Development of Novel CO_2 Adsorbents for Capture of CO_2 from Flue Gas

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ABSTRACT

Carbon Sequestration, the capturing and storing of carbon dioxide (CO_2) emissions generated from fossil fuel-based power plants has received widespread attention and is considered a vital course of action for CO_2 emission abatement. Efforts are underway at the Department of Energy's National Energy Technology Laboratory to develop viable energy technologies enabling the capture and separation of CO_2 from large stationary point sources. Solid, immobilized amine sorbents (IAS) formulated by impregnation of liquid amines within highly porous substrates are reactive towards CO_2 and may offer an alternative means for cyclic capture of CO_2 eliminating, to some degree, the inadequacies related to chemical absorption by aqueous alkanolamine solutions. CO_2 capture technologies are envisioned to offer significant cuts in global CO_2 emissions devoid of significant costs related towards energy services.

This paper describes the synthesis, characterization, and CO_2 sorption properties for a series of IAS materials previously tested to bind and release CO_2 and water vapor in a closed loop life support system. Specifically, tetraethylenepentamine (TEPA), acrylonitrile-modified tetraethylenepentamine (TEPAN), and a single formulation consisting of both TEPAN and N, N'-bis(2-hydroxyethyl)ethylenediamine (BED) were individually supported on a poly (methyl methacrylate) (PMMA) substrate and examined. CO_2 adsorption profiles leading to substantial reversible CO_2 adsorption capacities under anhydrous conditions were obtained using a Cahn TG-131 Thermogravimetric Analyzer. Under a dry mixture of 10% CO_2 in nitrogen at 25°C and 1 atm, TEPA supported on PMMA (TEPA/PMMA) over the initial 60 minutes of exposure adsorbed ~3.2 mmol/g of sorbent whereas TEPAN supported on PMMA (TEPAN/PMMA) along with TEPAN and BED supported on PMMA (TEPAN_BED/PMMA) adsorbed ~1.7 mmol/g of sorbent and ~2.3 mmol/g of sorbent respectively. Furthermore, cyclic experiments with an IAS formulation of a 1:1 weight ratio of TEPAN and BED supported on poly (methyl methacrylate) beads utilizing a fixed-bed flow system with a gas mixture simulating a flue gas environment (9% CO_2, 3.5% O_2, nitrogen balance with water vapor) with trace contaminants were also completed. CO_2 sorption capacity of the IAS material is ~ 3

mmols CO_2/g of sorbent at 40°C and 1 atm for a humidified 9% CO_2/N_2 gas mixture. No apparent beneficial effect on IAS material performance was found using a moisture-laden flue gas mixture (9% CO_2, 3.5% O_2, N_2 balance + 2% H_2O) over a series of cyclic experiments. Additional testing with 750 ppmv NO present in a humidified gas stream revealed negligible NO sorption onto the IAS material. A high SO_2 concentration (750 ppmv) resulted in incremental loss in IAS performance and visually revealed progressive degrees of "staining" or discoloration upon testing. Adsorption of SO_2 by the IAS material necessitates the need for upstream removal of SO_2 prior to CO_2 capture.

INTRODUCTION

Carbon dioxide capture and storage technologies are increasingly being considered a potentially significant contributor to the energy infrastructure changes required to stabilize atmospheric CO_2 concentrations.[1] To attain stabilization of atmospheric CO_2 concentrations at a near doubling of pre-industrial levels, carbon emissions estimated at 7 gigatons per year (GtC/year) will need to be diminished by about two thirds by the end of the century.[1] Therefore, the concept of capturing and storing CO_2 has progressively evolved from an obscure idea to an ever important climate change mitigation option.

Chemical absorption and chemical/physical adsorption are methods under consideration for large scale CO_2 capture systems.[2] Chemical absorption with aqueous alkanolamine solutions, including monoethanolamine (MEA)-based processes, has been widely used in capturing CO_2 from natural gas sources. This well-established technology absorbs CO_2 in a packed column by injecting a gaseous CO_2-containing stream at the bottom of an absorber column while the aqueous alkanolamine solution is sprayed in a counter-current fashion from the top of the column. Dissolved CO_2 reacts with primary and secondary alkanolamines forming carbamates and bicarbonates by the following reactions.

