Quality monitoring of salt produced in Indonesia through seawater evaporation on HDPE geomembrane lined ponds

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Abstract. Salt is one of the primary ingredients that humans always need for various purposes, both for consumption and industry. The need for high-quality salt continues to increase, as long as industry growth. It must improve product quality through the development of salt production process technology. In this research, the quality monitoring of salt produced in Indonesia by evaporation of seawater on ponds lined using high-density polyethylene (HDPE) geomembrane has been studied. The manufacturing of salt carried out through the gradual precipitation principle on prepared ponds. HDPE geomembrane is used to coat evaporation ponds with viscosity 12-22°Be and crystallization ponds with a viscosity of 23°Be. The monitoring of the product is carried out in the particular periods during the salt production period. The result of control shows that the quality of salt produced in HDPE geomembrane coated salt ponds has an average NaCl content of 95.75%, so it has fulfilled with Indonesia National Standard (SNI), that is NaCl> 94.70%. The production of salt with HDPE geomembrane can improve the quality of salt product from NaCl 85.4% (conventional system) to 95.75%.

1. Introduction
Sodium chloride (NaCl), which is often called table salt, is one of the chemicals that are widely used for various purposes. Besides being used as the salt intake, iodized salt, sodium chloride also used as the starting material for different industrial purposes. NaCl is traditionally used as a food additive in food processing because, in addition to influencing the product taste, it plays an essential role in texture and storage [1]. Therefore, its function cannot be replaced by other materials, and the salt positioned as a strategic commodity. NaCl easily obtained by evaporation of seawater. The making salt from seawater evaporation carried out the public, in general, is still conventionally to produce salt with low quality. About 20% of the international salt production is destined for human consumption, whereas 55% used in the chemical industry and 15% for de-icing roads in winter [2]. For industrial and chemical reagents, the salt must be reprocessed so that the NaCl levels approaching 100%. As for iodized salt consumption and processes, salt must meet the requirements of Indonesia National Standard (SNI) which contains at least 94.7% NaCl [3]. Crystallization method by evaporation of seawater will produce salt is still mixed with other compounds that dissolved, such as MgCl₂, MgSO₄, CaSO₄, CaCO₃, KBr, and KCl in small quantities. Thus, the stage crystallization method directly through the evaporation of seawater has not been able to produce the high purity NaCl.
The Indonesia salt needs from year to year has increased with population growth and industrial development. For 2000 the domestic salt in Indonesia needs both for consumption and industry, projected total estimated projections 2,100,000-2,200,000 tons while the production of salt is only about 300,000-900,000 tones [4]. This salt consumption means that to fulfill the needs of the Indonesia salt for at least 2000 to import as much as 1.2 million tons of salt. Until now, high-quality salt needs are imported from abroad, mainly industrial salt. The total of the Indonesia salt production in 2009 reached 1.371 million tons, while the total demand for salt, out of consumption salt, amounted to about 2.395 million tons [4-5]. Consequently to fulfill the needs of salt the government takes the salt import policy. It is especially ironic with the condition of the Indonesian natural resources which is an abundant marine, besides lead to dependency on other countries to fulfill the needs of the salt in the future.

Meanwhile, demand for iodized salt to improve the nutrition of food continues to rise, as long as the increase in disturbance caused by lack iodine. Likewise, for industrial purposes or as a chemical reagent, a chemical compound must have a high enough purity ~ 100%. Therefore, it is necessary to repair method of salt production so obtained salt with high quality (NaCl concentration> 98%). NaCl in nature may be collected from seawater, salt lakes or as a deposit that exists in salt mines [6]. The sea water contains an average of 3.5% by weight of the solute and more than 75% of the solute NaCl. The extraction of salt from seawater consists of progressive evaporation of brine in ponds using solar and natural wind [7]. During the evaporation process, salt crystallized from the ocean between the densities of 24°Be and 24°Be [8].

Problems are often encountered by the manufacture of NaCl through directly crystallization method is still the presence of impurities, which is quite a lot, so that the purity of the salt has not yet reached the maximum. The presence of compounds MgCl₂, MgSO₄, CaSO₄, CaCO₃ KBr, and KCl that simultaneously crystallized in the process of manufacturing salt causes lower purity of NaCl produced. The evaporation process of will increase the concentration of each solute and continues until the concentration reached saturation. The deposition process will take place based on the order of solubility in water. Substances that have a lower constant of solubility product (Ksp) will settle in advance of the elements that have a larger Ksp [9-10]. If the manufacture of salt carried out by direct evaporation of seawater, regardless of the viscosity of water, it will obtain the salt with high impurities, especially the content of CaSO₄, MgSO₄, and MgCl₂. The salt produced is low quality, not only less whiteness but also somewhat bitter. This salts are known as coarse salt, the NaCl content of 70-80%. Therefore, production of high-quality salt is paramount importance.

