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Reject Brine Management

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1. Introduction

Desalination has been growing rapidly as an industry and as a field of research that combines engineering and science to develop innovative and economical means for water desalting. Many countries in the world, especially in the Middle East, depend heavily on seawater desalination as a major source of drinking water and have invested considerable efforts and financial resources in desalination research and training. Desalination plants have seen considerable expansion during the past decade as the need for potable water increases with population growth. It is estimated that the world production of desalination water exceeds 30 million cubic meters per day and the desalination market worldwide is expected to reach $ 30 billion by 2015.

One of the major economical and environmental challenges to the desalination industry, especially in those countries that depend on desalination for potable water, is the handling of reject brine, which is the highly concentrated waste by-product of the desalination process. It is estimated that for every 1 m^3 of desalinated water, an equivalent amount is generated as reject brine. The common practice in dealing with these huge amounts of brine is to discharge it back into the sea, where it could result, in the long run, in detrimental effects on the aquatic life as well as the quality of the seawater available for desalination in the area.

Although technological advances have resulted in the development of new and highly efficient desalination processes, little improvements have been reported in the management and handling of the major by-product waste of most desalination plants, namely reject brine. The disposal or management of desalination brine (concentrate) represents major environmental challenges to most plants, and it is becoming more costly. In spite of the scale of this economical and environmental problem, the options for brine management for inland plants have been rather limited. These options include: discharge to surface water or wastewater treatment plants; deep well injection; land disposal; evaporation ponds; and mechanical/thermal evaporation. Reject brine contains variable concentrations of different chemicals such as anti-scale additives and inorganic salts that could have negative impacts on soil and groundwater.

This chapter highlights the main concerns as well as the environmental and economical challenges associated with the generation of large amounts of reject brine as a by-product of the desalination process. The chapter also outlines and compares the most common options for the treatment or disposal of reject brine. The chapter focuses on a novel approach to the management of reject brine that involves chemical reactions with carbon dioxide in the

presence of ammonia, based on a modified Solvay process. Reject brine is mixed with ammonia and then exposed to carbon dioxide using different contact techniques. The end result is the conversion of NaCl and CO_2 into a useful solid product, namely sodium bicarbonate, and the reduction of the salinity of the treated brine, which may then be used for irrigation. Besides brine management, the new approach will reduce the emissions of CO_2 as a major contributor to global warming. Carbon dioxide can be used as a pure gas from gas sweetening units or in the form of flue or exhaust gas from chemical or power plants.

2. Current brine disposal options

Since desalination processes generate considerable amounts of reject brine, the industry has adopted numerous disposal options that usually depend on the location of the desalination plant and type of process used. These options include: discharge to surface water or wastewater treatment plants; deep well injection; land disposal; evaporation ponds; and mechanical/thermal evaporation. Management of reject brine has recently become an increasingly difficult challenge due to many factors that include: growing number and size of desalination plants which limits disposal options; increased regulations of discharges that make disposal more difficult; increased public concern with environmental issues; increased number of desalination plants in semi-arid regions where conventional disposal options are limited (Mickley, 2006). Cost plays an important role in the selection of a brine disposal method and it is believed to range from 5% to 33% of the total cost of desalination (Ahmed et al, 2001). Mickley et al. (1993) identified the factors that influence the selection of a disposal method. These include the quantity and quality of the brine; composition of the concentrate; physical or geographical location of the discharge point of the concentrate; availability of receiving site, permissibility of the option, public acceptance, capital and operating costs, and ability for the facility to be expanded. The cost of disposal depends on the characteristics of reject brine, the level of treatment before disposal, means of disposal, volume of brine to be disposed of, and the nature of the disposal environment (Ahmed et al, 2001). A detailed review of the different brine disposal methods can be found in a report by Mickley (2001). The following sections will present a brief summary of the main brine disposal options and highlight the main drawbacks of each option.

2.1 Discharge into surface water

It has been a common practice for coastal desalination plants to dispose reject brine into the close-by surface water body, namely sea or ocean. For these plants, such disposal operation has always been deemed the most practical and least expensive. Costs for disposal are typically low provided that pipeline conveyance distances are not excessively long and the concentrate is compatible with the environment of the receiving water body. An assessment of salinity or TDS impact as well as those of specific constituents on the receiving stream must always be considered (Mickely et al, 2006). The main factors that determine the costs of reject brine discharge to surface water include: costs to transport the brine from the desalination plant to the surface water discharge outfall; costs for outfall construction and operation; and costs associated with monitoring the environmental effects of the brine discharge on the surface waters (Mickely et al, 2006).

The impact of brine disposal operations on coastal and marine environment is still largely unknown, but the high temperature and salinity associated with reject brine may have detrimental effects on marine life. Moreover, the high level of chemicals could reduce the

amount of dissolved oxygen available for the marine organisms. Other harmful chemicals that may be present in the reject brine such as hydrogen sulfide and chloride may have negative effect if the brine is not treated before disposal. In addition, the continuous disposal of reject brine into water body near the desalination plants could, in the long run, affect the suitably of the feed water. This is especially true for small and rather closed water bodies such as the Arabian Gulf, where most of the desalination activities in the world take place.

