

A two-step process for removal of carbon dioxide and production of desalinated water using ammoniated saline water

OMAR CHAALAL

MD. MONWAR

College of Engineering
United Arab Emirates University
Address P.O, Box 15551 Al Ain
COUNTRYUNITED ARAB EMIRATES
chaalal@scientist.com

Abstract: - The emission of CO₂ has been increasing steadily and reached the critical concentration of 400 ppm in 2013 for the first time. CO₂ removal from the sources such as fossil-fuel power plants and similar sources is of paramount importance to these industries and to reduce the effect on global warming. A two-step process is investigated experimentally to remove CO₂ from a synthetic mixture of natural gas containing it. The first-step of the process is based on the modified Solvay process and involves the chemical reaction between CO₂ and ammonia in saline solution. This process can reduce CO₂ by about 99% and at the same time it can reduce water salinity by 40%. The process produces sodium bicarbonate and ammonium chloride which are at high concentrations. The second step uses a membrane extraction method to reduce the concentration of ammonium chloride to produce treated water that can be used for irrigation purposes. This combined process is potentially more effective and less harmful than the conventional amine scrubbing process. This innovative process has been applied to the sweetening of natural gas in the laboratory and can be extended to treat similar sources. Simultaneous reduction of salinity to produce treated water is an additional benefit of this process.

Key-Words: - removal, carbon dioxide reduction, desalinated water, ammonia, extraction.

1 Introduction

Power plants, oil refineries, desalination plants, steel mills, paper mills, cement factories and other facilities create megatons of manmade CO₂ emissions that are beyond the earth's ability to absorb and neutralize. The emission of CO₂ has been increasing steadily and with the increasing demand of desalinated water (especially in GCC countries) this is expected to increase at a faster rate (Dawoud and Al Mulla, 2001). Saline water is also coproduced during oil and gas exploration. Further, the produced gas contains up to 10% carbon dioxide. The huge amount of saline water, which is discharged, rejected or dumped back in the oil and gas fields, is a real production problem (Jibri and Abraham, 2001; Abdel-Aal, 1997).

Carbon dioxide is very corrosive in presence of water, it has no heating value and is a major contributor to the greenhouse effect. The co-existence of carbon di-oxide and saline water in oil

and gas extraction industries are creating problems and require urgent solution. Therefore, the available commercial processes are being evaluated and new processes are being investigated for complete or partial removal of CO₂ preferably using the huge amounts of saline water around (or produced in) the GCC countries.

There are processes available for carbon dioxide capture (David and Kishore, 1999; Ritter and Ebner, 2007; Washim Uddin and Hagg, 2012; Scholes et al., 2008; Madsen, 2011). They are effective, but have disadvantages in large-scale applications. Furthermore, CO₂ absorbed in these processes cannot be released and require additional handling systems. Amine scrubbing is successful but expensive and has corrosion problems. Carbon dioxide capture by cryogenic distillation requires large amounts of energy and have problems dealing with high temperature gases. Various membrane-based processes are being investigated in last two decades (Mohshim et al., 2013; Strathman, 2001;

Ismail and David, 2001). The processes are becoming competitive but yet to be economical for commercial applications.

In this paper a simple process is considered that can substantially remove CO₂ from either natural gas or exhaust gases (a conceptual view is shown in Fig. 1a) by chemically reacting with the salt in the brine in presence of ammonia (Abdel-AAL et al., 1996; Chaalal et al., 2007; Chaalal, 2007). The objectives of the project are to provide an effective method: (1) to reduce carbon dioxide from natural gas and similar sources, (2) to transform saline water (discharged from desalination or oil and gas plants) into irrigation water and (3) to produce chemicals such as soda ash that has use in chemical, medical and food industries.

2 Experimental procedure

Step A: Removal of carbon dioxide and desalination of seawater

Initial experiments were performed to determine the absorption of pure carbon dioxide in ammoniated seawater. The effect of temperature and the molar ratio of ammonia/sodium chloride was also examined. In the next stage 1.5 l of seawater (the composition is listed in Table 1) were mixed with 0.5 l ammoniated solution. A synthetic mixture of natural gas composed of 90% methane and 10% carbon dioxide was passed continuously through the solution. Similarly the exhaust gas from a car diesel engine containing 4.8% carbon dioxide was also trialled and allowed to pass through the ammoniated seawater. The gas flow rate was maintained at 0.7 l/min and the experiments were conducted at of 25 °C and 1 atm. The carbon dioxide and the ammonia contents in the exit gas were measured by using a gas chromatograph (Model CP-300, Varian, Netherlands). The NaCl content in the desalted water was measured by atomic absorption using an ICP spectrophotometer (Varian 710-ES 03, Australia). Also, samples were taken from the solution, filtered and analysed for salt ions. The precipitate formed during the carbonation reactions was filtered and heated at 300 °C for two hours to transform the sodium bicarbonate to sodium carbonate.

