Iodization of Local Salt Based on Purification Technique using Saturated Brine Washing Method

T Widjaja1*, A Altway1, I Gunardi1, L Pudjiastuti2, D F Nury1, A F Nabila1, N Prasetyawati3, M Saifulloh3, Noviyanto4

1Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember Surabaya, Sukolilo, 60111, Surabaya, Indonesia
2Technical Implementation Unit of Social Sciences and Humanities, Institut Teknologi Sepuluh Nopember Surabaya, Sukolilo, 60111, Surabaya, Indonesia
3Department of Industrial Chemical Engineering, Institut Teknologi Sepuluh Nopember Surabaya, Sukolilo, 60111, Surabaya, Indonesia
4Department of Mathematics Education, STKIP PGRI Sumenep, Sumenep, 69451, Indonesia

E-mail: triw@chem-eng.its.ac.id

Abstract. Based on Indonesia National Standards (SNI), Indonesian local-salt is currently unavailable to produce high-quality salt. This study was aimed to investigate the purification process of local salt that has been carried out by local salt farmers in Sumenep, Madura Island, Indonesia and to determine the highest level of NaCl content from local salt using a washing method to make iodized salt. Purification process involves washing technique using a nearly saturated brine. The research was conducted in various particle-size (10-20 mesh and 20-35 mesh), salt/brine ratio (1:20, 1:40, 1:60), duration (10, 30, 60 minutes) and stirring speed (100, 200, 300 rpm). The highest NaCl content of 94.45 % was obtained at the washing process using the salt of 20-35 mesh at 1:60 ratio with washing time of 30 minutes at a speed of 100 rpm. The result of the process shows a decrease of Calcium and Magnesium levels by 95.56 %. In iodization process, the determination of the highest NaCl concentration was carried out using washing brine method and spray mixing injection was also done to develop a stable salt formulation. The optimum stability of KIO3 in salt was observed as a function of time.

1. Introduction
Salt is one of the primary commodities in Indonesia, which has a strategic role that staple for both consumption and industrial needs. However, the quality of salt produced by salt farmers who are still mainly using conventional technology (utilizes solar thermal energy) has an average sodium chloride of 85-89 % of sodium chloride content. The salt produced also contains impurities such as MgSO4, CaSO4, MgCl2, KCl and soil impurities[1]. This local salt could not be consumed directly both for consumption and industrial needs because its NaCl content is still under Indonesian National Standard (SNI) Number 01-3556-2000 for consumption needs and Indonesian National Standard (SNI) Number 06-0303-1989 for industrial needs[2]. Those salt quality are still below to Indonesian National Standard (SNI) 3556-2016 standard for consumption salts, National Standardization Agency of Indonesia SNI 0303-2012 standard for industrial salts 94.7 % and 98.5 % (dry base), respectively. Cooking salt is salt which is
used for consumption with NaCl content of at least 94.7 % calculated from the dried base, included maximum water content 7 %, Iodine as KIO$_3$ minimum 30 ppm. While industrial salt is usually used as raw material or supporting industrial activities, auxiliary materials for petroleum industry needs, textile, pharmaceutical and CAP (Chlor-Alkali Plant) with a minimum of 97 % NaCl content (dry base), impurities such as: Calcium 0.1 %, 0.05 % Magnesium, Sulphate maximum of 0.2 %, and maximum water content of 2.5 %, (% w/w) [3].

To obtain a good quality salt, the impurities should be precipitated. Salt which produced using the conventional methods still could not meet the standards of salt both for consumption and industrial determined by the Indonesian National Standard (SNI). Based on the quality of salt production requirements, there are several methods of purifying in order to fulfilled the requirements, included chemical and physical method. There are some salt purification technologies namely brine washing [4], evaporation (recrystallization) [5], and chemical addition [1].

