IMPROVEMENT IN PROCESS ECONOMY BY USING RO RETENTATE FROM SEAWATER DESALINATION INTO SODIUM CARBONATE PRODUCTION

Supriya S. Dhume[1], Yogesh J. Chendake[2], Rahul K. Kulkarni[3]

[1, 2, 3] *Chemical Engineering Department, Bharati Vidyapeeth Deemed University, College of Engineering, Pune, (India)*

ABSTRACT

Seawater desalination by reverse osmosis generates two streams generates permeate stream of pure potable water and retentate stream containing high salt concentration. This retentate stream contains high concentration of NaCl as major component, which is either dispensed as landfill or sent to water stream used as sink. This becomes waste of valuable resource, which can have undesirable effect on environment and soil. It can be utilized as a feed in chemical processes for production of sodium carbonate. This high concentration NaCl (~ 27 %) containing retentate can be useful feed option for soda ash industry which uses NaCl solution as feed stream from either sea water having NaCl concentration of ~ 3.0 % or rock salt. Its application for production of soda ash would lead to conservation of energy required for removal of water from feed seawater or product concentration. It would in turn result in economical benefits. As an analysis such reuse can lead to large economical benefits (to the extent of Rs. 91.00×10^6) by use of retentate from 1000 lit/h seawater as feed.

Keywords: Desalination, Economical Benefits, Retentate, Reverse Osmosis, Soda Ash

I. INTRODUCTION

Reverse osmosis can be applied for seawater desalination which removes dissolved salts and minerals, to produce potable water suitable for human consumption [1]. The salt NaCl from seawater is potential byproduct of desalination which can be utilized in further applications. The cost of desalinating seawater is generally higher than alternatives (fresh water from rivers or groundwater, and water conservation), due to energy requirements for desalination [2]. Such alternatives may not always be available or feasible, which makes desalination as only reliable source, in the areas with scarcity of fresh water. According to Henthorne Lisa; worldwide 15,988 desalination plants were in operation in June 2011 [3]. They produce 66.5 million cubic meters of water per day which satisfies need of 300 million people. Still drinkable water is not available to a large part of world population [3]. This makes seawater desalination as a major process these days.

Desalination can be carried out by two methods: 1) thermal processes or 2) membrane based processes. The traditionally used thermal process is vacuum distillation. It can be advantages at places where excess heat is available from other process e.g. heat from engine boilers in ships or submarines [4]. For regular application, thermal processes are highly energy intensive and costly in absence of availability of excess heat from other operations [4]. Other option is to use membrane based processes for seawater desalination. Reverse osmosis is one of the important technologies in the same [5]. They use semi-permeable membranes with pressure higher than osmotic pressure to transport water across, retaining salts. . Reverse osmosis plant membrane systems typically use less energy than thermal distillation, which has led to a reduction in overall desalination costs over the past decade [6]. Desalination remains energy intensive, however, and future costs will continue to depend on the price of both energy and improvements in desalination technology [6].

Though desalination by RO is popular and beneficial; there are hardly any reports on use or disposal of retentate. It contains high concentration of salts e.g. calcium, magnesium, potassium, silica, sodium, sulphates, etc. [7]. Though there are few reports of their utilization in preparation of pure brine solution, as food preservatives but majorly they are used in tacking out salts for landfills or disposed in streams used as sink [8]. This disposal or landfill would lead to pollution of soil and ground water contamination. To minimize the pollution and ground water contamination issues requires disposal in form of solid salt by pretreatment for removal of water using process like distillation, evaporation, multieffect reboiler, etc. This requires high amount energy and affects process economy. If this retentate is used in further processes like production of chemicals, it would reduce environmental issues along with positive impact on industrial economy.

Retentate from seawater desalination by RO contains high amount of salt (*viz*. sodium chloride, NaCl). It can be used as feed for different industries e.g. chlor-alkali industry, sodium bicarbonate, soda ash industry, food industry, medicine & agriculture, etc. [9]. These industries use sea water as feed or NaCl from rock salt [10]. Use of desalination retentate as feed for these industries would reduce of energy costs and lead to economical benefits.

Presently there are rarely any reports on use of desalination RO retentate in chemical industries and their economical befits, as per best of our knowledge. Though purification of sodium chloride and potassium chloride for application in electrochemical work is reported [11], applicability in large scale chemical production is neglected uptill now. Hence we thought to explore this area. In this work, we have explored possibility of using retentate stream as a feed in the production of soda ash and analyzed its economical aspects.