Step B: Reduction of ammonium chloride in desalinated water

In this step a membrane-based solvent extraction technique was applied using a hollow-fiber membrane contractor (Hossain and Chaalal, 2012). The hollow fiber membrane contractor, 5PCM-218, was purchased from Hoechst Celanese Corporation, Charlotte, NC, USA. The contractor had a shell and

tube configuration with hollow fibers (Celgard X-30 type) potted with polyethylene case. This type of contactor allows flow of two phases without being dispersed and provides large surface area per unit volume, compared to the conventional contactor. These are also available with very large area for mass transfer and can be used for both liquid and gas phase separation processes. A schematic diagram of the hollow-fibre membrane contactor is shown in Fig. 1b.

Table 1: Composition of seawater in GCC region

Description	Concentration (mg/l)
Total solids	43977
Sodium	14100
Calcium	511
Magnesium	1490
Chloride	24300
Bicarbonate	166
Sulphate	3410
Bromide	52
pH	7.8-8.5

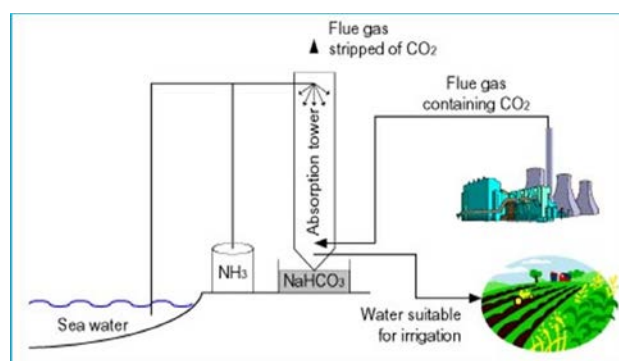


Figure 1a. A schematic drawing of the proposed process.

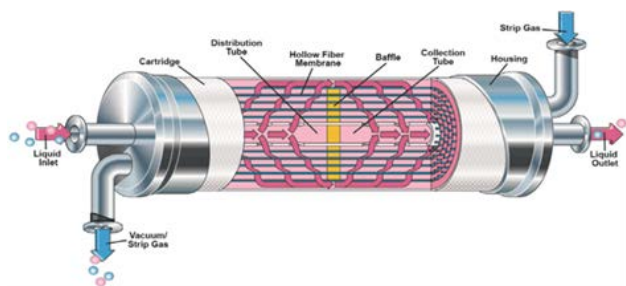


Figure 1b. A schematic diagram of the membrane contactor for removal of ammonium chloride.

3 Results and Discussion

The sodium percentage removal is shown as a function of time in Figure 2. Approximately 40% of sodium can be removed (as ammonium chloride) from seawater using a molar ratio of NH_3/NaCl more than 1 and within 1.5 hours of contact time. This removal performance increased slightly with the increase in the ratio of initial concentration of ammonia to sodium chloride.

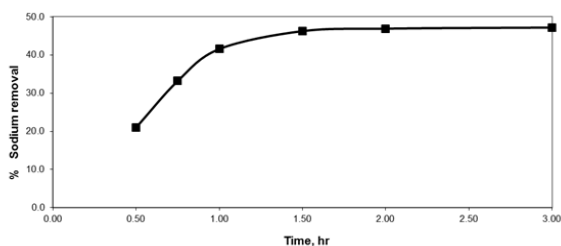


Figure 2: Removal (%) of sodium from seawater (3.5% sodium chloride) as a function of time.

The experiments for the removal process were conducted using two sources of CO_2 : (1) a synthetic natural gas mixture, containing 10% CO_2 and 90% CH_4 and (2) a sample of exhaust gas collected from a diesel car (4.8% carbon dioxide) by contacting with ammoniated seawater. A white cloud was observed immediately after adding the ammonia to the seawater samples, which disappeared a few minutes after the injection of the streams with carbon dioxide through the solution. The changes in concentration of carbon dioxide for the exit gas samples of (1) and (2) are shown in Table 2. It is observed that the CO_2 concentration decreased from 9.5% to 0.2% producing a sweetened gas of CH_4 composition of 99.8%. It is observed in Figure 3 that after 200 minutes the concentration of carbon dioxide increases again, the system reached

saturation with respect to ammonia concentration as it was not added continuously. This also suggests that had the process been made continuous by supplying ammoniated solution it would have performed similarly and the carbon dioxide would have been removed at such a high rate.

