

REVIEW OF CO₂ CAPTURE TECHNOLOGIES AND SOME IMPROVEMENT OPPORTUNITIES

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ABSTRACT

Reducing CO₂ emissions for addressing climate change concerns is becoming increasingly important as the CO₂ concentration in the atmosphere has increased rapidly since the industrial revolution. Many mitigation methods, including CO₂ sequestration and novel CO₂ utilization, are currently under investigation. Most of these processes require CO₂ in a concentrated form. However the CO₂ from large sources such as fossil fueled power plants is mixed with nitrogen, water vapor, oxygen, and other impurities. A typical CO₂ concentration from coal fired power plants is around 15 %, while CO₂ concentrations for natural gas fired plants are less than 10 %. Therefore, capturing CO₂ from flue gas is an important common link for many mitigation methods.

The current commercial operations for capturing CO₂ from flue gas use a chemical absorption method with Monoethanol Amine (MEA) as the sorbent. The method is expensive and energy intensive. The cost of capturing a ton of CO₂ including removing impurities and compressing CO₂ to supercritical pressure using existing MEA technology would be in the order of \$40, and the power output would be significantly reduced by the energy consumption in capturing and compressing CO₂. The high capture cost and energy consumption would be a major barrier for implementing CO₂ mitigation methods. Alternative technologies may offer improvement. This paper reviews several separation technologies applicable to capture CO₂ from flue gas, and discusses improvement opportunities and research needs.

INTRODUCTION

Concern over the increased concentration of CO₂ in the atmosphere and its effect on global climate change has increased the awareness and investigation for reducing CO₂ emissions. Most of the methods for mitigation require CO₂ in a concentrated form, while the CO₂ from fossil fueled power plants is mixed with nitrogen, water vapor, oxygen, and other impurities and has low concentrations (15 % for coal fired power plants, and less than 10 % for natural gas fired plants). Therefore, capturing CO₂ from flue gas is an important common link.

The current commercial operations for capturing CO₂ from flue gas use a chemical absorption method with Monoethanol Amine (MEA) as the sorbent. The method is expensive and energy intensive. An estimate by Pergman *et al* [1] using data from an ABB/Lummus Crest brochure [2] indicated the cost of capturing a ton of CO₂ including removing impurities and compressing CO₂ to a supercritical pressure would be in the order of \$40. While compression is an energy intensive and expensive component, the capture part of MEA method actually uses more energy and costs more than compression. The high capture cost is a major barrier for implementing near term carbon sequestration methods such as injecting CO₂ for enhanced oil recovery [1].

The other major shortcoming of the current technology is its high-energy consumption. The amine based method uses a large amount of low-pressure steam for sorbent regeneration, and the total power output is significantly reduced. It could lead to 20% reduction in electricity production for a PC plant (107MW/554MW) as a study by Booras and Smelser indicated [3].

Following is a preliminary analysis of several separation technologies applicable to CO₂ capture, new power generation configurations that may simplify CO₂ capture, as well as a discussion of some improvement opportunities

GAS SEPARATION METHODS APPLICABLE FOR CO₂ CAPTURE

Capturing CO₂ from the flue gas is essentially a gas separation process. Several separation methods, including Chemical Absorption, Physical Absorption, Physical Adsorption, Membrane Technologies, and Cryogenic Separation, can achieve such a goal. The judging criteria are capture effectiveness, process economy, energy consumption, and other technical and operational issues. Other measures such as modifying of power generation configurations by using O₂/CO₂ Combustion mode and oxygen blown Gasification Combined Cycle, could alter the flue gas composition and pressure that could help the CO₂ capture. Such strategy has some benefit but also raises new technical challenges.

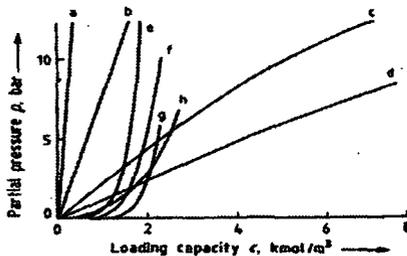


Figure 2. Equilibrium Curves of CO₂ in Various Solvents [Ref. 5]

Physical Adsorption: a) H₂O (30 °C); b) N-methyl-2-pyrrolidone (110 °C); c) Methanol (-15 °C); d) Methanol (-30 °C); Chemical Absorption: e) Hot potassium carbonate solution (110 °C); f) Sulfinol solution (50 °C); g) 2.5 molar diethanolamine solution (50 °C); h) 3 molar Amisol DETA solution.

Physical Adsorption

In physical adsorption, gas is adsorbed on the solid surface by a Van der Waals force. Most important adsorbents are activated carbon, zeolite, silica gel, and aluminum oxide [4]. The separation is based on the difference in gas molecule sizes (Steric Effect), or different binding forces between gas species and the adsorbent (Equilibrium Effect or Kinetic Effect)[4]. Like physical absorption, two types of processes: Pressure Swing Adsorption and Temperature Swing Adsorption are used. Because the gas molecules are attached on the solid surface and form mono or multi-layers in *physical adsorption*, the gas loading capacity could be lower than in *physical absorption*, even though many adsorbents have large surface area per unit volume. Because of the large volume of CO₂ in the flue gas, it appears physical adsorption might not be an effective and economical solution for separating CO₂ from flue gas. The other limit in using physical adsorption for this purpose is the low gas selectivity of available sorbents [6]. However in combining with other capture methods, physical adsorption may become attractive. Such applications include membrane technologies.

Membrane Technologies

Many membranes are made with similar materials used for physical adsorbents, because the physical quality, such as porous structure and selective gas affinity, are also useful for making membranes. Membranes are microscopic sieves. Under an applied pressure some molecules will pass through the micropores in membranes, and some molecules will be stopped.

The driving forces for gas separation using membranes are generally hydrostatic pressure and concentration gradient. There has been some work done in electrically driven separation of gases via ion conduction. Two types of membrane technologies can be used for separating CO₂ from other gases: *gas separation membranes and gas absorption membranes*. In using gas separation membranes a hydrostatic pressure is applied and the difference in permeability of gas species leads to separation of these gases. Although using separation membranes to separate CO₂ from light hydrocarbons has met with considerable success in the petroleum, natural gas and chemical industries, this technology may not be preferable to separate CO₂ from flue gas because of the large volume of the flue gas and the compression energy requirement. A study shows that a good separation using a two-stage system would cost twice much of the conventional amine separation processes [6].

In using gas absorption membranes, a liquid sorbent is used to carry away CO₂ molecules that diffuse through the membranes, and no high hydrostatic pressure is required. In this technology, the membranes serve as an interface between the feed gas and liquid sorbent. The membranes can be made in the forms of parallel hollow fibers, and feed gas and sorbent are moving on the opposite sides of the fibers. This configuration provides significantly greater liquid-gas contact area than packed absorbers, and can reduce the size, and possibly the cost of the absorber. Additional benefits include the independent control of gas and liquid flows, and minimization of flooding, channeling, or foaming of liquid sorbent in the absorber [6]. This configuration was under investigation by Norwegian researchers as a choice for offshore operation where the space and weight of the absorber are important factors. Considerable research is still required to

address issues such as how to deal with possible clogging of hollow fibers by fine particles in the flue gas.

Cryogenic Separation

Cryogenic separation of gas mixtures uses the difference in boiling points of various gas species to separate them. Because all gas species have a distinctive boiling temperature, the cryogenic method can provide effective gas separation. The critical temperature and triple point of CO₂ are 31.6 °C and -56.8 °C respectively. Between these temperatures, CO₂ can be liquefied by compression and cooling. The major disadvantage of cryogenic method is the high-energy consumption and costs associated with gas compression and cooling. For CO₂ sequestration, liquid CO₂ is required in many cases, and the work spent on liquefying CO₂ is not wasted. However, since the concentration of CO₂ in flue gas is about 15 % or less, the energy used to compress the rest 85% of flue gas is substantial. A simple calculation for the energy requirement for liquefying CO₂ by isothermally compressing the flue gas near the critical temperature to 74 bar would spend about 30% total power output in compressing 85% of the remaining gases, and this is about 50% more than MEA process. Methods to recover that amount of compression energy spent on 85% gas components could lower total energy consumption. Generally speaking, unless novel process schemes can be developed, cryogenic separation is an energy intensive operation.

New Configurations

Reduction of capture cost may be achieved in new power plants by designs that integrate CO₂ capture with power generation. In oxygen/CO₂ combustion mode, the flue gas would consist of mostly CO₂, and its capture is simplified. The oxygen production is also expensive and energy intensive, but the benefits from oxygen combustion including better thermal efficiency, reduction in the volume of flue gas and heat loss, and simplification or elimination of NO_x control [6] can partially offset the costs. A more advanced configuration can be an oxygen-blown coal gasification combined cycle plant. In order to achieve more than 90% removal of CO₂ that would be emitted from the gas turbine by combusting the syngas, shift reactors are included to turn CO and water vapor to CO₂ and H₂. In this configuration, CO₂ needs to be separated from H₂. Because the gasifier operates at an elevated pressure, a physical separation, such as Selexol can be used. As no steam will be required to regenerate the sorbent, and no additional compression is required for the absorption process, the energy consumption for CO₂ capture is small. Booras and Smelser [3] indicated the energy consumption for 90% CO₂ removal together with compressing the captured CO₂ to a supercritical pressure would reduce power production by about 12 %, and the majority of it is spent on compressing captured CO₂ to the supercritical pressure.

Because the existing oxygen production is energy intensive and will also generate a large amount CO₂, efforts should be dedicated to the reduction of energy consumption in oxygen production such as developing oxygen separating membranes.

As the vast majority of fossil power plants will not retire for many years, developing effectively CO₂ capture technologies applicable for existing plants is an urgent task. For those plants, *because of the large volume of flue gas and the low partial CO₂ pressure, chemical absorption appears to be a rational choice, as compared with other method. Productive approaches in the near term would be tapping the potentials for improving the chemical absorption, incorporating new membrane technologies, and encouraging innovative ideas.*

DISCUSSION - IMPROVEMENT OPPORTUNITIES IN CHEMICAL ABSORPTION

A major limitation of using MEA as a sorbent is its high heat of absorption with CO₂ (72 KJ/mole [8], equivalent to 18% of the combustion heat of carbon (393.5 KJ/mole)). Second, the concentration of MEA is used at 15 - 20%; this means energy has to be applied to heat the solution in the stripper and to evaporate some water. The total regeneration energy required is about 900 kcal/kg CO₂ [9] or 165 KJ/mole CO₂, equivalent to 42% heat from burning a mole of carbon, and 25% of the total combustion energy generated by burning coal. Although the stripper uses a low grade steam and some heat it contains was not used for generating power anyhow, it still causes 20% reduction of power generation for a PC power plant. Several aspects should be explored to improve this process.

