

Comparison of pre and post-combustion CO₂ adsorbent technologies.

T.C. Drage¹, A. Arenillas², K. Smith¹ and C.E. Snape^{*1}

¹*Nottingham Fuel and Energy Centre, School of Chemical, Environmental and Mining Engineering, University of Nottingham, NG7 2RD, UK*

²*Consejo Superior de Investigaciones Cientificas Instituto Nacional del Carbon, Apartado 73, 33080 Oviedo, Spain*

Abstract

Adsorption is considered to be one of the most promising techniques for the capture of CO₂ from flue gases. The application of adsorption to both post-combustion capture at pressures close to ambient and for high pressure pre-combustion capture applications, for example IGCC, are explored. Adsorption capacities as a function of adsorbent properties as well as strategies for regeneration, both thermal swing and pressure swing are described. Adsorption at both low and high pressures requires chemical and physical adsorbents respectively. Adsorption at high pressure has the advantage of potential temperature swing regeneration whilst maintaining CO₂ pressure, reducing the overall costs associated with re-compression of the gas for transportation.

Keywords: CO₂, capture, adsorption

1. Introduction

CO₂ capture can be achieved either by post-combustion capture at ambient pressure or pre-combustion capture at high pressure using IGCC. Aqueous solutions of amines have been used by industry as absorbents for acid gas (CO₂, H₂S) removal, for example monoethanol amine MEA. However, they have a number of shortcomings for the post-combustion treatment of flue gases, for example sorbents corroding mild steel components, vaporisation losses and energy intensive regeneration [1]. Physical adsorbents, for example Selexol are currently used for the pre-combustion capture of CO₂. However they incur a large energy penalty due to the loss of pressure during PSA regeneration, estimated to be approx 6%. Adsorption is one of the more promising technologies for capturing CO₂ from flue gases, with solid adsorbents potentially avoiding the shortcomings of the absorption systems described above. In this paper two approaches to CO₂ capture using adsorption under simulated post and pre-combustion conditions, at ambient and high pressure respectively, will be compared. Chemical adsorbents either basic amine polymers, for example polyethylenimine (PEI) supported on inorganic templates and a range of high nitrogen content carbons are investigated for post-combustion capture. Whilst a range of active carbon, physical adsorbents, for pre-combustion capture have been explored. The adsorbents will be described and compared in terms of their adsorption capacity and ease of regeneration.

* Corresponding Author: colin.snape@nottingham.ac.uk, +44 115 951 4166

2. Materials and Methods

2.1. Post-combustion / low pressure adsorption

A wide range of adsorbents have been studied. The modification of the surface chemistry of proprietary inorganic supports with polyethylenimine (PEI) has been applied to generate a range of adsorbents (BET surface areas from approximately 250 – 400 m²g⁻¹). PEI (average molecular mass 1800) was used and adsorbents were prepared using a wet impregnation technique [2,3]. A wide range of high nitrogen content adsorbents have also been developed and were also studied [4,5].

The CO₂ adsorption capacity of the adsorbents, expressed as the percentage of CO₂ adsorbed by mass (on a dry basis), was measured using thermogravimetric analysis. Temperature-resolved CO₂ adsorption profiles were generated by heating the adsorbents in an atmosphere of CO₂ at 0.25 °C min⁻¹ up to 100 °C [4]. Thermal swing adsorption / regeneration cycles (TSA) of the adsorbents was studied using a 3 cycle thermal swing adsorption programme to determine the optimal conditions for regeneration [6]. A specially constructed dynamic testing rig was used to undertake thermally assisted pressure swing desorption of the PEI-based adsorbents [6]. Adsorption up to complete saturation of the adsorbent was undertaken at 75 °C in a simulated flue gas of 15% CO₂ in balance N₂ at a flow rate of 100 ml min⁻¹. Desorption was undertaken in a stream of pure nitrogen to simulate pressure swing by lowering the partial pressure of CO₂.

2.2. Pre-combustion / high pressure adsorption

A wide range of active carbon (ACs) adsorbents were investigated. A general purpose commercial AC for purposes of comparison (Chorcarb) as was a high BET surface area commercial carbon (Picazine, ca. 1500 m² g⁻¹). A non-activated polyacrylonitrile (PAN) carbon and a highly activated PAN sample (BET surface area of 3000 m² g⁻¹) were also investigated. As well as three phenolic resin ACs with varying porosity characteristics (PR1, PR2 and PR3 and a chemically activated UF carbon with a relatively high nitrogen content (10 wt.% nitrogen, 452 m² g⁻¹). Equilibrium uptake measurements have been conducted in (i) a dual limb differential pressure rig [7] at up to 50 bar pressure at ambient temperature [8] and (ii) a commercial Hiden (IGA-001; Hiden Isochemical Ltd, Warrington, UK) Intelligent Gravimetric Analyser (IGA) up to 20 bar and elevated temperatures [8]. The IGA although operating at a lower maximum pressure than the dual limb differential pressure rig, facilitated evaluation of temperature swing adsorption (TSA).