II. MATERIALS AND METHODOLOGY

2.1 Materials

Approximately 97 % of world water reservoirs are made up of sea-water [1]. They are salty with ~ 3.5 % salinity [12]. It contains sodium (Na+) and chloride (Cl−) ions as major components with upto 3 % concentration along with other salts *viz*., Ca^{++}, Mg^{++}, K^{+}, Fe^{3+} at concentrations of 0.41, 1.28, 0.40 and 0.4 %, respectively. It also poses some other negligible concentrations.

2.2 Desalination by Reverse Osmosis (RO)

Desalination is used to remove salts from seawater making it suitable for desired application. RO is one of the important desalination methods, which fractionates seawater into permeate potable water and retentate containing major part of salts (e.g. NaCl) [13]. The RO membranes have minimum 90 % retention (*viz*., NaCl), normally. Considering fractionation of water 90 % permeate [14], remaining quantity as retentate posses NaCl with 27 % concentration. It also contains large quantities of other (*viz*., Ca^{++}, and Mg^{++}) salts as summarized in Table 1.

2.3 Feed to Sodium Carbonate (soda ash) Industry

NaCl is used as feed for industrial production of soda ash, in the form of 300 – 315 g/lit concentration brine solution. Conventional sources for NaCl are rock salt and sea water. Their details about available concentrations and impurities are listed in Table 1. Retentate from seawater desalination by RO can be another source for NaCl, which contains NaCl as major component with concentration 27%. Other components and their concentrations are given in Table 1.

Table 1. Nacl Sources, Their Compositions and Steps Needed For Application As Feed In Sodium Carbonate Production [7, 15, And 16]

NaCl Source	Composition		Processing for use as feed in soda ash industry
	Components	Concentration (gm/kg)	
Feed brine composition for soda ash	NaCl	300 – 315	• Purification needed • Product needs to be concentrated post generation
Direct use of seawater	Na^{+}	10.8	• Purification • Energy required for water evaporation to obtain brine concentration • To remove impurities brine needs purification • Required chemicals for precipitation
	K^{+}	0.40	
	Mg^{++}	1.28	
	Ca^{++}	0.41	
	Cl^{-}	19.4	
Rock salt	NaCl	900-970	• Cost of rock salt • Make solution salt plus water for conventional concentration • Needs Purification
	Mg^{++}	0.01	
	Ca^{++}	0.02	
	K^{+}	0.02	
RO retantate use as feed	Cl^{-}	38.8 ± 0.4	• Need purification
	Na^{+}	20.8 ± 0.3	
	Mg^{++}	2.64 ± 0.2	
	Ca^{++}	0.83 0.04	

III. RESULT AND DISCUSSION

3.1. Desalination of sea water by RO

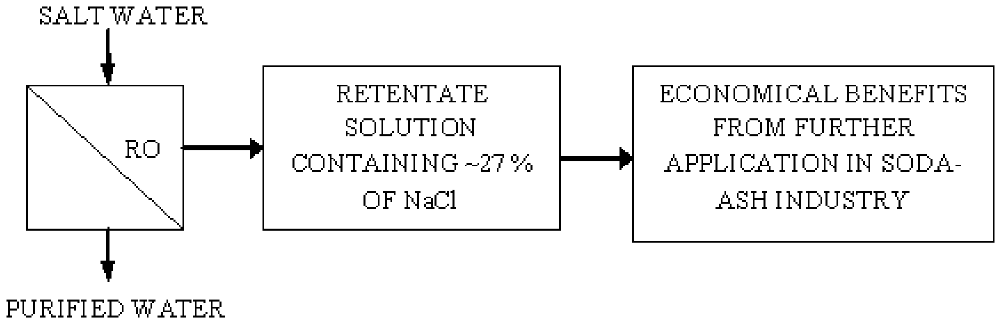

Fig. 1. Schematic Representation of Application of RO Retentate from Desalination Process

Desalination is used to separate salt content from seawater to desired level. RO is one of the prominent desalination technology, which uses semi-permeable membranes which allow selective passage of solvent (water) under influence of external pressure higher than osmotic pressure of solution [17]. This fractionates solution into pure solvent as permeate and major part of salts from feed solution is present in retentate [17]. Seawater desalination permeate is potable water with less than 500 mg dissolved solids [18]; suitable for most domestic, industrial, and agricultural uses. Its retentate contains major salts from feed seawater at very high concentrations. Practically, it can be said to be concentrated salt brine containing more than 35,000 mg dissolved solids with NaCl as major component [19]. During seawater desalination by RO purification takes place without phase change, which is a major advantage as compare to thermal process [20]. Due to This separation without phase change, it requires low energy and maintenance costs are less compared to conventional thermal processes [20]. This is addition to conventional benefits of membranes process such as, ease of operation, lowering operational and maintenance costs and environmental friendly nature. This benefit makes desalination by RO, an attractive option over thermal processes these days.