Figure 1. Chemical reactions related to post-combustion CO_2 scrubbing with amines
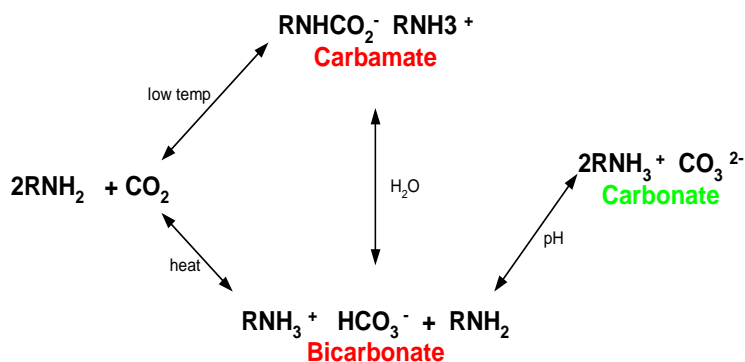
The interaction between a primary amine and acidic CO_2 molecules produces the formation of a carbamate ion as illustrated in Figure 1. Additionally, water may also hydrolyze the carbamate producing bicarbonate and regenerating a free amine; however, owning to the stability of carbamate, this reversible reaction does not transpire at a readily appreciable rate. Hence, the CO_2 capture capacity for primary (and secondary

amines) is impacted by the stoichiometric requirement of two amines molecules for each CO_2 molecule reacted.[3,4]   Release of the absorbed CO_2 from the CO_2-rich solvent is accomplished by thermal regeneration at temperatures in excess of ~120°C within a stripper column.   Although liquid amine scrubbing is a credible, mature process, its usage for capturing CO_2 from power plant effluents is found to be energy intensive.[3] Post combustion capture utilizing chemical absorption represents up to 80% of the total energy cost for carbon sequestration.

High capacity, CO_2 selective sorbents may offer an attractive option for the reversible capture of CO_2. Dry CO_2 scrubbing processes have the potential of being more energy efficient owing to their higher CO_2 adsorption capacities, coupled with substantially lower regeneration energy requirements. The combination of liquid amines with solid substrates to afford solid, regenerable CO_2 sorbents for the post-combustion capture of CO_2 has been examined by several groups.[4-15] Chuang et al.[4] utilizing aminopropyl SBA-15 found CO_2 to absorb on primary amine sites in the form of carbonate and bicarbonate with a total CO_2 adsorption capacity of 17.6 mg/g of sorbent at 25°C from a 4% CO_2 gas mixture. Cyclic adsorption—regeneration of this adsorbent exhibited hydrothermal stability resulting in no loss of CO_2 capture capacity. Huang et al.[5] formulated and synthesized amine-surface-modified silica xerogel and MCM-48 materials for acid gas removal applications. With large quantities of basic amine groups on the surface, these organic-inorganic hybrid materials, including aminopropyl-MCM-48, were reported to selectively bind CO_2 and H_2S. The presence of water vapor was found to significantly enhance the amount of CO_2 absorbed. Hiyoshi et al.[6] reports CO_2 sorption capacities for aminosilane modified SBA-15 materials in the presence of water vapor comparable to those tested in the absence of water vapor. Their CO_2 efficiency was reported to be directly related to the surface density of the amine. Filburn et al.[7] showed by immobilizing liquid amines, i.e., ethanolamines, within the pores of a polymeric support, regenerable CO_2 sorbents could be formulated and successfully applied in removing low concentrations of CO_2 by a pressure swing adsorption process. Furthermore, alteration of these organic amines by reaction with acrylonitrile resulted in a factor of two increase in CO_2 removal capacity compared to the unaltered, supported amines. Secondary amines were identified largely to be beneficial in adsorbing low concentrations of CO_2 from a gas stream typically found within a closed loop life support system. Supported amines have been identified as potential solid, regenerable sorbents capitalizing on their ability to capture CO_2 and water vapor together with minimum regeneration power requirements for long term human space flight applications.[8]

In this work, the interaction of CO_2 with linear ethyleneamine, TEPA, acrylonitrile-modified, tetraethylenepentamine (TEPAN), and a single formulation consisting of TEPAN and N, N'-bis(2-hydroxyethyl)ethylenediamine (BED), all individually impregnated within the pores of a high surface area, poly (methyl methacrylate) support were investigated. Organic ethyleneamines, TEPA, and TEPAN display considerably lower vapor pressures relative to alkanolamines, thus making them less susceptible to loss due to volatilization within a temperature range of 25°-100°C. Furthermore, the chemical interaction between TEPA, or TEPAN, and CO_2 is deemed to benefit from the presence of moisture, which within a power generation setting, will typically exist. CO_2

uptake profiles for these IAS materials were determined using thermogravimetric analysis (TGA) under a dry 10% CO_2 gas mixture at 25^oC. Cyclic experiments utilizing a fixed-bed flow system with a gas mixture simulating a flue gas environment (9% CO_2, 3.5% O_2, nitrogen balance with water vapor) with trace contaminants were also performed. The goal of this present work is to determine CO_2 adsorption properties for the IAS materials along with investigating the effects of trace gas constituents (moisture, O_2, NO/NO_x, and SO_2) present in flue gas on the IAS performance over a series of temperature swing cycles.