2.2 Deep well injection

Deep well injection is often considered for the disposal of industrial, municipal and liquid hazardous wastes (Saripalli et al, 2000). In recent years, this approach has been given serious consideration as an option for brine disposal from inland desalination plants, where surface water discharge is not viable or very costly. Deep wells can offer a feasible and reliable solution to disposing reject brine. However, deep wells are not feasible in areas subject to earthquakes or where faults are present that can provide a direct hydraulic connection between the receiving aquifer and an overlying potable aquifer (Mickely et al, 2006). Therefore, prior to drilling any injection well, a careful assessment of geological conditions must be conducted in order to determine the depth and location of suitable porous aquifer reservoirs (Glator and Cohen, 2003). The capital cost for deep well injection is usually higher than surface water disposal, where the latter method does not require long brine transport pipelines. Although deep well injection may be a feasible option for reject brine disposal, it still suffers from many drawbacks such as the need for selecting a suitable well site; the extra costs involved in conditioning the reject brine; corrosion and subsequent leakage in the well casing; and seismic activity which could cause damage to the well and subsequently contamination of groundwater (Glator and Cohen, 2003). Performance, design consideration and modeling of deep well injection have been addressed by many researchers (Rhee and Reible, 1993; Saripalli et al, 2000; Skehan and Kwiatkowski, 2000).

2.3 Evaporation ponds

This option has always been considered the most effective and economical method for brine disposal for inland desalination plants, especially for dry, arid regions similar to those in North Africa and Middle East. Inland plants in these regions are usually located in areas known to have high dry weather, relatively high temperature and, consequently, high evaporation rates. Ahmed et al. (2000) reviewed the relevant literature and presented the design aspects of evaporation ponds, highlighting the importance of selecting the main design parameters, namely surface area and pond depth. In another study (Ahmed et al, 2001), the authors surveyed the application of evaporation ponds in Arabian Gulf countries, namely United Arab Emirates and Oman. The authors reported that the newer plants have lined evaporation ponds, whereas the older ones have unlined disposal pits. The primary environmental concern associated with evaporation pond disposal is pond leakage, which may result in subsequent contamination of groundwater in the region. Recent evaporation ponds are always lined with polyethylene or other polymeric materials to prevent leakage and seepage of contaminants into the nearby groundwater.

A key factor in the effectiveness of evaporation ponds is the evaporation rate, which depends heavily on the weather conditions, mainly humidity and surrounding temperature. Attempts have been made, with limited success, to improve evaporation through the use of wind-aided intensified evaporation (Gilron et al, 2003). This technique claims to increase the evaporation rate by 50% for dry climate, but still depends on weather conditions. Improving the

evaporation rate could in principal reduce the size of the evaporation ponds and enhance their efficiency and potential of application in many parts of the world. Although high temperature and, consequently, high evaporation rates may speedup water reduction, evaporation ponds still suffer from many drawbacks including the need for huge areas and the possibility of contaminants dissipation into soil and groundwater.

3. Characteristics of reject brine

By definition, brine is any water stream in a desalination process that has higher salinity than the feed. Reject brine is the highly concentrated water in the last stage of the desalination process that is usually discharged as wastewater. Several types of chemicals are used in the desalination process for pre- and post-treatment operations. These include: Sodium hypochlorite (NaOCl) which is used for chlorination to prevent bacterial growth in the desalination facility; Ferric chloride ($FeCl_3$) or aluminum chloride ($AlCl_3$), which are used as flocculants for the removal of suspended matter from the water; anti-scale additives such as Sodium hexameta phosphate $(NaPO_3)_6$ are used to prevent scale formation on the pipes and on the membranes; and acids such as sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) are also used to adjust the pH of the seawater. Due to the presence of these different chemicals at variable concentrations, reject brine discharged to the sea has the ability to change the salinity, alkalinity and the temperature averages of the seawater and can cause change to marine environment. The characteristics of reject brine depend on the type of feed water and type of desalination process. They also depend on the percent recovery as well as the chemical additives used (Ahmed et al., 2000). Typical analyses of reject brine for different desalination plants with different types of feed water are presented in Table 2.1.

Parameters	Abu-fintas Doha/Qatar Seawater	Ajman BWRO	Um Quwain BWRO	Qidfa I Fujairah Seawater	Qidfa II Fujairah Seawater
Temperature, °C	40-44	30.6	32.4	32.2	29.1
pH	8.2	7.46	6.7	6.97	7.99
Electrical conductivity	NR	16.49	11.33	77.0	79.6
Ca, ppm	1,300-1,400	312	173	631	631
Mg, ppm	7,600-7,700	413	282	2,025	2,096
Na, ppm	NR	2,759	2,315	17,294	18,293
HCO_3, ppm	3,900	561	570	159	149.5
SO_4, ppm	3,900	1,500	2,175	4,200	4,800
Cl, ppm	29,000	4,572	2,762	30,487	31,905
TDS, ppm	52,000	10,114	8,276	54,795	57,935
Total hardness, ppm	NR	NR	32	198	207
Free Cl_2, ppm	Trace	NR	0.01	NR	NR
SiO_2, ppm	NR	23.7	145	1.02	17.6
Langlier SI	NR	0.61	0.33	NR	NR

Table 2.1. Characteristics of reject brine from desalination plants in the Gulf region (adapted from Khordagui, 1997). NR: Not reported; BWRO: brackish water reverse osmosis.