The purification process of salt is done using a washing technique and evaporation (recrystallization). Washing technique is done with a nearly saturated brine while evaporation (recrystallization) process. The evaporation process is one method to purify (purity) a solid material from its impurity through the dissolution process and crystallization. The evaporation process based on the solubility of the material in a solvent in which the solubility of the material will increase as the temperature rises and vice versa. The impurities may have different properties where the solubility of the impurities will be low at high temperature and vice versa. This process requires considerable heat energy to be able to evaporate the remaining water and recrystallize the purified salt [6]. The use of a nearly saturated solution was aimed to dissolve the impurities and other impurities to obtain salt with higher sodium chloride (NaCl) content. Salt can reach up to 5 % or NaCl levels reached from 91 to 96 % using this washing method. Conducted the comparison of the physical method using both recrystallization and washing method in resulting salt with the highest NaCl content. The purity of sodium chloride could be enhanced up 99.21 % from the re-crystallization method, while the washing method enhanced up to 96.64 % using the particle size of 20-30 mesh. The result showed that washing method is more efficient than the re-crystallization method because the re-crystallization method requires heat energy and could be used both for industrial and consumption needs.

The iodized local salt was done using the spray system mixing. The mechanical iodization process of salt can be carried out in three ways, namely the first method, dry mode (solid-solid mixing). The second method wet way of drying (mixing of liquid-solid) where the salt is mixed with iodine-containing liquids by dripping or spraying in this process. This method further guarantees the homogenization of the results, but the water content in the salt will increase. The third method is the wet (liquid-liquid mix). In this process, the mixing is carried out during the crystallization process, in which iodine increases in the crystallization process. The resulting results are evenly distributed but require a more significant cost and higher technology [7].

The objective of this research is to determine the most effective and efficient method to make iodized salt from the local’s salt. Salt crystals in varied coarse size of 10-20 mesh and 20-35 mesh, were introduced into brine with concentration 23°Be and the ratio of salt and brine solution used 1:20, 1:40, and 1:60. The solution was stirred for 10, 30, and 60 minutes, as well as at stirring speeds of 100, 200 and 300 rpm. These variables were tested to get lower Calcium and Magnesium level and increased NaCl concentration to 94.7 % as same as the National Standards Indonesia (SNI). From the best variation, after the improved quality of salt generated by the washing process, combined with iodized salt by the process of spray mixing method in which the homogeneity and stability of iodine in iodized salt as a function of time.

2. Experimental section

2.1. Raw material
Local-salt was kindly obtained from the local salt farmer in Sumenep, Madura island, Indonesia. Aquadest, sulfuric acid, potassium iodate, sodium thiosulfate, starch indicator were purchased from...
Merck. Sharp EM-S53-WH Standing Mixer was used for iodization and purchased from local market Surabaya, Indonesia.

**Figure 1.** Mixer set-up, (1): Motor; (2): Vessel; (3): Mixer; (4) Salt

2.2. **Salt preparation**
Salt was firstly determined gravimetrically. Salt was weighed and then dried at 110 °C to reduce its water content of the salt solid. After the drying process, salt was varied by size, coarse size, 10-20 mesh and 20-30 mesh, respectively. The impurities can be dissolved when salt solids contacted with the brine solution. Chemical composition of local salt as the raw material in brine washing method resulting in 82.335 % (dry base) using Argentometric method. All parameters, such as Calcium 0.235 %, Magnesium 1.104 %, Sulphate 1.411 % were analyzed using titrimetric. Impurities was analyzed by gravimetric.