3. Results

3.1 Low pressure / post combustion Adsorption.

The adsorption of CO₂ at pressures close to atmospheric requires chemical type adsorbents, with basic nitrogen or amine groups the principal functional groups required [2]. Adsorbents have been developed using two techniques, the modification of the surface chemistry of inorganic and fly ash derived supports with a range of amine polymers, for example, polyethylenimine (PEI) [3] and the generation of a range of high nitrogen content carbon matrix adsorbents by the carbonisation and activation of a series of nitrogen containing compounds [4,5]. Both techniques result in the generation of adsorbents that have a rapid rate of CO₂ adsorption. CO₂ adsorption capacity is high for all adsorbents at room temperature, with 8 – 10 wt.% uptakes achieved (Figure 1). The principal difference between the two methods is performance versus temperature, which decreases at elevated temperature for the high nitrogen content adsorbents. Overall the supported amine polymer adsorbents have the greatest

performance with the high adsorption of CO₂ over flue gas temperatures (60 – 80 °C).

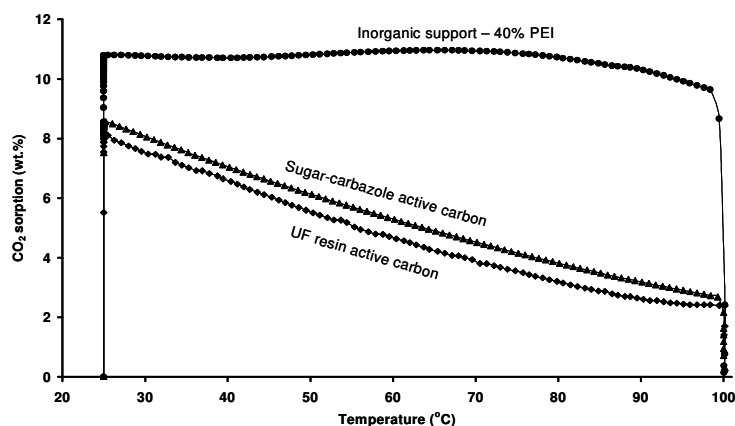


Figure 1 CO₂ uptake for a range of novel adsorbents as a function of temperature.

Regeneration of the inorganic template-PEI adsorbents has been explored [6]. The influence of temperature on the recovered adsorption capacity of the inorganic support impregnated with 40 wt% PEI (1800 MM) is presented in Figure 2. Increasing regeneration temperature results in increased recovered adsorption potential, which steadily increases from 110 – 145 °C. Above and including 145 °C approximately 90% of the original adsorption capacity is recovered. Recovered adsorption capacity below 145 °C is similar for both the first and second regeneration cycle (Figure 2). However, above 145 °C, whilst approximately 90 % of the original adsorption capacity is recovered, the capacity on the second regeneration cycle decreases, culminating at 180 °C with a greater than 10 % loss in recovered adsorption capacity.

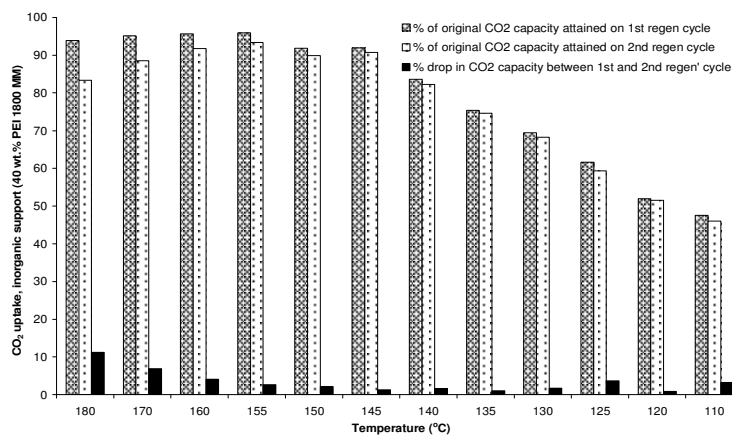


Figure 2. Effect of regeneration temperature over two successive TSA cycles (1 minute regeneration cycles) on the regeneration performance of an inorganic support impregnated with 40 wt.% PEI