Search for new sorbents

New sorbents that have high CO₂ loading capacity and lower heat of absorption should be studied. Some amines are less corrosive and can be used at a higher concentration. For example

Diglycol amine (DGA) can be used at 40% concentration thus has twice as much CO₂ loading capacity as MEA (currently used at 18%). A search should be directed to amines that have a lower heat of regeneration. Several sterically hindered amines have been examined and it is found that some hindered amines can reduce the heat of regeneration by 20 % [9]. Sterically hindered amines use geometrical effect to weaken the binding between the CO₂ and amine molecules. An alternative approach is to search for amines that have weaker chemical bindings with CO₂ molecules. Other non-amine sorbents and mixture of sorbents should also be evaluated.

Increase loading of sorbent

Increasing the amine concentration could reduce the amount of sorbent solution and the requirement of regeneration heat. Ref [10] indicated that regeneration energy requirement of a 50% MEA solution will be 40% lower than a 30% MEA solution. Additional benefits of using higher sorbent loading include reduced sorbent circulation, the size of reactors, and associated costs. Using higher series amines together with increasing the sorbent concentration may offer even better benefits. Regeneration energy requirements for a 50% MDEA (Methyldiethanolamine) solution would be 50 % less than those of a 30% MEA solution [10]. Current commercial restrictions on using higher MEA concentrations are related to excessive corrosion and solvent chemistry [10]. Assessment of the material requirements, performance of concentrated solutions, overall improvement in energy consumption, and costs need to be conducted.

Improve gas-liquid contact

Better gas-liquid contact can reduce the size of absorber and costs, improve practical CO₂ loading, and reduce the sorbent circulation and regeneration energy requirement. This becomes more important for new sorbents that have lower reaction rate constants along with their lower regeneration energy requirements. A study indicated that structured packing in an absorber can provide a much higher overall mass transfer coefficient than the currently used random packing [11]. Using the membrane technology can reduce absorber size because membranes provide large contact surface between the gas and liquid. A study indicated that an absorber using membrane technology can reduce its size by 72% and its weight by 66% compared with a conventional absorption column [12].

SOME CURRENT EFFORTS IN THE US AND OTHER COUNTRIES

Because CO₂ capture is critical for CO₂ sequestration, many countries are actively engaged in research in this area. Japanese researchers are testing various sorbents and have reported sterically hindered amines that save 20% in regeneration energy. Japan is also studying membrane materials to separate CO₂ from N₂ [13]. It has also reported a Cardo polyamide that has a higher selective permeability for CO₂/N₂, and hollow fiber membranes utilizing the Cardo polyamide were tested. In addition, a pilot plant with capacity of 1000 m³N/h (~30 TPD) was set up [7]. Canadian scientists at the University of Regina in Saskatchewan built a 1.77m high absorption column, and tested new sorbents and absorber packings [11]. The Norwegian efforts include increasing amine loading, testing new chemical sorbents, using hollow fiber membranes to reduce the size of absorber, modifying reactor designs for reducing corrosion, and reducing sorbent degradation [12]. In the Netherlands, hollow fiber membrane absorber and new sorbents were studied for capturing CO₂ for feeding a greenhouse [14].

The United States built the first commercial plant capturing CO₂ from flue gas using MEA for industrial application in Trona, California. Another facility in Poteau, Oklahoma used the similar technology to produce chemical grade and food grade CO₂ from flue gas. The National Energy Technology Laboratory (NETL) has initiated a study to improve the MEA-based absorption method. Current efforts include testing hindered amines and improving gas-liquid contact in the absorber. NETL has also supported studies of innovative approaches for capturing CO₂ including "CO₂ Capture from Industrial Process Gases by High-Temperature Pressure Swing Adsorption" by Air Products, "A Novel CO₂ Separation Systems" by TDA Research Inc., "Oxygen Enriched Combustion" By CANMET, and "CO₂ Separation using Thermally Optimized Membranes" by a team led by Los Alamos National Laboratory.

SUMMARY

Recognizing improvement potential

Present operations for separating CO₂ from flue gas are used for commercial CO₂ production in which the CO₂ can be utilized for producing a revenue (carbonation of liquids, enhanced oil recovery, etc.). The new demand from climate change concerns would stimulate research efforts to examine new opportunities. Capturing CO₂ for climate change also offers more flexibility

than industrial separation because high CO₂ capture and purity may not be necessarily required. Technologies not suited for industrial applications can still serve as a candidate for climate change concerns if the costs and energy consumption are favorable.

Improved chemical absorptions

A high priority in the near term would be tapping improvement potentials in chemical absorption to reduce the energy requirement. Significant reduction in cost and energy consumption could be achieved by studying new sorbents, increasing loading, improve gas/liquid contact, etc.

Physical absorption can be incorporated in advanced IGCC plants

Physical absorption can be effective when the partial gas pressure is high and the temperature is low. In integrating CO₂ capture in the power or fuel generation cycles, physical absorption will be a good choice. Examples include the O₂-blown pressurized gasifier and combined cycles.

Collaboration with Industry

Capturing CO₂ for climate change poses a new challenge for the gas separation industry, and provides new incentives and opportunities. The progress made in improving CO₂ capture in turn will benefit other gas separations. There could be many potential collaborations between DOE sponsored research and industrial interests that would speed up the progress in developing advanced CO₂ capture technologies.

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Study of CO₂ Absorption and Desorption in a Packed Column

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ABSTRACT

Carbon dioxide, a major greenhouse gas, may need to be removed from flue gas produced by combustion of fossil fuels in order to manage future climate changes. Although conventional wet scrubbing techniques exist for removal of carbon dioxide from gas streams, the wet scrubbing techniques must improve to process large volumes of flue gas at acceptable thermal efficiencies and minimal costs. Amine scrubbing is one such technique to remove CO₂. In order to make the process more efficient, two areas of improvement were investigated: gas-liquid contacting area and the type of reactant. Pertaining to the former, various absorption tests with conventional packing material and structured packings were conducted with mono-ethanolamine (MEA), a traditional solvent, as well as with novel amines. Significant improvements in CO₂ removal were obtained with the structured packing. With respect to the amine investigation, a key to improved efficiency is the ease of regeneration of the CO₂-loaded solvent. Testing with a sterically hindered amine, 2-amino-2-methyl-1-propanol, revealed that, although absorption was somewhat less as compared to MEA, thermal regeneration was far easier. The impact of various process parameters on the absorption and desorption steps will also be discussed.

INTRODUCTION

Chemical solvent absorption is based on reactions between CO₂ and one or more basic absorbents such as aqueous solutions of mono-, di-, or tri-ethanolamine. An advantageous characteristic of absorption is that it can be reversed by sending the CO₂-rich absorbent to a desorber (or stripper) where the temperature is raised. In the case of physical absorption, CO₂ is absorbed under pressure, and the gas desorption can be achieved at reduced pressure. The regenerated absorbent is then returned to the absorber thereby creating a continuous recycling process. The disadvantages of chemical absorption processes include their limited loadings and high energy requirements resulting from the reaction stoichiometry and the heats of absorption, respectively. There are also problems of corrosion and degradation. Physical solvents include methanol, polyethylene glycol, dimethylether, and others.

All currently available CO₂ separation processes are energy intensive. In ranking energy penalty of the processes, combustion with pure oxygen is the least energy intensive (about 30% energy penalty), and is followed by chemical solvent absorption processes (about 35% energy penalty) [2]. Also it has been concluded that even the current most efficient technology will reduce energy efficiency of utility steam plants by about 30% and will increase the price of electricity by 80%, even before disposal costs are added. These results are consistent with an EPRI study on CO₂ capture and disposal [3]. Combustion with pure oxygen requires redesign of the entire combustion and boiler system, and therefore, can not be retrofitted. The chemical solvent absorption process for CO₂ capture can be retrofitted in existing boiler systems and provides a rationale to pursue near-term evolutionary capture techniques. Emerging and future electricity generation technologies and novel CO₂ capturing methods have the potential to significantly reduce electricity costs if the control of CO₂ emissions is mandated.

EXPERIMENTAL

Absorption

Figure 1 shows a typical liquid chemical absorption process for CO₂ capture. The flowsheet represents a continuous absorption/regeneration cycling process. CO₂ is captured in the absorber at approximately 38 °C and is released from the regenerator at approximately 121 °C at a much higher concentration.

In our investigation, the experimental apparatus consists of a packed-column absorber to promote

gas-liquid contact and reaction in a counter-current flow pattern. Figure 2 shows the schematic diagram of the packed column absorber. The glass absorber is 7.7-cm ID and packing height varied from 18 to 71 cm during this series of tests. It has an exterior jacket with hot water flowing in this outer jacket for absorber temperature control. The heat-jacketed section is 82.6-cm high. CO₂ absorbent enters from the top of the absorber through a spray nozzle to ensure good initial liquid distribution to the packing material. The spray nozzle, which delivers fine mists, is placed 1 inch above the packing. The liquid is electrically preheated to the reactor control temperature in the stainless steel inlet line. The baseline absorber temperature is normally set at 38 °C during CO₂ absorption. Liquid flow rate is controlled by a MicroMotion mass flowmeter. Flow rate data are continuously stored in a computer at a predetermined time interval.

Simulated flue gas enters from the bottom of the absorber. Gas flow rate is controlled by a mass flow meter controller manufactured by Tylan General. Gas flow rate data are also stored in computer files. The baseline gas composition is 15% CO₂ and 85% N₂. Sulfur oxides, hydrogen chloride, nitrogen oxides, and oxygen are not included in the simulated flue gas to avoid possible interferences with the test objectives for this series of experiments. These acid gases are known to cause degradation of the solvents. Coal-fired flue gas nominally consists of 15% CO₂ on a dry basis when the combustion takes place with 20% excess air.

The initial objectives of the experiments are: (1) to obtain first-hand data on the effect of structured packing versus traditional random (or dumped) packing on the CO₂ capture rate; (2) to obtain CO₂ capture rate data by monoethanolamine (MEA) and by a sterically hindered amine; and (3) to compare CO₂ stripping rates between CO₂-rich MEA and CO₂-rich sterically hindered amine. The sterically hindered amine used during this test series was 2-amino-2-methyl-1-propanol (AMP). AMP is a tertiary amine which reacts with CO₂ at a slower rate than MEA. Though AMP reacts with CO₂ at a slower rate, less energy is required to drive out CO₂ from its CO₂-rich solution [1]. There is a wide selection of sterically hindered amines. Recently, in Japan, Kansei Electric Power Company, in conjunction with Mitsubishi Heavy Industries Limited, has developed a sterically hindered amine specifically for CO₂ recovery from flue gas [4]. TNO, in the Netherlands, also is developing liquid absorbents for flue gas applications [5]. However, the identities of those absorbents were not disclosed.

The basic reaction chemistry for monoethanolamine and CO₂ is represented by the following reversible reaction:



This is an exothermic reaction and 72 KJ of thermal energy is released per mole of CO₂ absorbed in MEA solution. Absorption usually takes place at 38 °C. During regeneration, more thermal energy (about 165 KJ/mole CO₂) is added to the solution to release the CO₂, because a large amount of water in the 20% by weight aqueous solution must be heated to regeneration temperature. Regeneration usually takes place at 121 °C. It has been estimated that up to 80% of total cost in the CO₂ absorption/regeneration cycle is due to the regeneration procedure.

