Available online at www.sciencedirect.com
SCIENCE DIRECT®
Separation and Purification Technology 35 (2004) 31–36
Separation and Purification Technology
www.elsevier.com/locate/seppur

CO_2 capture by amine-enriched fly ash carbon sorbents

M.L. Gray [a,*], Y. Soong [a], K.J. Champagne [a], John Baltrus [a], R.W. Stevens, Jr [b], P. Toochinda [b], S.S.C. Chuang [b]

[a] *US Department of Energy, National Energy Technology Laboratory, P.O. Box 10940, Pittsburgh, PA 15236, USA*
[b] *Chemical Engineering Department, University of Akron, Akron, OH 44325-3906, USA*

Received 21 September 2002; received in revised form 20 February 2003; accepted 26 February 2003

Abstract

The capture of CO_2 from gas streams has been achieved by the utilization of amine-enriched fly ash carbon sorbent system. The initial fly ash carbon sorbents were generated by the chemical treatment of carbon-enriched fly ash concentrates with a 3-chloropropylamine-hydrochloride (CPAHCL) solution at 25 °C. It was determined that these amine-enriched fly ash carbon sorbents performed at a 9% CO_2 capture capacity based on commercially available sorbents. The chemical sorption performance of these amine-enriched fly ash carbon sorbents will be described within this paper.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Carbon dioxide; Capture; Amine sorbent

1. Introduction

The concentration of CO_2 in our atmosphere is promoted by the combustion of fossil fuels for the generation of electricity. Capturing CO_2 from flue-gas streams is an essential parameter for the carbon management for sequestrating of CO_2 from our environment. Current technologies [1] being considered for CO_2 sequestration include: disposal of CO_2 in deep oceans; depleted oil and gas fields; deep saline formations (aquifers); and recovery of enhanced oil, gas, and coal-bed methane. However, the current cost for the utilization of these types of technologies has proven to be too expensive. Consequently, reducing the cost for the capture of CO_2 will be a critical step in the overall carbon management program.

The physical and chemical adsorption of CO_2 can be achieved by using solvents, cryogenic techniques, membranes, and solid sorbents. The large-scale operation of these technologies is energy intensive when applied to capturing CO_2 in dilute stream, such as flue gas, which consist of 15% CO_2 by volume for most coal combustion systems. Amine-based, solvent-capture systems are the most energy efficient option, but are energy intensive due to the large amount of water needed in these system. Excessive water is required because of the corrosion and air flow problems created by the use of monoethanolamine (MEA), diethanolamine (DEA), or methyldiethanolamine (MDEA) in these aqueous-based, CO_2-capture systems. The proposed reaction sequences for using primary, secondary, and tertiary alkanolamines reacting with

* Corresponding author. Tel./fax: +1-412-386-4826.
E-mail address: gray@netl.doe.gov (M.L. Gray).

1383-5866/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S1383-5866(03)00113-8

dissolve CO_2 are shown below. Formation of the zwitterion ion:

$$R_1R_2NH + CO_2 \leftrightarrow R_1R_2NH^+CO_2^- \quad (1)$$

Formation of amine carbamate:

$$R_1R_2NH + R_1R_2NH + CO_2 \leftrightarrow R_1R_2NH^+ + R_1R_2NCO_2^- \quad (2)$$

Protonation of amine:

$$R_1R_2R_3N + H_2O + CO_2\ (aq) \leftrightarrow R_1R_2R_3NH + HCO_3^- \quad (3)$$

Solid-amine CO_2 sorbents should have similar reactions with airborne CO_2, water vapor, and the amine functional group on its surface. Consequently, these types of sorbents are being used in aircraft, submarine, and spacecraft technologies [2–4]. However, the cost of these sorbents is too expensive for large-scale applications in the utility industry. Consequently, the development of economical amine-enriched sorbents based on a fly ash carbon concentrate will be discussed within this paper.

2. Experimental procedures

2.1. Samples

A fly ash containing 9.5% of unburned carbon was collected from the bag house of the 500-lbs/h-combustion unit at the National Energy Technology Laboratory (NETL). The fly-ash sample examined in this study resulted from the combustion of a Pittsburgh-seam coal from the Black Creek mine. A column agglomeration process [5,6] developed at NETL was use for the collection of the fly ash carbon concentrates.

The 3-chloropropylamine-hydrochloride (CPAHCL) and the potassium hydroxide were regent grade chemicals purchased from Aldrich Chemical Company.