EXPERIMENTAL METHODS

Synthesis of IAS.
Tetraethylenepentamine (TEPA), an organic amine consisting of both primary and secondary amino groups supported on a highly porous substrate, poly (methyl methacrylate) (PMMA) was used in the synthesis of the initial IAS. The support before amine impregnation provided sufficient surface area (~500 m^2/g), and pore volume (1.2 mL/g) to adequately retain the amine within the pores of the support. In a second IAS synthesis, modification of TEPA was carried out by reaction with acrylonitrile prior to immobilization within the pores of the polymeric support. For this reaction, TEPA was added to a 500 mL round bottom flask followed by slow addition of acrylonitrile with stirring. To help minimize the exothermic reaction, an ice bath was utilized. The TEPA/acrylonitrile solution was slowly heated to 50^oC and stirred for one hour. The reaction product formed a Michael adduct, TEPAN, that altered the original structure (see figure 2). Acrylonitrile reacts largely with primary amine functionalities in forming secondary amines upon completion of reaction.[7] In the last IAS synthesis, equal mass percentages of TEPAN and N, N'-bis(2-hydroxyethyl)ethylenediamine (BED) together with the PMMA support were utilized.

To immobilize the amines within the pores of the polymeric support, a solvent evaporation method was used. Initially, PMMA beads were uniformly dispersed in methanol within a rotary evaporator flask. The amines (solubilized in methanol) were then added to the beads, followed by the solution rotated at ambient temperature for 5-10 minutes producing a homogeneous slurry. Subsequent removal of the solvent was conducted by heating the rotary evaporator flask in a heated water bath. The procedure produced IAS materials with a high percentage of its theoretical pore volume filled with liquid amine(s).

CO_2 adsorption studies.

Thermogravimetric Analysis (TGA)
CO_2 uptake profiles were obtained using a Cahn TG-131 unit. Gas composition was controlled by blending high purity gases (CO_2, N_2) using mass flow controllers. For each experiment, approximately 50 mg of the IAS was placed into a round bottom quartz bucket and slowly heated to 105^oC to remove any pre-adsorbed CO_2 and moisture. Upon conditioning the sample for 60 minutes, the IAS was cooled to 25^oC and exposed to a dry mixture of 10% CO_2 and nitrogen for 90 minutes (total gas flow rate = 200 ml/min),

which was found to be sufficient to reach equilibrium. Nitrogen was continuously flushed through the top of the microbalance assembly and utilized as a purge gas at a flow rate of 100ml/min during testing.

Figure 2. TEPAN, Michael adduct produced by reaction of TEPA with acrylonitrile.

Tetraethylenepentamine (TEPA)

$50°C$ 2.3 $H_2C=CHCN$

Tetraethyleneamineacrylonitrile (TEPAN)
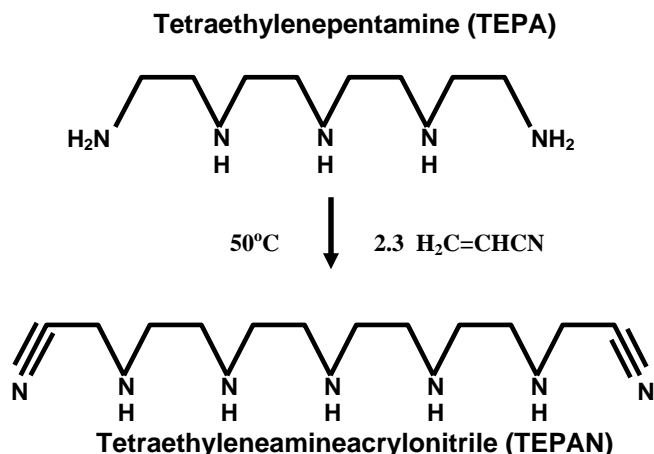
Fixed-bed flow system.
In order to determine the effects of trace flue gas contaminants on IAS performance, CO_2 adsorption, desorption, and thermal regeneration measurements were also conducted utilizing a fixed-bed flow system. For these tests, 90 cc of the IAS was placed onto a fritted disc located in the center of a 450 mm long quartz tube and at the center of a 400 mm split-tube furnace. Bed temperature was measured and controlled using a dual type K thermocouple located ~2 mm above the frit. Secondary temperature controls for heater tapes along the gas inlet path regulated the temperatures of several gas mixing chambers and a water humidification chamber. Gas compositions were established in blending respective gases from cylinders using thermal mass flow controllers; moisture content was determined using a variable flow dispensing pump. The system was configured with a series of gas analyzers for continuous monitoring of CO_2 (infrared), O_2 (paramagnetic), NO/NO_x (chemiluminescent), and SO_2 (infrared). Prior to entering the analyzer section, process gas was passed through a Perma Pure™ drying tube removing moisture from the gas stream. Data acquisition was obtained utilizing an automated Linseis™ data logger.

