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

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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

<table>
<thead>
<tr>
<th>Description</th>
<th>Concentration (mg/l)</th>
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<tbody>
<tr>
<td>Total solids</td>
<td>43977</td>
</tr>
<tr>
<td>Sodium</td>
<td>14100</td>
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</tr>
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Figure 1a. A schematic drawing of the proposed process.
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 NH3/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.

The experiments for the removal process were conducted using two sources of CO2: (1) a synthetic natural gas mixture, containing 10% CO2 and 90% CH4 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 CO2 concentration decreased from 9.5% to 0.2% producing a sweetened gas of CH4 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 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 with excellent reduction of CO2 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.

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**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

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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: