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INVESTIGATION ON CALCIUM AND MAGNESIUM IN TRADITIONAL SALT PLOTS: PROMOTING UTILIZATION WASTE BY-PRODUCT

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ABSTRACT: Calcium and magnesium are two major anions found in seawater naturally after chlorine and sodium. Calcium and magnesium widely used for industrial and human health. Seawater salt productions produce salt and wastewater as concentrated sea water. Sodium and chloride produced as salt from seawater in traditional salt production while calcium and magnesium need to be considered for promoting recovery mineral. As alkaline earth metal, calcium and magnesium potentially interfere with each other in the chemical process. The investigation was conducted at the peak of the dry seasons in Indonesia by collecting a water sample from each plot in traditional salt production. Each water sample measured using complexometric titration and hydrometer to count its density. The objective of this study is to prove calcium and magnesium behavior in traditional salt productions in Indonesia with a view to achieving integrated production of salts and mineral from sea water. This information can support marine environment sustainability through recovery from traditional salt production wastewater. During evaporation, calcium concentration increases but starting from BE 13-16 will get down. Magnesium concentration increases steadily during the salt-making process. Recovery magnesium from bittern has advantages since calcium ion as impurities have deposition at 53.5% seawater evaporation.

Keywords: Baume degree (BE), Bittern, Environment Sustainability, Recovery

1. INTRODUCTION

Traditional salt production is highly dependent on the season, production process only establishes on the dry season by using traditional solar evaporation method [1]. Salt production in Indonesia was produced more than 70% from the traditional process in Java Island [2], which supported by a salt farmer in East Java Province as a second largest salt buffer zone after East Nusa Tenggara. Recently, the traditional farmer did not produce salt caused by the rainy season that lasts almost a full year in 2016. This condition causing salt stock is decline and farmers have no income from salt production. Salt farmer started production at the end of July in 2017 when the dry season comes, three months later than usual. Limited stock of salt provides benefit to the farmer because of the price of salt that originally IDR 400-750 can reach IDR 3000. However, the salt farmer only gained the benefit for a short time. Since due to the continuing shortage of salt, the government issued a policy to import salt at harvesting time caused salt price decline. It is encouraging to start considering utilizing seawater to produce other mineral production from seawater beside salt. It requires integration of seawater utilization for salt production as well as for the mineral products such as magnesium and calcium to increase salt farmer income.

Magnesium and calcium are major ions that are commonly encountered in seawater after sodium and chlorine [3–6]. Magnesium and calcium are an anion bivalent and possible as impurities to each for its separation [7]. Calcium carbonate salts needed to support food processing, paper making, and construction industries [8]. Magnesium carbonate minerals widely used for the industrial process of rubber, ceramic, paper, paint and cosmetic [9]. Magnesium and calcium are important elements for a human to maintain the body function and has a simultaneous role in human health [10].

Sustainability means that ability to meet the needs at present without sacrificing the fulfillment in the future [11]. Environment sustainability connected economic and social sustainability. Productive environment sustainable provide resource foundation to support social sustainability. Economic sustainability depends on the sustainable flow of environmental, energy and material resources. These three aspects influence economy system condition. However, environmental sustainability is independent, not affected by either society or economy. Environment sustainability can stand alone as a sustainable system [12].

