

Production of chemicals from desalination blow down

A.A. Ibrahim and B.Y. Jibril

Chemical Eng. Dept., College of Eng., King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

The issue of disposal of desalination blow-down is becoming important due to its detrimental effects on the aquatic environment. This work presents a process that could decrease the concentration of the brine by production of useful chemicals such as NaHCO_3 , Na_2CO_3 , NH_4Cl and MgCl_2 . The conversion depends on the initial concentration of the brine and ammonia. The pH level of the solution is also critical parameter. The optimum range of pH for the proposed process is found to be 8 – 10. High ammonia consumption was observed. This may be a draw back for the process.

إن قضية تصريف مخلفات تحلية المياه المالحة أصبحت ذات أهمية نتيجة لتأثيراتها السلبية على البيئة المائية. هذه الدراسة تهتم بطريقة معالجة يمكنها من تقليل تركيز المحلول الملحي (brine) وذلك عن طريق إنتاج كيماويات مفيدة مثل بركونات الصوديوم، كبرونات الصوديوم، كلوريد الأمونيوم و كلوريد الماغنسيوم. هذه التحولات تعتمد على التركيز الأولى للأمونيا وال brine. أيضاً الأسى الهيدروجيني pH للمحلول يعتبر من المتغيرات المهمة و المؤثرة. المدى الأمثل للأسى الهيدروجيني pH لتلك العمليات وجد بين القيم ٨-١٠. أيضاً لوحظ إستهلاك عالٍ للأمونيا مما يمثل أحد عيوب هذه الطريقة.

Keyword: Desalination, Brine, Pollution control, NaHCO_3 , Na_2CO_3

1. Introduction

Desalination continues to be the most important source of drinking water in the arid regions such as the Arabian Gulf. In Riyadh, Saudi Arabia, for instance, 66% of drinking water demand is supplied by desalinated sea-water while the balance is produced from ground water sources [1, 2]. The ground water however, is becoming less reliable. This is because recently there has been alarming rate of depletion of ground water sources in the aquifers of the kingdom due to agricultural, urban and industrial water requirements [3, 4]. Therefore, the desalination process would be further intensified as a source of drinking water as demonstrated in fig. 1. The figure shows the increase in installed capacity of desalination plants in Saudi Arabia from 1978 to 1989. This reflects the demands in the period. According to recent official statistics, the kingdom will need 170 billion cubic meters of water annually by 2020, which is more than ten fold of today's requirements [5].

The intensified desalination process would increase the amount of concentrated brine, which is its major by-products. The issue of disposal of the brine is becoming important concern for policy decisions and environmental protection. Generally, there are six

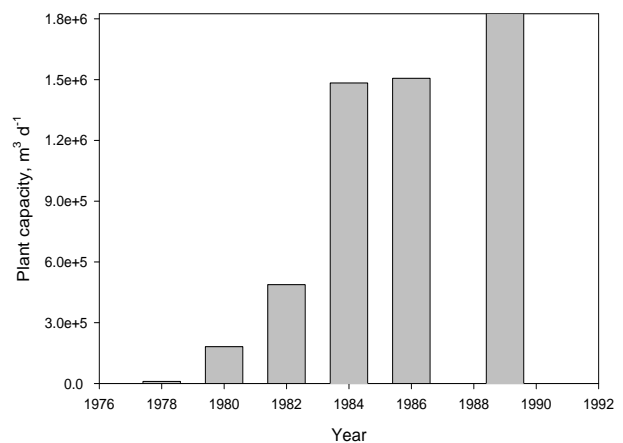


Fig. 1. Major desalination plants in Saudi Arabia.

major monetary cost effective methods for disposing the brine [6]. These are; (i) surface water discharge, (ii) discharge to the sewers, (iii) deep well injection, (iv) evaporation ponds, (v) spray irrigation and (vi) zero-liquid discharge. Clearly, deep well injection increases the plant construction cost, as arrangement must be made to avoid contaminating the drinking water aquifer. The high construction costs have also been a major disadvantage of zero-liquid discharge. The evaporative pond will ultimately pose a problem of precipitated salts that must be handle properly. In some cases, irrigation may