Three types of column packings are compared for their CO₂ absorption rates at identical test conditions: Intalox saddle (ceramic, random packing), 1.9-cm and the smallest available from the supplier (Norton Chemical Process Products); Flexipac structured packing supplied by Koch Engineering Company; and BX Gauze structured packing also supplied by Koch Engineering Company. Structured packing provides more gas-liquid contact surface area per unit packed volume than random packings. Thus the overall CO₂ capturing capacity and rate by the liquid absorbent is increased. The packing height ranged approximately 18 cm to 71 cm during this series of tests.

CO₂ Absorption Rate Determination

Inlet nitrogen flow, inlet CO₂ concentration (vol%), and outlet CO₂ concentration (vol%) are used to calculate instantaneous absorption rates every 10 seconds during an absorption test. The nitrogen flow is measured by a mass flow controller. The inlet and outlet CO₂ concentrations are measured by an Horiba infrared gas analyzer, which is calibrated immediately before the test. The inlet CO₂ flow rate is calculated using the following equation:

$$G_1 = [(F \times D/M)/(1 - y_1)]y_1 \quad (1)$$

where

G_i = CO₂ inlet flow rate, lb-mol/hr
 F = nitrogen gas flow rate, ft³/hr
 D = density of nitrogen, lb/ft³, at standard conditions
 M = molecular weight of nitrogen
 y_i = CO₂ mole fraction at inlet of absorber, vol%

The inlet CO₂ concentration, y_i , is averaged for the 20 data points (232 s) recorded immediately before solvent flow is initiated and is assumed constant throughout the test duration. The CO₂ inlet flowrate is controlled by a mass flow controller. The calculated flow rate, G_i , is used in the absorption calculation for data accuracy purposes. Since nitrogen gas is inert in the absorber, the outlet CO₂ flowrate is calculated using the nitrogen flow rate and outlet CO₂ concentration using the following equation:

$$G_o = [(F \times D/M)/(1 - y_o)]y_o \quad (2)$$

where

G_o = CO₂ outlet flow rate, lb-mol/hr
 y_o = CO₂ mole fraction at outlet of absorber, vol%

The CO₂ absorption rate is the difference between the inlet and outlet CO₂ flow rates. Total CO₂ absorbed in the absorber can be obtained by integrating the instantaneous rates over a selected time period. Efficiency of CO₂ absorption is defined as $[(y_i - y_o)/y_i] \times 100\%$ at steady state.

Regeneration

The CO₂ - rich liquid chemical absorbent can be regenerated by heating. CO₂ evolves from the rich liquid absorbent during the heating. This regenerated liquid absorbent is CO₂ - lean and recirculated to the absorber for reuse. The regeneration temperature is usually set at 121 °C under slightly elevated pressure in the carbon dioxide industry. In our investigation, the uniqueness of the laboratory regenerator is that the absorber was used as the regenerator during the regeneration phase of the absorption/regeneration cycle. The only difference is that higher temperature is maintained in the packed column in order to drive away CO₂ from the rich amine solution. The structured packing accelerates the CO₂ release from the CO₂ - rich amine solution. The CO₂ - rich solution, which is sprayed into the reactor, is trickling in a thin film down the extensive surface area provided by the packing. No purge gas is required during the regeneration; the recovered CO₂ is pure after condensing out the vapor. A bag meter is used to measure the total mass of CO₂ evolving from a known amount of CO₂ - rich amine solution; the time at every 2830 cm³ (0.1 ft³) advance at the bag meter is manually recorded.

RESULTS AND DISCUSSIONS

Absorber Efficiencies

Effects of absorbent (MEA) flow rate and packing type on CO₂ absorption efficiencies are compared. The test results are shown in Table 1. Higher absorbent flow rate increases CO₂ absorption efficiency as expected. Absorbent utilization is defined as efficiency divided by the stoichiometric ratio. Since it takes 2 moles of MEA to react with one mole of CO₂, the stoichiometric ratio for MEA is equal to the mole ratio divided by 2.

Three types of packings were studied for their effectiveness in CO₂ absorption: BX gauze, Flexipac, and random saddle (ceramic) packings. BX gauze and Flexipac structured packings are the products of Koch Engineering Company. At an absorbent to CO₂ mole ratio of 1.4, BX gauze improves packed column absorber efficiency by about 50% over the use of random saddle packing. Flexipac minimally improved efficiency over random saddle packing.

Comparison of CO₂ Absorption Rates

Table 2 shows that the sterically hindered amine, AMP, attained near equal CO₂ absorption rate using structured packing as compared to random saddle packing for MEA processing. In these tests, 29.2 wt% of AMP solution is used while only 20 wt% of MEA solution is used, because the molecular weight of AMP is larger than MEA. Thus equal mole concentration is maintained for both MEA and AMP in the absorbent solution, respectively. Flexipac structured packing did not significantly improve the CO₂ absorption rates.

Rate of CO₂ Regeneration: AMP vs MEA

To compare CO₂ regeneration rate between MEA and AMP, CO₂-saturated MEA and AMP solutions are prepared. The packed absorber, used as the regenerator, is only heated to 93 °C, since in the present reactor setup, this is the highest temperature that can be safely maintained to prevent the water or solution from boiling. CO₂ - saturated AMP or MEA solution is sprayed on the top of the packing, while the CO₂ releasing rate is recorded with the aid of a bagmeter. The data in Table 3 show that CO₂ releasing rate from AMP solution is about 80% faster than from MEA solution. No purge gas is used. The packed column has not been optimized, and a taller packed column is expected to improve the operation.

CONCLUSIONS

Investigations of amine-based scrubbing for CO₂ capture were performed to elucidate ways to improve this chemical absorption process. Increasing the gas-liquid contacting area has a major impact on scrubbing. Absorption tests revealed that for a particular amine, structured packing improves the absorber efficiency and absorption rate as compared to the more traditional random packing. The type of amine is also a consideration. At the same bed geometry, the conventional MEA performed much better during absorption studies than the sterically hindered amine, AMP. However, in the regeneration step, the CO₂ releasing rate from the saturated AMP solution is over 80% greater than from saturated MEA solution. By extracting information from the above results, it can be speculated that if the more easily-regenerable AMP is substituted for MEA, an overall process benefit will be obtained if a structured packing is used as compared to the random packing. Other techniques to improve the amine-based scrubbing will be investigated in the future.

DISCLAIMER

Reference in this report to any specific commercial process, product or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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TABLE 1
Absorber Efficiency and Absorbent/CO₂ Mole Ratio

Mole ratio	Efficiency, %	Packing	Utilization, %
1.4	61.3	BX gauze	87.6
1.4	60.9	BX gauze	87.0
1.4	62.2	BX gauze	88.8
2.2	97.2	BX gauze	88.4
2.3	98.9	BX gauze	86.0
1.4	41.4	Flexipac	59.1
1.4	40.1	random saddle	57.3

Absorbent: 20 wt% MEA

Mole ratio: Mole absorbent inlet/mole CO₂ inlet

Absorber temp: 38 °C

Absorber ht: 53 cm

NOVEL SOLID AMINE SORBENTS AND APPLICATIONS FOR CARBON DIOXIDE REMOVAL

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KEY WORDS: Carbon dioxide removal, space life support systems, solid amines

ABSTRACT

In this paper, we report on our solid amine sorbent (HSC⁺) previously developed and used for space life support applications, which may also be of interest for CO₂ removal in greenhouse gas control and other industrial processes. Adsorption capacities of the material for CO₂ pick up were determined, and long term test data show excellent performance. In addition, we have determined the heat of adsorption associated with CO₂ pickup by HSC⁺ and the effect of moisture, using isothermal flow calorimetry. We have also performed thermal gravimetric analyses on the materials to gain insight into the stability of the material and determine the temperatures at which CO₂ and constituents of HSC⁺ desorb from the surface.

INTRODUCTION

In order for CO₂ capture to be implemented as a method for climate change mitigation, technologies must be developed that are efficient, cost-effective, environmentally benign, and easily applicable. Liquid amines, used as sorbents for removing CO₂ in the natural gas industry for roughly 50 years, represent the primary competing commercial technology (lowest cost to date). However, there are several disadvantages in the use of liquid amines¹:

- High temperatures are required for regeneration (typically 100-120 °C)
- Equipment costs and maintenance for pumping or spraying liquids
- Corrosive effects of liquid amines and byproducts (corrosion inhibitors and high maintenance costs required); particularly accelerated by contaminants and acid gases
- Loss of amine due to evaporation (continual maintenance) and latent energy penalty
- Difficulty in handling liquids (as compared to solids)
- Amines must typically be maintained at <20% (occasionally up to 30%) concentration (to reduce corrosion), thereby compromising CO₂ removal capacity^{2,3}
- Additives are required to prevent foaming; and
- Oxygen typically has to be limited to prevent reaction with the solvent³ (<8%)

The focus of our work has been on solid amine sorbents^{4,5}, originally developed for space life support systems, but with several key advantages rendering them attractive for other applications: high capacity, low regeneration costs, long-term stability, intrinsically fast kinetics, no need for moisture removal from gas stream, and ease of handling. Through our Hamilton Sundstrand Space Systems International (HSSSI) Division, we previously developed a regenerable sorbent consisting of solid amine beads, known as HSC⁺. This material contains a liquid amine bonded to a high surface area, solid acrylic-based, polymeric support, followed by a coating to enhance the rate of CO₂ adsorption and desorption. Because a solid bed of material is used instead of liquids, there is minimal corrosion, and no equipment is needed to circulate or spray liquids. Our original use was for removing low concentrations of CO₂ at atmospheric pressure (typically less than 1%) and thus a key advantage is applicability to either high or low CO₂ partial pressures- i.e., compression of waste gas such as flue gas above atmospheric pressures is not mandatory. In addition, the sorbent may be made from low cost, commercially available amines and

the consumer cost is anticipated to be roughly the same as that for conventional liquid amines. Due to the anticipated long term stability of the material, periodic addition of amine, which is a necessity in conventional liquid amine systems, should not be required.

In order to design sorbents with higher capacities and favorable kinetics, a detailed study of the currently used sorbent, HSC⁺ is essential. In this paper, we report on a preliminary experimental investigation of thermodynamic data for HSC⁺ such as heats of adsorption, adsorption capacity, and thermal gravimetric analyses. Due to the exothermic nature of the CO₂ absorption reaction and the variability of CO₂ capacity with temperature, physical property data is essential to optimize system parameters (power, weight and volume). Our overall goal is to maximize the cyclic CO₂ capacity of the system while adhering to system power, weight and volume specifications. By reporting on fundamental property data, this sorbent may also be found applicable for other CO₂ removal processes as well.

