

Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO₂ Capture Project

**Capture and Separation of Carbon Dioxide
from Combustion Sources**

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Chapter 8

REMOVAL OF CO₂ FROM LOW PRESSURE FLUE GAS STREAMS USING CARBON FIBRE COMPOSITE MOLECULAR SIEVES AND ELECTRIC SWING ADSORPTION

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ABSTRACT

A novel separation technology based on electric potential field desorption of CO₂ from a carbon fibre composite adsorbent was proposed by the Carbon Materials Technology Group at Oak Ridge National Laboratory. This paper describes the experimental work and results from laboratory testing of the concept by the CCP Post-Combustion Technology Team. It was determined that the desorption step was controlled by surface heating of the composite adsorbent rather than a change in surface potential so originally believed. Electric power demands would make commercial application at the required scale uneconomic.

INTRODUCTION

The CCP contracted with the Carbon Materials Technology Group of Oak Ridge National Laboratory to evaluate the performance of carbon fibre composite molecular sieve (CFCMS) for the removal of CO₂ from industrial flue gas streams containing low quantities (3–10 mol%) of CO₂ at low (0.7 Barg) pressure.

CFCMS is a monolithic adsorbent carbon material composed of petroleum pitch-derived carbon fibre and a phenolic resin-derived carbon binder. Because of its unique construction, CFCMS is electrically conductive which facilitates rapid desorption of adsorbed species upon application of a low voltage, hence “Electric Swing Adsorption”. This desorption mechanism is not fully understood. It is postulated that the application of a low voltage generates a current flow, which disrupts the weak “Van der Waals” forces between the carbon adsorbent and the adsorbed species, releasing the latter.

This chapter describes the results from laboratory scale tests conducted for the CCP during the second and fourth quarters of 2002. The gas composition selected for the study was 3 mol% CO₂, 14.3 mol% O₂ and 82.7 mol% N₂. This is a typical exhaust gas composition from an industrial gas turbine fired on natural gas.

EXPERIMENTAL

Dynamic CO₂ Adsorption Testing Procedure

CFCMS billets were mounted in a test cell according to the schematic shown in Figure 1. Two test billets were produced (24.8% and 30.1 wt% burn-off). The test data reported below relate to the 24.8 wt% burn-off case.

Each cell was prepared by machining the CFCMS billet so that electrodes can be attached to it in order to power the cell during regeneration. The design is such that the feed gas has a mixing chamber both at the entrance to and exit from the cylindrical cell. The electrodes and other required mountings were shrunk-wrapped onto the cell to form an airtight system. The cell was then mounted into the modified gas flow loop.

Abbreviations: CFCMS, Carbon fibre composite molecular sieve; ESA, Electric swing adsorption; ORNL, Oak Ridge National Laboratory.

Flow through the cell can be reversed. There is a by-pass that carries the feed gas directly to the sampling system, which consists of a real-time mass spectrometer and a real-time CO₂ analyser. The gas is then passed through the cell and into the sampling system. The flow rate in and out of the cell and the pressure drop across it are measured. The feed gas temperature, the temperatures one inch into either end of the cell, and the temperature on the outside of the cell, were all recorded. The feed gas pressure was set at 10 psig.

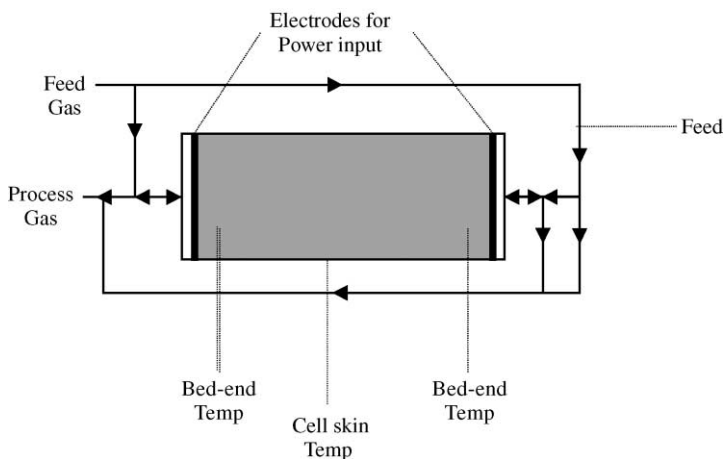


Figure 1: Schematic of the CFCMS cell set-up.