More data about the characteristics of reject brine and feed water for several desalination plants in Gulf counties such as Oman, UAE and Saudi Arabia can be found elsewhere (Ahmed et al, 2001; Mohamed et al, 2005).

4. Environmental impact of reject brine

Reject brine has always been considered as waste by-product of the desalination processes that can not be recycled and must be disposed of. Its harmful effects on the surrounding environment have always been underestimated in spite of the high concentrations of chemicals and additives used in the pretreatment of the feed water. Numerous studies have evaluated the environmental impact of reject brine disposal on soil, groundwater and marine environment. The surface discharge of reject brine from inland desalination plants could have negative impacts on soil and groundwater (Rao et al, 1990; Mohamed et al, 2005; Al-Faifi et al, 2010). Other researchers have highlighted the impact of reject brine composition and conditions on marine life (Lattemann and Hopner, 2005; Sadhawani et al, 2008). Sánchez-Lizaso et al (2008) have reported that the high salinity associated with reject brine discharges has detrimental effects on sea grass structure and vitality.

Soil deterioration and groundwater contamination is a major concern when reject brine is discharged into concentration ponds, which is the most common means of brine disposal for inland desalination plants. Disposal of reject brine into unlined ponds could have significant environmental impacts and the improper disposal has the potential for polluting the groundwater resources and can have a profound effect on subsurface soil properties (Mohamed et al, 2005). However, the environmental implications related to brine discharge have not been adequately considered by the concerned authorities. Mohamed et al (2005) have conducted a comprehensive evaluation of the impact of land disposal of reject brine from desalination plants on soil and groundwater. The authors assessed the effect of reject brine disposed directly into surface impoundment (unlined pits) in a permeable soil with low clay content, cation exchange capacity and organic matter content. The study indicated that concentrate disposal in unlined pond or pits can pose a significant problem to soil and feed water and can increase the risk of saline brackish water intrusion into fresh water. The authors recommended considering proactive approaches such as using lining systems, long term monitoring programs, and field research to protect groundwater from further deterioration. They have also highlighted the importance of implementing and enforcing regulations and polices related to reject brine chemical composition and concentrate disposal.

Soil structure may deteriorate due to the high salinity of the reject brine, when calcium ions are replaced by sodium ions in the exchangeable ion complex (Al-faifi et al, 2010). This in turn results in reducing the infiltration rate of water and the soil aeration. Sodium does not reduce the intake of water by plants, but it changes soil structure and impairs the infiltration of water and hence affects plant growth (Hoffman et al, 1990; Maas, 1990). In addition, the elevated levels of sodium, chloride, and boron associated with reject brine can reduce plants productivity and increase the risk of soil salinization (Maas, 1990).
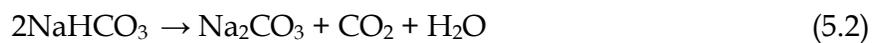
5. A new approach to reject brine management

The current options for reject brine management are rather limited and have not achieved a practical solution to this environmental challenge. There is an urgent need, therefore, for the

development of a new process for the management of desalination reject brine that can be used by coastal as well as inland desalination plants. The chemical reaction of reject brine with carbon dioxide is a new approach that promises to be effective, economical and environmental friendly (El-Naas et al, 2010). The approach utilizes chemical reactions based on a modified Solvay process to convert the reject brine into useful and reusable solid product (sodium bicarbonate). At the same time, the treated brackish water can be used for irrigation. Another advantage is that the main gaseous reactant, carbon dioxide, can be pure or in the form of a mixture of exhaust or flue gases, which indicates that this approach can be utilized for the capture of CO_2 from flue gases or sweetening of natural gas. El-Naas et al (2010) reported that the reactions of CO_2 with ammoniated brine can be optimized at 20 °C and can achieve good conversion using different forms of carbon dioxide. Details of this promising approach are presented in the next sections.

5.1 Solvay process

The Solvay process was named after Ernst Solvay who was the first to develop and successfully use the process in 1881. It is initially developed for the manufacture of sodium carbonate (washing soda), where a saturated sodium chloride solution -in the form of concentrated brine- is contacted with ammonia and carbon dioxide to form soluble ammonium bicarbonate, which reacts with the sodium chloride to form soluble ammonium chloride and a precipitate of sodium bicarbonate according to the following reactions:

$$NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4Cl \tag{5.1}$$

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \tag{5.2}$$

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O \tag{5.3}$$

The overall reaction can be written as:

$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2 \tag{5.4}$$

The resulting ammonium chloride can be reacted with calcium hydroxide to recover and recycle the ammonia according to Reaction 5.3. Although the ammonia is not involved in the overall reaction of the Solvay process, it plays an essential role in the intermediate reactions, especially Reaction (5.1). The ammonia buffers the solution at a basic pH; without the presence of ammonia, the acidic nature of the water solution will hamper the precipitation of sodium bicarbonate.

The sodium bicarbonate ($NaHCO_3$), which precipitates from Reaction (5.1), is converted to the final product, sodium carbonate (Na_2CO_3) at about 200 °C, producing water and carbon dioxide as byproducts (Reaction 5.2). A well designed and operated Solvay plant can reclaim almost all its ammonia, and consumes only small amounts of additional ammonia to make up for losses. The only major feeds to the Solvay process are sodium chloride (NaCl) and limestone ($CaCO_3$), and its only major byproduct is calcium chloride ($CaCl_2$), which is usually sold as road salt or desiccant.