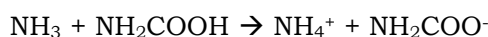
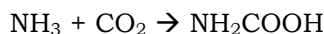
be a suitable means of disposal, but the level of ions concentrations of the water may not always be suitable for vegetative nutrient requirements. These drawbacks and the absence of strict regulations encourage improper disposal of the brine. At present, it is mainly discharged to the sea despite the detrimental effect to marine ecology. Based on the experience concerning the environment regulation applied to for instance, the petroleum industry, it is obvious that soon the brine discharges by desalination process will be subjected to stringent regulations. The alternatives or improved methods need to be developed for brine disposal.

In an earlier study, we proposed a process for production of chemicals from the brine in attempt to abate the sea pollution [7]. The process starts with absorption of ammonia in brine. The ammoniated brine is then contacted with CO₂. This converts the NaCl into products such as NaHCO₃, Na₂CO₃, NH₄Cl and MgCl₂. In this paper; we present the results of further studies on the effects of initial concentration of NaCl, NH₃ and the extent of carbonation on the conversion of NaCl to other products.

2. Experimental

The process involves absorption of ammonia in brine. The brine solution was prepared synthetically in the laboratory by adding pure NaCl in deionized water to obtain concentrations of 3.2 – 5.1 mol/dm³. The respective concentrations used are indicated in the results. The salt solution (100 ml in each case) was then contacted with 33 ml/s of pure ammonia to give the ammoniated brine of known concentrations. The resultant solution was placed in a batch gas bubbler. Then, carbonation of the ammoniated brine was carried out using pure CO₂ at fixed flow rates and periods. The major reactions involved are given in the following equations.

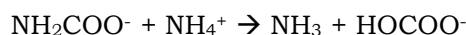
Primary reactions:



The overall reaction is



Secondary reaction:



The bicarbonates ions precipitate as sodium bicarbonate



The experiments were conducted at 22 ± 1 °C. The temperature of the system was regulated by the use of a cooling water jacket. The experimental setup is given in fig. 2. The solution was then passed through a filter to separate the precipitate from the mother liquor. The filtrate was analyzed for carbonates, chlorides, NaCl and NH₄Cl. The Na⁺ ions were determined using an atomic absorption spectrophotometer model 3100, Perkin Elmer. Details on the experimental setup and theoretical background to the reactions are given elsewhere [8].

3. Results and discussion

In this study, a series of reactions was employed to convert sodium and chloride ions in saline water into sodium bicarbonate and ammonium chloride. The effects of pH and carbonation time on the formation of carbonates and bicarbonates were studied. For this purpose, the experiment was carried out using 100ml of 3.5M NH₃ solution with no sodium chloride solution. The CO₂ gas was then bubbled until formation of precipitates was visible.

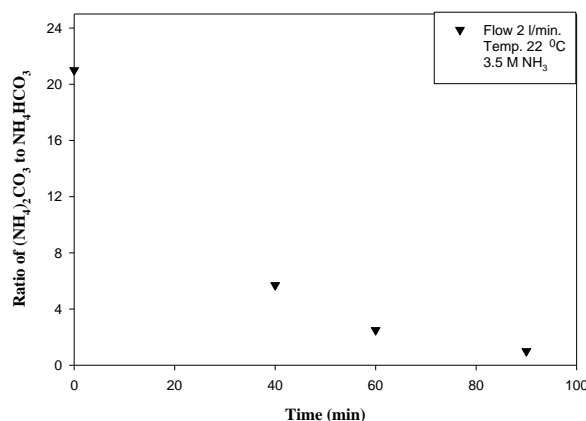
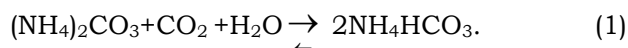


Fig. 2. Equilibrium conversion of (NH₄)₂CO₃ and NH₄HCO₃.