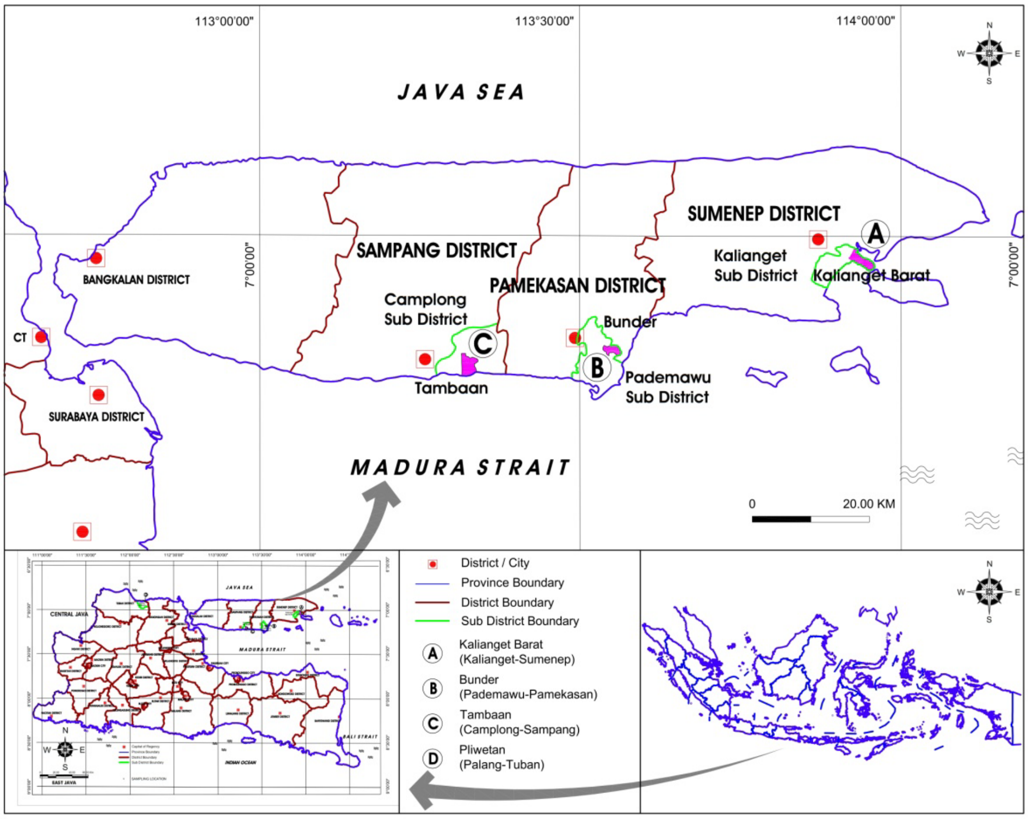

Fig.1 Sampling location in Madura Island
(District: A.Sumenep; B.Pamekasan; C.Sampang)