RESULTS & DISCUSSION

IAS Characterization
Nitrogen adsorption at 77K was employed to determine the physical characteristics of the poly (methyl methacrylate) support and IAS materials.   Prior to N_2 adsorption measurements, the samples were degassed by evacuation (10^{-3} Torr) at ambient temperature under vacuum. Based on its structural characteristics as shown in Table 1, PMMA was impregnated individually with TEPA, TEPAN, and equal mass loadings of both TEPAN and BED. Pore saturation was employed, resulting in the largest quantity of

amine(s) retained by the PMMA support. The N_2 adsorption isotherms (not shown) produced by the IAS materials noticeably shifts to lower relative pressures as a function of amine loading. These results visibly point to a significant reduction in mesopore diameter owing to pore filling of the PMMA substrate by the organic amines. Amine impregnation within the PMMA substrate was also validated by the reduction in the measured surface areas and pore volumes. Most noticeably, the values for (BET) specific surface area and (BJH) pore volume obtained for the TEPAN_BED sorbent were 39 m^2/g and 0.27 cm^3/g respectively.

Table 1. Characterization of PMMA support by N2 physisorption at 77 K

Support	S_{BET}, m^2/g	V, cm^3/g	D_{BJH}, Å	particle diameter, μm
PMMA	579	1.12	104	425-850

In addition to N_2 adsorption, TGA weight loss curves were used to help estimate organic amine loading (wt% concentration) for each IAS as shown in Figure 3. The onset of thermal decomposition for the PMMA support starts at approximately 252°C. Based on these weight loss curves, amine loadings for TEPA/PMMA, TEPAN/PMMA, and TEPAN_BED/PMMA were estimated at 38.6 wt%, 35.2 wt%, and 35.4 wt% respectively.

Figure 3. Thermogravimetric Analysis of Immobilized Amine Sorbents
Thermal Stability of Immobilized Amine Sorbents (IAS)
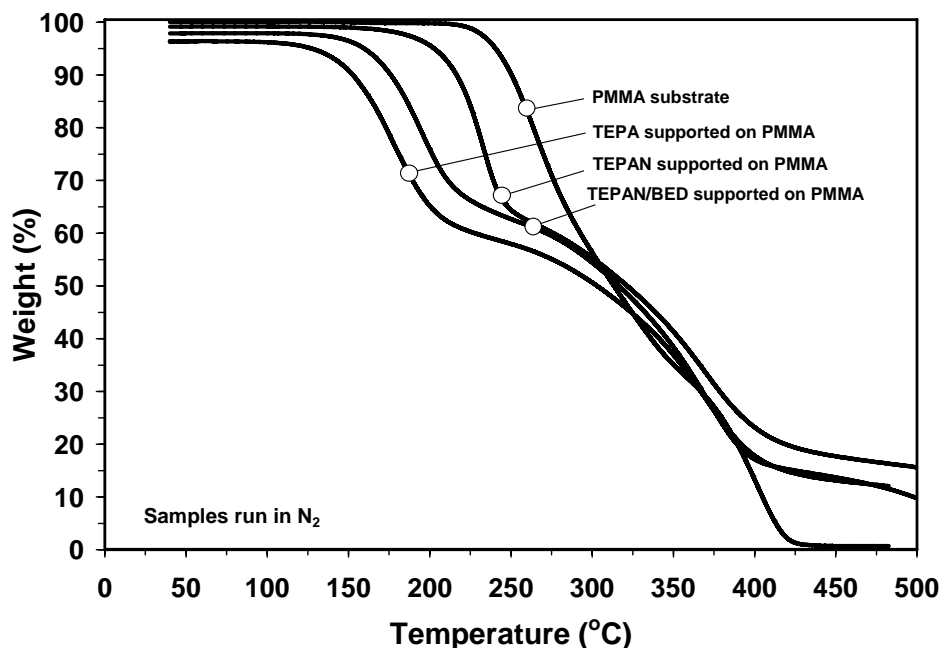
The same weight loss profiles in Figure 3 also show the thermal stability of each IAS material synthesized. Owning to the pre-conditioning step initially conducted for each IAS sample within the experiments, no apparent weight loss was observed from 40°C to 125°C clearly demonstrating the removal of pre-adsorbed CO_2 and moisture. In defining the onset temperature(s) representing the start of thermal decomposition for each organic

amine constituent, the figure clearly identifies TEPAN/PMMA as being the most stable, followed by the multiple constituent TEPAN_BED sample; followed by the sample impregnated with TEPA. From this figure, one can conclude that the organic amines are thermally stable in N_2 at temperatures required for CO_2 desorption, making it possible for these materials to be successfully tested in cyclic adsorption/desorption operations.

## CO_2 Sorption Capacity – Thermogravimetric analysis

Table 2 lists the CO_2 sorption capacity (based on mass %) determined for each material over the initial 60 minutes of exposure to CO_2 under anhydrous conditions at 25^oC. These preliminary results show that all IAS materials exhibit higher adsorption capacities compared to the PMMA substrate. The highest CO_2 capacity was observed for TEPA/PMMA sample, owning to its ability to accommodate the largest quantity of amine.