EXPERIMENTAL

The adsorption capacity for CO₂ and temperature increase associated with adsorption was determined using a flow apparatus, consisting of a pyrex tube packed with HSC⁺. A thermocouple was placed at the center of the bed, the concentration of CO₂ was measured at the inlet and exit of the tube using an infra red detector (Horiba, model PIR-2000), and the mass of the tube was measured after equilibrium to determine equilibrium adsorption capacities. In order to determine the thermal stability of HSC⁺, thermal gravimetric methods (TA Instruments, model 2950) were used. All TGA experiments were taken under consistent conditions and typical sample sizes varied between 20 and 50 mg. The runs were initiated at room temperature (approximately 25°C), and the temperature was increased at a ramp rate of 10°C per minute. Nitrogen was used as a purge gas at a flow rate of roughly 70 ml/min throughout all experiments. We have also measured heats of adsorption using isothermal flow microcalorimetry. This highly sensitive technique is valuable for thermochemical measurements in which equilibrium is attained in a relatively short time. Rather than maintaining adiabatic conditions (i.e., eliminating heat flow to or from the sample cell), we maintain isothermal conditions and measure heat flow to or from the cell. Integration of the heat flow over the time period of the adsorption process provides the heat of adsorption. The instrument (CSC, model 4400) is a differential (dual cell) unit and can measure heat flows as low as 0.1 μW (25 nanocalories/sec). Operating temperatures range from 0 to 100 °C with an adsorbent bed volume of approximately 3 cm³.

RESULTS

Figure 1 shows a typical breakthrough curve using an initial mass of 11.4 g of HSC⁺, packed in a 1 inch-diameter tube. The flow rate of CO₂ (2% in N₂) was varied between ~0.5 and 2 slpm. The maximum temperature determined in the center of the bed was 53 °C, and the maximum adsorption capacity was found to be roughly 4% by mass. These experiments employed a bed packed solely with beads of HSC⁺, whereas in practical applications, the use of a reticulated aluminum foam provides several advantages: the foam acts as a heat transfer and a bed retention medium, allowing for small scale changes in sorbent size without introducing a short-circuit path for channeling. These features are also in-place with the full-scale cycling sorbent system on-board the space shuttle orbiters.

TGA (thermal gravimetric analysis) data allow us to determine the range of temperatures at which CO₂, the coating material, and the amine(s) leave the surface of HSC⁺ under controlled conditions. As shown in Figure 2, the initial peak in the mass loss derivative curve (at ~ 60 °C) is due to removal of CO₂, with a maximum rate in mass loss between 60 and 70 °C. The second peak at ~ 200 °C is due to removal of both amine and coating.

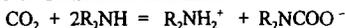
There is a change in the mechanism beginning at roughly 230 °C and complete decomposition occurs at ~ 450 °C. It is clear that loss of additional components (e.g., amine or coating) do not begin to take place until over 100 °C, illustrating thermal stability under the operating conditions we employ for space life support systems.

Figure 3 shows heat of adsorption data for the adsorption of CO₂ (2% in air) on HSC*. In this example, an approximately 0.6 g sample of HSC* was exposed to a 2% mixture of CO₂ in N₂, at a flow rate of 30 ml/min. The heat of adsorption was calculated to be -94 (±8) kJ/mol CO₂ which is consistent with results anticipated for amine + CO₂ reactions. The value we have reported is an average for 5 sample trials, and the mass % of CO₂ adsorbed is 3.7 (±0.4) %. One of the predominant sources of error is believed to be incomplete degassing to remove CO₂ and moisture, and absorption of CO₂/H₂O during material handling and sample transfer. Note that the heat of adsorption reported here represents a total heat of adsorption for adsorption of the maximum concentration of CO₂, rather than a differential or isosteric heat of adsorption for a specific CO₂ coverage.

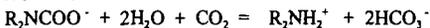
DISCUSSION

In order to design CO₂ scrubbers for various applications, detailed performance studies of the sorbent are essential. We have performed a set of preliminary experiments to determine thermophysical properties and reactivity of the solid amine sorbent HSC*. Some of the key issues to address in designing improved sorbents are: capacity, ease of reversibility, and stability. TGA and capacity measurements have shown the material to be favorable for space life support applications although a detailed understanding of the mechanism is still lacking. This is the first report of a direct measurement of the heat of adsorption of CO₂ on the material which may provide insight into the mechanism and ease of reversibility of the process.

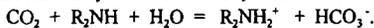
The mechanism for CO₂ removal using amines is known to be dependent on the presence of water^{7,8}. Without moisture present, the main reaction believed to account for CO₂ removal is carbamate formation:



This shows that for every one mole of amine, only ½ a mole of CO₂ is removed. However, when moisture is present, further reaction of the carbamate ion to form bicarbonate occurs:



Bicarbonate may also form directly from the amine + CO₂ + water reaction:



Therefore, in the presence of water, one mole of amine is effective in removing one mole of CO₂. This mechanism has been discussed in the literature for several years⁷. In our results, based on a measurement of mass increase alone, it appears as if roughly 3 times more CO₂ is removed in the presence of water as compared to the absence of water. An additional possibility is that reaction on the surface, and/or moisture adsorption, allows more of the active sites of the material to be available for CO₂ removal.

Measuring heats of adsorption can also provide important information on the interaction between CO₂ and the sorbent. For the case of water vapor on HSC* ΔH was found to be -47.2 (±1.0) kJ/mol H₂O, with nearly 17% mass capacity for water. As anticipated, a physisorptive process typically results in a ΔH similar to the heat of condensation of the adsorbed gas (ΔH ~ -44.0 kJ/mol at 25 °C for water). The heat released during adsorption of CO₂ is significantly larger (-94 (±8) kJ/mol CO₂) than the heat of condensation of water vapor, indicative of a strong interaction between the CO₂ and the amine surface. An illustration of mechanistic differences is shown by the measurement of mass % adsorbed in the presence of water versus in the absence of water. In the case of a dry (CO₂, N₂ mixture), there is a 3.7 (±.4) % mass gain; while the gain is 16.8 (± 3.6)% in the case of

pure water vapor, and 27.3 (\pm 2.2)% in the case of CO₂ + water vapor. It is therefore clear that higher CO₂ capabilities are achieved by coadsorption of water. Future studies will investigate the mechanism by which coadsorption aids in carbon dioxide removal and on optimizing solid amine sorbents.

CONCLUSIONS

We have measured the equilibrium CO₂ adsorption capacity for HSC⁺ to be \sim 4 % at ambient pressures, and have shown that the sorbent may be regenerated using vacuum desorption at \sim 1 Torr. Thermal gravimetric analysis was used to show that the amine is strongly bonded to the substrate and the material does not begin to lose amine/coating components until over 100 °C, while CO₂ is desorbed at roughly 60°C in a non pressure swing adsorption mode. The material has been tested for hundreds of cycles with no loss in performance.

ACKNOWLEDGEMENTS

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Carbon Dioxide Concentration and Temperature Profiles

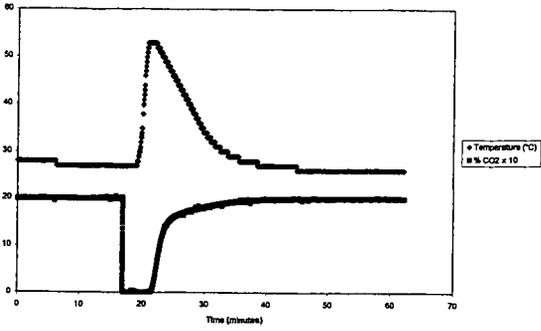


Figure 1.

TGA Data

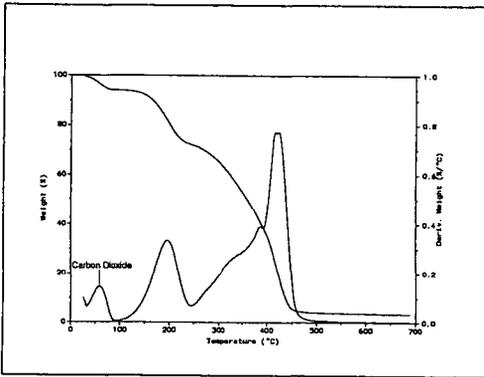


Figure 2.

HSC + 2% CO₂ in N₂

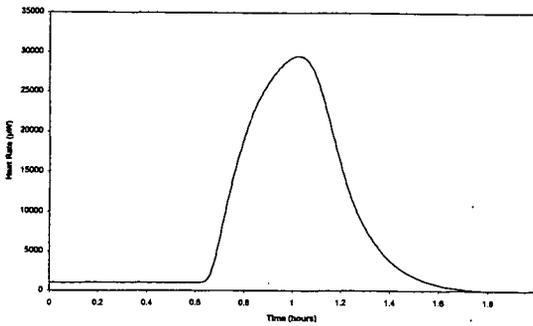


Figure 3.

DUAL ALKALINE APPROACHES FOR THE CAPTURE AND DISPOSAL OF CO₂

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KEYWORDS: Ammonia, Activated Carbon, and Carbon Dioxide

Abstract

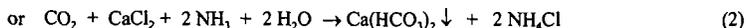
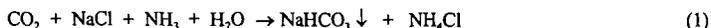
A new method being investigated to capture CO₂ uses a dual alkaline approach with the use of chloride salts in an alkaline solution. The capture of CO₂ leads to the precipitation of environmentally benign bicarbonate salts, which can be safely disposed of in the ground or ocean. A secondary alkaline is then employed to regenerate the first alkaline at ambient temperatures. During regeneration of the secondary alkaline, hydrochloric acid is produced which is subsequently injected into the ground to produce calcium chloride. The aqueous solution of calcium chloride can be either safely stored in the ground or pumped out as a salt source for the initial capture step. Another source of salt is the sodium chloride naturally available in the ocean. The dual alkaline approach offers an alternative method for CO₂ capture, separation, and disposal with the advantage of being able to avoid any new environmental problems that might occur as a result of the storage of supercritical CO₂ liquid.

1. Introduction

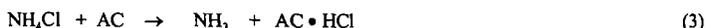
The existing approach for the sequestration of CO₂ from stationary power plants involves two steps: 1. The use of an amine (as an alkaline) to capture CO₂ from flue gas followed by steam stripping of the absorbed CO₂ at high temperatures, 2. The concentrated CO₂ gas is then pressurized to a supercritical CO₂ liquid for disposal in geologic formations and/or the deep ocean. It is known that both steps are energy intensive, especially the first step which accounts for two thirds to three fourths of the entire cost. Also, the reagent loss is substantial if flue gas contains a large amount of SO₂ and NO_x due to the difficulty in regenerating amines from heat stable salts such as amine sulfates or nitrates. Additional energy is also needed to pressurize the CO₂ gas into supercritical liquid for injection into the ground or deep-ocean. Besides the high cost of implementing the existing CO₂ sequestration approach, there is a concern about the ecological consequence resulting from the storage of CO₂ in the ocean and geological formations.

An alternative approach is the conversion of CO₂ to carbonate salts that can be safely returned to the environment. Weathering of alkaline rocks is a natural method of CO₂ sequestration. To enhance the rate of the natural process, Kojima et al. suggested that alkaline minerals could be pulverized, dissolved, and reacted with power plant CO₂ to form magnesium and calcium carbonates. Lackner et al. has extensively investigated the thermodynamics and processes of using chlorides to accelerate the carbonate formation from various minerals, including Serpentinite and Peridotites.