2.3. **Brine washing method**
The process was conducted in a batch laboratory scale. Brine solution was used for washing the solution. Brine solution contains 98.5 % NaCl content. The brine washing method is an extraction process or a separation of a component which is in a solid phase by a liquid phase as a solvent (Wu et al., 2017). In this case, the salt is the solid phase and the salt solution as the solvent (Wu et al., 2017). The performance of brine washing method was influenced by the concentration of brine solution which the 23 °Be have been measured by Baume meter. According to (Sedivy, 1996), the brine solution includes a saturated solution at 24.6 °Be and becomes a salt crystal at 25 °Be - 30 °Be. Salt crystals in varied of coarse size, 10-20 mesh, and 20-35 mesh was contacted on brine with concentration 23 °Be with the ratio of salt and brine solution used 1:20, 1:40, 1:60, time of stirring 10, 30, and 60 min., as well as stirring speeds of 100, 200, and 300 rpm is constant. After the washing process, the filtration separation process is performed. The next stage performs a complexity titration analysis to determine the content of Ca and Mg after washing with brine. The initial content of Ca and Mg obtained were 3.6072 and 2246.392 milligrams using titration, respectively.

2.4. **Iodization**
Local salt was used to prepare the fortified salt sample. Duration of 1, 2, 3, 4, 5, 10 and 15 minutes, stirring speed of 100 rpm, and particle size of salt 20and 60 mesh was carried out in the present study. Salts were weighed and mixed in a static mixer using a stirring speed of 100 rpm. 1 ml of potassium iodate was sprayed with mixed salt. Iodized salt samples were stored in a desiccator at 25 °C for 90 d. Iodine content analysis was estimated as described by iodometric titration method in Indonesian National Standard (SNI) number:01-3556 which can be titrated by Sodium Thiosulphate using starch as color indicator.

2.5. **Statistical analysis**
Data from chemical assays were obtained for once and examined as the homogeneity of KIO₃ in salt. Stability KIO₃ in salt was observed as function time every 10 d (days) once. The results of this observation will be obtained the response as index homogeneity.
3. Results and discussion
NaCl levels after the washing process are presented in Table 1. From the best variation, i.e., in the size of 20-35 mesh, 100 rpm, 1:60 ratio with 30 minutes washing time, salt quality improvement of 12 %, from the initial salt before washing 82.22 % to 94.45 %. Salt produced by quality 94.45 %, combined with the process of iodized salt by mixing spray method in which the homogeneity and stability of iodine in iodized salt as a function of time.

3.1. Decreasing Calcium and Magnesium in varied particle size
By using the washing method, the impurity content can be reduced because ions Ca\(^{2+}\) and Mg\(^{2+}\) can dissolve in the brine solution. In this study, the concentration of brine solution used is 23\(^{o}\)Be which means the solution contains 23 % salt and 77 % water. Water will dissolve Ca and Mg so that there is a solvation process. In the solvation process, the ion or molecule is surrounded by a solvent molecule having a particular arrangement. So the reaction that occurs when the washing process of salt solids as follows:

\[
\begin{align*}
2\text{H}_2\text{O} + \text{Ca}^{2+} & \rightarrow \text{Ca(OH)}_2(\text{aq}) + \text{H}_2(\text{g}) \\
2\text{H}_2\text{O} + \text{Mg}^{2+} & \rightarrow \text{Mg(OH)}_2(\text{aq}) + \text{H}_2(\text{g})
\end{align*}
\]

(a) \hspace{1cm} (b)

Figures 2. (a) Calcium content; (b) Magnesium content after washing process, varied particle size

From Figures 2 (a) and (b), it can be seen that decrease in Calcium and Magnesium in various particle size variations of the best variation at washing time of 30 minutes and 100 rpm. Washing time becomes one of the factors determine the quality of salt on salt refining with washing method. The longer the wash time than the longer the salt contacts with the brine solution, so impurities present in the salt crystals can be reduced more lot and impurities left in salt crystals a little more. Besides, levels of Magnesium which was obtained tend to be larger than Ca because the concentration of Magnesium in salt crystals was higher than Calcium so that the difference of concentration of Mg with brine was also more significant [8].