2.2. Amine treatment process

The 10 g fly ash carbon concentrate was treated with a 500 ml 1×10^{-3} molar 3-CPAHCL salt solution with and without 1×10^{-2} molar potassium hydroxide for 1 h at 25 °C. The treated amine-enriched fly ash carbon concentrate was filtered and dried in an oven for 1 h at 105 °C. The final amine-enriched fly ash concentrations were then tested as CO_2 capture sorbents in the DRIFTS/TPD reactor systems (refer to Fig. 1).

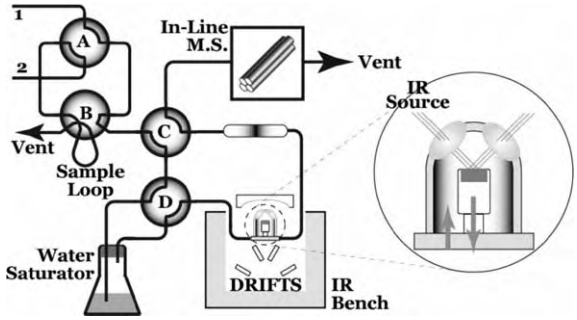

Fig. 1. Schematic drawing of the DRIFTS\TPD CO_2 capture reactor system.

2.3. CO_2 capture capacity

The chemical CO_2 capture capacities were determined by the combination of diffuse reflectance infrared transform spectroscopy (DRIFTS) temperature programmed desorption (TPD) and mass spectroscopy (MS) analyses. The evolution of CO_2 between the temperature range of 30–115 °C was not analyzed due to the limitations of the experimental reactor systems. Consequently, the CO_2 desorption capacities were calculated at 120 °C. The detailed operating conditions for this procedure were previously described in the literature [7].

2.4. XPS analysis

The amount of nitrogen of the surface of the amine-enriched fly ash carbon sorbent was determined by XPS (N1s peak) analysis. The details of this experimental procedure have been reported in the literature [8].

3. Results and discussion

The proposed reactions of the 3-CPAHCL with the fly ash carbon concentrate are illustrated in Fig. 2. With the incorporation of the amine group onto the

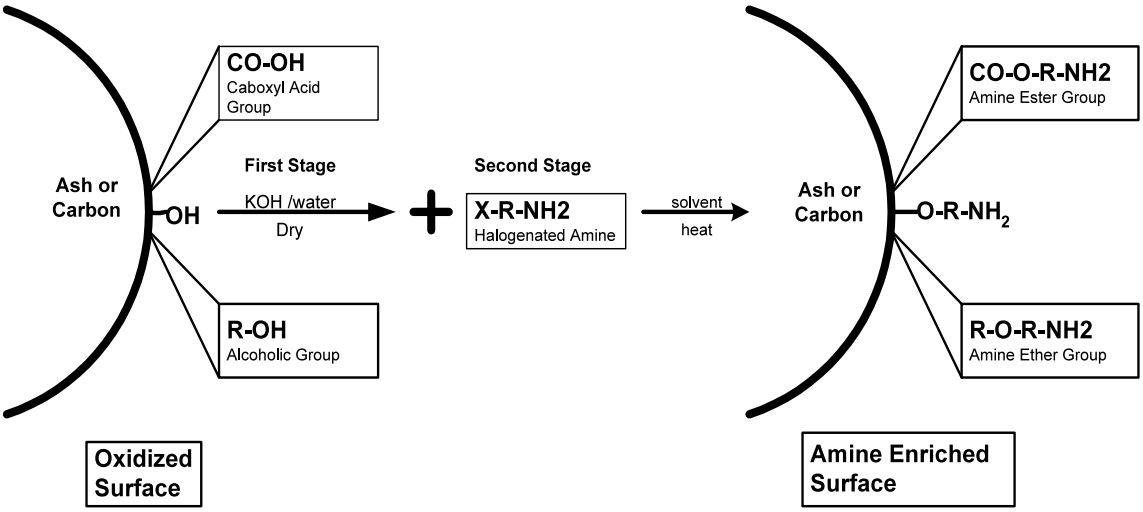

Fig. 2. Proposed reactions for preparation of the amine-enriched fly ash sorbent.

surfaces of this fly ash carbon concentrates should enable them to capture CO_2 from gas stream in the present of moisture. The amounts of nitrogen incorporated onto the surfaces of these fly ash carbon concentrates were determined by XPS analysis and the results are shown in Table 1.