The decline in regeneration performance at 140 °C and above can be explained by TGA analysis of the inorganic support-PEI adsorbent using a slow heating rate of 0.25 °C min⁻¹ over the temperature range 25 to 200 °C (Figure 3). In the presence of CO₂ adsorption capacity is constant up to approximately 85 °C, above this temperature CO₂ adsorption becomes less favourable and adsorption capacity decreases to a minima at 135 °C. Whilst it would be expected that the adsorbent would undergo a further weight loss as seen in N₂ and air above 135 °C, an increase in weight is observed (Figure 3). This increase in weight is proposed to be as a result of reaction between the CO₂ and PEI amine functional groups, leading to the formation of an as yet unidentified thermostable complex. The formation of the thermostable complex above 130 °C is proposed to account for the successive decline in adsorbent performance with each successive regeneration cycle

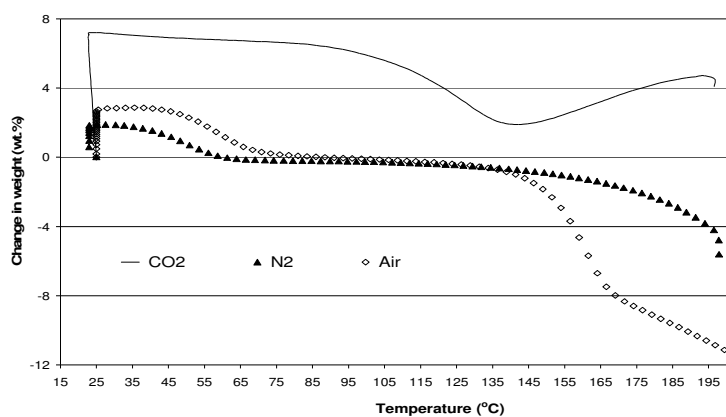


Figure 3 TGA profile for the behaviour of the PEI based adsorbent in N₂, CO₂ and air, whilst slowly heated from 25 - 200 °C at 0.25 °C min⁻¹.

Thermally assisted pressure swing desorption has been undertaken using a specially constructed dynamic testing rig [6]. Regeneration of the adsorbents at 75 °C is a lengthy process requiring a large ratio of N₂ to CO₂ (Table 1). The benefit of increased regeneration temperature is demonstrated by the dramatic reduction in the amount of nitrogen required to desorb the CO₂, by approximately 50 % with an increase in temperature from 120 – 140 °C (Table 1). Removal 100 % of the adsorbed CO₂ is inefficient compared to compared to 99 %, requiring a five fold increase on the moles of nitrogen (Table 1). Although nitrogen would not be used to regenerate adsorbents, the efficiency of the pressure swing method suggests that steam stripping could be applied for regeneration.

Regeneration Temp (°C)	Flow Rate ml min ⁻¹	Regeneration (mol N ₂ / mol CO ₂)			
		100 %	99 %	90 %	80 %
75	100	244	150	93	61
120	100	96	48	20	16
130	100	57	20	13	10
140	50	53	10	5	4
	100	51	14	10	8

Table 1 Moles of nitrogen required to desorb various proportions of the adsorbed CO₂ over a range of temperatures and flow rates for an inorganic support loaded with 40 wt.% PEI.

3.2. High pressure / pre-combustion adsorption

Adsorption isotherms generated from the differential pressure apparatus demonstrated adsorption to be rapid, with approximately 80% of the equilibrium uptake being achieved in seconds, and the final equilibrium uptake reached after *ca.* 4 minutes [8]. Figure 3 presents the adsorption isotherms up to 40 bar for all the carbons investigated. The activated PAN which gave the highest uptake possessed a surface area of 3000 m² g⁻¹. Differences between uptakes at 2 and 40 bar generally increase with increasing uptake (Figure 3), therefore demonstrating greater potential for pressure swing adsorption (PSA) cycles. Figure 5 shows a plot of the variation of equilibrium CO₂ uptakes at 40 bar with BET surface area for the carbons tested. The outlier on the plot is PR2 which possessed the highest proportion of micropores of all the polyphenol resin samples. This property could account for its higher adsorption capacity if all are accessible to CO₂. Thus, it can be concluded that the CO₂ uptakes at high pressure correlate well with micropore surface area.

PSA has been simulated by examining the difference in CO₂ adsorption isotherms at atmospheric and elevated pressures. Analysis of PR2 revealed that after a pressure swing from 40 to 1 bar, uptakes of 10% w/w could be achieved at high pressures, compared to *ca.* 16% for the initial carbon. However the difference between the uptakes of some of the other carbons at 1 and 40 bar, were higher, reaching

nearly 40% w/w for the activated PAN, highly promising for PSA application.