The analysis showed the formation of ammonium carbonate exclusively. The experiment was continued by bubbling more CO₂ gas and recording the time. Filtrate was analyzed to determine the ratio of carbonates to bicarbonates. Fig. 3 shows that the ratio of ammonium carbonate to ammonium bicarbonate decreases as the carbonation time increases. This is in accordance with the equilibrium as suggested by relationship as given in eq. (1).



The result of analyses indicates that the total moles of carbonates and bicarbonates remains constant, but transformation from one form to another takes place. Initially, the carbonate formation is predominant, but further carbonation leads to the formation of bicarbonate. Thus, bicarbonate increases with carbonation time at the expense of the carbonate. On the other hand, it is found that the pH value decreases with carbonation time due to acidity of the gas as shown in fig. 4. It indicates changes of pH with carbonation time for the reaction using brine of different compositions. An appreciable change in value of pH from 12 to 9 is observed in the initial period of carbonation (up to 30 min.). However, further carbonation time brings only slight changes in pH value. It suggests that over the pH range of 8-10, the formation of bicarbonate is favorable. Outside this range (pH greater than 11) other chemical reactions take place [9].

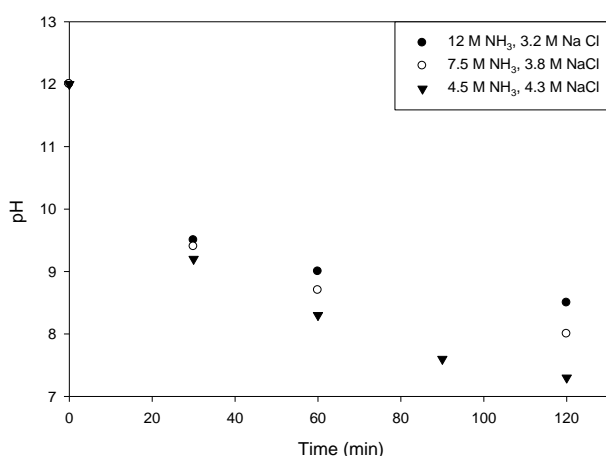


Fig. 3. Effect of carbonation on pH.

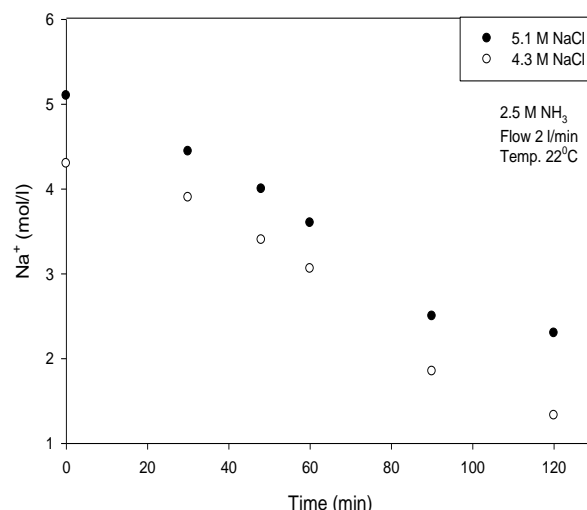


Fig. 4. Effect of initial salt concentration on Na⁺ removal.

Fig. 5 and 6 compare the effect of two different initial salinities (4.3M and 5.1M) in solutions of different ammonia concentrations 2.5M and 3.5M respectively. The trends shown are similar. The rate of conversion of sodium ions was higher when a higher saline feed sourced was used. However, there is a degree of dependence on the concentration of ammonia. At higher ammonia concentration the relative difference between NaCl conversions at the two NaCl concentration levels is smaller. The effect of ammonia concentrations is clearly shown in fig. 7, where the higher ammonia concentration favored the conversion of NaCl. It is known that a substance, which does not react with a solute, or form any complex ion with it, commonly decreases the solubility of the solute when it is introduced into the solution. Solubility of NaCl therefore, decreases with the increase of ammonia concentration. This in turn reduces the formation of sodium carbonates and bicarbonates. If a high concentration of NH₃ is employed then a large amount of NH₃ is going to coprecipitate with NaHCO₃ as ammonium carbonate exceeds its solubility limit. This may hinder the reaction since NH₃ is not taking part in the conversion of the salt. It indicates the need to adjust the initial salinity content of the solution with respect to concentrations of NH₃ to obtain higher degree of NaCl conversion.