From the results of carbon dioxide reduction in the synthetic natural gas with ammoniated seawater (3.5% w/w salinity) is shown in Table 2, it is observed that the time required is very short (in minutes) to reduce carbon dioxide concentration from 10 % to almost 0%. Similar performance in reducing CO_2 is also observed in the results with formation water(8% w/w salinity) from oil exploration plant. The reduction of CO_2 the exhaust gas of a diesel car is also shown in Table 2; again within a few minutes the reduction is complete. Therefore, it is evident that the process works well over a wide range of “real” industry samples with excellent reduction of CO_2 in a considerably shorter time of a few minutes.

Table 2: Carbon dioxide (%) at the exit of the absorber using (1) natural gas as feed and (2) exhaust gas from a diesel car.

description/Components	Concentration (mg/L)
Total solids	43977
Sodium	14100
Calcium	511
Magnesium	1490
Chloride	24300
Bicarbonate	166
Sulphate	3410
Bromide	52
pH	7.8-8.5

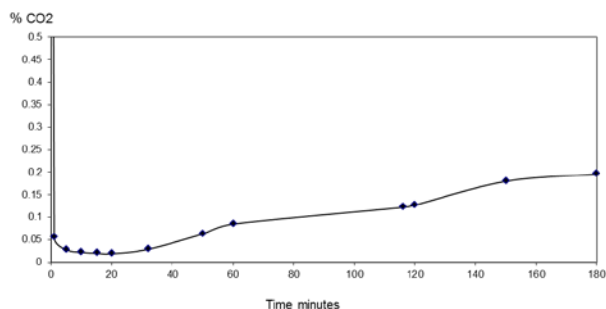


Figure 3. Concentration of carbon dioxide in the exit gas (sufficiently clean).

From the results of carbon dioxide reduction in the synthetic natural gas with ammoniated seawater (3.5% w/w salinity) is shown in Table 2, it is observed that the time required is very short (in minutes) to reduce carbon dioxide concentration from 9 % to almost 0%. Similar performance in reducing CO₂ is also observed in the results with formation water (8% w/w salinity) from oil exploration plant. The reduction of CO₂ the exhaust gas of a diesel car is also shown in Table 2; again within a few minutes the reduction is complete. Therefore, it is evident that the process works well over a wide range of “real” industry samples considerably shorter time of a few minutes. During the process sodium chloride in brine is transformed into ammonium chloride and the concentration is very high. So in the next step a membrane extraction process was examined to reduce its concentration so that the treated water can be used for irrigation purposes, where less than 5000 ppm of ammonium chloride is recommended. The results of the membrane extraction process is shown in Figure 4. It is observed that approx. 43% removal was possible in a once-through treatment. Further work is underway to determine more favourable conditions for the extraction of ammonium chloride from such high concentration feed.

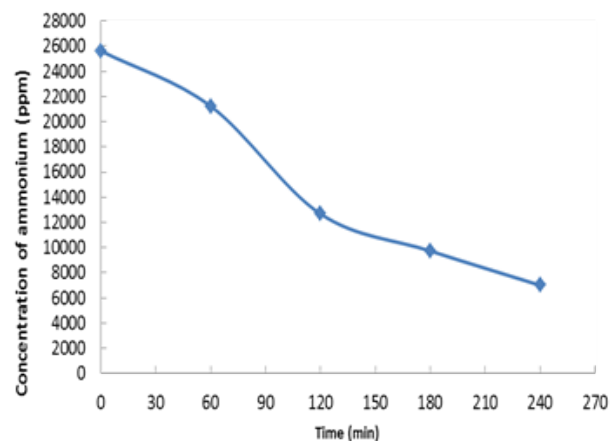


Figure 4. Concentration of ammonium in seawater (after removal with a carrier dissolved in sunflower oil).

4 Conclusions

The experimental results show the technical feasibility of sweetening of natural gas and reduction of CO₂ from exhaust gas through reactions of ammonia with high salinity water. The findings are summarized as

- (1) Excellent removal of carbon dioxide from natural gas (containing 10% v/v of CO₂) was obtained (reduced by 99%) and at the same time, the water salinity was reduced by 40%
- (2) Similar reduction of CO₂ was achieved from exhaust gas collected from a diesel car and within a very short time of a few minutes
- (3) The desalinated water contains high concentration of ammonium chloride that can be reduced for its use in irrigation purposes by adding a membrane extraction step after the carbon dioxide removal step.
- (4) The membrane process was upgraded to a bench-scale membrane contactor with an area of 1.4 m² and good percentage removal was achieved (in the range 43-73%).
- (5) This result was obtained from a high feed of concentrated ammonium chloride solution (25,600 ppm) and within a contact time of 4 hrs at a processing rate of 12-14 L/h.