In industrial practice, Reaction (5.1) is carried out by passing concentrated brine through two towers, where the brine is ammoniated in the first tower by bubbling ammonia gas through the saturated brine. In the second column, carbon dioxide is bubbled up through

the ammoniated brine to form sodium bicarbonate and ammonium chloride. The worldwide production of soda ash in 2005 has been estimated at about 42 billion kilograms (Kostick, 2005).

5.2 Thermodynamic analysis

The overall reaction in the Solvay process is not spontaneous as is, but it must go through the three steps given in Reactions 5.1, 5.2 and 5.3. The first step (Reaction 5.1) is the most important one, since it involves the initial contact of the three main reactants (CO_2, NaCl and NH_3). The prime target of the Solvay process is the formation of sodium carbonate, but for brine management the aim is to convert water-soluble sodium chloride into insoluble sodium bicarbonate that can be removed by filtration.

A chemical reaction and equilibrium software, HSC Chemistry (Roine, 2007) was used to carry out a thermodynamic analysis for Reaction (5.1) to determine the equilibrium composition at different temperatures and to estimate the heat of reaction as a function of temperature. For a fixed temperature and pressure the number of moles present at equilibrium for any species can be determined using the Gibbs free energy minimization method. The analysis indicates that Reaction (5.1) is spontaneous for the whole temperature range (0 to 90 °C) as indicated by the negative ΔG. At 20 °C, the values for ΔH and ΔG are -129.1 kJ/mol and -25.8 kJ/mol, respectively. The calculated thermodynamic properties for Reaction (5.1) are presented in Table 5.1. The reaction proceeds through the following two steps:

$$NH_4OH + CO_2 \rightarrow NH_4HCO_3 \tag{5.5}$$

$$NaCl + NH_4HCO_3 \rightarrow NaHCO_3 + NH_4Cl \tag{5.6}$$
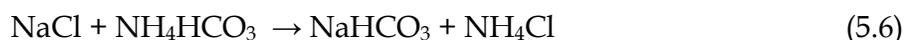
Temperature (°C)	ΔH (kJ/mol)	ΔS (kJ/mol. °C)	ΔG (kJ/mol)
0.0	-123.7	-332.4	-32.9
10.0	-129.4	-353.4	-29.3
20.0	-129.1	-352.4	-25.8
30.0	-128.8	-351.5	-22.3
40.0	-128.6	-350.6	-18.8
50.0	-128.3	-349.7	-15.3
60.0	-128.0	-348.9	-11.8
70.0	-127.7	-348.0	-8.3
80.0	-127.4	-347.2	-4.8
90.0	-127.1	-346.4	-1.3

Table 5.1. Thermodynamic data for Reaction (5.1)

Given its highly negative ΔH and ΔG (Table 5.2), Reaction (5.5) is an exothermic reaction that takes place as soon as the CO_2 gets in contact with the ammoniated brine. Once ammonium bicarbonate is formed, it reacts with sodium chloride according to Reaction (5.6). As can be seen from Table 5.3, Reaction (5.6) is not as spontaneous as Reaction (5.5) and it is believed to be the rate limiting step.

Temperature (°C)	ΔH (kJ/mol)	ΔS (kJ/mol. °C)	ΔG (kJ/mol)
0.0	-127.6	-241.6	-61.7
10.0	-129.5	-248.4	-59.2
20.0	-131.5	-255.1	-56.7
30.0	-133.4	-261.5	-54.1
40.0	-135.3	-267.8	-51.5
50.0	-137.2	-273.8	-48.7
60.0	-139.2	-279.7	-46.0
70.0	-141.1	-285.5	-43.2
80.0	-143.1	-291.0	-40.3
90.0	-145.0	-296.5	-37.3

Table 5.2. Thermodynamic data for Reaction (5.5)

The thermodynamic analysis indicates that Reaction (5.6) is exothermic with a negative heat of reaction up to a temperature of 40 °C. Beyond this temperature, the reaction becomes endothermic as shown in Table 5.3. This phenomenon was observed experimentally in a semi-batch reactor study (El-Naas, 2010). The reactor temperature was monitored with time and found to increase up to 41 °C, then drop and stabilize at 30 °C. Although this sudden change in the heat of reaction may be attributed to the reactor dynamics, a similar finding was reported by Yeh and Bai (1999) who attributed it to variations in the concentration of NH_3 in the solution. This, however, is unlikely to be the case, since the heat of reaction obtained by the thermodynamic analysis (Table 5.3) is per mol of NH_3, and it is only a function of temperature. The phenomenon is believed to be due to the mechanisms of Reaction (5.6).