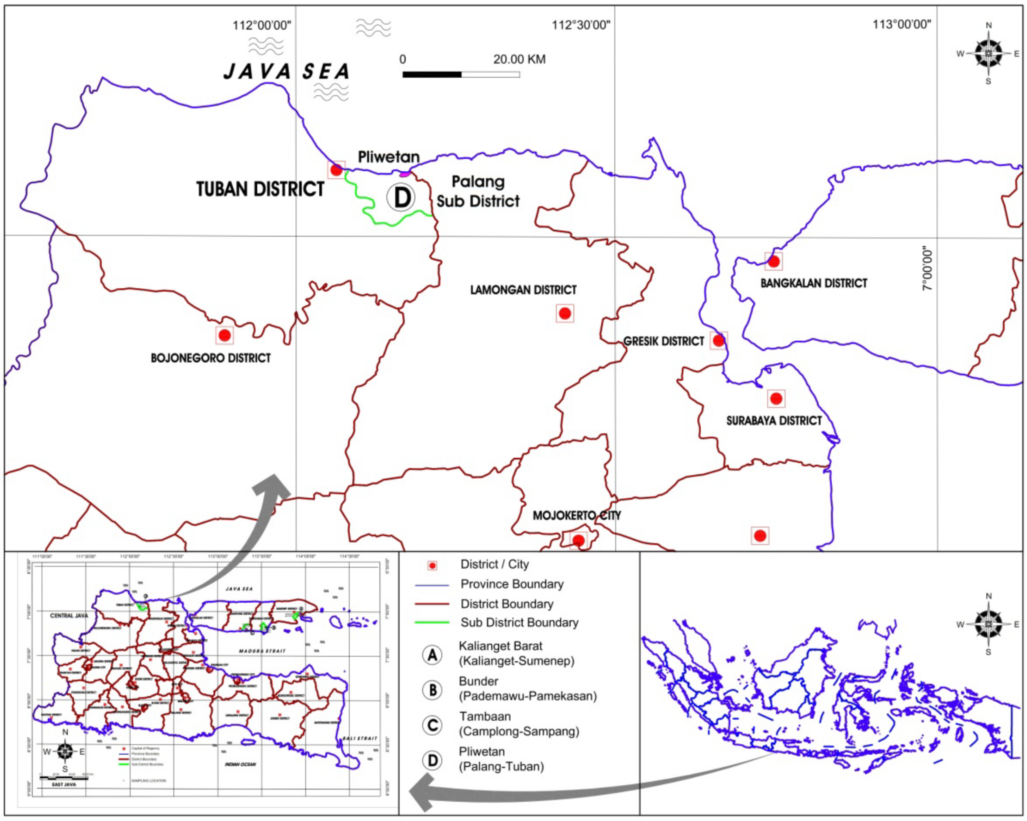

Fig.2 Sampling location in Java Island (D.Tuban District)

Traditional salt production promoted supporting marine environment sustainability. In addition to producing salt, the traditional salt production also produces wastewater. Wastewater is a concentrated solution that remains after crystallized salt deposition called bittern [13,14]. Bittern characteristic has mineral concentration 10 larger than seawater so it can influence marine life balance [15]. Bittern could be a pollutant when it discharged directly to the sea. Bittern could be mangrove growth inhibitor even cause deforestation and mortality [5]. Bittern has potential to be mineral resources when it is treated with mineral recovery. Mineral recovery needs analysis to investigate the anions behavior in salt processing. Calcium and magnesium are both alkaline earth metal and potentially interfere with each other in chemical reactions.

The novel we have discussed is magnesium and calcium behavior at a certain Baume degree (BE) in each plot during salt production process and causes. This paper provides information in which BE of magnesium and calcium has the valuable concentration for its recovery and fewer impurities. Although there have been some reports on the salt production, to our knowledge, there are no reports on the behavior of calcium and magnesium at a certain BE in each plot during salt production in Indonesia and its causes.

2. METHODS

The beginning of field study was conducted for reporting the schematic process flow layout which started from seawater inlet fill the plots in the salt pond. This study was conducted at the peak of the dry season in East Java Indonesia. The water sample was collected from each plot in plastics bottles prior to magnesium and calcium concentration analysis and measured its Baume degree (BE). Analytical methods to measure calcium and magnesium used complexometric titration with EDTA based on the American Water Works Association. Furthermore, the water sample density was determined by a hydrometer using BE unit.

The sampling was undertaken from three districts (Sampang, Pamekasan, and Sumenep) in Madura Island which is the largest salt producer in East Java Province and Tuban district in Java Island. Field study also conducted interviews with salt farmers about selling price in scarcity salt period and when imported salt from Australia has arrived. The location sampling was reported in Fig.1 and Fig.2.

3. RESULTS AND DISCUSSION

The main objective of this study is an investigation of the calcium and magnesium behavior in traditional salt production by solar evaporation. Salt pond consists of several ponds, started by stabilization, evaporation, concentration, crystallization or salt table. Each pond has several plots for evaporating sea water by sun naturally. A traditional salt pond can be illustrated in Fig.3 [2].

