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Modified Desalination Scheme for Handling Reject Brines Hussein K Abdel-Aal^{1,2*}, Maha Abdelkreem² and Khaled Zohdy²

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Abstract

The main goal of this work is to present a sustainable modified desalination scheme which incorporates a chemical conversion unit (CCU) that handles the reject brines exit the desalination unit. With the available technology, we have today this can change the paradigm of "waste product" into a "resource" aiming for the utilization of brine, as a feed stock for magnesium production plus other chemical products to take place.

It is a chemical process that involves bubbling CO_2 gas in "ammoniated" brine. The brine used contains about 25% NaCl and is obtained by concentrating the reject brine before entering the CCU. The proposed method, offers a vehicle to dispose reject brine and to utilize it, at the same time, to recover and extract valuable minerals found in these rejects. In the proposed method, ammonia used in the chemical conversion process is synthesized by using renewable hydrogen, obtained by water electrolysis.

A preliminary process analysis of the proposed system is presented along with computational results. For one cubic meter of reject brine, 0.64 ton ammonium chloride (found in partially desalinated water) and 0.63 ton soda ash are produced, while 0.203 ton ammonia and 0.526 ton carbon dioxide are consumed. In addition, the recovery of MgCl, from reject brine adds merits to the proposal.

Keywords: Desalination; Energy; Brine

Introduction

Technology possesses immense potential to aid in solving the world's most pressing problems. Through research, it is concluded that one of today's most needed breakthroughs is a cost-effective, energyefficient method for desalinating water using renewable energy. A breakthrough desalination technology could mitigate future problems associated with the need of water supply.

Along with the existing trends in chemical process industries, it is found that a strong bias exists towards integrated processing, co-generation, co-processing and minimization of waste product generation.

This gave the lead to initiate work towards our current proposal through what may be called co-processing and production. Considering the necessity to address theoretical and experimental investigations for an alternative route, this work presents a preliminary technical analysis for a sustainable modified multi-purpose desalination scheme. The challenge of further improving desalination schemes is addressed through the management by co-processing of reject brine.

Literature review

Research work in the area of bubbling ammoniated brine in carbon dioxide was initiated by many workers in line with the well-known Solvay process. Most notable are Abdel-Aal et al. [1-5] and El-Nass et al. [6,7]. This type of work handled the treatment of brines exit desalination plants using such approach. However, the integration of this treatment process, called Chemical Conversion Unit (CCU), to be part of desalination system is introduced for the first time.

Reject brine exit desalination plants is a highly-concentrated waste by-product. It is estimated that for every 1 cubic meter of desalinated water, an equivalent amount is generated as reject brine. The common practice in dealing with brine is to discharge it back into the sea, where it could result, in the long run, detrimental effects on the aquatic life as well as the quality of the seawater available for desalination in the area [8,9].

The lack of economically and ecologically feasible concentrate management options, is a major barrier to widespread implementation of desalination. The main concern in desalination is the management of the brines whose uncontrolled discharge has significant negative impacts on the environment [10-13].

Concentrate Management

The lack of economically and ecologically feasible concentrate management-options is a major barrier to widespread implementation of desalination. The main concern in desalination is the management of the brines whose uncontrolled discharge has significant negative impacts on the environment [10-13]. To these conventional methods, shown above, co-production or co-processing represents a promising alternative to be proposed in this paper, as explained next.

Objectives

Science is about more than just what happens in the lab. There are other factors including economic forces affecting the kinds of questions we ask and how we go about trying to answer them [14-16]. This is typically true for desalination, in particular, how to handle reject brine?

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Our present work focuses on utilizing these reject brines as a feed stock for further processing. This way, we are not only offering a solution to handle waste management for reject brine but we are also creating a means for additional income to the water desalination industry. Our proposal is a kind of a research into a suite of seawater desalination improvements, in order to make the process cheaper and more environmentally friendly. Two main reasons are in support for this proposed scheme:

1- It eliminates environmental problems, from displacing oceandwelling creatures to adversely altering the salt concentrations around them. No reject brine is dumped back to the sea.

