Application of Ion Exchange Method on Removal of The Ca^{2+}, Mg^{2+}, K^+ and $SO4^{2-}$ Salt Solution

Caecilia Pujiastuti[1], Ketut Sumada[2]
Chemical Engineering Department
Universitas Pembangunan Nasional "Veteran" Jawa Timur
Surabaya, Indonesia
[1]caeciliapujiastuti@gmail.com

Yustina Ngatilah[3]
Industrial Engineering Department
Universitas Pembangunan Nasional "Veteran" Jawa Timur
Surabaya, Indonesia

Abstract— **Salt product of Indonesian country is produced through the process of evaporation and crystallization of seawater. The salt product contains sodium chloride (NaCl) levels ranging between 80-92% and the other are impurities such as magnesium chloride ($MgCl_2$), calcium carbonate ($CaCO_3$), potassium chloride (KCl) and magnesium sulfate ($MgSO_4$). The quality of salt produced has lower quality compared to salt consumption and industry standards, The salt for salt consumption, minimum sodium chloride (NaCl)contain is 94.7%, industrial is more than 98% and pharmaceuticals more than 99.5%. therefore is needed a method to improve the quality of the salt. In this research is selected ion exchange method to improvement the quality of salt. This research focuses on study the effect of cationic resins amount (50-150) grams per liter of salt solution and anion solution (75 grams) and contact time (5-25) minutes on removal of Ca, Mg, K and SO4 ions. The study was conducted in a stirred tank with a fixed rotation speed of 200 rpm, and the initial quality of the salt solution contained Ca ions: 0.07%, Mg: 0.09%, K: 0.04% and SO4: 0.4%. Based on the result of the research, the removal of Ca ion: 82.86%, Mg: 62.22%, K: 25.00% and SO4: 72.50% at condition of cationic resins amount: 100 gram / liter and contact time 25 minutes.**

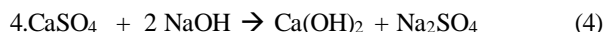*Keywords*— *Salt, impurities, ion exchangers, removal.*

I. INTRODUCTION

Salt product of Indonesian country is produced through the process of evaporation and crystallization of seawater. The salt product contains sodium chloride (NaCl) levels ranging between 80-92% and the other are impurities such as magnesium chloride ($MgCl_2$), calcium carbonate ($CaCO_3$), potassium chloride (KCl) and magnesium sulfate ($MgSO_4$). The quality of salt produced has lower quality compared to salt consumption and industry standards, The salt for salt consumption, minimum sodium chloride (NaCl) contain is 94.7% [1], industrial is more than 98% [2] and pharmaceuticals more than 99.5%. Therefore is needed a method to improve the quality of the salt. Some processing processes that have been carried out in order to improve the quality of salt are:

1. Physical process, the physical processes such as washing process (hydro-extraction) is a process of extraction of impurities by salt saturation solution. This hydro-extraction
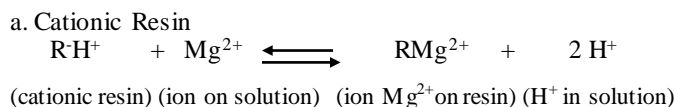
process can produce salt products with a NaCl content of 95-97%, this is more high than salt consumption standard. The recrystallization process, a process that re-crystallizes the salt product, this process through two stages of the process, namely the process of salt dissolving and crystallization (evaporation), this process can produce salt products with NaCl 98-99 % content, this quality more high than salt consumption and industry standard