According to Table 1, there was an in increase in the nitrogen content when these fly ash carbon concentrates were reacted with 3-CPAHCL with and without the presence of potassium hydroxide. Based on these results, it is apparent that these fly ash carbon concentrates are slightly reactive with the 3-CPAHCL under these conditions. Since 95C resulted in the highest nitrogen content, the presence of potassium hydroxide is not required for the incorporation of amine onto the surfaces of these fly ash carbon concentrates.

Previous work [9] on these similar sorbents have shown that they have the ability to capture CO_2 from gas stream with the presence of moisture. Initially, the original fly-ash concentrates (95) were generated from the feed fly ash (59) by using the column agglomeration process. The amine treated fly ash carbon concentrates (95A, 95B, and 95C, refer to Table 1) were then examined as CO_2 capture sorbents. These sorbents were placed in a 10% $CO_2/H_2O/He$ gas stream and DRIFTS, TPD, and MS analyses were conducted to determined the CO_2 capture capacities. The adsorption/desorption of CO_2 for these sorbents were determined at 25 °C (adsorption) and 120 °C (desorption). Typical DRIFTS and TPD/MS spectra are shown in Figs. 3 and 4. According to the DRIFTS spectra, the formation of the corresponding carbamate-amine product was indicated by the presence of the two peaks at 1087 and 1148. The other major peaks at approximately 2380 are the adsorption of CO_2. The desorption of the CO_2 was observed as the temperature was increased to 120 °C. At this elevated temperature, the TPD/MS spectra indicates the mass numbers (*m*/*e*) for the desorption of CO_2 (*m*/*e* 44), H_2O (*m*/*e* 18), O_2 (*m*/*e* 32) and CO or N_2 (*m*/*e* 28). The *m*/*e* value of 28 may be the decomposition of the surface amine compound or the breakdown of the carbamate amine product. If this is the decomposition of the surface amine compound, it will have a direct effect on the regenerable properties of these sorbents. The overall CO_2 capture capacities are summarized in Table 2.

As shown in Table 2, the adsorption of CO_2 in samples 59 and 95 increased with the amine chemical

Table 1
XPS analysis of amine-enriched fly ash carbon sorbents

Sample	Chemical treatment	XPS N1s (%) on surface
59 Feed fly ash	None	Not detected
95 Carbon	None	0.81
95A Carbon	CPAHCL and KOH	1.11
95B Carbon	KOH only	0.83
95C Carbon	CPAHCL only	1.29