One factor is the low purity of the salt due to the presence of impurities in the salt of Ca\(^{2+}\) and Mg\(^{2+}\) as the largest impurities [1]. In salts, Ca\(^{2+}\) and Mg\(^{2+}\) ions in the form of MgSO\(_4\), MgCl\(_2\), CaSO\(_4\), CaCl\(_2\). With the solubility of these compounds affects the salt purity itself, because with a small solubility it will be difficult to be removed or dissolved. The decrease of Ca\(^{2+}\) and Mg\(^{2+}\) was influenced by several factors such as salt size, washing time, the salt ratio with brine, and stirring rate. Data were obtained by using titration. From the results, at a speed of 100 rpm and 30 minutes washing time gave the best data.
Table 1. NaCl levels after washing using AAS analysis

| Particle size (mesh) | Ratio (salt/brine) | Analysis result (%) | Particle size (mesh) | Ratio (salt/brine) |
|----------------------|--------------------|---------------------|----------------------|--------------------|
| coarse               | 1:20               | 88.12               | coarse               | 1:20               |
|                      | 1:40               | 93.18               | coarse               | 1:40               |
|                      | 1:60               | 88.2                | 10-20                | 1:60               |
|                      | 1:20               | 91.93               | 10-20                | 1:20               |
| 10-20                | 1:40               | 90.65               | 10-20                | 1:40               |
|                      | 1:60               | 90.65               | 10-20                | 1:60               |
|                      | 1:20               | 90.65               | 20-35                | 1:20               |
| 20-35                | 1:40               | 89.38               | 20-35                | 1:40               |
|                      | 1:60               | 94.45               | 1:60                 |                     |

Also, the solubility of Mg is much higher than that of Ca solubility. One factor is the low salinity of salt due to the presence of impurities in the salt of the compound Ca\(^{2+}\) and Mg\(^{2+}\) as the most considerable impurities in the salts of Ca\(^{2+}\) and Mg\(^{2+}\) ions in the form of MgSO\(_4\), MgCl\(_2\), CaSO\(_4\), CaCl\(_2\). At smaller particle sizes, Calcium and Magnesium tend to move more easily from within the salt crystals to the brine.

Figures 3. (a) Removal Calcium; (b) Magnesium in varied particle size

From Figures 3, particle size 20-35 gave a significant decrease results. In Figures 2(a), Calcium content 3.6072 to 0.160 milligrams produce a percentage of removal Calcium 95.556 %, where the percentage decrease in Calcium and Magnesium can be seen in Figures 2 (a) and (b), respectively. The largest decrease in Magnesium also occurs in particle size of 20-35. At 20-35 mesh, a large decrease of Calcium and Mg compared to the size of coarse and 10-20 mesh. This is due to the reduction of size so that impurities in the salt can go out into the salt surface and dissolve with brine. Ratio (Salt/brine) also affects the salt quality resulting from the washing process. In Figures 3 (a) and (b) show that the ratio is at 1:60, for each Calcium and Magnesium a significant decrease in coarse size10-20 mesh, as well as the size of 20-35 mesh. On size 10-20 mesh with variable 60 minutes, a ratio (salt/brine) which can result in a decrease in Calcium and Magnesium % the highest amounted to 93.333 % occurred in the variable comparison 1:60. The higher the ratio (salt/brine), the more brine solution used so that impurities that can be removed from the salt crystals are also more numerous. This caused the Calcium...
and Magnesium in the washing salts to decrease, and the salt becomes purer with higher NaCl content. Comparison of salt and brine also determine how effective and efficient washing process performed. By NaCl levels of 94.45% using AAS analysis after saturated washing brine process, the salt could be formed as both for consumption and chemical needs.