To initiate a breakthrough run, the feed gas flow was routed through the by-pass to the sampling system, where the feed gas composition was recorded. The feed gas was then swept clean from the by-pass piping with N₂, the carrier and regenerant gas. The feed gas was sent through the cell, which was saturated with N₂ after regeneration. The composition of the exit gas was recorded by the sampling system. All the other parameters such as temperatures and pressure drop across the cell were recorded. The dry gas mixture was run through the cell under set conditions and breakthrough curves were plotted for each run.

RESULTS AND DISCUSSION

Dynamic CO₂ Adsorption Testing

The data derived from test breakthrough curves are shown in Tables 1 and 2. Table 1 shows the data on the gas mixture adsorption for the CFCMS cell at 24.8% burn-off. In Table 2, the data describes the capacity of the beds as a function of temperature at a feed rate of 1 l/m and for two different electrode heating systems, the mesh and the ring.

TABLE 1
CO₂ ADSORPTION ON CFCMS—O#1 (24.8% BURN-OFF)

Feed rate (L/m)	Del P(psi)	L Scrubb	CO ₂ Ad (g)	g/g CFCMS	g/L CFCMS
1	0.02	26.0	1.42	0.0046	0.801
3	0.04	33.0	1.80	0.0058	1.017
5	0.05	36.5	1.99	0.0064	1.125
10	0.10	40.0	2.19	0.0070	1.232

Mass = 312.0 g, Volume = 1.773 L, Burn-off = 24.8%.

TABLE 2
CO₂ ADSORPTION CAPACITY VERSUS BED TEMPERATURE AT 1 L/M

Temp (°C)	Litres Scrub.	CO ₂ Ad (g)	g/g CFCMS	g/L CFCMS	Electrode type
22	29.8	1.63	0.0049	0.902	No heating
45	20.8	1.14	0.0034	0.629	Mesh
60	17.8	0.97	0.0029	0.539	Mesh
42	12.3	0.67	0.0020	0.372	Ring
60	7.0	0.38	0.0011	0.212	Ring

Regeneration of the CO₂-Saturated CFCMS Cell

Tables 3 and 4 correspond to the breakthrough curves in Figures 2 and 3. In Table 3 the actual high and low temperatures are shown; these are indicative of the temperature changes in the cell as the mass transfer zone moves through it. There is an initial temperature rise at the inlet end due to adsorption, followed by a temperature fall later as the CO₂ desorbs, with a simultaneous temperature rise at the outlet end due to adsorption there. Later, the temperature at the outlet end also falls as the CO₂ desorbs. When there is power input, it completely masks these effects at the outlet end. Table 4 only shows the difference between the high and low temperature in the cell.

TABLE 3
RAW DATA FROM THE BREAKTHROUGH CURVES

Feed (L/m)	Regen. (L/m)	Litres Scrubbed	Energy (kJ)	Litres N ₂ Regen.	High T (°C)	Low T (°C)
5	5	37.0	0.0	97.0	26	19
5	5	37.0	3.0	92.0	37	21
5	5	36.5	6.0	81.5	53	22

TABLE 4
DATA DERIVED FROM THE BREAKTHROUGH CURVES

Feed (L/m)	Regen. (L/m)	CO ₂ Ad (g)	g/g CFCMS	Energy (kJ)	L Scrubbed/ L N ₂ Regen.	Del T (°C)
5	5	3.02	0.0065	0.0	0.381	7
5	5	2.02	0.0065	3.0	0.402	16
5	5	1.99	0.0064	6.0	0.448	31

The tables show the interaction between nitrogen purge rate and energy input during regeneration. The amount of feed gas scrubbed, and hence the CO₂ adsorbed, is constant as expected, because the same feed rate of 5 l/m was used. However, the amount of N₂ required for complete regeneration decreases as energy input increases. Table 4 shows the ratio of gas scrubbed to regenerant gas increasing with power input. It also shows the increased temperature difference with power input.