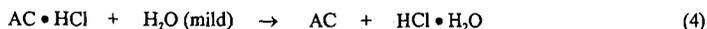
With previous research on the conversion of CO₂ to benign carbonate in mind, a new method is addressed, a dual alkaline approach. The approach involves the use of a salt in an alkaline solution, such as ammonia, to capture CO₂, leading to the formation of a bicarbonate salt.



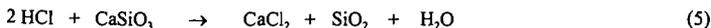
We have found that an activated carbon (AC), a secondary alkaline in solid form, can then be employed to regenerate the first alkaline at ambient temperature (25°C).



The AC can then be regenerated by the extraction of the adsorbed hydrochloric acid with water washing at a mild temperature (<100°C).



The hydrochloric acid extracted by the water may then be injected into the ground where it would react with calcium silicate minerals to produce calcium chloride.

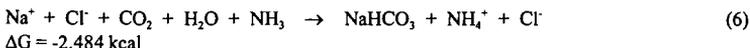


The aqueous solutions of calcium chloride produced underground can either be safely stored in the ground or provide a source of salts for the first step as shown in Eq. (2). In addition to the man-made salts produced by Eq. 5, another source of salt is brine (NaCl), which can be obtained from the ocean.

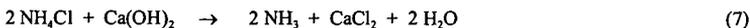
The dual alkaline approach requires low temperatures and little heat input in the regeneration of bases. The approach is self-sustaining, the needed chloride salt is supplied by the ground (Eq. 5) or can be obtained at low costs from the ocean (about \$5/ton sodium chloride based on Encyclopedia of Chemical Technology, Kirk-Othmer, Vol 21), which is especially suitable for power plants located near the coast.

Proven Process

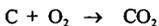
Ammonia has been demonstrated to be an effective catalyst for the reaction of CO₂ with sodium chloride in the production of sodium carbonate (the Solvay process). The reaction was performed by first saturating brine with ammonia, and then with carbon dioxide.



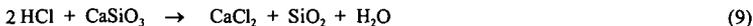
Following the reaction, sodium bicarbonate, which is fairly insoluble, was separated by filtration. Sodium carbonate is subsequently obtained by heating sodium bicarbonate. The ammonia was recovered by the reaction of ammonium chloride with lime, Ca(OH)₂ where limestone served as the source of lime



However, this scheme poses several drawbacks when applied to coal-fired power plants. Among others, the use of limestone for the regeneration of ammonia renders the process ineffective mainly because for every mole of CO₂ captured and transformed, two moles of NaCl are consumed, wasting a mole of NaCl that is needed to react with CO₂ produced during the calcination of limestone to lime:



To circumvent these drawbacks, activated carbon is used as a base to replace lime for the regeneration of ammonia. The HCl subsequently produced may be disposed of by reacting it with silicate minerals to produce benign CaCl₂ and SiO₂. This reaction is performed in subsurface areas by injecting HCl underground, where silicates are abundant in the Earth's crust. Plagioclase (NaAlSi₃O₈ or CaAl₂Si₂O₈), Feldspar (KAlSi₃O₈), and Amphibole [(Ca, Mg, Fe)₇Si₈O₂₂(OH)₂] constitute about 42%, 22%, and 5% in vol, respectively.



The soluble CaCl₂ salt may be pumped out of the ground for use in the fixation of additional CO₂ according to Eq. (2).

2. Experimental Approaches and Results

The use of an aqueous solution of ammonia and sodium chloride for the reaction with CO₂ to produce sodium bicarbonate precipitate is a proven process as mentioned previously. After the reaction and the separation of a sodium bicarbonate precipitate, the remaining solution contains ammonium chloride.

We have discovered that ammonium chloride can be separated into hydrochloric acid and ammonia. Experiments were performed by passing an aqueous solution of ammonium chloride ($\text{pH} = 4.7$) through a column of activated carbon. The resultant liquid was analyzed by ion chromatography. Results indicated that the liquid after the column contained more ammonium ions than chloride ions (Figure 1). The pH of the liquid also increased from 4.7 to as high as 9.5, indicating that the ammonia is regenerated from the ammonium chloride solution.

The kinetics of the decomposition of ammonium chloride and subsequent adsorption of hydrochloric acid by the acid adsorbent was studied. It was found that the reaction order was first order and 0.617 order with respect to the concentration of the adsorbent and ammonium chloride, respectively (Figure 2). The temperature dependence on the adsorption of hydrochloric acid from an ammonium chloride solution was investigated. The Van't Hoff plot indicates that the adsorption is exothermic (-2.48 kcal/mol).

The regeneration of the activated carbon with water as a function of temperature was also investigated. The kinetics of the desorption of hydrochloric acid from the adsorbent was studied at 298, 313, 333, 353, and 373°K (Figure 4). The desorption rate increased with an increase in temperature. The Van't Hoff plot showed that the enthalpy of the desorption of hydrochloric acid was 6.25 kcal. This energy was substantially less than that (47.85 kcal) required in the regeneration of MEA from an MEA-carbamate.

The capability of repeated use of the activated carbon was also demonstrated. Several cycles were performed (Figure 5). The results show that the cyclic process can sustain itself.

3. Conclusion

The research performed has demonstrated that: 1. It is feasible to capture CO_2 and directly transform it into a bicarbonate precipitate using an aqueous mixture of an alkaline and a chloride, 2. It is possible to regenerate ammonia from an ammonium chloride solution using an activated carbon. Future work includes the study of the effectiveness of different types of activated carbon and adsorbents for the regeneration of ammonia from ammonium chloride solutions.

Acknowledgments

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Fig. 1 Production of NH₃ from NH₄Cl using Carbon

Conditions: 10 g AC, 100 ml 10 mM NH₄Cl solution was pumped at 1 ml/min flow rate at room temp.

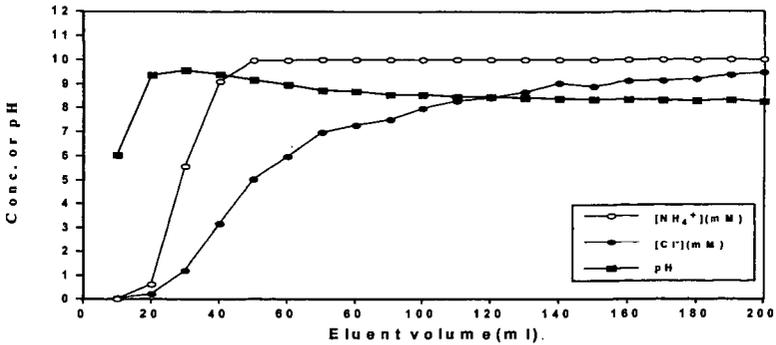


Fig. 2 Reaction order for the adsorption of HCl from NH₄Cl by Carbon

Conditions: 2g AC, 100ml L NH₄Cl solution, room temp., stirring speed: 800 rpm

Forward reaction rate expression: Rate = 0.0028 [AC][NH₄Cl]^{2.617}

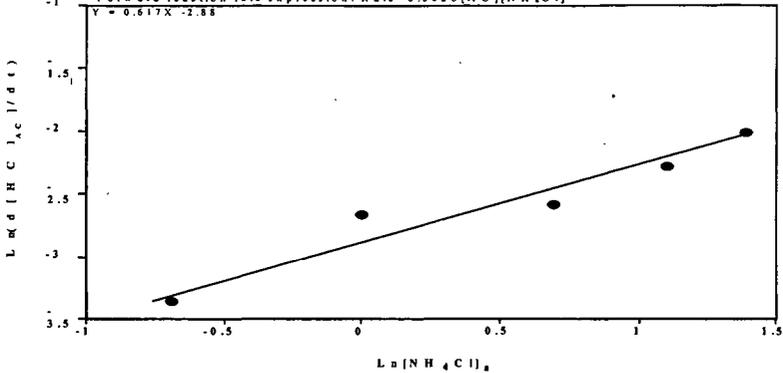


Fig. 3 Van't Hoff plot for adsorption of HCl on Carbon from NH₄Cl solution

Conditions: 10 g AC, 500 ml 2mM NH₄Cl solution, stirring speed: 800 rpm at 293, 313, 333, 353 K, respectively

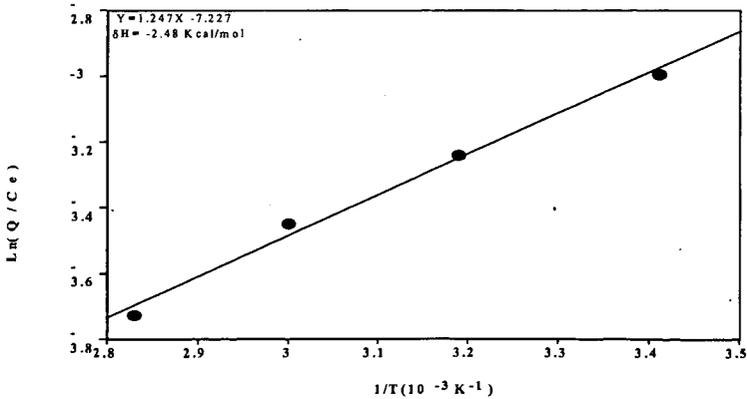


Fig. 4 Van't Hoff plot for desorption of HCl from Carbon in water

Conditions: 10 g AC, 500 ml, 2mM NH₄Cl solution, stirring speed: 800 rpm at 298, 313, 333, 353, 373 K, respectively

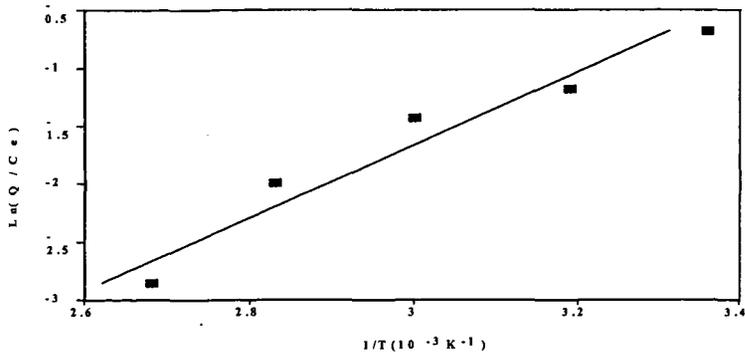
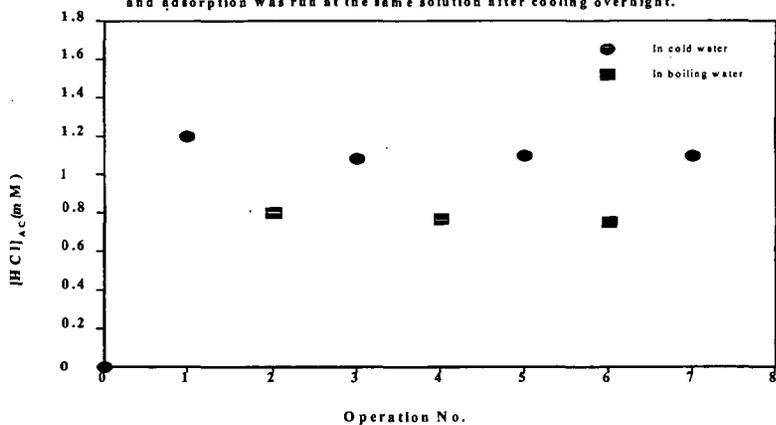


Fig. 5 Regenerability of Carbon for HCl adsorption

Conditions: 2 g AC adsorbed 1.225 mM HCl from 100ml 1.3 mM HCl solution at room temp. The desorption was run at 100 ml boiling water, and adsorption was run at the same solution after cooling overnight.