2- It provides additional income from the sales of valuable products by the integration of the chemical conversion unit CCU).

The road map to our proposed multi-purpose desalination scheme

Our proposed overall desalination scheme is represented first, by the following black box shown in Figure 1. Next, to reveal the contents of this black box, our proposed scheme consists basically of three main units: MSF, Brine concentration unit and chemical conversion unit (CCU) as shown in Figure 2. In addition, an auxiliary unit is hooked to the set up to supply solar heat source for the whole plant and to provide the required raw materials for unit 3.

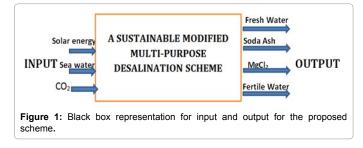
Solar evaporation unit (brine concentration)

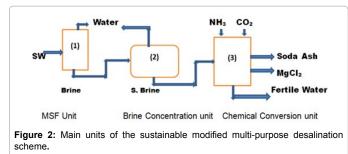
Brine exit desalination unit has to be concentrated from about 6% sodium chloride to saturated brine, about 26-30%. This is a prerequisite for the next stage that takes place in the desalting unit. Evaporation is carried out using heat provided by solar flux as will be explained next [17,18]. This unit provides additional fresh water to our system.

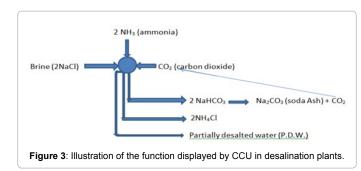
Chemical conversion unit

The chemical conversion unit (CCU), uses saturated brine as feed. Chemical reactions taking place will lead to the production of soda ash, magnesium chloride and fertile water that contains ammonium chloride. The unit is schematically illustrated in Figure 3.

Auxiliary units







The unit consists basically of 3 subunits:

(a) Source of solar heat supply for the whole desalination scheme. It is proposed to be a parabolic solar collector, capable to provide heat to the desalination unit, water electrolysis for hydrogen production and others [19-21].

(b) Renewable hydrogen production by water electrolysis using solar energy.

(c) Ammonia synthesis.

Solar energy is a cornerstone in our proposal. The facilities provided by the auxiliary unit are exemplified as shown in Figure 4.

Case Study: Process Analysis and Material Balance Calculations

In order to carry out this study, the following two-step procedure is outlined:-

 $1^{\mbox{\tiny st}}$: Define the chemical reactions underlying our system. They are as presented next:

Main Reactions

The basic reactions involved could be visualized to take place as follows:

Reaction between CO₂ and NH₃ can be described as:

$$CO_2 + 2NH_3 \rightarrow NH_2COO^2 + NH_4^+$$
 (1)

In the bulk of the solution, the carbamate hydrolyses comparatively slowly to bicarbonate:

 $\rm NH_2COO^- + H_2O \rightarrow \rm NH_3 + H_0COO^-$ (2)

In the presence of NaCl, the following instantaneous reaction takes place:

$$NH_4^+ + HCO_3^- + NaCl \rightarrow NaHCO_3 + NH_4Cl$$
 (3)

Soda ash is produced as an end product:

$$2\text{NaHCO}_{3} \rightarrow \text{Na}_{2}\text{CO}_{3} + \text{CO}_{2} + \text{H}_{2}\text{O}$$
(3-a)

This leads to the precipitation of sodium bicarbonate leaving ammonium chloride in a partially desalinated water.

In addition, the following reaction could take place, leading to the production of $MgCl_2$, as well.

$$2NH_4Cl+Mg(OH)_2 \rightarrow MgCl_2+2NH_3+2H_2O$$
(4)

 $2^{\rm nd_{\text{-}}}$ Apply the stoichiometric principles to these reactions, as presented in the next table.