Table 2. CO_2 capture properties for Immobilized Amine Sorbents (IAS)

Sorbent ID:	Time of Exposure, min	CO_2 absorbed, mass %	CO_2 adsorbed, mmol/g of sorbent
TEPA	60	14.0	3.2
TEPAN	60	7.5	1.7
TEPAN_BED	60	9.9	2.3

Figure 4 illustrates the CO_2 uptake profiles acquired for the IAS materials with a dry mixture of 10% CO_2 in nitrogen at 25^oC along with the corresponding desorption curves obtained with dry nitrogen at 100^oC. Critical factors pertaining to the selective adsorption of CO_2 were taken into account during these experiments—the highest value of weight uptake representing the sorption capacity of the IAS materials, the uptake rate, i.e., the time necessary in reaching this maximum value, and the desorption capacity, relating to the regeneration potential of the IAS material(s). For these materials, very similar initial adsorption kinetics was observed resulting in a rapid increase in sample weight upon exposure to dry CO_2, followed by a slower continuous uptake of carbon dioxide. Their CO_2 sorption efficiency for each IAS material was found to be directly related in part to their amine content. The highest capacity obtained was achieved by the TEPA/PMMA sample; both TEPAN/PMMA and TEPAN_BED/PMMA produced lower CO_2 capture capacities compared to the unaltered TEPA/PMMA sample. These results were somewhat surprising in that the TEPAN/PMMA sample was specifically tailored with an increased abundance of secondary amines. Validation of utilizing reaction-modified amines stems from earlier work described by Giavarini et al. and Rinaldi et al,[16-17] who modified TEPA by reaction with phenol, formaldehyde, and combinations of the two to increase its capacity for gas phase CO_2 removal in aqueous solutions. One plausible cause for the lower sorption capacity for these samples may stem from poor dispersion of the active amine sites, which influences the final adsorption of CO_2. Due to its inherently low viscosity as compared to TEPA, TEPAN alone has a much greater tendency to aggregate within the pores of the polymeric support, thus leading to a higher potential of pore pluggage resulting in increased diffusional resistance. Such a result appears to have occurred as illustrated in Figure 4.

Figure 4. CO_2 adsorption—desorption profiles obtained with 10% CO_2 and nitrogen gas mixture at 25°C and 1 atm for (a) TEPA/PMMA, (b) TEPAN/PMMA, and (c) TEPAN_BED/PMMA
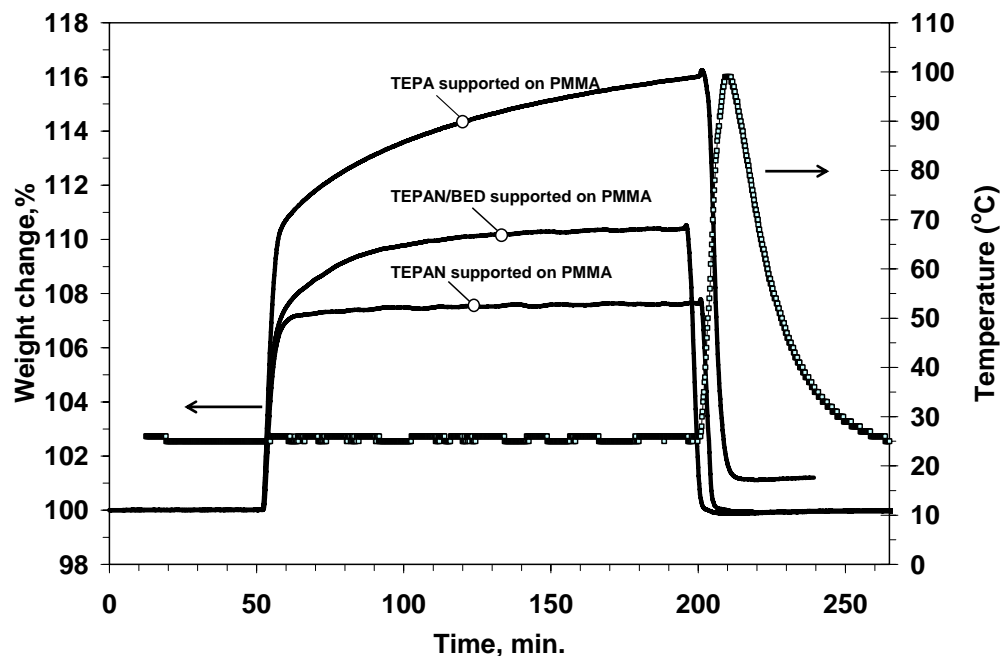

Further evidence to this hypothesis may be drawn from the examination of the TEPAN_BED/PMMA sample. Improved accessibility of the CO_2 molecules by this sample compared to TEPAN/PMMA stems from the fact that the TEPAN concentration is significantly lowered upon mixing with a second, organic amine, BED, thus changing to some degree the viscosity of the amine mixture by dilution. Available hydroxyl groups present within the BED molecule may also influence the ratio of CO_2 to N atoms, thus enhancing its CO_2 sorption capacity. In rapidly heating the IAS materials (10°C/min) to 100°C in N_2, the TEPA/PMMA sample showed some evidence of incomplete desorption; whereas both TEPAN/PMMA and TEPAN_BED/PMMA exhibited complete desorption of CO_2 during experimentation.