More work is underway to extend the method to recycle ammonia (partially) to reduce the requirement in initial feed and to determine the effect of other operating conditions.

5 Acknowledgement

The authors would like to thank Almobdioon Centre for Studies and Research, King Abdul Aziz University (especially Dr. Essam Hassan Kawther, CEO, ACSR), Kingdom of Saudi Arabia, for providing the financial assistance of the project. They also appreciate the UAE University for the travel grant to present this work.

6 Biography

Dr. Omar Chaalal graduated from the Stevens Institute of Technology USA with his MS in chemical process and design Engineering. In 1990, he graduated from New Castle Upton Tyne University, England with a PhD in chemical and process engineering. He worked for the United Arab University from 1997 to 2010 as an Associate Professor in the Faculty of Engineering. Dr. Omar Chaalal has conducted research in the areas of offshore and onshore oil spills and bioremediation on contaminated UAE soils. He designed a unique barge that had the ability to skim leaking oil from the oceans. His plan was recognized and written up in the New Scientist Magazine. Dr. Omar Chaalal has published over 50 papers in regards to desalination, global warming, offshore and onshore oil contamination, and soil bioremediation. The work was patented in 2007.

References:

- [1] Dawoud MA, and Al Mulla MM, Environmental Impacts of Seawater Desalination: Arabian Gulf Case Study, Intl. J. Environment and Sustainability, 1: 287 (2001).
- [2] Jibri BEY and Abraham AA, Chemical conversion of salt concentrates from desalination plants, Desalination, 139: 287 (2001).
- [3] Abdel-AAL HK, Dual purpose chemical desalination process, Desalination, 113: 19 (1997).
- [4] David D and Kishore D, Recent development in CO₂ Removal Technology, UOP, (1999).
- [5] Ritter JA and Ebner AD, Carbon dioxide separation Technology-R&D needs for the chemical and petrochemical industries, Chemical Industry Vision, 2020: 287 (2007).
- [6] Washim Uddin M and Hagg MB, Natural gas sweetening-the effect of CO₂-CH₄ separation after exposing a facilitated transport membrane to hydrogen sulfide and higher hydrocarbons, J. Membr. Sci., 423-424: 143 (2012).
- [7] Scholes CA, Kentish SE and Stevens GW, Carbon dioxide separation through polymeric membrane systems: Flue gas applications, Recent Patents on Chem. Eng., 1: 52 (2008).
- [8] Madsen HT, Investigation of fouling formation during H₂S scavenging with 1,3,5-tri-(2-hydroxyethyl)-hexahydro-s-triazine, Esbjerg Institute of Technology, Aalborg University, 2011.
- [9] Vorsana Radial Counterflow Solutions: Post-combustion carbon dioxide capture, <http://www.vorsana.com./fluegas/carboncapture.html>.
- [10] Mohshim DF, bin Mohshim H, bin Mukhtar H, Man Z and Nasir R, Latest development of Membrane fabrication for natural gas purification: a review, J. Eng., Article ID 101746 (2013).
- [11] H. Strathmann, Membrane separation processes: current relevance and future opportunities, AIChE.J., 47: 1077 (2001).
- [12] Ismail AF and David LIB, A review on the latest development of carbon membranes for gas separation, J. Membr. Sci., 193: 1 (2001).
- [13] Abdel-AAL HK, Ibrahim AA, Shalabi MA, and AL-Harbi DK, Chemical separation process for high saline water 1: Parametric experimental investigation, Ind. Eng. Chem. Res., 35: 799 (1996).
- [15] Chaalal O, El-Nass MH, and Marzouqi AH, A simple global warming solution in a novel technique for natural gas formation water desalting,' 9th Conference on Energy for a Clean Environment, 2 - 4 July, 2007, Povaa de Vazim, Portugal.
- [16] Chaalal O, Patent WO/2007/139392, 'Modified Solvay process, and uses thereof for processing CO₂ containing gas streams and for desalination.
- [17] Hossain Md M and Chaalal O, Solvent extraction of ammonium ions from seawater using sunflower oil, The 2012 World Congress on Advances in Civil, Environmental, and Materials Research, 26-30 August, Seoul, Korea.