

## CO<sub>2</sub> Removal From Gas Streams Using a Carbon Fiber Composite Molecular Sieve

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### Abstract

*A novel adsorbent carbon monolith has been developed at Oak Ridge National Laboratory. The monolith is fabricated from isotropic-pitch-derived carbon fibers and powdered phenolic resin via a slurry molding process. The resultant green-form is dried, cured, and carbonized to convert the phenolic resin to carbon, and then activated to develop a connected network of micropores within the carbon fibers and resin-derived carbon binder. The monolith is also macroporous, exhibiting large (>50 μm) pores between the fibers. The resultant open structure allows the free flow of fluids through the monoliths such that gases can reach the micropores where they may be selectively adsorbed.*

*This novel adsorbent has been named a “carbon fiber composite molecular sieve” (CFCMS). Several separations have been demonstrated such as the separation of hydrogen from experimental gas mixtures containing H<sub>2</sub> and H<sub>2</sub>S or H<sub>2</sub> and CO<sub>2</sub>; the separation of CO<sub>2</sub> from CH<sub>4</sub>; the separation of CO<sub>2</sub> from air; and the separation of CO<sub>2</sub>, CO, H<sub>2</sub>S, and H<sub>2</sub>O from a variety of proprietary gas mixtures. The CFCMS is being investigated as a CO<sub>2</sub> separation and capture device in carbon mitigation strategies for natural gas processing, fuel cells, and gas turbines.*

*The monolithic material is rigid and strong, resistant to attrition and dusting, and because of its continuous carbon skeletal structure, electrically conductive. An adsorbed gas may be quickly and efficiently desorbed by the passage of an electric current, thereby allowing for a low-energy, electrical-swing separation system. It is possible to regenerate the carbon monoliths in the absence of a temperature increase, potentially reducing swing cycle times and improving separation efficiency.*

*The structure and properties of the adsorbent CFCMS monoliths are reported. Some information on the experimental apparatus is provided. Breakthrough plots and performance data for CO<sub>2</sub> separation and capture are presented, and the electrical swing adsorption process is discussed.*

## 1. Introduction

There is a great need for a versatile (i.e., applicable to a wide range of process conditions), effective, and regenerable CO<sub>2</sub> separation and capture device that is cost effective, produces minimal waste, and is readily adaptable to a variety of carbon sequestration schemes. Separation and capture of CO<sub>2</sub> has been identified in numerous forums as a critical issue for sequestration of carbon as a carbon emission mitigation option. An innovative concept using an activated carbon adsorbent called a carbon fiber composite molecular sieve (CFCMS) is being investigated at the Oak Ridge National Laboratory (ORNL) and at other laboratories around the world. The CFCMS has distinct adsorption-capacity and adsorption-kinetics advantages over conventional granular activated carbons.

The CFCMS is a monolithic carbon adsorbent material composed of petroleum-derived isotropic pitch carbon fibers and phenolic-resin-derived carbon binder. The material was developed jointly by ORNL and the University of Kentucky Center for Applied Energy Research. High micropore volumes (0.5–1.0 cm<sup>3</sup>/g) and BET surface areas (1000–2000 m<sup>2</sup>/g) are routinely attained in this material. In addition, the monoliths have an open structure that allows the free flow of fluids through the material (see Fig. 1). The CFCMS has been shown to be highly efficacious in the adsorption of polar molecules and for some flat nonpolar molecules, such as CO<sub>2</sub> (variants of the CFCMS have an affinity for other nonpolar molecules, such as CH<sub>4</sub>).



Fig. 1. Micrograph of the CFCMS showing the open structure of the material.

Moreover, the continuous nature of the monolith's structure imparts electrical conductivity to the material. Advantage has been taken of this property by ORNL to develop a novel desorption process, which has been named "electrical swing adsorption" (ESA). On saturation of the CFCMS with, for example, CO<sub>2</sub>, immediate desorption of perhaps 90 to 95% of the adsorbed gas can be accomplished by application of a low voltage across the adsorbent. There are many important operational implications of this desorption process. The system pressure and temperature do not have to be altered as in other parametric swing processes such as pressure swing adsorption (PSA) or thermal swing adsorption (TSA). The ESA process is extremely fast in comparison to PSA and TSA. It is an inherently low energy process compared to PSA and TSA. All of these features suggest a great deal of system and operational simplicity and indicate that CFCMS and the ESA technique may be the basis of a new unit operation system for energy and environmentally relevant separations.