Temperature (°C)	ΔH (kJ/mol)	ΔS (kJ/mol. °C)	ΔG (kJ/mol)
0.0	-6.3	-11.8	-3.1
10.0	-4.6	-5.5	-3.0
20.0	-2.8	0.6	-3.0
30.0	-1.1	6.5	-3.0
40.0	0.7	12.2	-3.1
50.0	2.5	17.8	-3.3
60.0	4.2	23.2	-3.5
70.0	6.0	28.5	-3.8
80.0	7.9	33.8	-4.1
90.0	9.7	38.9	-4.4

Table 5.3. Thermodynamic data for Reaction (5.6)

5.3 Role of ammonia

Although ammonia is a major reactant in the first step of the Solvay process, it can be fully recovered in the process and, therefore, it is not seen in the overall reaction. Ammonia buffers the solution at a basic pH of greater than 9 and hence allows the precipitation of $NaHCO_3$, which is less water-soluble in basic solution than NaCl. Only a small amount of ammonia is needed to raise the pH to above 9; the increase of pH beyond this point is a little slower as

shown in Figure 5.1. In the absence of ammonia, the acidic solution will deter the precipitation of sodium bicarbonate regardless of the concentrations of other salts. This reiterates the importance of ammonia as a catalyst in Reaction (5.1) and the importance of controlling sodium bicarbonate solubility in the overall process, which will be discussed in the next section.
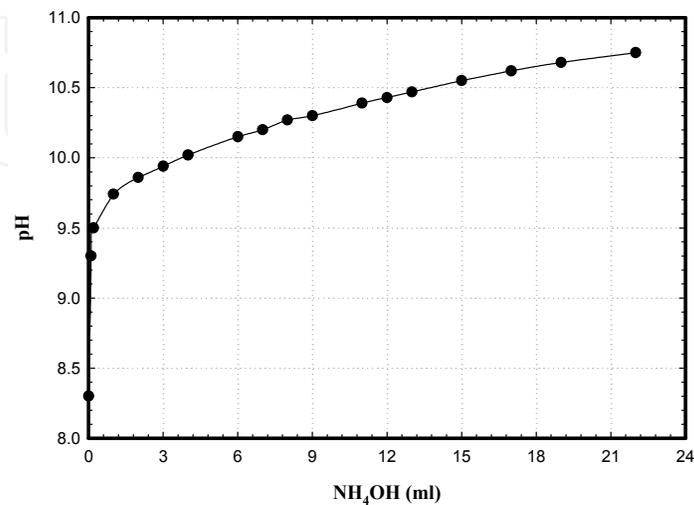

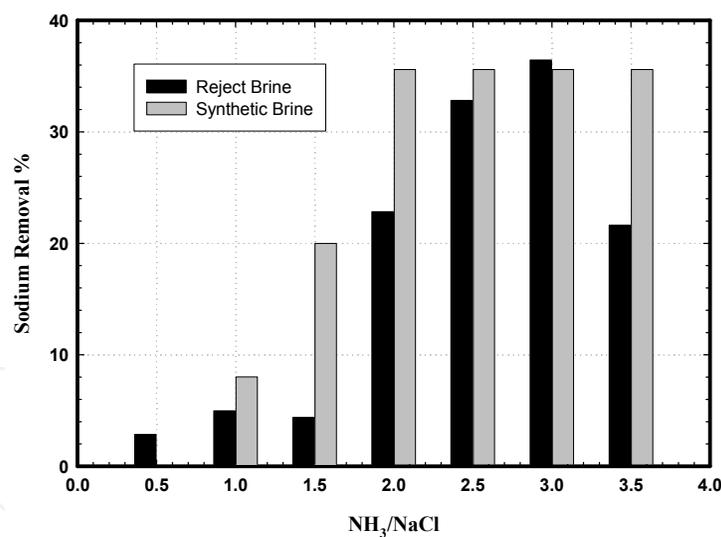Fig. 5.1. Variation of solution pH with ammonia addition at 25 °C

Fig. 5.2. Variation of sodium removal with $NH_3/NaCl$ molar ratio at 20 °C

It is important to note that the stoichiometric amount of ammonia required by Reaction (5.1) is one mole. However, in a real process excess ammonia may be needed for the reaction to reach completion. An experimental evaluation of the effect of excess ammonia on the removal of sodium at 20°C (El-Naas et al, 2010) indicated that the percent removal of sodium increased with increasing the $NH_3/NaCl$ ratio, reaching a maximum at 3 as shown in Figure 5.2. Similar experiments with synthetic brine solution, containing only NaCl in distilled water, in this study and in a previous study (Jibril and Ibrahim, 2001) revealed that the optimum sodium removal was achieved at a lower molar ratio ($NH_3/NaCl$) of 2. In both

cases, the molar ratio is higher than that required stiochiometrically, which may be due to the fact that the reaction was carried out in a semi-batch reactor, where the CO_2 gas leaving the reactor stripped away some of the ammonia from the solution. This will not be the case for an industrial process, where the reactor will be run in a continuous mode and the ammonia is recycled within the system. As for the even higher molar ratio observed for the reject brine ($NH_3/NaCl=3$), it is believed to be due to the presence of other impurities in the brine.

Metal carbonates in the brine may compete for ammonia and reduce its availability for reaction with CO_2. Magnesium carbonate ($MgCO_3$), which is always present in the reject brine, consumes ammonia to form magnesium hydroxide and ammonium bicarbonate according to the following reaction:

$$NH_3 + MgCO_3 + 2H_2O \rightarrow NH_4HCO_3 + Mg(OH)_2 \qquad (5.7)$$

Thermodynamic analysis of Reaction (5.7) indicates that this reaction is spontaneous for temperatures less than 22 °C. Thus one additional mole of ammonia is consumed by Reaction (5.7) to form magnesium hydroxide. This was confirmed experimentally, where milky colored turbidity was observed after mixing the reject brine with ammonium hydroxide.