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Keywords: CO₂, Separation, Liquid membranes

Introduction

Gas separation using facilitated transport membranes (FTM) has been extensively investigated. Major advantages of FTM over conventional polymeric membranes include higher permeabilities for reacting species like CO₂ and the resultant high selectivities over nonreacting species like N₂. This is due to the facilitating reaction mechanism in FTMs compared to the solution-diffusion mechanism in polymeric membranes. FTMs are particularly attractive at low reacting species concentrations where the driving force is very low. This is especially advantageous for removal and sequestration of carbon dioxide when it is present in low concentrations. Facilitated transport membranes include immobilized liquid membranes (ILMs) where the carrier in a solvent, usually water, is immobilized in the pores of the membrane.

Despite the obvious advantages offered by the ILMs, commercialization of these membranes is restricted because of the inherent limitation of stability of the liquid membrane. The reasons for the ILM instability are: (a) absence of any chemical bonding to the support matrix; (b) evaporation of the solvent liquid into gas phases during operation; (c) lower breakthrough pressures. To improve the ILM stability, the feed and sweep sides are completely humidified minimizing solvent loss by evaporation. Another alternative is to use low-volatile and hygroscopic solvents for the ILM preparation.

We have been studying replacement of water by glycerol in the ILMs for separating CO₂ from N₂ streams (Chen et al., 1999, 2000). Since glycerol is very viscous when dry and has higher viscosity than polyethylene glycol (PEG) 400 at ambient temperatures, we can expect lower permeabilities for the non-reacting species like N₂ and higher selectivity for the reacting species like CO₂. The general objective of this work is to investigate CO₂ permeation characteristics through glycerol-based ILMs using different carriers like sodium carbonate and sodium salt of glycine.

Both carriers mentioned above require a solvent, either water or glycerol, to dissolve them. The use of novel carrier liquids/oligomers which do not require any additional solvent was also explored. These carrier liquids are non-volatile and have high densities of reactive functional groups for CO₂ separation. Such carrier liquids eliminate the necessity of a solvent; the liquid membranes formed can be inherently stable.

Experimental Details

Hydrophilized polyvinylidene fluoride (PVDF) and hydrophilized polypropylene Celgard 2500 were used as flat membrane substrates; hydrophilized polysulfone was used as the hollow fiber substrate. ILMs were prepared by immersion or coating techniques. After immersing the substrate in the solution for a pre-determined period of time, it was removed from the solution; the extra liquid on the substrate surface was wiped away. If the immersion time is long enough, the ILMs prepared can be assumed to fill the entire pore length of the substrate. For hollow fibers, immobilization was carried out on the shell side before the fibers were placed in a shell casing.

The CO₂/N₂ permeances were measured by the flow cell technique which involved passing an inert sweep gas on the permeate side whose flow rate and compositions were continuously monitored. The feed gas stream was humidified with water before passing into the cell. For feed gas relative humidities (RHs) less than 100%, dry and humidified gases were blended to achieve the required RH. Sweep gas used was dry helium. The experimental procedure consisted of setting the feed gas flow rate such that the partial pressure of CO₂ remained essentially constant along the feed side of the membrane which had a small area. The sweep flow rate was set to keep the partial pressure of CO₂ in the permeate relatively small, yet high enough for accurate measurement. The permeation rates of CO₂ and N₂ were determined from their concentrations in the sweep gas and sweep gas flow rate.

Results and Discussion

Glycerol-based ILMs having average thicknesses ranging from 15 to 100 microns were studied. The concentrations of carriers examined were: 0 to 4.0 mol/dm³ for sodium carbonate, 0.3-5 mol/dm³ for glycine-Na. While 1M sodium carbonate solution was clear and stable, higher carbonate concentrations in glycerol led to turbid solutions at room temperature. Most of the glycine-Na based ILMs were prepared using less than 3M solutions; higher concentration solutions tend to be turbid. An oligomer providing high liquid density of reactive functional groups was also studied with and without the presence of glycerol as solvent in the ILM.

Table 1 compares the effect of carrier concentration of sodium carbonate and glycine-Na in glycerol systems in hydrophilized PVDF membranes. The entering feed gas was completely humidified with water. For a sodium carbonate concentration of 0.1M, the CO₂ permeability through the ILM increased by a factor of nearly 100 compared with that through pure glycerol. In the higher carrier concentration range, the permeability of carbon dioxide did not increase proportional to the carrier concentration, but there was an increase in the selectivity of ILM for CO₂, possibly due to increase in solution viscosity and ionic strength and the resultant decrease in solubility and diffusivity of N₂ in the ILM. Similar behavior was observed for glycine-Na-glycerol based ILMs also. Some data were obtained for membranes having both carriers, glycine-Na and sodium carbonate. The mixed carriers-based ILMs gave CO₂/N₂ permeation performances close to the glycine-Na based ILMs of corresponding concentration.

Table 1. ILM performance in hydrophilized PVDF membranes: effect of carrier concentration

Carrier concentration (M)	CO ₂ partial pressure (cm Hg)	CO ₂ permeability (Barrer)	N ₂ Permeability (Barrer)	CO ₂ /N ₂ Selectivity
Na₂CO₃				
0	0.55	14	3.83	3.7
0.1	0.55	1420	3.98	359
1	0.55	2880	3.34	850
4	0.55	2540	1.75	1460
Glycine-Na				
0.3	0.44	4280	1.98	2210
2.25	0.41	9730	1.89	5140
3.5	0.42	8510	1.16	7310
5.0	0.38	7370	1.27	5780
1.0 M Na₂CO₃+ 1.0 M Glycine-Na	0.48	4980	2.22	2240

The partial pressure of carbon dioxide affected the CO₂ permeance according to the expected facilitated transport behavior. At lower CO₂ partial pressures, the CO₂ permeance of sodium carbonate-glycerol ILM or glycine-Na-glycerol ILM is greater than those of DEA-PEG 400 ILM (Saha and Chakma, 1995), but lower than MEA-water ILM (Teramoto et al., 1996). At higher CO₂ partial pressures, fixed-carrier membranes (Quinn and Laciak, 1997) achieve higher CO₂ permeances than these ILMs.

The glycine Na-glycerol ILMs were operated for more than 600 hours with no change in performance. The mechanical stability of the glycerol-based ILMs was studied by subjecting the ILMs to different feed inlet relative humidities. In one such experiment, a 0.6 M sodium carbonate-glycerol ILM was subjected to feed inlet relative humidity varying with time to observe any deterioration in performance. The feed stream was 10.6% CO₂-balance N₂ gas mixture. The feed RH was 100% for the first 48 hrs. Then it was decreased to 13% and maintained at that level for 100 hours. Finally, the feed RH was increased to 100% again. The ILM was not at all damaged during the 100 hour flow of very low RH feed stream: the ILM performance could be restored to normal levels when the feed RH was increased to 100% again. The low volatility and highly hygroscopic nature of glycerol are responsible for the observed stability, which is a marked improvement over water-based ILMs. Glycine-Na-glycerol based ILMs also demonstrated similar behavior.

Table 2 shows the performances for glycerol based ILMs in hydrophilized Celgard 2500 membranes. The permeabilities obtained in the Celgard-based ILMs were lower than those obtained in PVDF membrane based ILMs. The Celgard-based membranes in general showed lower selectivities which may be attributed to imperfect hydrophilization.

Table 3 presents the results for hollow fiber based ILMs. The effective CO₂ permeance for a 0.53% CO₂-balance N₂ feed gas mixture can be as high as 3.13 x 10⁻⁵ cc/cm².s.cmHg with CO₂/N₂ separation factors in the range of 2000-2700. These data represent so far the highest carbon dioxide permeances observed in this study for hollow fiber membranes. Further, they compare very well with the highest CO₂ permeances obtained with flat film ILMs in our studies. The stability of these ILMs was excellent over the period studied, namely, 300 hours with no apparent deterioration in CO₂ permeance or CO₂/N₂ selectivity.

Table 2. Effect of carrier concentration on the ILM performance in hydrophilized Celgard 2500 membranes

Carrier concentration	CO ₂ partial pressure (cm Hg)	CO ₂ permeability (Barrer)	N ₂ Permeability (Barrer)	CO ₂ /N ₂ Selectivity
1 M Na ₂ CO ₃	0.52	863	1.24	698
2.25M Glycine-Na	0.46	3920	2.23	1770

Table 3. Performance of hydrophilic polysulfone fiber modules for 3.0 M glycine-Na-glycerol solution.

Δp_{CO_2} cmHg	Feed in/out RH %	$(Q/t)_{eff,N_2}$ cc/cm ² .s.cmHg	$(Q/t)_{eff,CO_2}$ cc/cm ² .s.cmHg	CO ₂ /N ₂ selectivity
0.335	91.7/n.a.	1.34e-8	3.13e-5	2330
0.390	100/n.a.	2.54e-8	2.93e-5	1150
0.410	87.6/50.0	1.54e-8	2.98e-5	1930
0.410	93.0/66.0	1.36e-8	3.08e-5	2260
0.410	92.3/32.4	1.14e-8	2.81e-5	2460

The novel use of non-volatile highly functionalized oligomers for selective CO₂ separation was also studied. Pure oligomer was used as the ILM. The results were remarkable. The CO₂-N₂ separation factor could go very close to 19,000 at a low CO₂ partial pressure of 0.36 cm Hg. The corresponding CO₂ permeability was 4100 Barrers. At higher CO₂ partial pressures of about 30 cmHg, the CO₂-N₂ separation factor was around 700. This behavior reflects the classical carrier saturation behavior of facilitated transport membranes. This particular ILM was used continuously for more than 35 days without any visible signs of any membrane leaks or instability. During this period, the ILM was subjected to different carbon dioxide partial pressures, transmembrane pressures, and feed inlet relative humidities. The oligomer-based ILMs appear to function almost as a molecular gate for CO₂ vis-à-vis other inert gases, N₂, O₂ etc at low partial pressures and high feed RHs. Addition of glycerol to the oligomer in forming the ILM tends to reduce the CO₂-N₂ selectivity because of higher N₂ solubility in glycerol.