Seawater desalination by RO has many attractive features, with only major issue of disposal or utilization of high salt containing retentate. This area is largely neglected up till now. Permeate forms major section (~90 %) of solute-water from feed seawater to RO system, while retentate consists of remaining ~10 % of water, with > 90 % of salt and other impurities [14]. Generally, feed seawater posses ~3.5 % salinity, having NaCl as a major component with concentration upto 3 % [15]. This leads to formation of retentate with NaCl as major component with concentration upto 27 %; along with other components whose concentrations are given in Table 1.

3.2 Disposal of RO Retentate

Disposal of retaining containing high concentrations of salt is major issue. Currently one of the major methods is its release into water bodies used as sink [21]. Such disposal of salt containing streams into deep seas requires large pumping costs. Additionally, sudden change in salt concentration near disposal area caused from this disposal could adversely affect marine life. Another method can be disposal as a landfill [21]. Such disposal of salt solution can lead to seepage of salt containing water through the soil and contaminate of ground water. This would affect soil quality around the disposal ponds. Hence it is necessary to evaporate water and dispose salts in solid forms. Such solid disposal requires removal of water by evaporation to concentrate the solution. It would require high amount of energy, in turn large fuel costs.

The retentate solution can be concentrated to a level (~ 96 %) where it can be disposed without possibility of water seepage through soil. Consider 1000 lit/hr of seawater with 3.5 % salinity as feed to RO unit, which fractionates to produce 900 lit/hr potable water and 100 lit/hr retentate. For the RO membrane minimum NaCl retention is 90 %, while other salt and organic molecules are being larger in size assumed to be retained completely [13]. This would give us permeate stream with potable water and retentate stream containing salts having NaCl as major component of 27 % concentration. For disposal of this high concentration stream as landfill, major component of water from this retentate needs to be removed by considering increase in NaCl concentration upto 96 %. Thus evaporator is used to evaporate water and remaining salts as bottom product. During evaporation of water, the heat capacity of solution would change due to presence of NaCl. Considering all these factors annual total energy requirement can be calculated as described earlier [22].

Thus considering 1000 lit/hr seawater as feed, RO retentate volume would be 100 lit/hr. For 300 days/annum plant operation heat required for evaporation of water from RO retentate before its disposal would be ~59.00 × 10^4 kJ. If this heat is provided by direct fire tube boiler having efficiency of 80 %, amount of black coal required would be 95 × 10^5 kJ/ton. As per Indian market the cost of this coal is Rs. 150/ton. Thus an estimated amount of Rs.73. × 10^6 would be required per annum for disposal of salts from desalination of 1000 lit/hr seawater as feed. This is a large cost requirement.

3.3RO Retentate Utilization

Sea water is common available material, which cover more than 97 % of the Earth's surface [1]. In the Reverse Osmosis unit salt water is pumped to make it potable water as shown in Fig. 1. The salinity of sea water is due to variety of dissolved ionic compounds. Major components present are sodium (Na^+) ions and chloride (Cl^-) ions. Also a significant amounts of magnesium (Mg^{2+}), calcium (Ca^{2+}), potassium (K^+), sulfate (SO_4^{2-}) and hydrogen carbonate (HCO_3^-) ions are present [16]. Their concentrations in seawater are shown in Table 1 [15]. Upon passing through RO membranes this seawater is fractionated into permeate and retentate solution. This retentate contains high concentrations of sodium chloride. Concentrations of calcium, magnesium and potassium salts are low (Table 1). Conventional method of solid disposal of these salts requires large amount of energy, in turn fuel cost as discussed in Section 3.2. Additionally, this disposal of retentate would be loss of valuable resource. This high concentration saline solution can be used for different applications such as a feed for the production of chemicals, which uses NaCl as feedstock.

Production of sodium carbonate is one of such industry where NaCl is used as starting material [23]. We thought to investigate economical impact for use of RO retentate as feed for Na_2CO_3 production. Na_2CO_3 is considered in this investigation for possible use on RO retentate during production due its large applications in various industries like manufacture of glass, electrolyte, water softener in laundering, etc. Sodium carbonate is a food additive used as an acidity regulator, anti-caking agent, raising agent, and stabilize; also used by the brick industry as a wetting agent to reduce the amount of water [24].