High-density polyethylene (HDPE) geomembranes have been commonly used in composite liners at the bottom of modern municipal solid waste landfills, and they have shown excellent performance in containing a broad range of chemicals [11-12]. Due to the advantages of HDPE geomembranes, then in this study will be applied to produce salt with high purity. Various methods of high purity salt production have been exploited by using binder agent impurity. The use of HDPE geomembranes was introduced in the manufacture of super quality salt. Also, the removal of impurities by using Na₂CO₃ and NaOH [13-15], as well as Na₂CO₃ and Na₂C₅O₆ in high-quality salt production also reported [16-18]. Although the method can improve the quality of salt produced, the method is not appropriate when applied and industrial scale, because of not only high production costs but also not environmentally friendly. Therefore, it is necessary to develop alternative methods that can solve the problem. In a previous study, using black plastic as a liner in the manufacture of salt can be produced the high-quality salt [18]. This research studies the quality monitoring of the quality of salt production using HDPE geomembrane as an agent of the liner in the salt ponds. The parameters of product quality include the content of NaCl, Mg, Ca, and H₂O.

2. Methods
This study includes a series of laboratory research, field research and testing results of research on a variety of related laboratory. Implementation of field research provides preparation of area salt ponds, the treatment process conditions, product sampling, harvesting products and direct observation field
conditions. The laboratory tests of the salt product composition include determining the content of NaCl, water, Mg, Ca were conducted in the laboratory of Chemistry, Universitas Negeri Semarang. The analysis of salt based on Standard National Indonesia (SNI) was carried on Waste and Environmental Testing Laboratories and Miscellaneous Commodities Research and Development Institute for Industrial Semarang. Analysis NaCl was determined by argentometry method, while Mg and Ca were determined by atomic absorption spectrometry. The research was conducted in salt ponds of Garam Mas, Ltd., Kaliori, Rembang, Central Java, Indonesia.

2.1. Site selection and settings of saltwater.
The setting pond consists of a brine pool, pool salt ponds control (conventionally system) and a salt pond with HDPE plastic coated treatment. The wide of salt ponds with plastic coated treatment HDPE is 1561 m², while the conventional pond is 1955 m². Figure 1 showed the conventionally salt ponds (without HDPE), and salt ponds with treatment HDPE lined respectively.

![Figure 1. Setting of ponds: (a) conventionally salt ponds and (b) salt ponds with HDPE lined](image)

The production process began with the manufacture of salt production land through the gradual precipitation. The HDPE geomembrane was used to coat the evaporation ponds with viscosity 12-22 °Be, as well as for the crystallization table with viscosity 23ºBe. The salt production was taken place by making land checkered in stages so that the sea water can gravitationally flow to the downstream anytime. To produce a high-quality salt was made by the principle of gradual precipitation, as presented in the following flowchart (Figure 2)

![Figure 2. Salt productions by gradual precipitation](image)

2.2 Equipment and material
The equipment used in the research comprise meter, pump, the pipe, stop valves and rubber hoses, hoes, crowbars, spades, rakes, a set of glasses, pH meter, and Baume meter. The materials needed include sea water free of pollution, silver nitrate, aquadest and geomembrane HDPE.

2.3. Production process

The production process of salt carried out by running of seawater gradually to settling ponds that have been made, sedimentation ponds (SP). The sedimentation ponds (SP I, SP II and SP III), serves as evaporation and precipitation ponds. In these ponds, sea water was evaporated by solar evaporation and controlled, so that the salinity of the water is in the range 10-12 °Be. Also, SP IV and V are further evaporation ponds, which accommodate sea water with salinity 12-17 °Be and 17-23°Be. Bunker is a pond to store old water (viscosity 23°Be) and serves as a reservoir of ancient water. The crystallization process took place in crystallization table lined by HDPE geomembrane. Evaporation process begins after passing through the settling ponds of seawater for four days by flowing into evaporation ponds.