This investigation has demonstrated that energy input enhances the regeneration of the cell and the recovery of the CO₂. No attempt has been made to optimise the process. For example, neither the effect of power input alone nor the optimum N₂ regenerant flow rate was investigated. Such comprehensive investigation will be required before a detailed process design is undertaken.

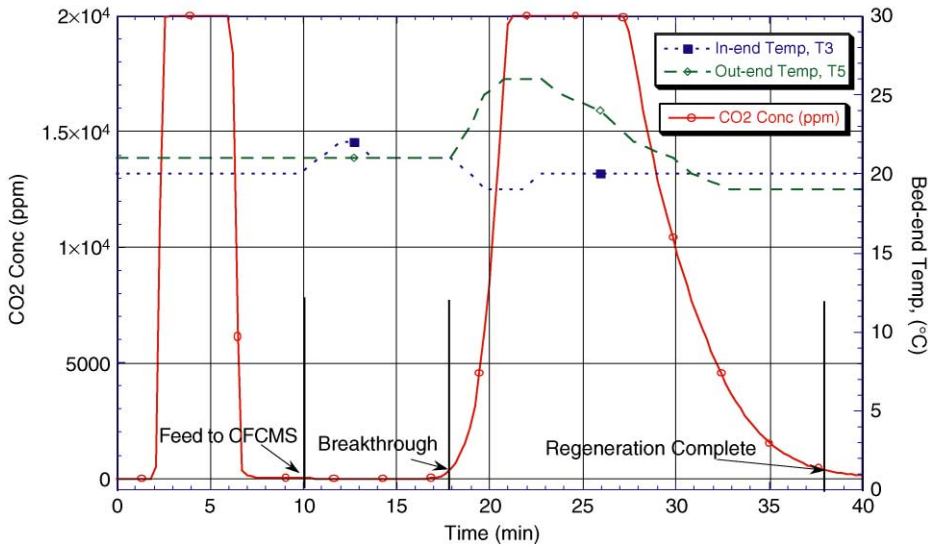


Figure 2: CFCMS 24.8% burn-off—breakthrough and regeneration at 5 l/m. (full concentration profile).

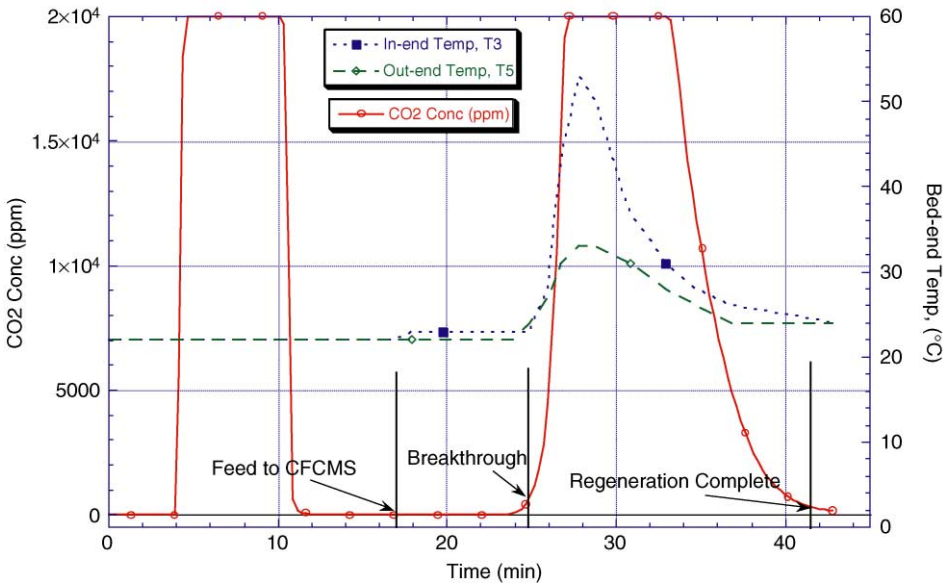


Figure 3: CFCMS 24.8% burn-off—breakthrough and regeneration at 5 l/m with energy input (5 v 10 A for 2 min) (full concentration profile).