3.4 Present Feed Conditions in Soda Ash (Na_2CO_3) Industry

Currently, Na_2CO_3 industry uses NaCl in the form of purified brine solution with 300 - 315 g/lit concentration as feed solution for Solvay process. It uses NH_3 which dissolved in an NaCl solution and reacted with CO_2. A precipitate of $NaHCO_3$ was obtained which could be calcined to produce high purity Na_2CO_3. Saturated salt brine is purified in series of wash towers with NH_3 and then with CO_2 to remove Ca, Mg, and Fe as sludge [24]. Thus RO retentate reduce burden over all this NH_3 and CO_2 towers.

Seawater is one of the important and abundantly available source of NaCl. It has low salinity of 3.5 % and just ~ 3 % of NaCl is present with other impurities like magnesium, potassium, calcium etc. (Table 1). It requires major purification for removal of calcium and magnesium salts. Additionally it requires concentration of solution to obtain NaCl concentration in the desired range of 3 to 35 %, which can be used as brine solution for Na_2CO_3 production [24]. This requires evaporation of water, in turn requires large quantities of energy (~ 24.00 × 10^5 kJ/hr) and fuel costs (Rs. 94.00×10^6 /annually) (calculated). Additionally it requires additional costing for purification of brine for precipitation of Ca^{++} and Mg^{++}. This precipitation of $NaHCO_3$ requires chemicals like lime; which adds costs to the order of 26.00 × 10^3 Rs. /annum of feed solutions.

Another source of NaCl is rock salt. The availability rock salt is low. It is available in the regions of Africa, Bulgaria, Canada, US, Italy, Pakistan, Germany etc. It contains almost 90-98% of NaCl with negligible quantities of calcium, magnesium and potassium (Table 1). It needs to be dissolved in water to form brine solution. Though impurities are present very negligibly still they need purification for better production of chemicals, which adds costs of brine solution (Rs. 62.00 × 10^5/annually) (calculated).

3.5 Benefits from Application of RO Retentate

RO retentate from seawater desalination can provide major economical benefits in production of soda ash. This RO retentate can be successfully used as feed in Na_2CO_3 industry compared to seawater and rock salt. RO retentate has the higher concentration of NaCl. NaCl concentration is almost 27 % (calculated). It needs evaporation of water to increase its concentration, but it is very less compared to energy required to increase concentration of seawater to required NaCl concentration of 300 - 315 g/lit.

Successful implementation of such combined process would lead to utilization of stream which currently treated as waste, for preparation of useful products in an economical way. Additionally, the combined operation would eliminate costs required for disposal of salts from RO retentate. This can be a source of large economical benefits in soda-ash production. Thus overall utilization of this retentate would best option for industries to use it for further process like manufacturing of chemicals. Also it minimizes the environmental issues like effect on marine aquatic life possible due variation in salts concentration by disposal of RO retentate, and soil and ground water quality degradation due to disposal of salts in solid form.

IV. CONCLUSION

Though seawater desalination by using RO is very beneficial technique for produce potable water, it has issues with generation of large quantities of retentate solution with high concentration of salts. Conventionally methods of disposal of RO retentate lead to large losses of important feedstock and harm to environment. The use of retentate in Na_2CO_3 production leads to large economical benefits. Use of RO retentate from 1000 lit/hr seawater desalination as a feed in Na_2CO_3 production can provide benefits worth 91.6 × 10^6 Rs/annum (calculated) as compared to use of direct seawater as feed. Though soda ash preparation process has excess energy available from other operations they can be utilized for applications like production of cheap electricity On the other hand it provides benefits worth 38.00 × 10^5 Rs/annum (calculated) compared to use of rock salt as feed. This is in addition to elimination of energy costs 73.74 × 10^6 Rs/annum (calculated) required for water evaporation during solid disposal of salts from RO retentate. Such economical and environmental benefits make use of RO retentate in further processes an attractive option.

REFERENCE

[1] Thomas M. Missimer, Noreddine Ghaffour, Abdullah H.A. Dehwah, Rinaldi Rachman, Robert G. Maliva, Gary Amy (2013), "Subsurface intakes for seawater reverse osmosis facilities: Capacity limitation, water quality improvement, and economics", Desalination 322 (2013) 37–51.