The manufacture of CFCMS, characterizations of its pore structure, and its physical properties, as well as adsorption data for CO<sub>2</sub> are reported here. The novel ESA process is discussed, and breakthrough experimental data are presented. The experimental ESA system that is being used to acquire process-relevant separation data is described, and experimental data demonstrating the efficacy of the material under a variety of system conditions are presented.

## **2. Objective**

The objective of the work described here was to demonstrate the performance potential of CFCMS for CO<sub>2</sub> separation and capture. This broad objective imposed the condition for the development of a novel processing as well as the need for a test system with broad flexibility for simulation of systems of interest. It was not intended that this work would result in an optimized material for any specific system application. Rather, it was intended that this work would establish the feasibility of CFCMS as an adsorbent and would help to define further work on material optimization and system integration.

This work was also intended to develop all processing parameters required to consistently produce CFCMS and to identify or develop the necessary characterization methods required to demonstrate consistency of quality. Furthermore, there was a need to develop a laboratory test system that could be used to simulate conditions of systems of interest in a carbon sequestration scenario.

## **3. Approach and Technology Description**

The CFCMS material utilized in this work was manufactured via the slurry process [1,2] outlined in Fig. 2. Isotropic-pitch-derived carbon fibers are mixed with powdered phenolic resin and water to form a slurry. The slurry is transferred to a molding tank, and the water is drawn through a screen under vacuum. A schematic diagram of the molding apparatus is also shown in Fig. 2. The resultant green artifact is dried in air at 60°C and stripped from the mold screen. The composite is cured at ≈ 150°C prior to carbonization

at 650°C in an inert gas. The final synthesis stage involves activation of the composite in moisture saturated He or in dry CO<sub>2</sub>.

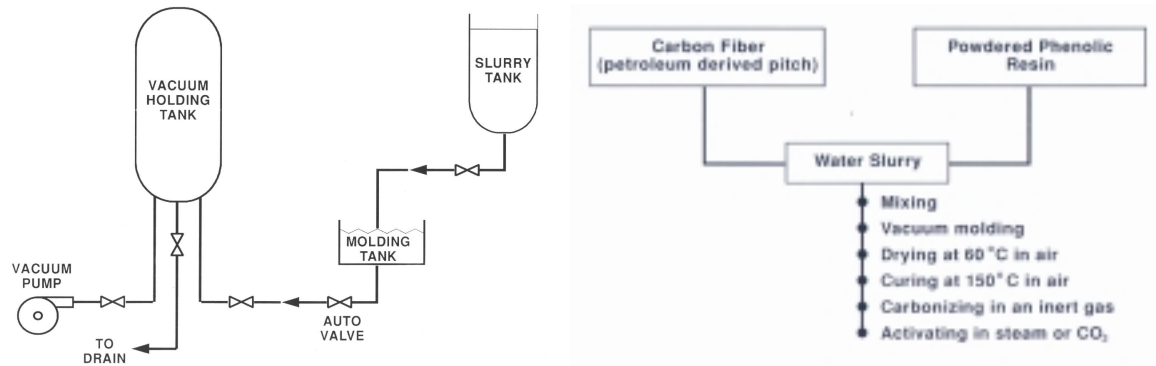


Fig.2. Schematic diagram of the slurry molding apparatus (left) and the synthesis route (right) for the CFCMS.

The thermal conductivity of CFCMS was determined by using the thermal flash technique. A sample was illuminated on one face with a laser, and the temperature of the other face was monitored with an infrared detector. The thermal diffusivity was calculated from the thermal transient; and the thermal conductivity was then determined from Eq. (1):

$$K = \alpha \cdot \rho \cdot C_p, \quad (1)$$

where  $\alpha$  is the thermal diffusivity at the test temperature,  $\rho$  is the bulk density, and  $C_p$  is the specific heat at the test temperature.

Pore structure characterization of CFCMS was conducted with a Quantichrome Autosorb-1 instrument to measure N<sub>2</sub> adsorption isotherms at 77 K. Parameters such as the BET surface area, Dubinin-Astakhov (DA) and Dubinin-Radushkevich (DR) micropore size and micropore volume, and the t-method micropore volume are determined from the isotherms. Meso- and macro-pore size distributions were obtained by using mercury intrusion analysis, optical microscopy, and scanning electron microscopy (SEM) examination.

A gas flow loop was constructed to determine and verify the performance characteristics of the CFCMS. A schematic diagram of the gas flow loop is shown in Fig. 3 and a general view of the loop is shown in Fig. 4. The gas flow loop has a capacity of about 50 L/h and can be operated up to 1000 psi. The gas flow loop is highly instrumented and provides a wealth of data for determination of adsorption capacity and adsorption kinetics as well as data that are helping to elucidate the mechanisms of adsorption and desorption associated with CFCMS.