Harvest of salt is done after seven days crystallization on regularly. Collection of salt is done by using a rake or shovel plastic timber on a table salt with a thickness sufficient water table or 3-5 cm. The process was taken place not only collecting salt but also washing the crystallized salt. Furthermore, the salt was transported from salt table to a pile while land surface mounted woven bamboo to drain the harvested salt. Also, the coarse salt was transported to the warehouse for the next process.

2.4. Analysis of quality salt produced

The product of the coarse salt, after storage in warehouses, further processed in a factory to produce various products. The quality of the salt product is determined from the results of chemical analysis of samples of salt in a Laboratory Chemistry, Universitas Negeri Semarang and Laboratory of Waste and Environmental Testing, Miscellaneous Commodities Research, and Development Institute for Industrial Semarang. The analysis parameters include the contains NaCl, water, heavy metals, color, taste, by Indonesia National Standard (SNI), and the content of Ca²⁺ and Mg²⁺, crystal form and whiteness of salt.

3. Result and discussion

3.1. Salt production on ponds lined geomembrane HDPE

Total production of salt has been obtained from the salt ponds coated HDPE geomembrane and controlled ponds (conventionally method) for one month around 1.5 are listed in Table 1.

| No | Ponds | Amount (ton) |
|----|-------|-------------|
| 1  | P 1   | 1.60        |
| 2  | P 2   | 2.70        |
| 3  | P 3   | 3.75        |
| 4  | P 4   | 2.30        |
| 5  | P 5   | 4.30        |
| 6  | P 6   | 2.45        |
|    | Total | 17.10       |
| 7  | Conventionally Ponds | 43.44 |

According to the table 1, it appears that the amount of salt products is increasing with the period the existing harvesting. This increasing shows an increase in the effectiveness of land-use HDPE plastic coated. In the harvest period, the number of salt products decreased. This decreasing is due to supply shortages of water for salt production. Effective production time is 6-7 days, so the salt production declined. The production in the next period resulted in more salt, which takes place one
week. This harvest period is the maximum results obtained during the production of salt. Hence the harvest period was changed to seven days (a week) so that the salt harvest can be done once a week.

Based on physical observation results in the salt table of crystallization HDPE plastic coated, it appears that the salt color is whiter, cleaner and without the dirt ground. Salt harvesting process easier can be directly scratched from the salt table, easily and quickly without damaging the table salt. Meanwhile, the salt table is easy to use for the next crystallization, without re-hardening process. Salt products from every period of production show the consistency of high quality, which indicated by similarity of products for each harvest. The salt fluctuation resulted due to old the water supply shortages. This occurs because the amount of salt products is highly dependent on many factors, such as the supply of sea water, sea water quality, temperature, weather, wind and seasons. Therefore, the productivity of salt can be different.

3.2 Quality monitoring of salt products

Monitoring quality of salt products aimed to determine the quality of the resulting salt product at a specified period. The control is done for the salt produced by both ponds with coated HDPE and conventional ponds. At this stage, preliminary analysis and advanced analysis. The initial investigation of the chemical content of products salt (coarse salt) is conducted in the Laboratory of Chemistry, Universitas Negeri Semarang. In this study determined the main component of salt products. The composition of the salt produced are listed in Table 2. (P 1- P 6: ponds lined HDPE, C1 - C2: conventional ponds)

Table 2. Composition of salt products

| No | Ponds | Composition (%) |
|----|-------|----------------|
|    |       | NaCl | H2O | Ca | Mg |
| 1  | P 1   | 95.87| 2.96| 0.4| 0.1|
| 2  | P 2   | 93.54| 5.79| 1.04| 0.14|
| 3  | P 3   | 95.3 | 1.981| 1.3 | 0.14|
| 4  | P 4   | 98.20| 3.61| 1.5 | 0.18|
| 5  | P 5   | 98.87| 3.78| 1.02| 0.16|
| 6  | P 6   | 92.9 | 3.58| 2.28| 0.12|
| 7  | C 1   | 84.18| 6.60| 1.62| 0.16|
| 8  | C 2   | 86.52| 10.30| 1.26| 0.18|

Table 3 showed that the salt product innovation using HDPE geomembrane (P1-P6) has an average content of NaCl 95.75% with a range of NaCl content of 92.9%-98.87%. Therefore the salt produced fulfills the NaCl concentration by SNI, i.e., at least 94.70%.

Advanced analysis conducted on refined salt is processed by Garam Mas, Ltd. using the salt product from ponds lined HDPE as primary materials. Fine salt analysis carried out at the Laboratory Center for Industrial Research and Development Semarang. Results analysis for salt products using SNI procedure is listed in Table 3.