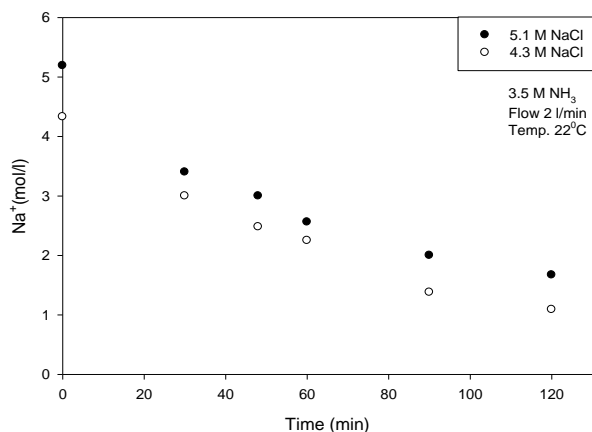


Fig. 5. Effect of initial salt concentration on Na⁺ removal.

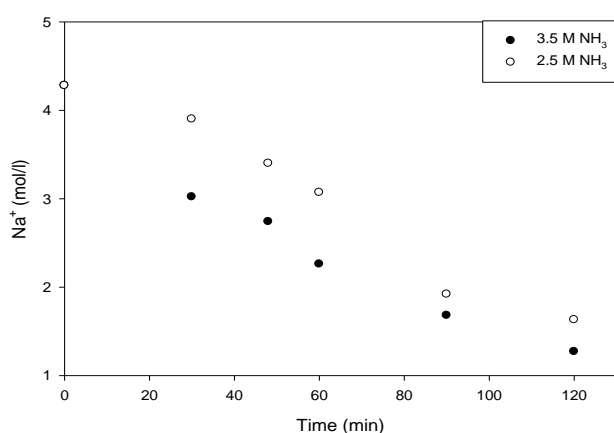


Fig. 6. Effect of low initial NH₃ concentration on na⁺ removal.

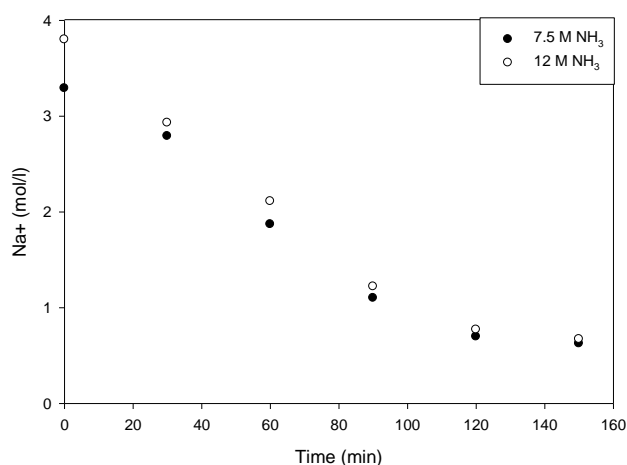


Fig. 7. Effect of high initial NH₃ concentration on na⁺ removal.

4. Conclusions

The issue of decreasing the concentration of the desalination plants blow down before disposal to the sea is important. It has been shown that contacting it with ammonia and then carbon dioxide may drastically decrease the concentration of the brine. This depends on the pH level of the solution. Useful products such as carbonates and bicarbonates could be obtained from the brine. Further studies are needed to establish the overall feasibility of the proposed process.

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