Conclusions

- 1) Glycerol-based immobilized liquid membranes provide mechanically stable performance even when exposed to low humidity feed gases. The performance of the ILM can be restored to the normal levels once higher feed humidity is reintroduced. This is a radical improvement over conventional water-based ILMs.
- 2) ILMs were operated for more than 600 hrs continuously without any deterioration in performance.
- 3) Increase in partial pressure of CO₂ reduces the CO₂ permeability and its selectivity as expected for the facilitated transport mechanism.
- 4) Novel non-volatile oligomeric liquids having high density of reactive functional groups appear to function as a CO₂-selective molecular gate, yielding very high CO₂-N₂ selectivities at low CO₂ partial pressures and high feed side RHs.

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ADSORPTION OF CO₂ ON MOLECULAR SIEVES AND ACTIVATED CARBON

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Key Words - Volumetric adsorption of CO₂, Pressure swing adsorption of CO₂, Adsorbents for CO₂ separation and removal

INTRODUCTION

Fossil fuels supply more than 98% of the world's energy needs. However, the combustion of fossil fuels is one of the major sources of the green house gas CO₂. It is necessary to develop technologies that will allow us to utilize the fossil fuels while reducing the emissions of green house gases. Commercial CO₂ capture technology that exists today is very expensive and energy intensive. Improved technologies for CO₂ capture are necessary to achieve low energy penalties. Pressure swing adsorption (PSA) is one of the potential techniques that could be applicable for removal of CO₂ from high pressure gas streams such as those encountered in Integrated Gasification Combined Cycle (IGCC) systems.

PSA processes are based on preferential adsorption of the desired gas (eg. CO₂) on porous materials at a high pressure. When the pressure is decreased, the gas is desorbed from the porous sorbent and the sorbent can be reused for subsequent adsorption. PSA technology has gained interest due to low energy requirements and low capital investment costs. Development of regenerable sorbents that have high selectivity for CO₂ and high adsorption capacity for CO₂ is critical for the success of the PSA process.

In this work three sorbents from United Catalyst, namely, molecular sieve 13X, molecular sieve 4A, and activated carbon were utilized to study the adsorption of CO₂. Volumetric adsorption studies of CO₂, N₂, or H₂ with the three sorbents were conducted at 25 °C up to a pressure of 300 psi (~2x 10⁶ Pa).

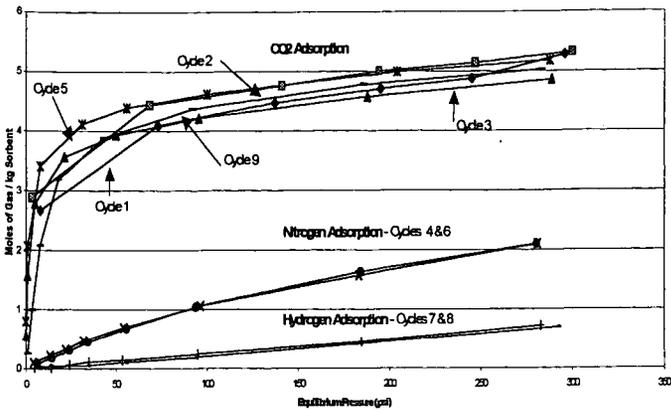
EXPERIMENTAL

The sorbents Zeochem-Z10-02/13X molecular sieve, Z4-01/4A molecular sieve and activated carbon were obtained from United Catalysts, Inc. Adsorption isotherms at 25 °C of pure CO₂, N₂, or H₂ on molecular sieve 13X, molecular sieve 4A, and activated carbon were measured up to an equilibrium pressure of about 300 psi (~2x 10⁶ Pa) utilizing volumetric adsorption apparatus. Approximately 10 ml of the sorbent materials were placed in the sample chamber, which was evacuated to ~ 5x10⁻⁵ Torr. The amount of CO₂ adsorbed was calculated utilizing the pressure measurements before and after the exposure of the sample chamber to CO₂. Base line data with CO₂ were obtained utilizing 10 ml of glass beads. A total of 9-10 adsorption cycles were performed with each sorbent. After each cycle the sorbent was evacuated overnight. After two cycles, each, were performed with hydrogen and nitrogen, a final cycle was performed with CO₂ to evaluate whether the adsorption was affected by the adsorption of the other gases.

RESULTS AND DISCUSSION

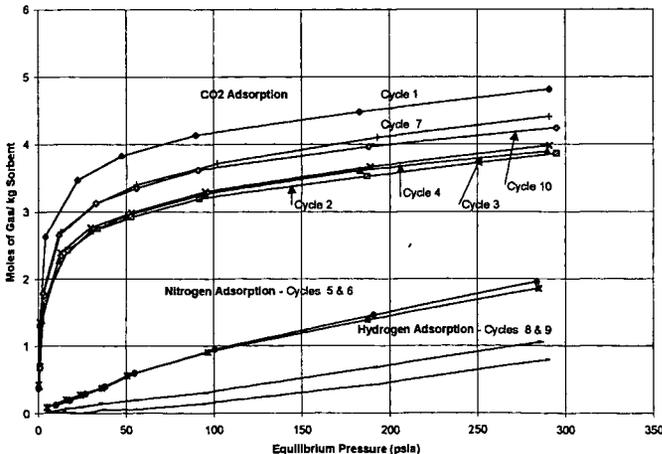
Volumetric adsorption isotherms of CO₂, N₂ and H₂ on molecular sieve 13X at 25 °C are shown in Figure 1. Up to 50 psi the CO₂ adsorption increased rapidly when the pressure was increased. The increase in CO₂ adsorption after 50 psi appeared to be gradual. The adsorption isotherms for repeated cycles were very similar. This indicated that the adsorption is fully reversible and complete regeneration can be obtained by evacuation of the material after adsorption. At all pressures, adsorption isotherms of nitrogen were lower than those of the CO₂, and adsorption isotherms of hydrogen were significantly lower than those of CO₂. Both nitrogen and hydrogen isotherms were completely reversible. Preferential adsorption of CO₂ indicates that this material can be used for separation of CO₂ from some gas mixtures. The final adsorption isotherm (cycle 9-which was obtained after the adsorption experiments with nitrogen and hydrogen) was conducted with CO₂ and it is very similar to the previous adsorption isotherms with CO₂. This indicates that the sorbent was not affected by the adsorption of nitrogen and hydrogen.

Figure 1 - Adsorption Isotherms on ZEOCHEM-Z1002P3



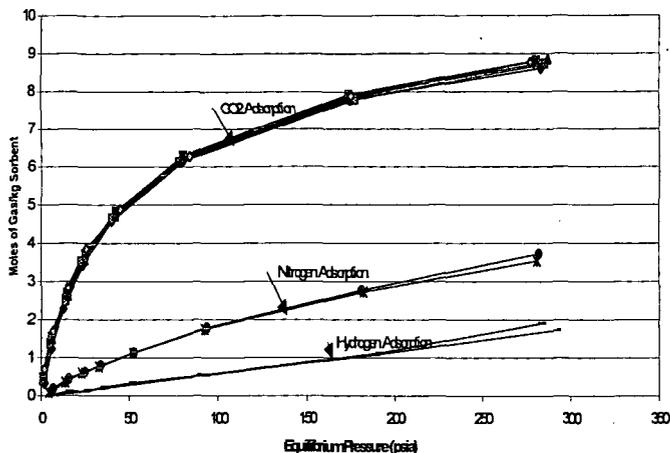
The volumetric adsorption isotherms for molecular sieve 4A(Zeochem Z4-01-4A) are shown in Figure 2. The adsorption isotherms indicate that the uptake of CO₂ is higher than the uptakes of the other two gases, nitrogen and hydrogen. This preferential uptake of CO₂ makes this sorbent suitable for the separation of CO₂ from gaseous mixtures. The adsorption isotherms of CO₂ for molecular sieve 4A are not highly reproducible, indicating that the adsorption is not completely reversible. The adsorption at the first cycle was the highest. The uptake of CO₂ for molecular sieve 4A was lower than that of molecular sieve 13X at all equilibrium pressures up to 250 psia. However, both nitrogen and hydrogen adsorption isotherms of molecular sieve 4A appear to be similar to those of molecular sieve 13X. The adsorptions of nitrogen and hydrogen did not affect the final adsorption isotherm of CO₂.

Figure2 - Adsorption Isotherms of ZEOCHEM Z4-01-4A/4x8



The adsorption isotherms for activated carbon are shown in Figure 3. It is interesting to note that all the isotherms are extremely reproducible, which indicates the excellent reversibility of adsorption. The CO₂ uptake for activated carbon was lower than that of the two molecular sieves at lower pressures (< 50 psi), but at higher pressures the CO₂ uptake for activated carbon was higher than that of the molecular sieves. Nitrogen and hydrogen adsorption isotherms appear to be very reproducible. The final CO₂ adsorption cycle (cycle 10) was very similar to the first cycle, which indicated that the sorbent was not affected by the adsorption of other gases.

Figure 3- Adsorption Isotherms of Activated Carbon



CONCLUSIONS

All three sorbents, molecular sieves 13X and 4A, and activated carbon, showed preferential adsorption of CO₂ over nitrogen or hydrogen at all pressures up to 250 psia. The molecular sieve 13X showed better CO₂ uptake than molecular sieve 4A. At lower pressures activated carbon had a lower CO₂ uptake than the uptakes of the molecular sieves, but at higher pressures the adsorption was higher for activated carbon than for the molecular sieves.

SEPARATION AND RECOVERY OF CO₂ FROM EXHAUSTED GAS BY HYDRATES

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Keywords: Separation, Phase equilibrium, Hydrate

ABSTRACT

Hydrates have the peculiar crystal structure that one guest molecule is surrounded with a cage composed by water molecules. These water molecules are connected by the hydrogen bonding each other, but there is no chemical bonding between the guest molecule and the water molecules. In this paper I will show the possibility of hydrate's application to solve environmental problems. The cage-like structure of hydrates can be utilized as an environmental pollutant gas separation method since in mixture hydrates the molar fraction of components in a hydrate phase is different from that in a gas phase. Firstly properties of hydrates concerning with the separation technology are summarized concisely. Potential function between the water molecules and the guest molecule is calculated for CO₂, N₂ and O₂. And hydrate-gas equilibrium in CO₂-N₂-O₂ mixture is predicted. Then, based on these data, the separation technology with hydrates is demonstrated.

INTRODUCTION

Hydrates have been classified as one of clathrate compounds and show the peculiar structure that one gas molecule exists in the cage composed by water molecules. The molecule in the cage is called a guest molecule and many kinds of gas molecules like argon, oxygen, nitrogen, xenon, carbon dioxide, nitric monoxide, sulfur dioxide, and hydrogen sulfide may become a guest molecule. The forming condition of hydrates is generally in low temperature and high pressure, and this condition is different with the type of the guest molecule.

