is gradually treated by adding those compounds, which were varied from 0.50 to 3.50 gram with the step size of 0.50 gram. The results showed that the purity of NaCl could be enhanced up to 99.6% that was achieved by adding 2.00 gram o f NaOH, 1.50 gram of* Na_2CO_3 *and 2.50 gram of* $BaCl_2$*. This purity is suitable to meet community and industrial demands.*

Key words: Chemical treatment; precipitation; public salt

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INTRODUCTION

Salt products have been consumed by human beings as an important food additive and as the raw material for industrial application. Salt has been produced from seawater that is easily available in the world. Indonesia is one of the salt producer countries where the salt is produced by salt industries and salt farmers. Particularly, salt in Indonesia is produced by solar evaporation of seawater in the salt fields. The seawater evaporation rate depends mainly on air humidity, wind velocity and solar heat . The evaporation of sea water in the salt field causes a high concentration of seawater and at a certain level salt concentration; the salt becomes crystallized gradually (Shreve, 1977).

The crystallization process is started at the level of 7.1° Be in terms of precipitation of calcium carbonate ($CaCO_3$) while still having a low level of salt (Anonymous, 1996). Therefore, the salt compound precipitated is calcium sulphate in the form of fine gypsum ($CaSO_4.2H_2O$). The range of calcium sulphate precipitation is wider than the other salt compound crystallization, especially for sodium chloride, so that the decrease of fine gypsum plays a role as a part of NaCl crystallization. Accordingly, the separation of gypsum crystal is difficult to carry out if it is done only through washing, due mainly to its existence within the NaCl crystal structure and the low solubility of the gypsum in the water.

The precipitation of magnesium compound cannot be avoided due to the similarity in range of the NaCl salt crystallization, 26.2° Be, in the form of $MgSO_4$ and $MgCl_2$. Particularly in Indonesia, the salt produced by salt farmers and known as public salt is about 70% of all national production. The low quality of the public salt produced cannot sufficiently meet the grade requirement of the table salt and industrial salt type. Consequently, a purifying process of public salt is needed in order to achieve the table and industrial salt grade quality. This purifying process is conducted by decreasing the polluter compound and increasing the NaCl content. The salt purifying process can be carried out by chemical treatment and gradual precipitation based on filtration process.

In this experimental work, the chemical treatment was conducted by the addition of chemical substances to the public salt in order to increase the NaCl content and to decrease the polluter compound especially for magnesium and calcium salt. Monod (1991) expressed that the gram equivalent of both Na+ and Cl- ions within seawater is not proportional . It can be shown in the Pacific seawater that has a gram equivalent of Na+ and Cl^- of 480 and 560 respectively. This phenomenon will make it necessary to add a chemical treatment such as Na+ donor in order to increase NaCl level. The chemical added as a Na+ donor is sodium hydroxide and sodium carbonate. The barium chloride compound is added to the solution in order to cover the SO_4^{2-} ion excess and to give more Cl- ion that will settle the sulphate salt to the form of barium sulphate ($BaSO_4$).

The chemical reaction of this treatment can be written as follows:

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$$
$$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2 + Na_2SO_4$$
$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$$
$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$
$$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2NaCl$$

On the basis of the above reaction it could be concluded that the pollutted ion will be reduced by precipitation. Hence, the NaCl content will be increased by formation in reaction.

MATERIALS AND METHODS

The material used in the experiment was public salt from Juwana, Pati, Central Java Indonesia with an NaCl content of 92.86% (dry base), participating agent, and reagent analysis. The precipitant substances used were sodium hydroxide, sodium carbonate and barium chloride, while the chemical materials used for the analysis were EDTA solution (0.1 N), $AgNO_3$ solution (0.2 N), hydroxylamine solution (5%) and EBT and Murexide indicators, respectively.

The public salt was dissolved in the water, stirred to achieve the saturation condition and filtrated from the polluter. 100 ml of the solution was poured into a measuring glass as a sample of brine solution. The settler solution was then added gradually to the sample. Afterwards, sodium hydroxide was added to the brine solution at varying weights and carefully stirred. The sediment formed was filtrated and measured for its weight, while the filtrate will be continued to the next process (Monod, 1991). The addition of sodium carbonate at various weights was implemented to this filtrate and then was carefully stirred. The sediment formed was filtrated, dried and then measured for its weight, while the filtrate will be continued to the next process. The last settling was implemented by adding barium chloride at various weights, followed by stirring. The sediment precipitated was then filtrated and measured, while the filtrate was analysed as a product. Schematically, the

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purification of public salt is presented in the following figure.