3.2. Homogeneity of the KIO₃ as function of time

Salt iodization was done using spray mixing. On the highest NaCl content of 94.45 %, salt iodization was done using spray mixing method and iodine content determination analysis using iodometric titration method. KIO₃ KIO₃ as much as 1 ml (% v / v) sprayed mechanically into the salt to be iodized using the variable rotation speed specified. In this study, an iodized product was analyzed to determine KIO₃ levels in (ppm). It is then calculated using a homogeneity index to compare each variation of a predetermined operating condition.

\[
\text{homogeneity index } = \left( 1 - \frac{\sum (y_i - \bar{y})^2}{\sum y_i} \right) \times 100\%
\]

Figure 4 shows the best variables of iodized result that is on the particle size of 20 and 60 mesh. In this case, the smaller the particle size indicates the more homogeneous KIO₃ present after injection with the spray system in the salt. In this case, time affects the homogeneity index of the resulting KIO₃. At (t) 5 min, the homogeneity index shows 85.13 for the particle size of 20 mesh and 88.62 at 60 mesh particle size. At (t) 6 to 15 minutes the homogeneity index shows more uniformity in both 20 and 60 mesh. The more serious issue arises with particle size of salt that has a large range of grain size. This causes an uneven distribution of KIO₃ due to surface area differences. As can be seen in Figure 4, at 20 mesh the homogeneity is found in smaller than 60 mesh. This because the salt will naturally separate by grain size. Fine salt may be ground to produce a more uniform grain size distribution.

3.3. Stability of KIO₃ as function of time

Table 2 shows the concentration of KIO₃ during 90 days stored in desiccators at 25°. It was observed that the stability of KIO₃ did not show the difference, apparently for 90 d (days). In summary, spray solutions of 1 ml KIO₃ are suitable for salt fortification as they retain the micronutrients and remain in solution for a minimum 4 months. These solutions may be used to fortify salt which retains sufficient.
micronutrient stability. As a result, impure iodized salt can lose most of the added iodine during extended storage. Therefore, the suggestion of 9 to 12 months storage should be investigated.

| Table 2. Stability of KIO₃ at 90 d (days) |
|----------------------------------------|
| Time (days) | 10  | 20  | 30  | 40  | 50  | 60  | 70  | 80  | 90  |
| KIO₃ concentration (ppm) | 80.1 | 80.1 | 80.1 | 80.1 | 80.1 | 80.1 | 80.1 | 80.1 | 80.1 |

4. Conclusion
The development of a novel, saturated brine washing method to make iodized local salt using spray mixing has been reported. The results of saturated brine washing method could enhance the NaCl content of 94.45 %, which was obtained at brine washing process of particle size 20-35 mesh at (Salt/brine) 1:60 ratio with washing time of 30 minutes at a speed of 100 rpm. This result of the process could decrease Ca and Mg by levels 95.56 %. The stability of KIO₃ local salt samples using brine washing method was confirmed stable for 90 d stored in the desiccator at 25 °C.

Acknowledgement
The authors would like to express their most profound gratitude to The Institute for Research and Community Services (LPPM) of Institut Teknologi Sepuluh Nopember Surabaya, Indonesia for funding this research with grant number [1457/PKS/ITS/2018]. The authors would also like to express special thanks to all member of Biochemistry Technology and Chemical Reaction Engineering laboratory for their unconditional help and support during the research process.

References
[1] Ihsan D and Djaeni M 2002 Improving public salt quality by chemical treatment J. Coast. Dev. 5 111–16.
[2] National Standardization Agency of Indonesia SNI 0303-2012 standard for industrial salts
[3] Anwar M A, Bakar A, Ahmad A, and Harun M 2017, Chem. Eng. Transc. 56 235–40.
[4] Sumada K, Dewati R and Suprihatin 2018 J. Phys.: Conf. Ser. 953 012214
[5] Chenli Z, Lian F, and Ma L 2016 5th Int. Conf. on Measurement, Instrumentation and Automation pp. 105–109.
[6] Caecilia P, Ketut S, Yustina N and Prasetyo H 2016 MATEC Web Conf. 58 01022 10–13.
[7] Li Y O, Diosady L L and Wesley A S 2010 J. Food Eng. 99 232–38.
[8] Clar C, Oxon D and Wu T 2002 Endocrinolog. Metab. Clinics North America 31 681-98.