[2] Asif Matin, H.Z. Shafi, Zafar Khan, Mazen Khaled, Rong Yang, Karen Gleason, Faizur Rehman (2014),"Surface modification of seawater desalination reverse osmosis membranes: Characterization studies & performance evaluation", Desalination 343 pp. 128–139.

[3] Henthorne, Lisa (2011), "The Current State of Desalination", International Desalination Association Retrieved 2012.

[4] Mohamed A. Eltawil, Zhao Zhengming1and Liqiang Yuan (2008), “Renewable energy powered desalination systems: technologies and economics-state of the art”, Twelfth International Water Technology Conference, IWTC12 2008 Alexandria, Egypt.

[5] C. Fritzmann, J. Lowenberg, T. Wintgens, T. Melin (2007), "State of the art of reverse osmosis desalination", Desalination 216 (2007) 1–76.

[6] Gregory P. Thiel (2015), "Salty solutions", Physics Today 68 (2015) 66–67.

[7] Monica Reig, Sandra Casas, Carlos Aladjem, Cesar Valderrama, Oriol Gibert, Fernando Valero, Carlos Miguel Centeno, Enric Larrotcha, Jose Luis Cortina, “Concentration of NaCl from seawater reverse osmosis brines for the chlor-alkali industry by electrodialysis”, Desalination 342 (2014) 107–117.

[8] J. L. Etchells, I. D. Jones, M. A. Hoffman, “Brine preservation of vegetables”, Institute of Food Technology, (1943) pg 176-182.

[9] Westphal, Gisbert et al. (2002) "Sodium Chloride" in Ullmann's Encyclopedia of Industrial Chemistry, Wiley.

[10] British geological survey natural environment research council, “mineral planning factsheet”, (2006).

[11] Gladys D. Pinching and Roger G. Bates, “Purification of Sodium Chloride and Potassium Chloride for Use in Electrochemical Work, and the Determination of Small Amounts of Bromide”, Journal of Research of the National BUTeau of Standards, Research Paper RPl749 Volume 37, October 1946.

[12] Robert H. Stewart (2008), “Introduction to Physical Oceanography”, September 2008 Edition, by University of Texas Center for Space Research and NASA.

[13] Marcel Mulder (1996), “Basic principles of membrane technology”, Kluwer academic publisher 1996, chap. 6, pp 280-412.

[14] Mousa S. Mohsen, Salem Gammoh (2010), “Performance evaluation of reverse osmosis desalination plant: A case study of Wadi Ma’in, Zara and Mujib Plant”, Desalination and Water Treatment, 14 pp. 265–272.

[15] James Murray, “Major Ions of Seawater”, (10/01/04) Univ. Washington

[16] Robert V. Titler, “Chemical analysis of major constituents and trace contaminants of rock salt”, USEPA. (2012).

[17] Michael E. Williams (2003), “A Brief Review of Reverse Osmosis Membrane Technology”, EET Corporation and Williams Engineering Services Company, Inc., pp. 1-29.

[18] Lauren F. Greenlee, Desmond F. Lawler, Benny D. Freeman, Benoit Marrot, Philippe Moulin (2009), “Reverse osmosis desalination: Water sources, technology, and today’s challenges”, water research 43 pp. 2317-2348.

[19] Mostafa H. Sharqawy, John H. Lienhard V, Syed M. Zubair (2010), “Thermophysical properties of seawater: a review of existing correlations and data”, Desalination and Water Treatment 16 pp. 354–380.

[20] Hari J. Krishna (2005), “Introduction to Desalination Technologies”, Texas Water Development Board (Report): http://www.beeindia.in/energy_managers_auditors/ema.php?id=4

[21] R. Taylor and A. Allen, “Waste disposal and landfill: Information needs”, (2004) Chapter 12 – p. 1

[22] Supriya S. Dhume, Yogesh J. Chendake, Rahul K. Kulkarni and Ankush Gupta (2015), "Improvement in Process Economy by Utilization of Ro Retentate from Seawater Desalination in Chemical Production", Water Science and Technology: Water Supply, Manuscript Draft, Manuscript Number:-WS-EM15258.

[23] Shakhashiri (2010), "Sodium Hydrogen Carbonate and Sodium Carbonate", chemical of the week, Chemistry 104-2 October 14, 2010: www.scifun.org

[24] M. Gopala Rao and Marshall Sitting, "Drydens outlines of chemical technology", third edition, Affiliated east-west press pvt. ltd. (2011) pp 185-207.