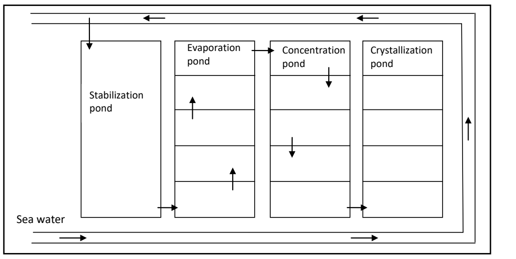

Fig.3 Illustration of the traditional salt pond [2]

Based on the result of field study and interviews with salt farmers, the whole process of making salt traditionally is done through the drain of seawater into the plots by gravity. Seawater in stabilization plot evaporated by the sun until BE 5 then will be flowed to evaporation plot. Salt farmers have to measure the density using hydrometer regularly. Seawater in evaporation plot has reached BE 11 will be flowed to concentration plot and allowed to evaporate until BE 22. Then seawater has BE 22 will flow to crystallization plot. Salt farmer has to investigate BE in order to control the salt quality since BE is higher than 29 have to be discharged from crystallization plot.

The mean of 21 concentration analyses is given in Fig.4 with both calcium and magnesium. In this study, we obtained water samples from the salt plot with the smallest BE 2. Calcium and magnesium concentration was increased started from BE around 1 when sea water was in the stabilization plot. Fig.4 shows the concentration of calcium increases continuously during evaporation of seawater, but after BE 13-16 will decrease.

As shown in Fig.4, this is contrary to the behavior of magnesium concentrations that continue to increase in line with the increase in BE. Fig.5 shows the order of separation of salts as evaporation of seawater occurs. During sea water evaporation down to 53.3%, deposition started by Fe_2O_3 and part of the calcium carbonate due to the decomposition of the bicarbonate (CaCO3). Ferric oxide was formed by reaction of ferrous ions in solution with oxygen refer to Eq.1 and part of the calcium carbonate was deposited due to the decomposition of bicarbonate refer to Eq.2.

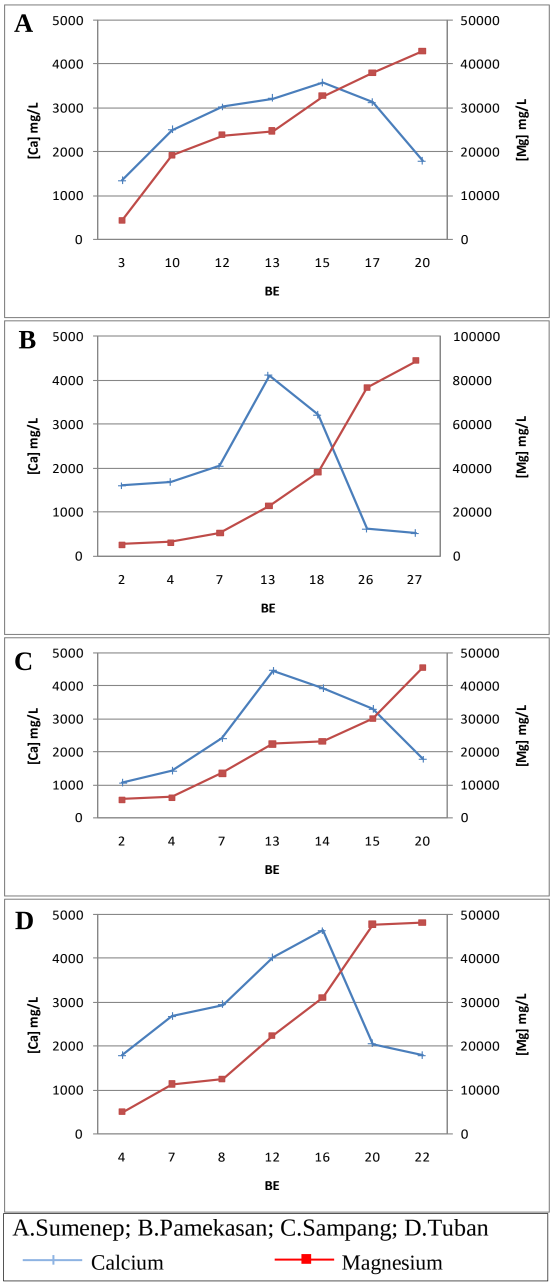

Fig.4 Calcium and magnesium concentration (mg/L as $CaCO_3$ and $MgCO_3$, respectively) from location study