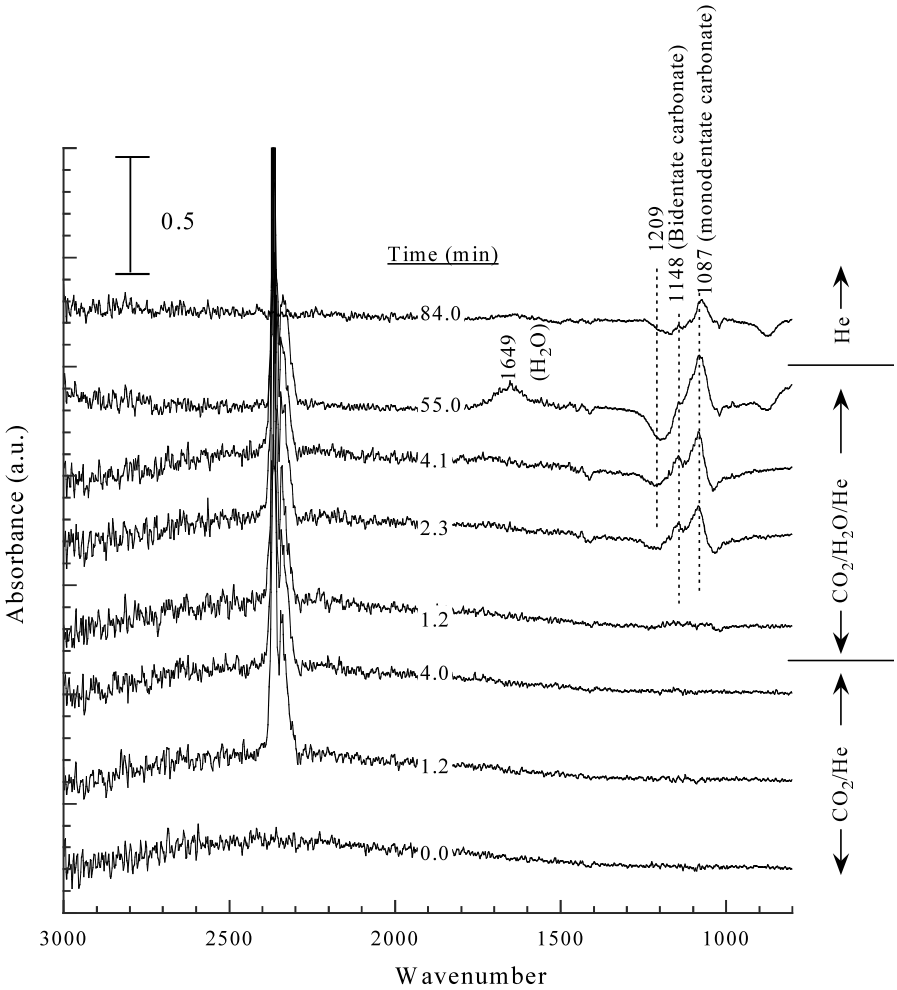

Fig. 3. A typical DRIFTS CO_2 absorption spectra over 95C sample.

Table 2
TPD CO_2 desorption result of amine-enriched sorbents

Sample #	Treatment methods	CO_2 release μmol/g sample
59 Feed fly ash	None	24.4
95 Carbon	None	72.9
95A Carbon	CPAHCL and KOH	81.1
95B Carbon	KOH only	117.9
95C Carbon	CPAHCL only	174.6
95C Carbon (regenerated)	CPAHCL only	140.6

treatment. The best sample was 95C, which had the CO_2 capture capacity of 174.5 μmol/g, and was regenerable for an additional test (140.6 μmol/g). In comparison to commercially available sorbents with surface areas of 1000–1700 m^2/g and CO_2 capture capacities of 1800–2000 μmol/g [10], the 95C was only able to achieve 9% of the CO_2 capture capacity. However, the surface area of the 95C amine-enriched sorbent was only 27 m^2/g, which may account for its low CO_2 capture capacity. Furthermore, additional modifications to the reaction conditions are required in order to improve the incorporation of amine onto the fly ash carbon concentrate under these reaction conditions.