CONCLUSIONS

Technical Highlights and Key CCP Interpretations

Adsorption cycle

- CFCMS CO₂ capacity—maximum achieved during testing 0.78 wt%. This may be enhanced to ca. 1.0 wt% assuming equilibrium loading is achieved. The low loading capacity is a direct consequence of the low CO₂ partial pressure in the feed gas.
- CFCMS capacity for CO₂ is reduced by the presence of water in the feed gas, due to competitive adsorption. A reduction of 7% (versus dry gas capacity) was noted during testing. Stabilisation was achieved after only a couple of adsorption cycles.
- CFCMS capacity is a strong function of operating temperature. Adsorption temperatures less than 30 °C are likely to be required for industrial scale units.
- Cycle times between 8 and 11 min were observed for adsorption during the laboratory testing.

Desorption cycle

- The gas analyser used for the tests had an upper range limit of 20,000 ppmv CO₂. The initial phase of the regeneration cycle could not be interpreted clearly. The “Electric Swing effect” was not observed directly. Nonetheless, it was clear that average CO₂ production during the peak evolution period was 15–20% higher when the “Electric Swing effect” was applied.
- The manner in which the power was applied during desorption step leads to the creation of a temperature spike within the CFCMS bed, such that it was not clear whether “Electric Swing” or “Resistive Heating” was primarily responsible for the increased CO₂ evolution rate.
- The laboratory regeneration technique utilised purge gas to create low CO₂ partial pressures during the desorption step. This approach cannot be used commercially, since it reverses the separation achieved by the process. A vacuum desorption system will be required to create low CO₂ partial pressures of around 5 kPa abs.
- The process clearly relies to some extent upon “Pressure Swing” effects to aid desorption.
- Cycle times between 15 and 40 min were observed for desorption during the laboratory testing. Around 65% of the absorbed CO₂ was evolved during the peak period, which varied over the range 6–14 min across the test programme, i.e. the first one-third of the full desorption cycle.
- When the “Electric Swing effect” was applied, this increased to about 70% of the adsorbed CO₂.
- Because of the limitations of the analytical instrument, it is not possible to say what the actual CO₂ evolution profile looked like during the peak period. Only the average figures can be deduced.
- Feed gas velocities and evolution rates are quite low across the range of tests conducted. The pressure drops are commensurately low. For industrial scale applications CFCMS open flow area and pressure drop are likely to be critical.

Industrial scale-up

The CCP sponsored two brief studies looking at the scale-up of the ORNL study results and applying these at industrial scale. Kvaerner undertook a review of the engineering issues that would have to be addressed, while the CCP reviewed the likely costs of an ESA unit versus a more traditional Amine removal unit based around the Fluor Econamine® process. The Kvaerner study highlighted the following issues:

- Short cycle times could be employed because of CO₂'s rapid adsorption onto carbon based substances.
- Cycle times as low as 2 s are feasible. Rapid opening/closing valves are available, but not at the scale of operation required. Engineering development is a likely requirement.
- Adsorber/Desorber vessel design will have to address both pressure drop limitations and good gas distribution requirements through the CFCMS bed.

CCP economic evaluation

An in-house CCP assessment was made for the likely capital cost for an ESA unit sized to capture 200,000 tonnes/annum of two LM2500 gas turbine exhausts. This basis was taken from an earlier BP study based on an Alaska scenario (not the CCP Alaska baseline) where a conventional Amine process was employed as the capture unit. The ESA process scheme is depicted in Figure 4.