On continued evaporation down to 19% calcium sulfate ($CaSO_4$) began to be deposited and continued until the volume was 3%. Sodium chloride (NaCl) started precipitating on evaporation down to 9.5% and was accompanied by small amounts of magnesium sulfate and chloride. There three salts, plus sodium bromide continued to crystallize until evaporation down to 1.62%. At this point, 91.3% of sodium chloride had crystallized. The mother liquor comprised all the potassium salts along with the remaining sodium, magnesium sulfates, and magnesium chlorides. This small volume could have been lost in a large deposit or washed away before it could crystallize [16]. This causes a difference in behavior between calcium and magnesium from the traditional salt production.

$$2Fe(HCO_3)_2 + \frac{1}{2}O_2 \rightarrow Fe_2O_3 + 4CO_2 + 2H_2O \quad (1)$$

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O \quad (2)$$

The utilization of concentrated seawater to extract the calcium minerals can be done from the traditional salt plot by considering the BE value to obtain the highest calcium value. Utilization of calcium minerals already presents in the solution can be utilized to support the chemical crystallization process to obtain a new material comprising calcium. The crystallization of the reaction to obtain another material can be carried out by utilizing a solution containing the required anions.

If attempts are made of the utilization of abundant mineral resources from the sea such as the use of calcium as a source of support, it can apply crystallization with chemical reaction [17,18]. This process can utilize concentrated seawater that has been evaporated naturally in the traditional salt pond before BE reaches about 13-16.

This is different from magnesium that will precipitate when BE reached 29 and above. Traditional salt farmer conducted regular BE measurement to control salt quality. Based on the occurrence of salt process magnesium was exist in seawater as mother liquid, the salt farmer had to discharge brine water with BE over 29 from crystallization plot. When seawater reaches BE over 29 then it should be removed to avoid magnesium deposition on NaCl salt. Magnesium deposition can cause bitter taste of NaCl salt [13].

The differences in calcium and magnesium behavior take apart as advantages for conducting recovery magnesium from salt wastewater. Calcium and magnesium are both alkaline earth metal and potentially interfere with each other in chemical reactions. Calcium and magnesium can compete to react with anions in chemical reactions.

As in the recovery struvite ($MgNH_4PO_4$) using wastewater contains calcium. The presence of calcium ion in the wastewater might preferentially react with PO_4 to produce hydroxyapatite, dicalcium phosphate, and octacalcium phosphate.

The presence of calcium ions can influence struvite formation, either by competing for phosphate ions or by interfering with the crystallization of struvite. The formation of calcium carbonate or calcium phosphate also is noticed causing an increase induction time from 2 minutes become 3 minutes [19-21].