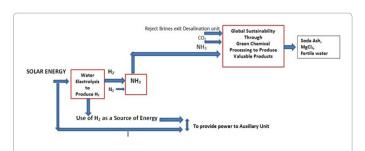
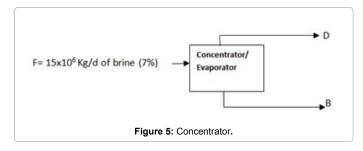


Figure 4: Role of solar energy to provide hydrogen for ammonia synthesis by water electrolysis.



Now, we are ready to seek the solution of our system, defined earlier as "chemical conversion unit" (CCU)- described above- by using Excel computations, as applied for the following case study:

Assuming that a feed of 7,700,000 gallon/day of sea water (equivalent to about 30,000 cubic meter/day), salinity is 35,000 ppm is to be desalinated using MSF plant. For calculation purpose, this feed input is converted to mass, to be 30×10^6 kg/day, approximately and to be taken as a basis. The feed input when flashed in the MSF plant, it produces 15×10^6 kg/d of brine, with a salt concentration of about 7%. Assume also that for every volume of desalinated water, an equivalent amount is generated as reject brine (Figure 5).

The reject is then subjected to solar concentration/evaporation to raise the salt content in the brine to the saturation point, nearly 30% concentration. A material balance on this concentrator is carried out as follows: Total Balance F = D + B

Component mass balance on the salt: $15 \times 10^6 (0.07) = B (0.3)$

Therefore, B = 3.5×10^6 kg/d of concentrated brine to be processed next for the chemical conversion step. The distillate rate of the fresh water obtained, as a result of this evaporation process is D = 11.5×10^6 kg/d.

Again, taking one day as a basis in our next calculations, we simply drop per day (Figure 5). NaHCO₃ does not come as a final product. The final product we obtain is Na_2CO_3 , known as soda ash, according to the reaction:

 $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

Cost Benefit Analysis (CBA)

Cost benefit analysis (CBA), sometimes called benefit costs analysis (BCA), is a systematic approach to estimating the strengths and weaknesses of alternatives (for example in projects investments); it is used to determine options that provide the best approach to achieve benefits while preserving savings. The CBA is also defined as a systematic process for calculating and comparing benefits and costs of a decision, policy. CBA has two main objectives:

1. To determine if an investment/decision is sound (justification/ feasibility)

2. To provide a basis for comparing projects

A cost benefit analysis is used to evaluate the total anticipated cost of a project compared to the total expected benefits in order to determine whether the proposed implementation is worthwhile for a company or project team, as shown next. For the proposed project presented in the paper, finding the cost of the project is too elaborate to be presented. The value obtained from the sales will be briefly given for two products: Ammonium chloride and Soda ash, with market values 130 and 200 \$/ ton respectively.

Assuming 50,000 m^3 of reject brine, the benefit realized from the values of the products are calculated as follow:

Ammonium chlor	ide = $50,000 \times 0.064 \text{ ton} \times 130 /\text{ton} = \text{\$} 400,000$
Soda ash	= 50,000 × 0.063 ton × 200 \$/ton = \$ 630,000
Total sales	= \$ 1,030,000

Discussion

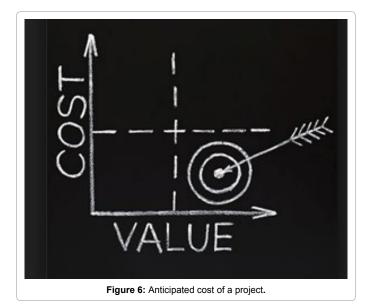
This work presents a preliminary technical analysis for a sustainable modified multi-purpose desalination scheme for handling waste brines. The challenge of further improving desalination schemes is addressed through the management by co-processing of reject brine (Figure 6).

Along with the existing trends in chemical process industries, it is found that a strong bias exists towards integrated processing, cogeneration, and minimization of waste product generation. This gave the lead to initiate work towards our current proposal through what may be called co-processing and production (Tables 1 and 2).

Two main reasons in support of this proposed scheme are:

• The elimination of environmental problems, from displacing ocean-dwelling creatures to adversely altering the salt concentrations around them. No reject brine is dumped back to the sea.