In these experiments, certified gas mixtures are typically used although the system has the capability to mix pure gases to produce desired mixtures for separation.

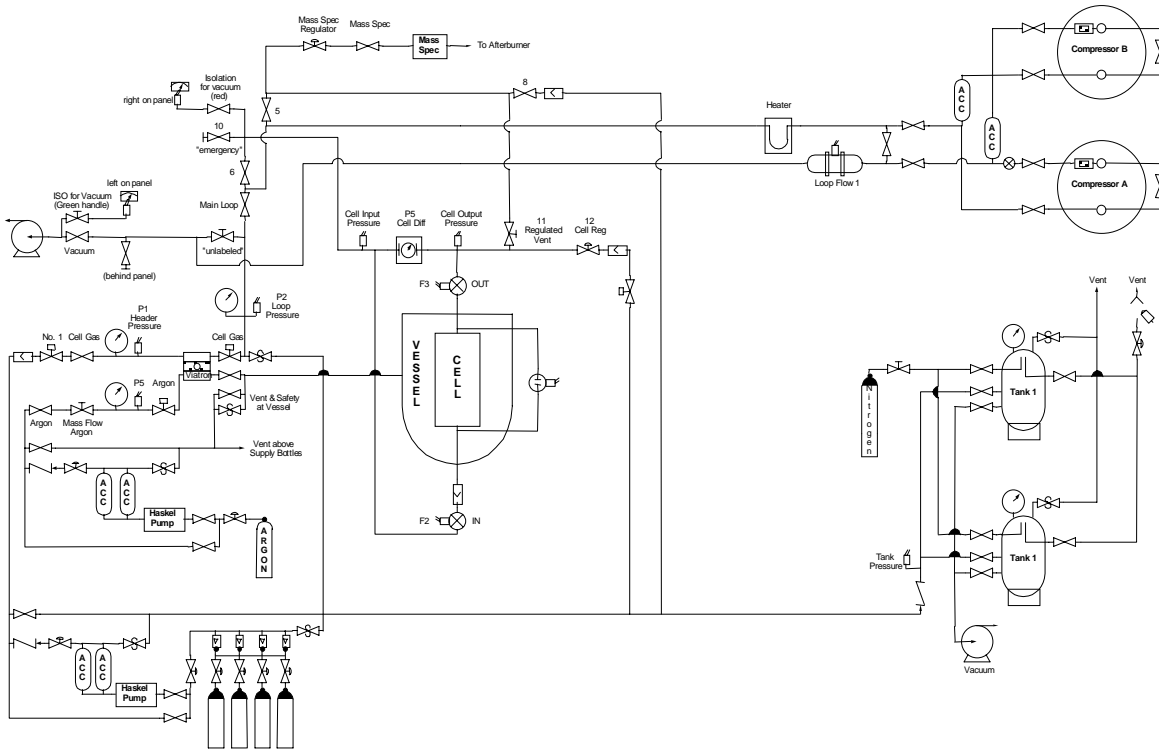


Fig. 3. Schematic diagram of the modified gas flow loop.



Fig. 4. General view of the gas flow loop.



A side stream is led from the loop and passes through an adsorption (Fig. 5) containing the activated CFCMS. Copper head ring connectors are attached at each end of the CFCMS, and electrical connections are led to a low-voltage (0–8 V DC) power supply. Gas pressure, temperature, and flow rates in the loop and adsorption cell are monitored and recorded. A sample of the cell outlet gas is led to a mass spectrometer or gas detector so that gas concentrations in the exit may be detected. The ESA subsystem of the loop imparts the ability to stimulate desorption of CO<sub>2</sub> from the CFCMS sample.

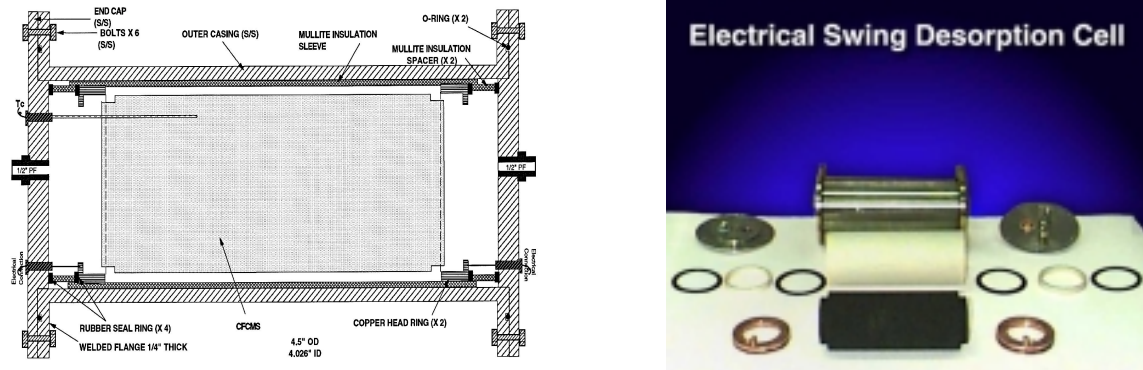


Fig. 5. Adsorption cell schematic (left) and exploded view of components (right).