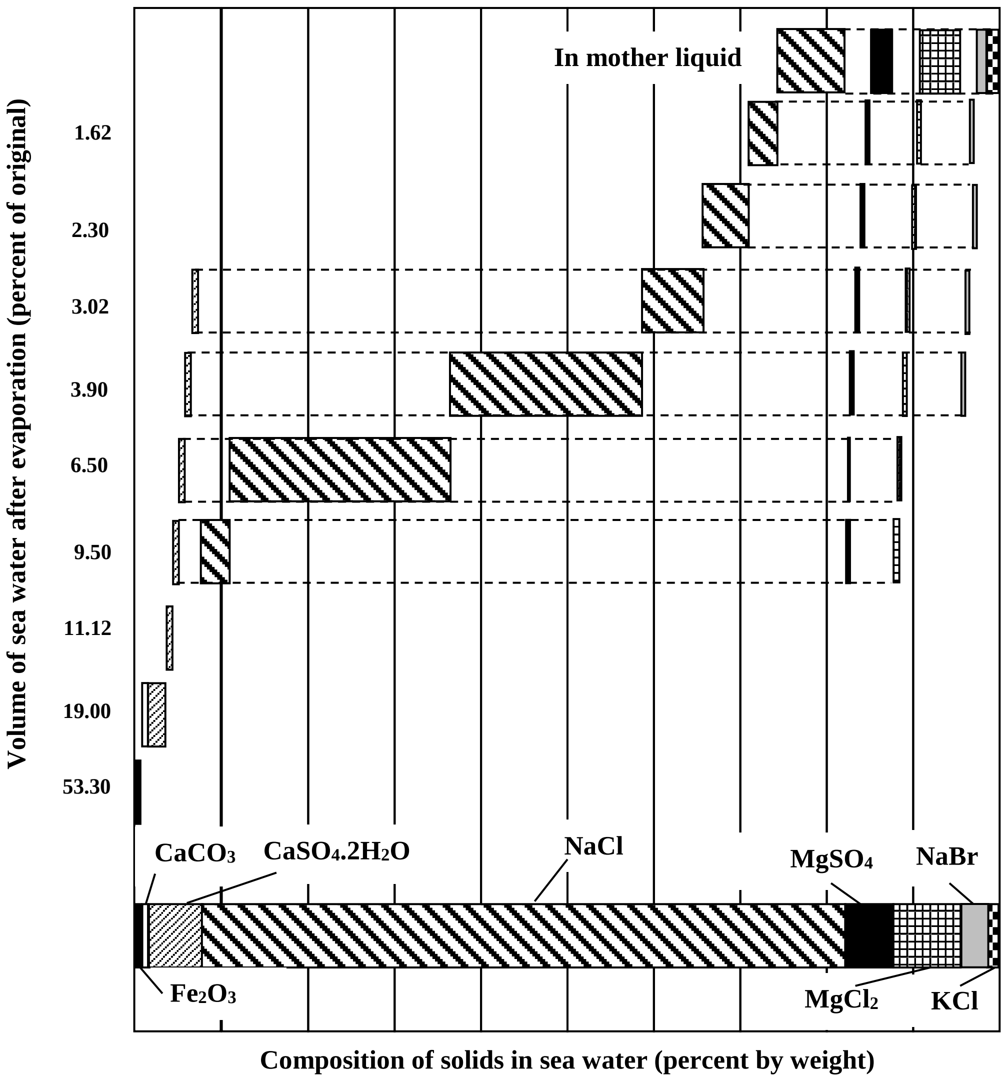

Fig.5 Order of separation of salts from evaporated seawater [16]

The different behavior between calcium and magnesium take apart as advantages for extraction magnesium from salt production wastewater. Some studies have been reported utilizing bittern as salt wastewater to magnesium recovery as magnesium oxalate, carbonate, sulfate, chloride, and hydroxide [22-25]. Utilization bittern can be one of the efforts in maintaining marine environment sustainability through treat wastewater from salt production. In addition to preventing pollution from bittern that is toxic to marine life, this effort can also help salt farmers in increasing production other than salt. It is promoted to diversify the products in an integrated manner not only salt production but also mineral recovery from wastewater. It is expected to contribute to increasing coastal community revenue since have been relying solely on salt at present. Salt farmers often get a low price because the time of harvesting is often followed by government policy to import salt. If salt farmers can integrate the production of salts and other minerals, it can increase revenue during harvesting that coincides with imports. Although in the utilization of salt wastewater requires a lot of effort but should be initiated a policy to the government in order to help salt farmers as a coastal community to create a sustainable economy. Economic sustainability will be able to support social sustainability that will also create a sustainable marine environment.

4. CONCLUSION

The results of this study can be valuable information for achieving marine environmental sustainability through the recovery of materials from seawater in salt production activity.

The utilization of concentrated sea water to extract its mineral can be done from a traditional salt plot by considering the BE value to obtain potential value.

The concentration of calcium that could potentially be utilized as recovery resources in concentration plot, prior to reaching BE 13-16. While magnesium concentration increases continuously during the process of making salt until harvesting as bittern.

5. ACKNOWLEDGEMENTS

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