2. Chemical process, the improvement of the quality of salt by chemical processes, is by adding of chemicals into the salt solution, the chemicals commonly added to the salt solution are sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), sodium phosphate (Na_2HPO_4) and others [3,4,5]. The addition of these chemicals is intended to bind impurities in salts such as magnesium (Mg), calcium (Ca), potassium (K) and sulfate (SO4) ions and form deposits. Some chemical reactions that occur in the addition of chemicals are as follows :
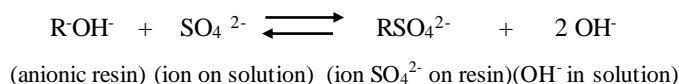
$$1.\ MgCl_2\ +\ 2\ NaOH\ \rightarrow\ Mg(OH)_2\ +\ 2\ NaCl \qquad (1)$$

$$2.\ MgCl_2\ +\ Na_2CO_3\ \rightarrow\ MgCO_3\ +\ 2\ NaCl \qquad (2)$$

$$3.\ CaSO_4\ +\ Na_2CO_3\ \rightarrow\ CaCO_3\ +\ Na_2SO_4 \qquad (3)$$

$$4.\ CaSO_4\ +\ 2\ NaOH\ \rightarrow\ Ca(OH)_2\ +\ Na_2SO_4 \qquad (4)$$

Based on some reaction above, the added of chemicals will form precipitates such as magnesium hydroxide ($Mg(OH)_2$, magnesium carbonate ($MgCO_3$), calcium carbonate ($CaCO_3$) and calcium hydroxide ($Ca(OH)_2$.This deposit shows the presence of separated impurities. this process can produce salt products with NaCl 98-99 % content, this quality more high than salt consumption and industry standard.

3. Ion Exchange (Ion Exchange), the improvement of the quality of salt by ion exchange method is carried out by 3 stages of process, namely the process of salt dissolution, ion exchanger, and crystallization . This process is a chemical processes (ion exchanger), positive ions (Mg^{2+}, Ca^{2+}, K^+ and Na^+) which are in the salt solution will be exchanged with hydrogen (H^+ or Na^+) ions in the ion exchange medium (cationic resin) and the negative ions (Cl^-, and SO_4^{2-}) will be exchanged with hydroxide ions (OH^-) which are in the ion exchange medium (anion resin) [6,7,8]. The ion exchange mechanisms are as follows [9].

a. Cationic Resin

$$R^-H^+ + Mg^{2+} \rightleftharpoons RMg^{2+} + 2H^+$$

(cationic resin) (ion on solution) (ion Mg^{2+} on resin) (H^+ in solution)

In the cationic resins, the positively charged of Mg^{2+} ion will be bound to the cationic resins, while the cationic resins itself will release H^+ ions, the release of H^+ ions can cause a decrease on the pH of the solution.

b. Anionic Resin

$$R^-OH^- + SO_4{}^{2-} \rightleftharpoons RSO_4{}^{2-} + 2OH^-$$

(anionic resin) (ion on solution) (ion $SO_4{}^{2-}$ on resin)(OH^- in solution)

In the canionic resins, the negatife charged of $SO_4{}^{2-}$ ion will be bound to the anionicnic resins, while the anionic resins itself will release OH^- ions, the release of OH^- ions can cause a inecrease on the pH of the solution.

The selectivity of ions

In ion exchange there is a certain rule (selectivity) of Montgomery [10], namely:

At low ionic concentrations and normal temperatures, ion exchange will increase with increasing ionic valence. As follows :
   $Th^{4+} > Al^{3+} > Ca^{2+} > Na^+$ or $PO_4{}^{3-} > SO_4{}^{2-} > Cl^-$ this shows that ions that have a higher valence will be exchanged first and so on

b. At low ion concentrations, normal temperatures, and the same valence of ions, ion exchange increases with increasing number of ion atoms. As follows :
   $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ or $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Be^{2+}$ this indicates that ions that have larger atomic numbers will be swapped first and so on.

c. At high ion concentrations, the potential difference lies in the difference in the valence of the ions, in some cases ions that have lower ionic valence have a higher potential exchange. As follows :
   $SO_4{}^{2-} > I^- > K^+ > NO_3{}^- > CrO_4{}^{2-} > Br^-$ this shows that ions that have a greater valence will not necessarily be exchanged first.