Recently, the separation technology that uses the functional material having recognition ability of molecules has been attracting many attentions. For instance, Crown ether, shown in Fig.1, can recognize and capture a molecule that fits the molecular space of the crown ether. This property of the crown ether can be utilized in the separation technology. In that case recognition and capture of the molecule are carried out based upon the molecular size. On the other hand, hydrates have the recognition ability based upon the potential energy between the guest molecule and water molecules in addition to the ability based upon the molecular size.

In this paper I take the possibility of hydrates as the functional material having the molecular recognition ability and report the result of applying this ability of hydrates to the separation of the carbon dioxide from the exhausted gas. Firstly the properties of hydrates concerning separation are introduced and the separation process using hydrates is explained. Then in relation to the molecular recognition ability of hydrates, the potential functions between the guest molecule and water molecules are presented for each guest molecule of carbon dioxide, oxygen or nitrogen. Some examples of the phase equilibrium calculation that can be used to recover carbon dioxide from the exhausted gas are shown. Lastly experimental apparatus demonstrating this technology is introduced and some experimental results are shown.

HYDRATES

Fig.2 shows models of the cage composed by water molecules and Table 1 indicates structural properties and geometric constants of the cage. Water molecules occupy summits of the polygon and are connected by the hydrogen bonding each other. And each cage contains one guest molecule. Though there are many kinds of molecules that can be held in the cage, some

restrictions exist to be contained in the cage. At first, the size of the molecule must be proper to be inside of the cage because the diameter of the cage is constant and fixed. In other words, hydrates have the molecular recognition ability depending on the molecular size. And the molecule whose size is extremely smaller than the cage size cannot make hydrates. Next, it is necessary not to make the hydrogen bonding between water molecules. Table 2 shows guest molecules that make hydrates and their van der Waals diameter.

SEPARATION BY HYDRATES

Each cage of hydrates contains one guest molecule, but considering bulk hydrates, there is no need for all guest molecules to be same. In other words, mixture hydrates exists. Mixture hydrates means the situation that different kinds of molecules are scattered in hydrates cages. Mixture gas that consists of many components shown in table 2 can form mixture hydrates.

The separation technology by hydrates is based on the fact that molar fraction of components in the hydrate phase is different from that in the gas phase. Fig 3 illustrates this situation conceptually. In this case, the gas phase contains same number of black molecules and white molecules but the hydrates phase includes larger number of black molecules. That is to say, the stability of the hydrate cage is different according to the type of the guest molecule.

Fig.4 expresses the situation illustrated in Fig.2 by a diagram. This figure is also conceptual. In this figure a vapor line and a hydrate line are drawn. By utilizing this figure we can design the separation process. For instance, the dotted line in this figure indicates that the vapor in which the molar fraction of black molecules is 0.5 forms hydrates at pressure P_1 and that the molar fraction of black molecules in the hydrates phase is 0.79. When dissolving these hydrates, you can obtain the vapor in which the molar fraction of black molecules is 0.79. The dashed line shows that the vapor in which the molar fraction of black molecules is 0.79 forms hydrates at pressure P_2 and that the molar fraction of black molecules in hydrates phase is 0.95. By same procedure in the former case, dissolving these hydrates, you can recover the vapor in which the molar fraction of black molecules is 0.95. The repeating process between forming and dissolving hydrates is necessary to separate mixture gas by hydrates.

MOLECULAR RECOGNITION BY HYDRATES

Molecular recognition of hydrates is carried out by two mechanisms. One is based upon molecular size and the other is based upon the difference of the potential function between the guest molecule and water molecules. Let assume that mixture gas is composed by carbon dioxide, oxygen and nitrogen, in this case each molecule can be clathrated in the cage as shown in Table 2. So next factor of the separation is the difference of potential functions among these three components. Fig.5 shows potential functions between the guest molecule and water molecules for carbon dioxide, oxygen and nitrogen. It is obvious from this figure that the depth of the potential well with carbon dioxide is deep comparing with that of oxygen and nitrogen. This fact suggests that the carbon dioxide molecule is easier to be captured in the hydrate cage than other two components.

To design the separation process for the mixture of carbon dioxide, oxygen and nitrogen, the phase equilibrium diagram for $\text{CO}_2\text{-N}_2\text{-O}_2$ mixture is necessary. After removing NO_x and SO_x , main components of exhausted gas are nitrogen, carbon dioxide, oxygen and water. Hydrate phase equilibrium calculation was carried out for the exhausted gas of this component. Fig.6 and Fig.7 demonstrate results of the phase equilibrium calculation based upon the van der Waals and Platteeuw theory. If the molar fraction of carbon dioxide in the exhausted gas is 0.12, carbon dioxide is separated and recovered by two steps of forming and dissolving hydrates.

EXPERIMENTAL APPARATUS AND RESULTS

Fig.8 illustrates the experimental apparatus. The high-pressure vessel was made by sus303

and its diameter was 150mm. The molar fraction of mixture gas was controlled by mass flow meters. The mixture gas was pressurized by a booster pump then introduced to the vessel. Hydrates were made by the spray method. Pressurized water was jetted out from a nozzle. Temperature was measured by platinum resistance thermometers and pressure was gauged by a pressure transducer. The molar fraction of the mixture gas and hydrates was measured by a gas chromatograph.

Table 3 shows one example of experimental results. Obviously the molar fraction of carbon dioxide in the hydrate phase is higher than that in the gas phase. But there is a gap between theoretical predictions and experimental results.

CONCLUSION

Properties of hydrates concerning with the separation were briefed. Potential function between the water molecules and the guest molecule was calculated for carbon dioxide, oxygen and nitrogen. And hydrate-gas equilibrium in CO₂-N₂-O₂ mixture was predicted. Then, based on these data, the separation technology with hydrates was demonstrated.

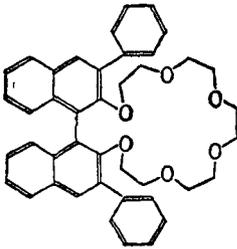


Fig.1 Crown ether

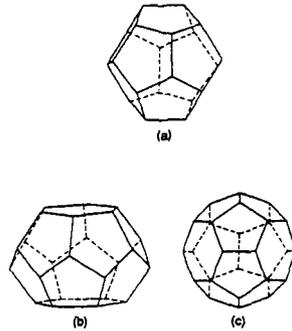


Fig.2 Cages of gas clathrate hydrates
(a) small cage. (b)(c) large cage

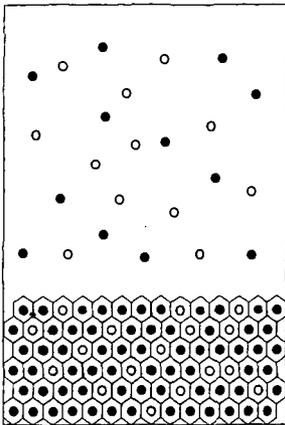


Fig.3 Mixture hydrates with vapor phase

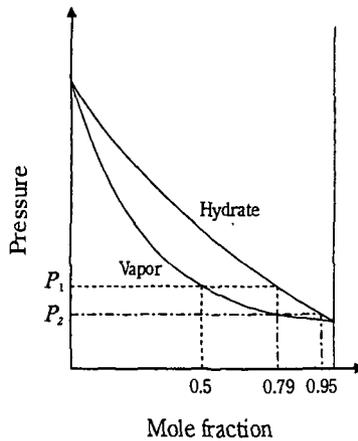


Fig.4 Hydrate-Vapor Equilibrium

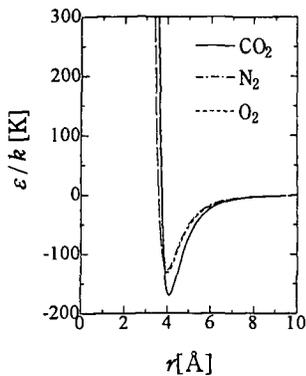


Fig.5 Potential function for the guest molecule

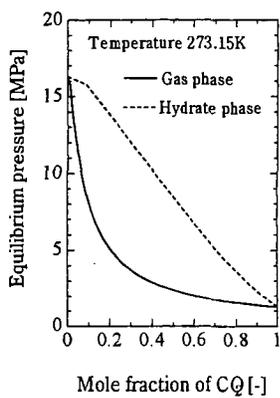


Fig.6 Phase equilibrium for $\text{CO}_2\text{-N}_2\text{-O}_2$ mixture hydrate where NO_2 is constant at 97.7:2.3

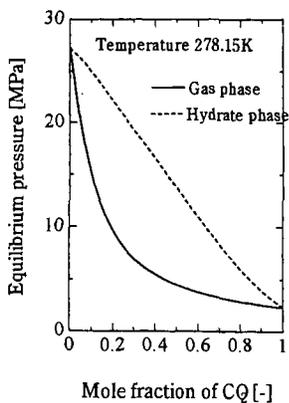


Fig.7 Phase equilibrium for $\text{CO}_2\text{-N}_2\text{-O}_2$ mixture hydrate where N_2O_2 is constant at 97.7:2.3

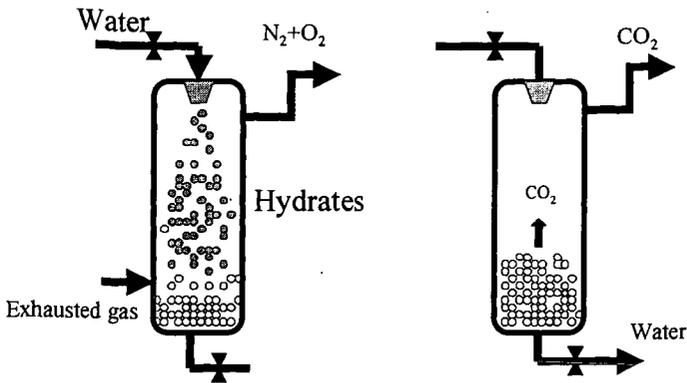


Fig.8 Experimental apparatus

Table 1 Geometry of cages

Crystal structure	I		II	
	Small	Large	Small	Large
Cavity type	5 ¹²	5 ¹² 6 ⁴	5 ¹²	5 ¹² 6 ⁴
Description	5 ¹²	5 ¹² 6 ⁴	5 ¹²	5 ¹² 6 ⁴
Average cavity radius [nm]	0.395	0.433	0.391	0.473
Coordination number	20	24	20	28
Number of cavities per water molecule	1/23	3/23	2/17	1/17

Table 2 Guest molecules that make hydrates

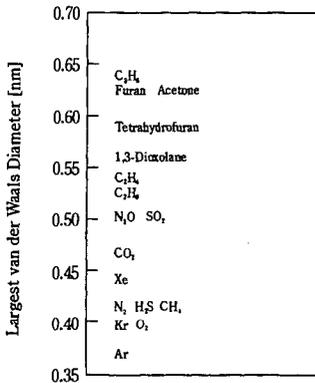


Table 3 Experimental results

Temperatuur: 276.75K		Pressure: 9.33MPa		
		N ₂	O ₂	CO ₂
Injection port (control of MFC)		50.0%	20.0%	30.0%
Measurement of gas component before injection		51.1%	21.1%	27.9%
Collection port (measurement of gas chromatograph)		41.8%	19.1%	39.1%