CO_2 Sorption Capacity – Fixed Bed Flow System

In evaluating its potential for CO_2 capture within an industrial application, IAS materials having high CO_2 selectivity, high adsorption capacity, together with proficient regenerability over numbers of adsorption/desorption cycles are favored. With this in mind, a second IAS was synthesized with TEPAN, (50% by weight) and BED (50% by weight) supported on poly (methyl methacrylate) beads. (*TEPAN50/BED50/PMMA*) This investigation focused on employing multiple, organic amine molecules of high molecular weight having a large number of secondary amino groups, making it a workable candidate for investigating its CO_2 sorption properties within a temperature range of 25°-150°C. Tertiary amine groups form a minor percentage of the active amine sites within this IAS. In contrast to single amine molecules, multi-amine materials may provide inherent advantages relating to sorbent specific kinetic, heat capacity, and heat of adsorption limitations.

Figure 5. CO_2 Breakthrough Curve for *TEPAN50/BED50/PMMA* Sorbent
Inlet gas composition: 9.0% CO_2, 3.5% O_2, N_2 balance + 2% H_2O
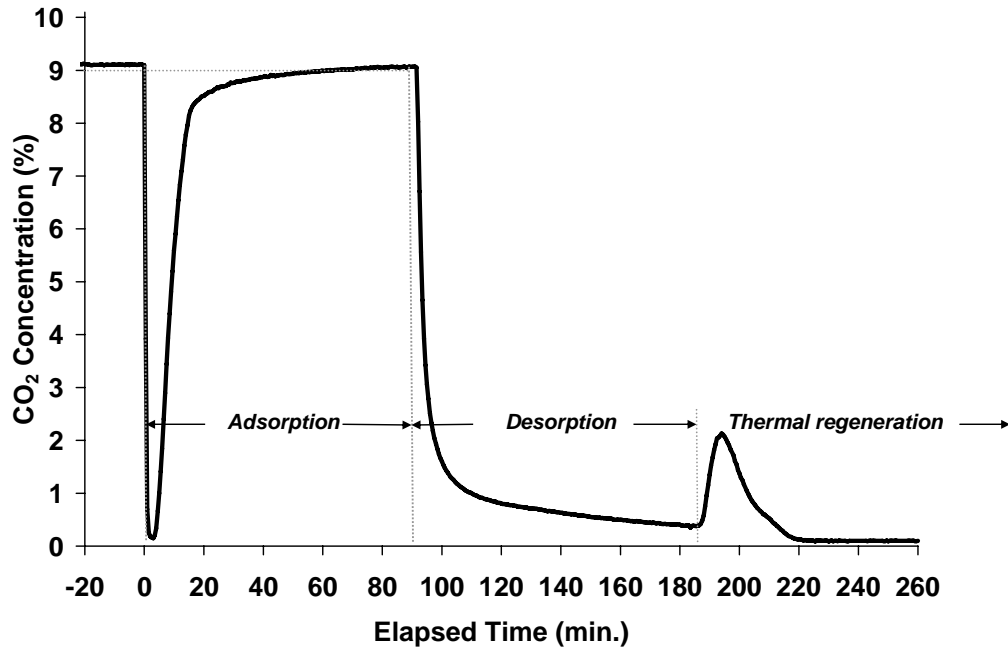
IAS performance for the newly, fabricated *TEPAN50/BED50/PMMA* sorbent was determined from cyclic adsorption/desorption/thermal regeneration data utilizing a fixed bed flow system. The variation of the CO_2 concentration in the gas downstream of the IAS bed for the fifth period of 40 adsorption/desorption/regeneration cycles as monitored by the CO_2 analyzer is shown in Figure 5. Upon upward delivery of a humidified 9% CO_2/3.5% O_2/N_2 gas flow to the IAS, an instantaneous drop in the exit CO_2 concentration during the initial minutes of adsorption transpired. A minimum CO_2 exit concentration less than 0.01% was observed. Upon the IAS bed approaching saturation, CO_2 started to exponentially rise in the exit stream defining a CO_2 breakthrough with respect to elapsed time. The adsorption of CO_2 continued until the exit CO_2 stream asymptotically approached the inlet CO_2 concentration. In every case during testing, the adsorption stage was accompanied by a rise in temperature due to the exothermic nature of the CO_2-amine reaction. Upon reaching the inlet CO_2 concentration, the input gas mixture with the exception of nitrogen was stopped. In conducting this action, (change in partial pressure of CO_2) CO_2 rapidly desorbed from the IAS accompanied by a sharp decrease in temperature presumably due to the endothermic desorption reaction. During this extended phase, the bed temperature characteristically proceeds through a minimum value and slowly approaches the initial adsorption temperature. In the final stage, regeneration of the IAS was accomplished by raising the bed temperature to a pre-determined value (typically 90°-100^oC) as evidenced by an additional quantity of CO_2 being liberated from the IAS. The IAS was fully regenerable, as evidenced by the baseline value shown in Figure 5. Clearly, the cyclic operation illustrates the reversibility of the IAS and its potential application for removing CO_2 derived from fossil fuel combustion. CO_2 adsorption capacity for the IAS was determined from the cyclic data