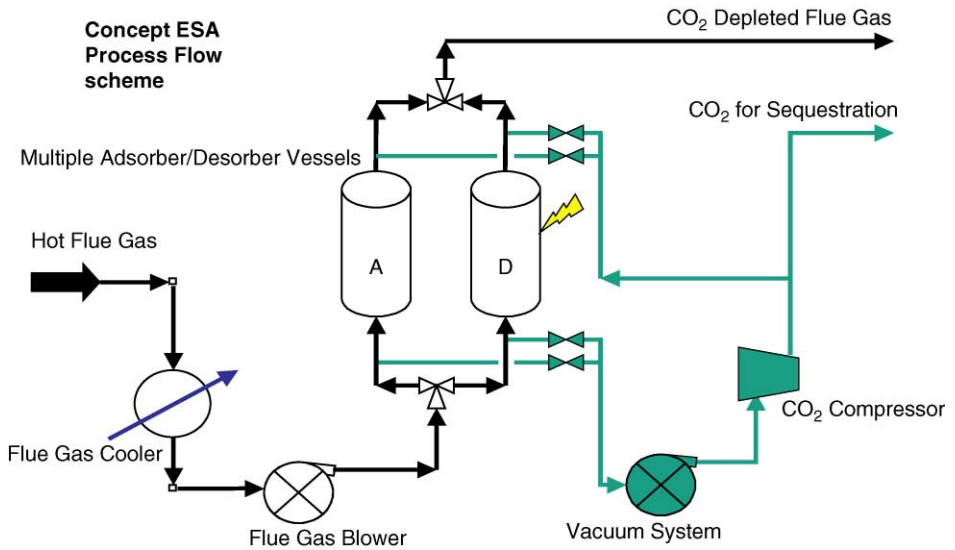


Figure 4: Conceptual electrical swing adsorption industrial process design.

Process assumptions and conditions for this evaluation were:

- 10 min adsorption and 10 min desorption/purge cycle times. This was based on observed times for the adsorption step, with desorption step time chosen to reflect that two-thirds of the CO₂ evolution occurs during the first one-third of the observed cycle time. This leads to an assumption of a delta loading of CO₂ on CFCMS of 0.65 wt% (based on a maximum loading of 1.0 wt%).
- Vacuum system capable of producing a pressure of 5 kPa in the desorber vessels.
- Flue gas cooler reducing flue gas temperature to 25 °C.
- Flue gas blower to compensate for CFCMS pressure drop.
- Compression to 220 barg for sequestration.

Conclusions from the evaluation are as follows.

Unit capital cost

- The number and size of adsorber vessels and the requirement to design for low (vacuum) pressures will result in high equipment cost. Furthermore, the number and size of switching valves combined with the complex arrangements required for power distribution are likely to add a further significant cost burden.
- The volumes of Carbon material are large (600 metric tonnes) and will add significant cost.
- Low gas velocities will be necessary if pressure loss is to be minimised. Based upon current observed pressure loss through CFCMS, a flue gas blower has been utilised for the economic evaluation. A pressure loss of 25 kPa has been assumed. Blower capital and operating cost is high because of the need to compress the entire flue gas stream.
- The vacuum pumping system will be a significant cost item.

Operating cost. A brief review of operating costs for the two approaches suggests that ESA will display higher costs due to its high import power requirement (for electrical regeneration). However, it should be noted that the laboratory experiments conducted by ORNL did not attempt to optimise, or even minimise

the power required for regeneration. This conclusion may not be reasonable without further work to confirm minimum (optimised) power needs for ESA.

The performance of the ESA process within the three CCP Post Combustion baseline scenarios is not expected to favour its use over current amine based technologies given its likely higher capital and operating costs.

RECOMMENDATIONS

Some rather fundamental technical issues need addressing before it is likely to compete with and/or better the performance of conventional amine systems in a Post Combustion CO₂ capture scenario:

- The low CFCMS loading;
- The “Electric Swing effect”—is it a real effect or is resistive heating the key mechanism.
- The impact of other gas components (water, NO_x, SO_x, etc.).
- Cycle pressure drop and its influence on cycle time (particularly desorption).
- Power requirements for desorption, which have clearly not been optimised here.

The CCP does not expect ESA technology to achieve CCP goals for reduced cost of CO₂ capture in Post Combustion scenarios, based upon its current stage of development. ESA technology is likely to be better suited to high-pressure applications where concentration in feed gas is high (high partial pressure). In such environments CFCMS loadings will be higher, vacuum assisted desorption will be unnecessary and the impact of CFCMS pressure loss can be more readily managed within the cyclic operation.