II. MATERIAL AND METHODS

In this study the materials were used is obtain from salt centers in East Java, and the medium for exchanging ion is cationic and anionic resin, while the levels of NaCl, Mg^{2+} and Ca^{2+} were analyzed by titrimetric method, K^+ ions were analyzed using AAS and SO_4 analyzed by the gravimetric method. Salt product (360 grams) dissolved in one (1) liter of distilled water where the condition is the solubility limit of salt, the salt solution is added by cationic resin to bind positive ions (Mg^{2+}, Ca^{2+} and K^+), filtration and filtrate are added anionic resin to bind ions negative ($SO_4{}^{2-}$), filtration and filtrate were analyzed for NaCl, Mg^{2+}, Ca^{2+}, K^+ and $SO_4{}^{2-}$ concentrations. The filtrate is crystallized through evaporation so that a salt product is produced, the salt produced is

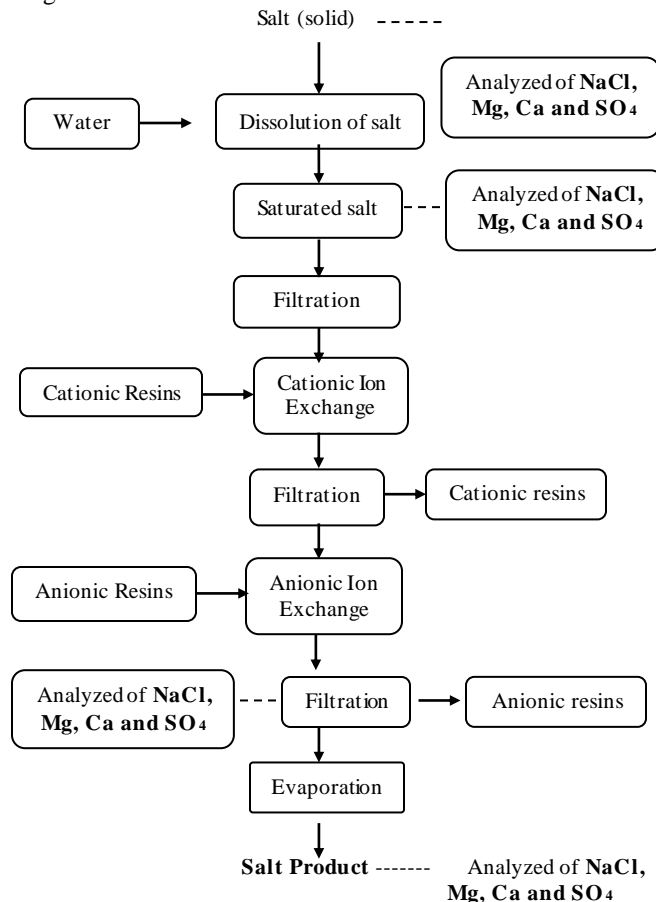analyzed for NaCl, Mg^{2+}, Ca^{2+}, K^+ and $SO_4{}^{2-}$. The block diagram is as follows:

Fig. 1. Schematic Diagram of Research

III. RESULT AND DISCUSSION

a. Chemical composition of the salt used as a raw material

The chemical composition of salt that used as raw material in this research is presented in the following table 1.

TABLE I. CHEMICAL COMPOSITION OF SALT

No	Parameters	Concentration (%)
1	Sodium chloride (NaCl)	92,03
2	Magnesium (Mg)	0,56
3	Sulfate (SO4)	2,03
4	Calcium (Ca)	0,50

b. Chemical composition of the saturated salt solution

The saturated salt solution is a solution obtained from 360 g of salt dissolved with 1 liter of water. The chemical composition of the saturated salt solution is presented in the following table 2.