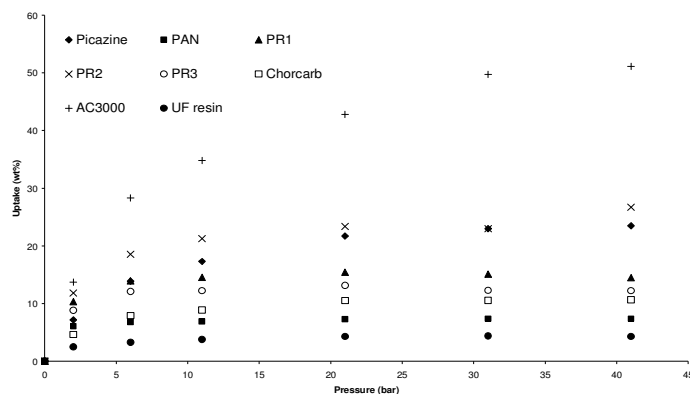


Figure 4 Adsorption isotherms for all of the adsorbents (differential pressure apparatus).

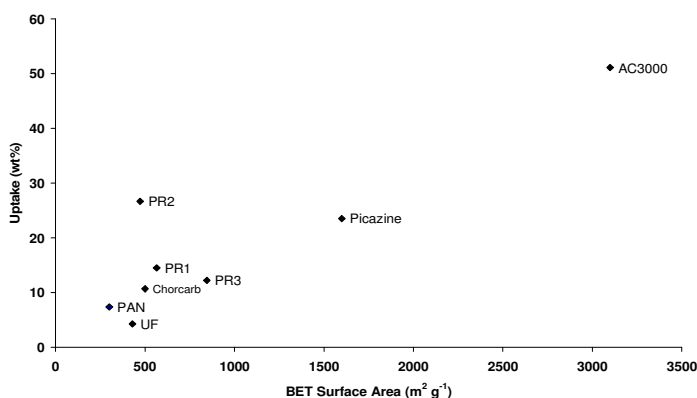


Figure 5. Correlation of equilibrium CO₂ uptakes at 40 bar with surface area for the carbons tested (differential pressure apparatus).

Intelligent gravimetric analysis gave rise to higher uptakes than in the differential pressure apparatus as a result of the high vacuum used for degas of the adsorbents. The adsorption isotherms the high surface area PAN AC indicate that equilibrium uptakes have increased giving an uptake of 100% w/w at 20 bar (Figure 7). The adsorption isotherm at 170°C (Figures 7) demonstrated that at least two-thirds of the CO₂ could be removed by TSA at this temperature with a CO₂ pressure of 20 bar. This demonstrates the potential for TSA, recovering a large proportion of the adsorption capacity whilst maintaining CO₂ at elevated temperature for transportation.

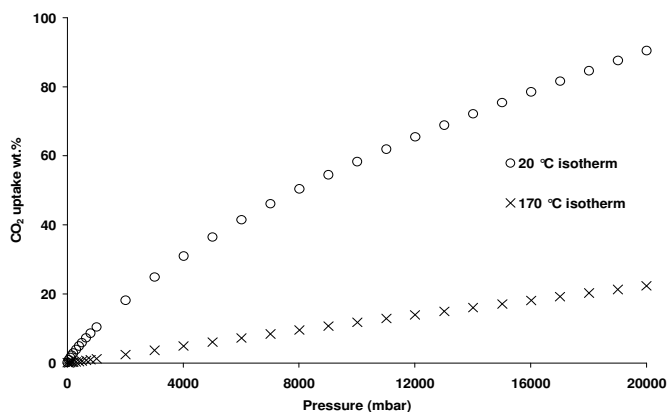


Figure 7. Adsorption isotherms for the highly activated PAN sample, showing the difference between ambient and 170 °C to simulate TSA. (IGA measurement).

4. Conclusions

A wide range of adsorbents have been generated for pre and post-combustion applications. Chemical adsorption is required for low pressure, post combustion capture. Overall immobilised amine polymer based adsorbents provide the best adsorption capacity at flue gas temperatures. Conditions for the regeneration of PEI based adsorbents must be selected carefully if degradation of the polymer is to be avoided, especially where TSA is used. Thermally assisted pressure swing regeneration illustrates the potential of steam stripping for the regeneration of the adsorbents. High pressure adsorbents for pre-combustion capture demonstrate high adsorption capacities, dependent upon the micropore surface area. Greater adsorption capacities can be achieved at high pressure than for chemical adsorbents. Regeneration has been demonstrated by both thermal and pressure swing techniques. Thermal swing regeneration has excellent potential in that over two thirds of the adsorption capacity can be regenerated whilst retaining pressure, therefore saving on the high energy penalties associated with re-compression of the gas. Both techniques offer good adsorption, and potential advantages over the current solvent absorption systems. The high pressure AC adsorbents are advantageous due to their ease of regeneration and potential to keep CO₂ at high pressures, thus avoiding energy penalty associated with re-compression.

5. Acknowledgments

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6. References

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