generated within fixed-bed flow system. Experimental conditions and results from selected IAS experiments are summarized in Table 3.

Effect of Moisture on IAS Performance

The presence of water vapor (2% and 4% moisture) appears not to influence CO_2 uptake for the IAS material. Each TEPAN molecule contains five secondary amines, so two NH_2 groups are necessary to bind one CO_2 molecule in the absence of water. When water is present, each NH_2 group can capture one CO_2 molecule as an ammonium bicarbonate salt. The observed rapid uptake of CO_2 by the IAS material probably reflects the fast kinetic nature of the intramolecular type carbamate formation. For the conditions examined, it appears that such intramolecular carbamate salts are favored over bicarbonate formation. These results were found in good agreement with cyclic adsorption—desorption studies with EDA-modified mesoporous silica materials.[13]

Effect of NO on IAS Performance

A series of experiments with 750 ppmv nitrogen oxide (NO) present in the simulated flue gas mixture were conducted to help determine the effect of NO on the performance of the IAS material. Negligible adsorption of NO was found during the cyclic adsorption—desorption process. Samples extracted before and after NO testing were examined afterwards by scanning electron microscopy (SEM) using a Aspex Personal SEM™ equipped with a Noran energy dispersive detector enabling X-ray detection of elements with atomic number 6 (carbon) and greater. The samples were examined in backscattered electron imaging (BSI) mode coupled with energy dispersive spectroscopy (EDS). Focusing on the exterior surface of the IAS particles, no additional elemental nitrogen was observed for the spent samples compared to fresh, virgin sorbent particles. Indirect validation of minute amounts of NO being present on the IAS material was examined by conducting subsequent CO_2 sorption tests in the absence of NO. On the basis of analyzing the data, tests revealed CO_2 sorption capacities to be very similar. Examination of the NO concentration during the stage of thermal regeneration showed only trace amounts (less than 5 ppmv NO) being eradicated with absorbed CO_2.

Effect of SO$_2$ on IAS Performance

The effect of sulfur dioxide (SO_2) on the performance of the IAS material was examined utilizing 750 ppmv SO_2 present in the simulated flue gas steam. The IAS material was found to adsorb simultaneously both CO_2 and SO_2. As in CO_2 adsorption, an instantaneous drop in SO_2 concentration within the exit gas stream was observed, however, during the desorption process at 90°-100^oC there was no indication of SO_2 being eliminated from the exterior surface of the IAS material. During periods between experiments visual inspection of the IAS within the fixed bed revealed progressive degrees of "staining" or "discoloration" to the IAS material. Upward delivery of the simulated flue gas mixture into the quartz column showed the lower portion of the sorbent bed to be darker in color compared to the upper section. In an attempt to desorb SO_2 from the sample at 120^oC, loss of the amine component N, N'-bis(2-hydroxyethyl) ethylenediamine (see Figure 6) was observed.

Figure 6. Digital photograph of N, N'-bis(2-hydroxyethyl) ethylenediamine crystals recovered after thermal regeneration of IAS at 120°C.

SUMMARY

The present study has shown an IAS material consisting of acrylonitrile-modified amine, tetraethylenepentamine TEPAN and N, N'-bis(2-hydroxyethyl)ethylenediamine supported on poly (methyl methacrylate) beads to reversibly adsorb and desorb carbon dioxide. The large pores of the polymeric substrate promote fast mass transport of CO_2 believed to proceed by the formation of an intramolecular carbamate salt providing favorable kinetics. CO_2 sorption capacity of the IAS material is ~ 3 mmols CO_2/g of sorbent at 40°C and 1 atm for a humidified 9% CO_2/N_2 gas mixture. In the fixed bed flow studies, negligible adsorption of NO onto the IAS material was found during adsorption—desorption testing. The IAS material was found to adsorb simultaneously both CO_2 and SO_2. Visual inspection of the IAS shows some degree of "staining" or "discoloration" upon SO_2 exposure at high SO_2 concentrations. Observations relating to SO_2 absorption necessitate the need for upstream removal of SO_2 prior to CO_2 capture.