The integration of the chemical conversion unit CCU), to be



Page 4 of 5

Reactents	Molecules	Units
Feed water to MSF	3.00E+07	Kg
Fresh water exit MSF	1.50E+07	Kg
Brine 7% exit MSF	1.50E+07	Kg
Brine, 30% exit Concentrat.	3.50E+06	Kg
Fresh water exit Concentrator	1.15E+07	Kg
NaCI in brine	1.05E+06	kg
Moles of NaCl	1.79E+07	Mole
Moles of NaHCO ₃	1.79E+07	Mole
Moles of NH₄CI	1.79E+07	Mole
Moles of NH ₃	1.79E+07	Mole
Moles of CO ₂	1.79E+07	Mole
Moles of Na ₂ CO ₃	8.97E+06	Mole
Quantity of NaCl	1.05E+06	kg
Quantity of NaHCO ₃	1.51E+06	kg
Quantity of NH ₄ Cl	9.60E+05	kg
Quantity of NH ₃	3.05E+05	kg
Quantity of CO ₂	7.90E+05	kg
Quantity of Na ₂ CO ₃	9.51E+05	kg

Table 1: Results of excel computations.

Consumption rate of Reactants versus Rate of Production of Products (Tons Per Cubic meter of reject Brine exit MSF)						
Per Cu. meter of reject Brine exit MSF	Reactants	Products				
NH3	2.03E-02					
CO2	5.26E-02					
NH₄CI		6.40E-02				
Na ₂ CO ₃		6.34E-02				

Table 2: Consumption rate of reactants versus rate of production of products.

	Reactants						Products					
	NH₄	H ₂ O	CO ₂	MgCl ₂	NaCl	NH₄OH	Mg(OH) ₂	NaHCO ₃	Na ₂ CO ₃	NH₄CI	CO2	Kg
No.1	-4	-4				4						
No.2				-1		-2	1					
No.3			-2		-2	-2		2		2		
No.4								-2	1		1	
net	-4	-4	-2	-1	-2	0	1	0	1	4	1	

Table 3: Stoichiometric principles.

part of desalination plants will lead to additional income from the sales of valuable products.

Conclusion

The results of Excel computations given above, reveals very interesting conclusions:

• The dollar values of the products obtained from the proposed system should add to its merits. These include two main products: soda ash and ammonium chloride. The latter could be produced dissolved in partially desalted water, to be sold as a fertilizer. The recovery of magnesium, as magnesium chloride makes the third product to be recovered as well. Details on this step are fully discussed by Abdel-Aal et al. [5]. It is a very viable option. This will promote the application of our proposed desalination system since magnesium chloride is the raw material to produce magnesium metal (Table 3).

• When we say sustainable energy, we are basically referring

to renewable energy resources, in particular solar energy. Hence, a sustainable desalination system would be one that is provided by a source of solar heat supply for the whole desalination scheme. It should be capable to provide heat to the desalination unit, brine evaporation/ concentration and for water electrolysis for hydrogen production as well. The concentration (evaporation) step of the reject brine exit the desalination unit to bring it to about 27% sodium chloride is of prime importance. Parabolic Solar collector is recommended for this task [19].

• To have a reliable and cheap source of ammonia, it is suggested to produce the hydrogen for ammonia synthesis by water electrolysis using solar energy. Figure 4 is a schematic representation of this cycle.. Solar energy is a cornerstone in our proposal.

• The option of producing fertile water (partially desalted water) containing $\rm NH_4Cl$, to be used for agriculture purposes, is a good choice. Salt content in this water is reduced from initial brine concentration of 25% to about 7%. Ammonium chloride is an excellent fertilizer used in the Far East for rice crops, and is recommended as an

extremely good source of both nitrogen and chloride for coconut oil.

• The proposed desalination scheme should find widespread support to be applied in many of the Arab Gulf Countries such as Saudi Arabia and the Arab Emirates. They will produce fresh water to drink along with valuable chemical products to sell, without harming the marine environment by reject brines exit desalination plants.

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Page 5 of 5