TABLE II. CHEMICAL COMPOSITION OF TRADITIONAL SALT

No	Parameters	Concentration (%)	Equivalent/L
1	Sodium chloride (NaCl)	28.40	
2	Magnesium (Mg)	0.09	0.018519
3	Sulfate (SO4)	0.40	0.021277
4	Calcium (Ca)	0.07	0.008733
5	Potassium (K)	0.04	0.010256

The chemical composition of the saturated salt solution that use as raw material in this research. The saturated salt solution contains magnesium (Mg), sulfate (SO_4), calcium (Ca) and potassium (K) ions that will be used on ion exchange process.

c. The influence of agitation time and amount of cationic resins to decrease of calcium concentration on ion exchange process
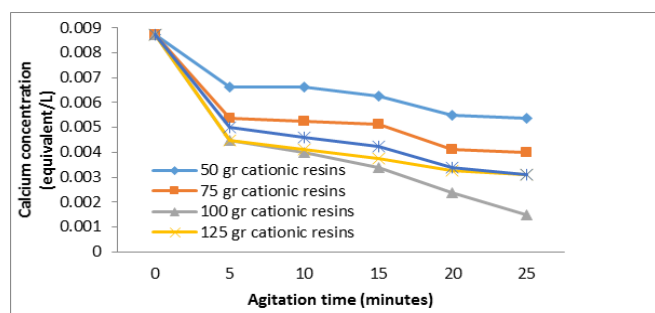

Fig. 2. Correlation agitation time to calcium (Ca^{2+}) decrease on amount of cationic resins

Figure 2 shows that the law magnesium concentration on salt solution is 0.001497 equivalent/Liter at the addition of 100 grams of cationic resins and agitation time for 25 minutes. The highest ion calcium (Ca^{2+}) removal percentage is reached 82.6%.

d. The influence of agitation time and amount of cationic resins to decrease of magnesium concentration on ion exchange process
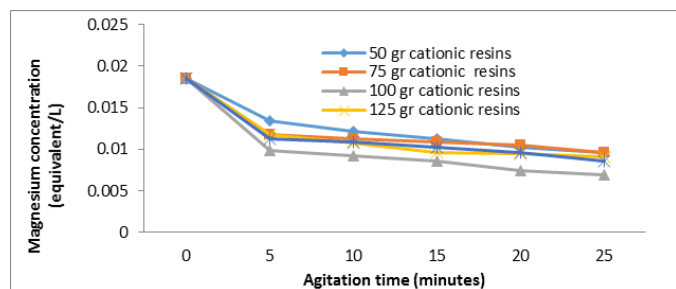

Fig. 3. Correlation agitation time to magnesium (Mg^{2+}) decrease on amount of cationic resins

Figure 3 shows that the law magnesium concentration on salt solution is 0.006996 equivalent/Liter at the addition of 100 grams of cationic resins and agitation time for 25 minutes. The highest ion magnesium (Mg^{2+}) removal percentage is reached 62.22%.

e. The influence of agitation time and amount of cationic resins to decrease of potassium concentration on ion exchange process
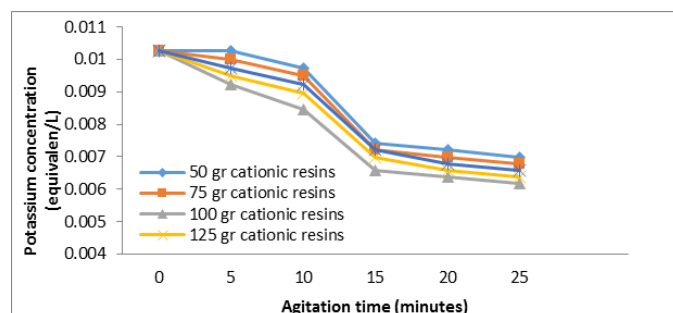

Fig. 4. Correlation agitation time to potassium (K^+) decrease on amount of cationic resins

Figure 4 shows that the law potassium concentration on salt solution is 0.006173 equivalent/Liter at the addition of 100 grams of cationic resins and agitation time for 25 minutes. The highest ion potassium (K^+) removal percentage is reached 25.00 %.