It is worth noting here that after treatment of the reject brine through reactions with carbon dioxide, other ions such as Mg^{+2} and Ca^{+2} were significantly reduced at the end of the experimental runs. In fact, Mg^{+2}, Ca^{+2} and Sr^{+2} were reduced by more than 98%. Sodium (Na^+), which is the main focus of the treatment, was reduced by about 42% at the optimum conditions. This low reduction in sodium, however, is believed to only represent the conversion to insoluble sodium bicarbonate, which is removed by filtration. Since the amount of sodium in the filtrate comes from NaCl and soluble $NaHCO_3$, the true conversion can not be easily determined, and it is expected to be much higher than the 42%. Controlling the solubility of $NaHCO_3$, therefore, is a crucial step in optimizing the Solavy process for reject brine management.

5.4 Role of NaHCO₃ solubility

Sodium bicarbonate ($NaHCO_3$) is an important intermediate product in the Solvay process and its solubility plays an important role in the success of the process, since it determines the amount of the solid product that can be removed by filtration. For the process to achieve high conversion, the solubility of $NaHCO_3$ must be as low as possible. It is imperative, therefore, to evaluate factors that can limit or reduce its solubility. At room temperature, the solubility was determined experimentally to be about 9.75 g/100g and found to be negatively affected by the presence of other intermediates and reactants in Reaction (5.1) such as NaCl and NH_4HCO_3.

5.4.1 Effect of NaCl

The solubility of $NaHCO_3$ was found to decrease drastically with increasing the concentration of NaCl in the solution, from 9.75 g/100g at 0wt% NaCl to 3.6 g/100g at 10wt% NaCl as Shown in Figure 5.3. This is attributed to the presence of the sodium ion (Na^+) in the aqueous solutions of both salts. In aqueous solutions, both sodium chloride and sodium bicarbonate are present in their ionic format:

$$NaCl\ (a) \Leftrightarrow Na^+ + Cl^- \qquad (5.8)$$

$$NaHCO_3 \text{ (a)} \Leftrightarrow Na^+ + HCO_3^- \tag{5.9}$$
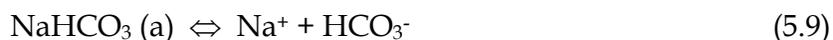
One would expect that increasing the concentration of the sodium ion (Na^+), by adding more NaCl into the solution, would force the equilibrium of Reaction (5.9) to the left and hence reduce the solubility of $NaHCO_3$. The solubility of NaCl in water at 25 °C is about 36 g/100g, which is almost four times that of $NaHCO_3$. The reduction in $NaHCO_3$ solubility with the presence of NaCl (Figure 5.3) seems to follow an exponential decay (**$y = 9.7e^{-0.095x}$**). According to this relation, the solubility of $NaHCO_3$ in a saturated NaCl solution will diminish to merely 0.3 g/100g. This highlights the necessity for using saturated brine in the Solvay process. It is to optimize the precipitation of $NaHCO_3$ by minimizing its solubility.
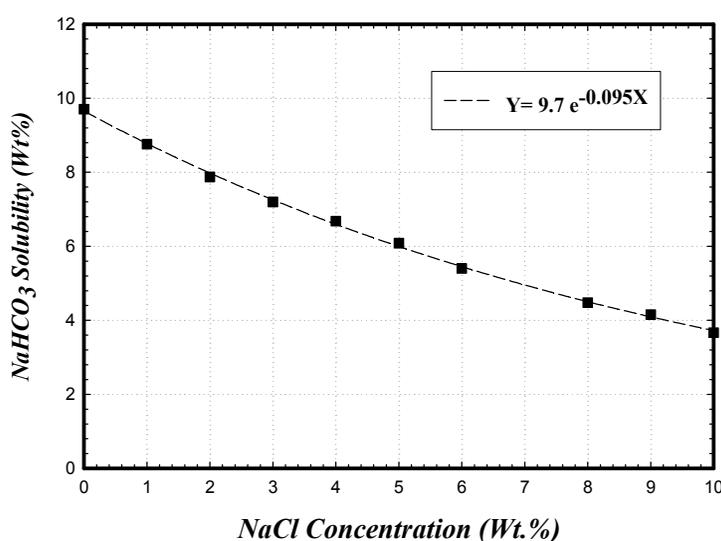
Fig. 5.3. Effect of NaCl on the solubility of $NaHCO_3$ at 25 °C

5.4.2 Effect of ammonium bicarbonate

Ammonium bicarbonate is another important intermediate in the formation of sodium bicarbonate according to Reactions 5.4 and 5.5. Its effect on the solubility of $NaHCO_3$ was evaluated for two aqueous solutions, containing 4% and 8% sodium chloride. The results are shown in Figure 5.4. Clearly, raising the concentration of ammonium bicarbonate seems to have a detrimental effect on the solubility of $NaHCO_3$. The rate of reduction in the solubility seems to be higher (about 33%) for the solution containing 8% NaCl. One may use similar argument to that used in the case of NaCl to explain this decline in the solubility. In this case, increasing the concentration of (HCO_3^-) by adding more ammonium bicarbonate would force the equilibrium in Reaction (5.11) below to the left and thus lower the solubility of $NaHCO_3$.