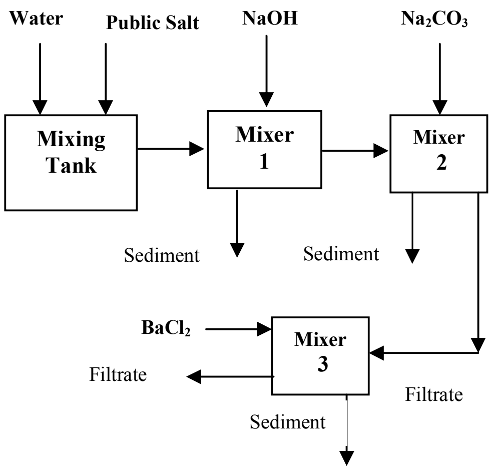

Figure 1. Schematic Diagram of Public Salt Purification

The chemical analysis has been conducted to the common seawater by volumetric titration for of Cl^-, $SO4^{2-,}$ Ca^{2+}, and Mg^{2+} to investigate their salt-compound concentration.

RESULTS AND DISCUSSIONS

The composition of public salt and salt produced by chemical treatment can be written in Table 1. The NaCl content of the salt produced as a result of the experiment work increased from 92.86% to 99.57 %.

Table 1. Composition of public salt and salt product from chemical treatment

Component	Public salt (% w/w)	Chemical treatment (% w/w)
NaCl	92.86	99.57
$CaSO_4$	2.87	0.28
$MgSO_4$	1.26	0.065
$MgCl_2$	3.02	0.083

The increase of the NaCl content of salt produced using chemical treatment was due to the precipitation of material impurities such as Mg $(OH)_2$, $CaCO_3$ and $BaSO_4$ on salt solution that were formed by chemical reaction between Ca^{2+}, Mg^{2+} and SO_4^{2} with NaOH, Na_2CO_3 and $BaCl_2$. The precipitation process could occur since the solubility of these compound are lower than NaCl. Comprehensively, the effect of chemical treatment by adding NaOH, Na_2CO_3 and $BaCl_2$ are described in the following sections.

The Effect of NaOH Addition

This step is aimed to reduce Mg^{2+} in public salt by adding NaOH ranging from 0.50 to 3.00 grams with the step size of 0.50 gram. This compound reacted with magnesium ion (Mg^{2+}) and calcium ion (Ca^{2+}) to produce magnesium hydroxide ($Mg(OH)_2$) and $Ca(OH)_2$. The solubility of these compounds in the amount of $3.4x10^{-11}$ and $5.5x10^{-6}$ are lower than NaCl solubility. The reaction NaOH with Mg^{2+} and Ca^{2+} is ionic reaction, as expressed in the following reactions.

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$$
$$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2 + Na_2SO_4$$
$$CaCl_2 + NaOH \rightarrow Ca(OH)_2 + 2NaCl$$

Hence, the formation of $Ca(OH)_2$ and $Mg(OH)_2$ is stoichiometrically equal to the amount of NaOH addition. In this step, only $Ca(OH)_2$ precipitated from the solution because of its lowest solubility as presented in Table 2. The result is also illustrated in Figure 2 in order to understand the trend of $Mg(OH)_2$ precipitation by adding the amount of NaOH. Referring to those results, the addition of more than 2.00 gram of NaOH could not increase the amount of precipitated $Mg(OH)_2$. The precipitated $Mg(OH)_2$ even tended to be constant, which indicated that the amount of Mg^{2+} concentration in the solution was equal to the solubility of $Mg(OH)_2$. Based on

Figure 2, it could be also concluded that the response of $Mg(OH)_2$ precipitation was exponential with the change of NaOH addition that indicated the process precipitation is first order process. Meanwhile, the $Ca(OH)_2$ could not be perfectly precipitated since its solubility is higher than $Mg(OH)_2$. This compound will be removed using Na_2CO_3 addition as described in the next section.

Table 2. The Addition of NaOH and the amount of precipitated $Mg(OH)_2$

NaOH addition (g)	Amount of precipitated $Mg(OH)_2$ (g)
0.50	0.30
1.00	0.70
1.50	0.85
2.00	0.94
2.50	0.94
3.00	0.94

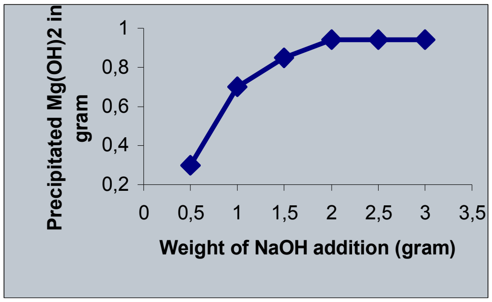

Figure 2. The effect of NaOH addition on $Mg(OH)_2$ precipitation

The Effect of Sodium Carbonate Addition

The objective of this step is to remove Ca^{2+} in the filtrate from the first treatment by adding Na_2CO_3. In this process, Ca^{2+} is combined with CO_3^{2-} by forming $CaCO_3$, as expressed as follows:

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$$
$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$
$$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 + NaOH$$

The $CaCO_3$ with the solubility of $4.8x10^{-9}$ is lower than $Ca(OH)_2$ solubility so that $CaCO_3$ was easily removed from the solution by precipitation. The result showed that the $CaCO_3$ commenced to precipitate at the addition of 0.5 gram Na_2CO_3 as seen in Table 3. The result was also plotted in graph as seen in Figure 3. Based on that figure, the response of precipitated $CaCO_3$ is exponential with the change of Na_2CO_3 addition In this case, the amount of precipitated $CaCO_3$ was maximally achieved at the addition of 1.5 gram of Na_2CO_3. It indicated the balance of Ca^{2+} in the solution equals to $CaCO_3$ concentration. Excessive addition (more than 1.5 gram) could not increase the amount of precipitated $CaCO_3$ since Ca^{2+} in solution is stoichiometrically equal to 1.5 gram of Na_2CO_3. Meanwhile, another anion. namely SO_4^{2-} , could not precipitate in the form of $CaSO_4$ due to its higher solubility. It would be perfectly precipitated in the form of $BaSO_4$ by adding $BaCl_2$.

Table 3. Addition of Na_2CO_3 and the weight of precipitated $CaCO_3$

Na_2CO_3 Addition (g)	Weight of precipitated $CaCO_3$ (g)
0.50	0.45
1.00	0.91
1.50	0.93
2.00	0.93
2.50	0.93
3.00	0.93

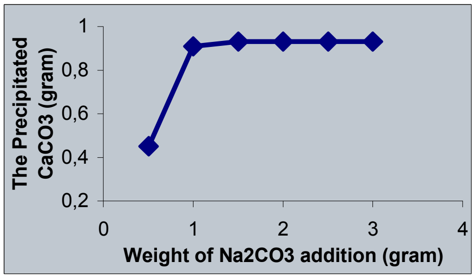

Figure 3. The effect of the addition of Na_2CO_3 on $CaCO_3$ precipitation

The Effect of Barium Chloride Addition

This method is objected to remove SO_4^{2-} by adding $BaCl_2$ to form $BaSO_4$, as expressed in the following equation.

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$
$$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2NaCl$$

The solubility of $BaSO_4$ in the amount of 9.2×10^{-11} is very low and it makes SO_4^{2-} precipitating from the solution. The total of precipitated $BaSO_4$ equals to the amount of $BaCl_2$ addition since the formation occur through ionic reaction. In this method, the amount of $BaCl_2$ was varied from 0.50 to 3.50 gram with the step size of 0.5 gram to obtain optimal precipitation. The result was listed in Table 4 and it was then presented in Figure 4. Refer to those results, the optimal of $BaSO_4$ precipitation is reached at adding 2.50 gram of $BaCl_2$. At this condition, the concentration of SO_4^{2-} in solution is similar to $BaSO_4$ solubility. When the addition of $BaCl_2$ was increased more than 2.50 gram, the amount of precipitated $BaSO_4$ is constant. This is due to the amount of SO_4^{2-} in public salt solution is stoichiometrically equal to 2.50 gram of $BaCl_2$.

Table 4. Addition of $BaCl_2$ and the weight of $BaSO_4$ precipitate

$BaCl_2$ addition (g)	Weight of precipitated $BaSO_4$ (g)
0.50	0.55
1.00	1.10
1.50	1.65
2.00	2.15
2.50	2.34
3.00	2.34
3.50	2.34

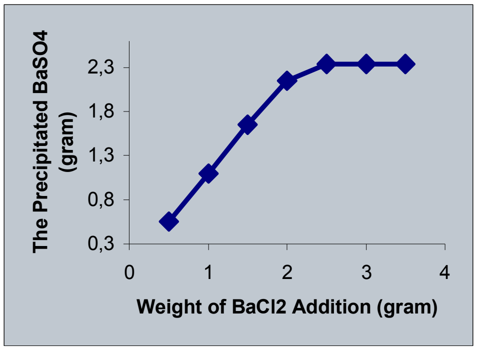

Figure 4. The effect of the addition of $BaCl_2$ on $BaSO_4$ precipitation

CONCLUSION

The improvement of public salt quality can be implemented by chemical treatment with the addition of Sodium hydroxide, Sodium Carbonate and Barium Chloride in three series mixer. It could remove the concentration of impure ion such as Calcium (Ca^{2+}), Magnesium (Mg^{2+}) and sulphate (SO_4^{2-}) ions in brine solution through ionic reaction. Hence, the method could also increase the purity of Sodium Chloride (NaCl) content from 92.86% to 99.57% (dry base) that is suitable to meet community and industrial demand.

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