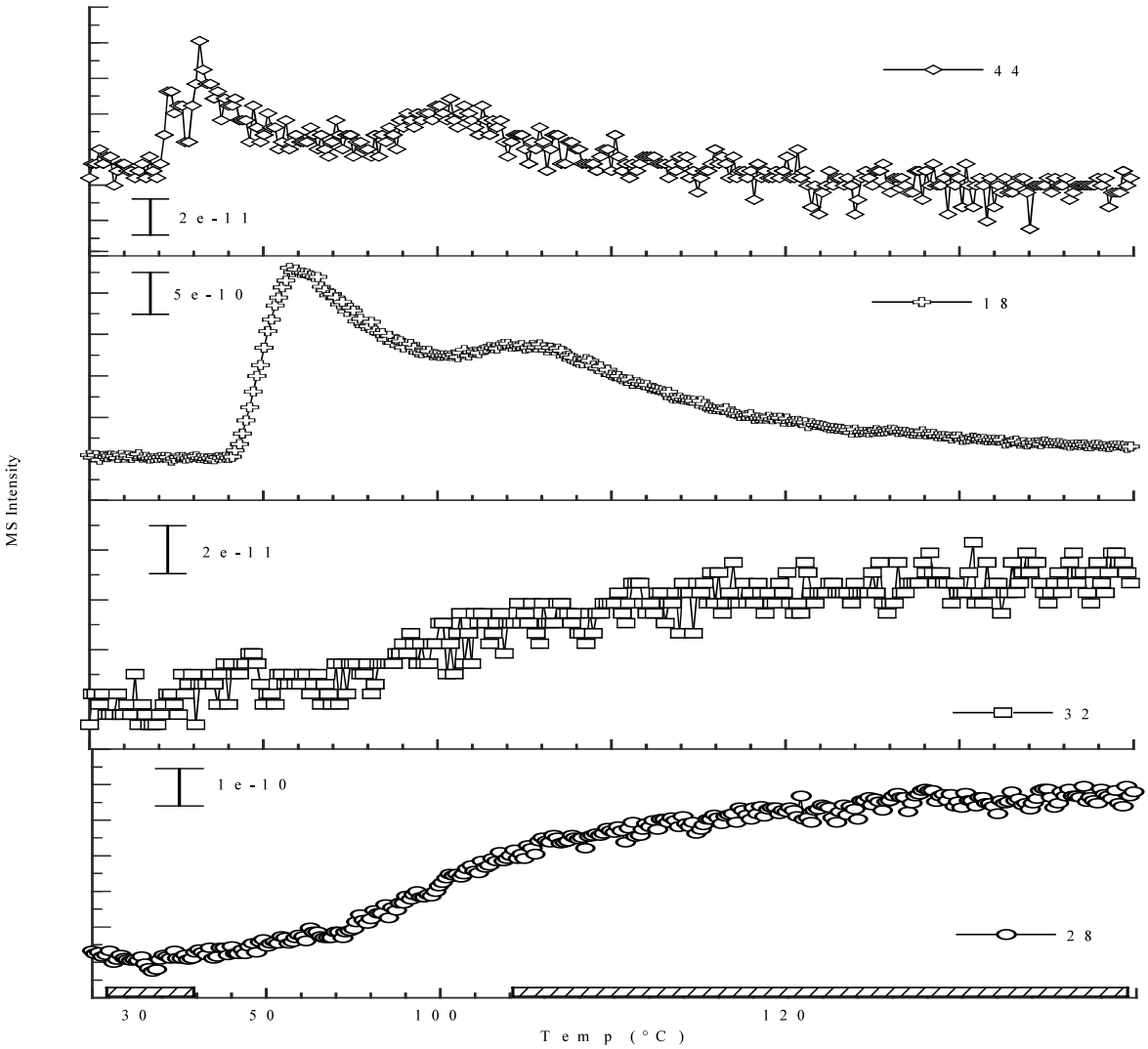

Fig. 4. Typical TPD/MS spectra for 95C sample.

4. Conclusion

The amine treatment process was successful in improving the CO_2 capture capacities of these fly-ash carbon concentrates. However, the performance of the regenerable sorbents was only able to reach 9% of the required CO_2 capture capacity to make them competitive with the existing CO_2 sorbents. Alternative low-cost, high surface oxygen-rich solid substrates and CO_2 capture procedures are being examined and will be reported in future publications.

References

[1] DOE Report Doe/ER-30194, "Research Needs Assessment for the Capture, Utilization and Disposal of Carbon Dioxide from Fossil Fuel-Fired Power Plants," 1993.

[2] US Patent 4,810,266, H.A. Zinnen, A.R. Oroskar, C.H. Chang, "CO_2 removal using aminated carbon molecular sieves," 1989.

[3] US Patent 5,492,683, P.J. Bibara, T.A. Naletta, "Regenerable support amine polyol sorbent," 1996.

[4] US Patent 5,876,488, P.J. Bibara, T.P. Filburn, T.A. Nalette, "Regenerable solid amine sorbent," 1999.

[5] US Patent 6,126,014, M.L. Gray, K.J. Champagne, D.H. Finseth, “Continuous air agglomeration for high carbon fly ash benefication,” 2000.
[6] M.L. Gray, K.J. Champagne, Y. Soong, D.H. Finseth, Parametric study of the column agglomeration of fly ash, Fuel 80 (2001) 867–871.
[7] Y. Soong, M.L. Gray, R.V. Siriwardane, K.J. Champagne, R.W. Stevens Jr, P. Toochinda, S.S.C. Chuang, Novel amine enriched solid sorbents for carbon dioxide capture, Fuel Preprint 46 (1) (2001) 285.
[8] M.L. Gray, K.J. Champagne, Y. Soong, R.P. Killmeyer, J. Baltrus, M.M. Maroto-Valer, J.M. Andersen, M.V. Ciocco, P.H. Zandhuis, ACS chapter book, in: Environmental Challenges and Greenhouse Gas Control for Fossil Fuel Utilization in the 21st Century, Kluwer Academic/Plenum Publishers, 2002, p. 403.
[9] M.L. Gray, K.J. Champagne, Y. Soong, R.W. Stevens Jr, P. Toochinda, S.S.C. Chuang, “Solid Amine CO_2 Capture Sorbents”, ACS, Fuel Chemistry Division Preprints, vol. 47 (1), 2002, p. 63.
[10] US Patent 5,876,488, P.J. Bibara, T.P. Filburn, T.A. Nalette, “Regenerable Solid Amine Sorbent,” 1999.