$$NH_4HCO_3 \text{ (a)} \Leftrightarrow NH4^+ + HCO_3^- \tag{5.10}$$

$$NaHCO_3 \text{ (a)} \Leftrightarrow Na^+ + HCO_3^- \tag{5.11}$$
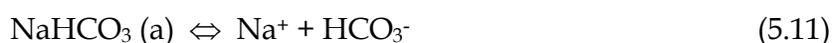
The experimental results (Figure 5.4) indicate that for an aqueous solution containing 8% NaCl, the solubility of $NaHCO_3$ can be reduced to 0.0 g/100g with the addition of about 13wt% ammonium bicarbonate, which can definitely have significant effect on the possibility of using the Solvay process for reject brine management.
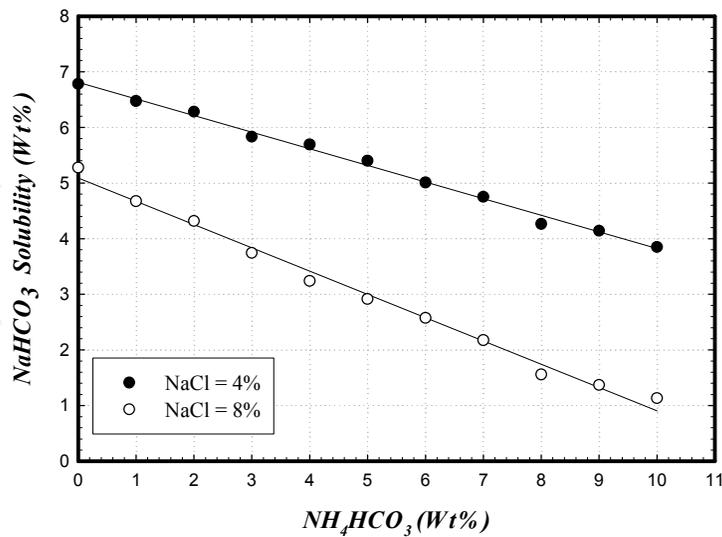
Fig. 5.4. Effect of NH_4HCO_3 on the solubility of $NaHCO_3$ at 25 °C

Ammonium chloride (NH_4Cl) is another byproduct formed in the Solvay process. Its effect on the solubility of $NaHCO_3$ was assessed in about the same way as that used with ammonium bicarbonate. The results, however, were not similar. The solubility of sodium bicarbonate does not seem to be affected by the presence of NH_4Cl regardless of the concentration of NaCl. This may be attributed to the fact that ammonium chloride is not involved in the formation of sodium bicarbonate and does not have any common ions with $NaHCO_3$; therefore, it does not affect its ionic equilibrium at these concentrations and temperature.

6. Industrial applications and CO_2 Capture

Application of the Solvay process for reject brine management has another important feature, which is the potential for carbon capture and storage (CCS). The process can be utilized for the removal of CO_2 from flue gases or for the sweetening of natural gas. Carbon dioxide is a major contributor to global warming and believed to have the greatest adverse impact on the observed greenhouse effect causing approximately 55% of global warming. The most common approach to CCS involves capturing CO_2 and then injecting it into rock layers in depleted or near-depleted oil and gas fields. The aim, off course, is to store the CO_2 and at the same time utilize it for Enhanced Oil Recovery (EOR). Although this option has gained the support of many industrialized and oil producing countries alike, it is not really problem-free and its long term effects are not yet known (El-Naas, 2008). Under typical storage conditions (1000 m below the surface), the density of CO_2 phase is approximately two-thirds that of the underground brine, which provides the driving force for escape (Bryant, 2007). Gradual seepage of CO_2 into the atmosphere may not pose much harm to human life, but it will certainly defeat the purpose of CCS.

Carbon dioxide reactions with ammoniated brine can offer a dual-purpose approach for the management of reject brine and capture of CO_2. The main unit of the process is the contact

reactor, where the flue gases are contacted with the ammoniated reject brine. Other units include the ammoniating tank, where the high salinity water is mixed with ammonia gas; the ammonia recovery reactor, where the ammonia is recovered through reaction with calcium hydroxide; and a filter to separate the precipitated sodium bicarbonate from the rest of the solution. A schematic diagram of the process is shown in Figure 5.5. The carbon dioxide captured through this process is stored in the form of sodium bicarbonate.
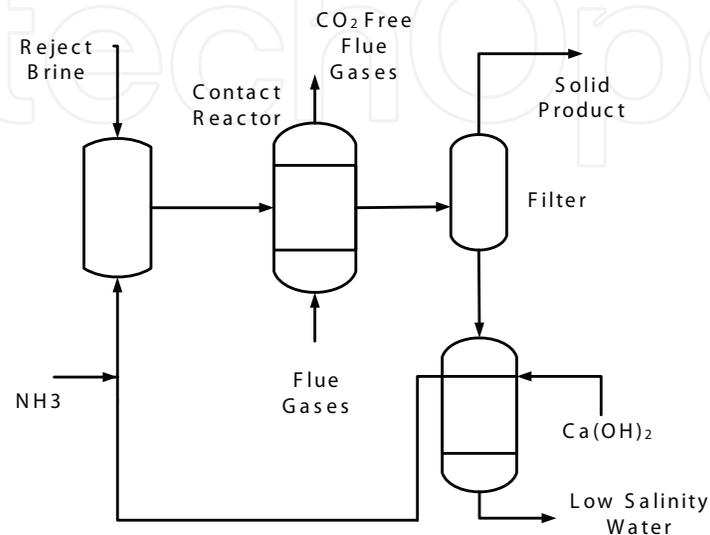

Fig. 5.5. A schematic diagram of a reject brine management process

The effectiveness of capturing CO_2 through the reaction with ammoniated brine was assessed experimentally. A gas mixture containing 10% CO_2 in methane was bubbled through one liter of ammoniated brine in three semi-batch bubble columns in series. The gas effluent of the first column was bubbled through the second and then the third. Half of the ammoniated brine was placed in the first column while the other half was divided equally between the other two columns. The total gas flow rate was controlled at 47 liter/hr using two mass flow controllers. The concentration of carbon dioxide and methane in the effluent gas stream were analyzed using a dual channel CO_2 and CH_4 infrared analyzer.