Table 3. Result of analysis salt products using SNI procedure

| Parameters | Unit | Result | Quality Standard |
|------------|------|--------|-----------------|
|            |      |        | SNI .01-3556-2000 |
| H2O        | (% wt) | 7 | Max. 7 | 
| NaCl       | (% wt) | 95.21 | Min. 94.7 |
| KIO3       | mg/kg | >30 | Min. 30 |
| Pb         | mg/kg | 1.22 | Max. 10.0 |
| Cu         | mg/kg | 2.17 | Max. 10.0 |
| Hg         | mg/kg | <0.01 | Max. 0.1 |
| As         | mg/kg | <0.01 | Max. 0.1 |
The test results with SNI procedure (Table 3) against a sample of refined iodized salt by crystallization technology innovation results showed NaCl 95.21%. The content of NaCl, H2O, KIO3 and heavy metals fulfilled the quality standards of SNI. The monitoring results indicate that salt manufactured in HDPE coated geomembrane pools is of a higher quality than without the HDPE geomembrane layer.

4. Conclusion
The quality monitoring of salt produced by seawater evaporation in HDPE coated salt ponds shows that the salt quality has fulfilled Indonesian Industrial Standards (SNI). The product of coarse salt had higher contains NaCl on average 95.75%, with a range of NaCl content of 92.9-98.87%, so that it fulfills the contains of NaCl according to SNI, i.e., > 94.70%. Therefore, the use of HDPE in the manufacture of salt needs to be expanded in various industrial centers of salt. Also, the quantity and quality of the salt product resulted using the HDPE can be improved through better management of water flow and will be useful when a set of water flow and old water supply smoothly available.

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References
[1] Carla G, Jéssica R, Heraldo J, João C, Tassyana F and Luísa F 2017 An. Acad. Bras. Cienc. 89 2505
[2] Korovessis N A and Lekkas T D 2009 Glob. NEST J. 11 49
[3] Susanto H, Rokhati N and Santosa G W 2015 Procedia Environ. Sci. 23 175
[4] Hamid A A and Aldianto L 2014 J. Bus. Manag. 3 316
[5] Bakosurtanal 2010 Map of Salt Land Indonesia, Edition Java and Madura (Cibinong, Indonesia: Natural Resource Survey Center)
[6] Westholm L J and Alderton D 2015 Reference Module in Earth Systems and Environmental Sciences: Mineral Resources (Amsterdam, Netherlands: Elsevier)
[7] Jhala D S 2006 Solar Salt Production Process (Santorini Island, Greece: Proceedings of the 1st International Conference on the Ecological Importance of Solar Saltworks (CEISSA 06)
[8] Rathnayaka D D T, Vidanage P W, Wasalathilake K C, Wickramasingha H W, Wijayarathne U P L and Perera S A S 2013 Int. J. Chem. Mol. Nucl. Mater. Metall. Eng. 7 12
[9] Civan F 2016 Phase Equilibria, Solubility, and Precipitation in Porous Media: Reservoir Formation Damage (Third Edition) (Amsterdam, Netherlands: Elsevier)
[10] Gaffney J S and Marley N A 2018 General Chemistry For Engineers: Solution Chemistry (Amsterdam, Netherlands: Elsevier)
[11] Rowe R K, Saheli P T and Rutter A 2016 Waste Manag. 55 191
[12] Booker J R, Brachman R, Quigley R M and Rowe R K 2004 Barrier Systems for Waste Disposal Facilities, Second Edition (London: CRC Press, Taylor & Francis Group)
[13] Bahruddin Z, Aman I, Arin and Nurfatihayati 2003 Indonesian Natur Journal 6 16
[14] Choi H-G, Shim M, Lee J-H, Yi K-W 2016 J. Cryst. Growth 474 69
[15] Fan J, Luo J, Chen X and Wan Y 2017 J. Chromatogr. A 1490 54
[16] Sun J, Dong Y and Kong C 2014 Sep. Purif. Technol. 136 309
[17] Hasan M, Rotich N, John M, Louhi-Kultanen M 2017 Chem. Eng. J. 326 192
[18] Kumar A, Mukhopadhyay I, Ghosh P K, Mohandas V P, Shukla J J and Sanghavi R J 2009 Process for the Preparation of Common Salt from Brines in Solar Pans (USA: U.S Patent Application 20090175781)