f. The influence of agitation time and amount of anionic resins to decrease of sulfate concentration on ion exchange process
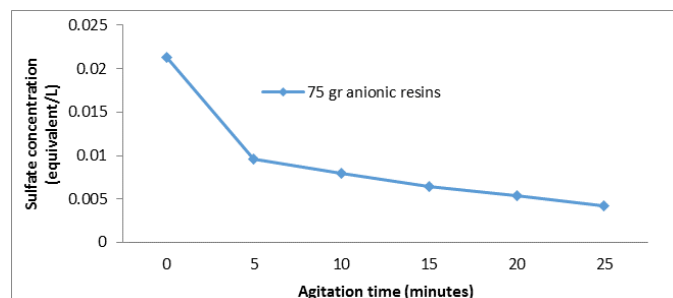

Fig. 5. Correlation agitation time to sulfate (SO_4^{2-}) decrease on 75 gr of anionic resins

Figure 5 shows that the law sulfate concentration on salt solution is 0.004255 equivalent/Liter at the addition of 75 grams of anionic resins and agitation time for 25 minutes. The percentage of sulfate ion removal is reached 72,50%.

IV. CONCLUSION

Based on the results of research can be concluded several things including
1. Ion exchange method can be applied to removal Ca^{2+}, Mg^{2+}, K^+ and SO_4^{2-} ions on salt solution
2. Percentage of magnesium (Mg^{2+}) ion removal is 82.62 %
3. Percentage of calcium (Ca^{2+}) ion removal is 62.22 %
4. Percentage of potassium (K^+) ion removal is 25.00%

5. Percentage of sulfate (SO_4^{2+}) ion removal is

6. Quality of salt product after evaporation process : NaCl : 99.41 % ; Ca^{2+} : 0.032% ; Mg^{2+} : 0.09% dan K^+ : 0.081 serta SO_4^{2-} : 0.195 %.

ACKNOWLEDGMENT

REFFERENCE

[1] National Standardization Agency of Indonesia SNI 3556-2016 standard for consumption salts

[2] National Standardization Agency of Indonesia SNI 0303-2012 standard for industrial salts

[3] C. Pujiastuti, K. Sumada, Y. Ngatilah, and P. Hadi, "Removal of $Mg^{2+}, K^+, SO4^{-2}$ ions from Seawater by Precipitation Methode," Matec Web Conf., vol 58, pp 01022, 2016.

[4] C. Pujiastuti, Y. Ngatilah, K. Sumada, and S. Muljani, "The Effectiveness of Sodium Hydroxide (NaOH) and Sodium Carbonate (Na2CO3) on the Impurities Removal of Saturated Salt Solution," IOP Conf.Series : J. Physics: Conf. Series, vol 953, pp 012215, 2017

[5] C. Pujiastuti, Y. Ngatilah, K. Sumada, S. Muljani, "A Chemical Effectivity Study on Removal of Seawater Mg^{2+}, K^+, Ca^{2+} and SO_4^{2-} Ions ," Adv. Sci. Lett., vol 23, pp 12252–12255, 2017.

[6] N. Kansara, L. Bhati, M. Narang, and R. Vaishnavi, "Wastewater treatment by ion exchangemethod: a review of past and recent researches,"Environmental Science an Indian J., Vol 12 (4), pp 143-150, 2016

[7] S. Mountadar, A. Hayani, A. Rich, M. Sinit, and S. Tahiri, "Equilibrium, kinetic, and thermodynamic studies of the Ca^{2+} and Mg^{2+} ions removal from water by Duolite C206A," Solvent and Extraction and Ion Exchange J., Vol 4 (5), pp 156-165, 2018

[8] B. Bandrabur, R.-E.T. Fărmuş, L. Lazăr, L. Bulgariu, and G. Gutt, "Use of Strong Acid Resin Purolite C100E For Removing Permanent Hardness of Water-Factors Affecting Cationic Exchange Capacity," Scientific Study & Research Journal, Vol 13 (3), pp 295 – 304, 2012

[9] N.N. Ismail, "Experimental study on Ion Exchange Rate of Calcium Hardness in Water softening process Using Strong Acid Resin DOWEX HCR S/S", Al-Nahrain University, College of Engineering J., Vol.91 (1), pp 107 – 114, 2016

[10] J. Montgomery, Water Treatment Principles and Design, John Wiley and Sons, 1985, pp 198-222