The experimental results for the CO_2 percent removal through the reaction with ammoniated reject brine solution are presented in Figure 5.6. It is evident that there is a considerable reduction in the CO_2 concentration in the effluent stream with 100% removal in the first two hours and more than 80% removal for the first five hours of run time. It is noticeable, nonetheless, that the percent removal is declining with time due to the consumption of the main reactants in the solution. Since the reactors were operated in the semi-batch mode, where only gases enter and leave the system, the other reactants in the ammoniated brine (NH_3 and $NaCl$) were consumed with time and hence less CO_2 was removed with time as shown in the figure. Although these results confirm the technical viability of the process for CO_2 capture and reduction of the reject brine salinity, more research is still needed to optimize the reactor design for continuous operation. An industrial process can be developed to offer an effective solution for the two major environmental challenges: reject brine management and CO_2 capture.
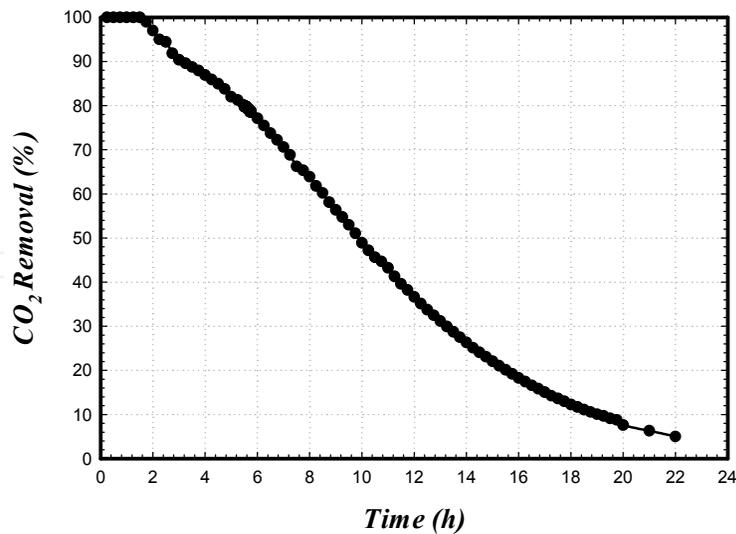
Fig. 5.6. CO_2 removal from a gas mixture containing 10% CO_2 in methane through reaction with ammoniated brine at 20 °C in a semi-batch three bubble columns in series.

7. Conclusions

Reject brine management represents a major environmental and economical challenge for most desalination plants. The current options for brine management are rather limited and have not achieved a practical solution to this environmental challenge. A new approach that involves reactions with CO_2 in the presence of ammonia has proven to be effective in reject brine management and capture of CO_2 .

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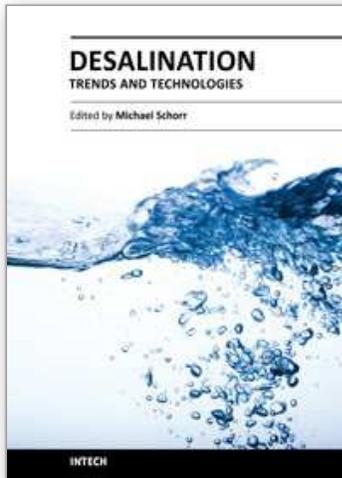
Desalination, Trends and Technologies

Edited by Michael Schorr

The book comprises 14 chapters covering all the issues related to water desalination. These chapters emphasize the relationship between problems encountered with the use of feed water, the processes developed to address them, the operation of the required plants and solutions actually implemented. This compendium will assist designers, engineers and investigators to select the process and plant configuration that are most appropriate for the particular feed water to be used, for the geographic region considered, as well as for the characteristics required of the treated water produced. This survey offers a comprehensive, hierarchical and logical assessment of the entire desalination industry. It starts with the worldwide scarcity of water and energy, continues with the thermal - and membrane-based processes and, finally, presents the design and operation of large and small desalination plants. As such, it covers all the scientific, technological and economical aspects of this critical industry, not disregarding its environmental and social points of view. One of InTech's books has received widespread praise across a number of key publications. Desalination, Trends and Technologies (Ed. Schorr, M. 2011) has been reviewed in Corrosion Engineering, Science & Technology – the official magazine for the Institute of Materials, Minerals & Mining, and Taylor & Francis's Desalination Publications. Praised for its "multi-faceted content [which] contributes to enrich it," and described as "an essential companion...[that] enables the reader to gain a deeper understanding of the desalination industry," this book is testament to the quality improvements we have been striving towards over the last twelve months.

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