DISCLAMER

Table 3. Test Conditions and Results for Selected Immobilized Amine Sorbent Experiments
Inlet Gas Composition (Vol %): 9.0% CO_2, 3.5% O_2, ppmv NO, ppmv SO_2, and N_2 balance

Run Identification Sample ID-Cycle No.	165A-2	165A-12	165A-14	165A-22	165A-23	165A-25	165A-26	165A-33	165A-34	165A-36
H_2O concentration (vol %)	0	4	4	2	2	2	2	2	2	2
SO_2 concentration (ppmv)	0	0	0	0	0	0	0	750	750	0
NO concentration (ppmv)	0	0	0	0	750	750	0	0	0	0
Adsorption										
Initial temperature (^oC)	40	38	38	39	41	40	39	40	41	37
Exotherm (^oC)	25	27	29	27	34	35	27	29	33	25
Breakthrough time (min)	14	12	12	13	12	11	14	11	9	10
CO_2 adsorbed (liter)	2.51	2.36	2.22	2.15	1.98	1.97	2.47	1.71	1.64	1.57
CO_2 adsorption capacity	3.1	2.9	2.7	2.7	2.4	2.4	3.0	2.1	2.0	1.9
Desorption										
Exotherm (^oC)	13	12	14	12	12	12	12	14	14	12
CO_2 desorbed (liter)	2.36	2.17	1.75	1.87	1.71	1.69	2.18	1.72	1.53	1.51
Thermal Regeneration										
Temperature (^oC)	90	90	90	90	90	90	90	90	90	90
Time (hrs)	1	1	1	1	1	1	1	1	1	1
CO_2 desorbed (liter)	0.14	0.46	0.42	0.40	0.42	0.44	0.71	0.17	0.17	0.14
Total desorbed CO_2 (liter)	2.50	2.63	2.17	2.27	2.13	2.12	2.89	1.90	1.70	1.65

ACKNOWLEDGEMENTS

REFERENCES

1. Stephens, J.C. van der Zwaan B. CO_2 Capture and Storage (CCS): Exploring the Research, Development, Demonstration, and Deployment Continuum" BCSIA Discussion Paper 2005-08, Energy Technology Innovation Project, Kennedy School of Government, Harvard University, 2005
2. Intergovernmental Panel on Climate Change, *Carbon Dioxide Capture and Storage,* ISBN-92-9169-119-4, 2006. See http://www.ipcc.ch/activity/srccs/
3. White, C.M.; Strazisar, B.R.; Granite, E.J.; Hoffman, J.S. *Journal of the Air & Waste Management Association*, **2003**, 53, 645.
4. Chang, A.C.C.; Chuang, S.S.C.; Gray, M.; Soong, Y. *Energy Fuels*, **2003**, 17, 468.
5. Huang, H.Y.; Yang, R.T.; Chinn, D.; Munson, C.L. *Ind. Eng. Chem. Res.* **2003**, 42, 2427.
6. Hiyoshi, N.; Yogo, K.; Yashima, T. *Micropor. Mesopor. Mater.* **2005**, 84, 357
7. Filburn, T.; Helble, J.J.; Weiss, R.A. *Ind. Eng. Chem. Res*. **2005**, 44, 1542.
8. Schladt, M.J.; Filburn, T.P., Helble, J.J. *Ind. Eng. Chem. Res*., **2007**, 46, 1590.
9. Khatri, R.A.; Chuang, S.S.C.; Soong, Y.; Gray, M. *Ind. Eng. Chem. Res*. **2005**, 44, 3702.
10. Satyapal, S.; Filburn, T.; Trela, J.; Strange, J. *Energy Fuels*, **2001**, 15, 250.
11. Xu, X.; Song, C.; Anderson, J.M.;, Miller, B.G.; Scaroni, A.W. *Energy Fuels*, **2002**, 16, 1463.
12. Knowles, G.P.; Graham, J.V.; Delaney, S.W.; Chaffee, A.L. *Fuel Processing Technology*, **2005**, 1433.
13. Zheng, F.D.; Tran, N.; Busche, B.J.; Fryxell, G.E.; Addleman, R.S.; Zemanian, T.S.; Aardahl, C.L. *Ind. Eng. Chem. Res*., **2005**, 44, 3099.
14. Franchi, R.S.; Harlick, P.J.E.; Sayari, A. *Ind. Eng. Chem. Res*., **2005**, 44, 8007.
15. Arenillas, A.; Smith, K.M.; Drage, T.C.; Snape, C.E. *Fuel*, **2005**, 84, 2204.
16. Rinaldi, G. *Ind. Eng. Chem. Res.,* **1997**, 36, 3778.
17. Filipsis, P.; Giavarini, C.; Maggi, C.; Rinaldi, G.; Silia, R. *Ind. Eng. Chem. Res*., **2000**, 39, 1364.