## 4. Results and Discussion

### 4.1 Structure

The macrostructure and porosity of CFCMS are illustrated in Fig. 6. The carbon fibers are bonded at their contact points creating an open and permeable structure. Macroscopic voids in the structure are approximately 50–250 μm. Fiber lengths are 50–1000 μm, and diameters are 12–16 μm. The N<sub>2</sub> isotherm for CFCMS in Fig. 7 exhibits the characteristics of a Type I isotherm (i.e., typical of a microporous solid).

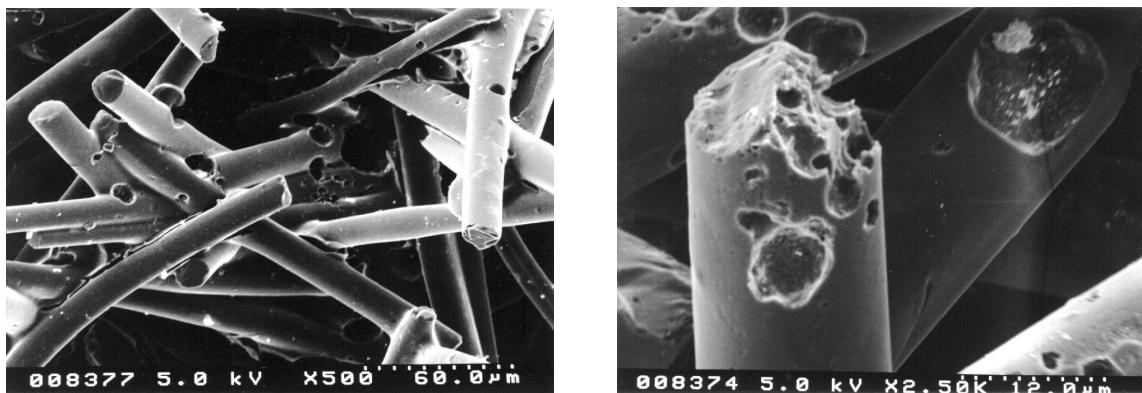


Fig. 6. The microstructure of activated CFCMS (left) and a scanning electron micrograph of an activated carbon fiber from a CFCMS sample.

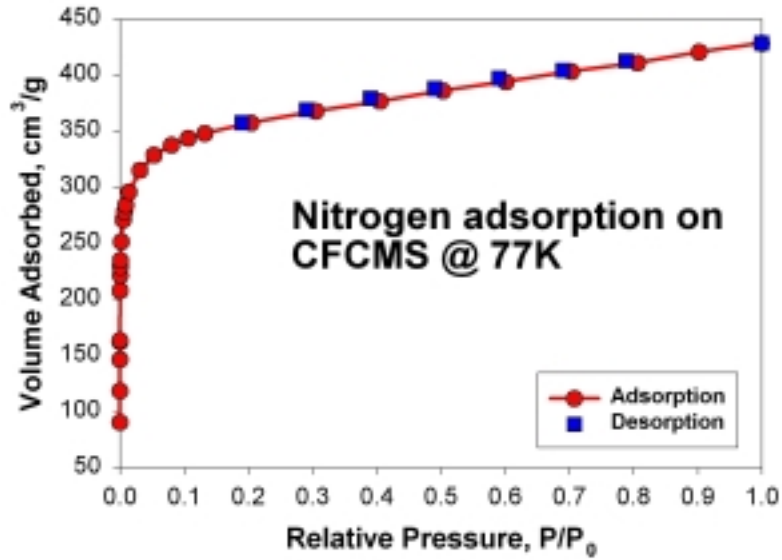


Fig. 7. Type I isotherm of CFCMS, which is indicative of a microporous solid.

#### 4.2 Thermal Conductivity

The thermal conductivity of CFCMS monoliths (Fig. 8) is several times higher than that of packed beds of conventional granular or powdered activated carbon. Typically, the thermal conductivity of CFCMS is anisotropic, the value parallel to the fibers being three to four times greater than that perpendicular to the fibers [2]. The thermal conductivity of an adsorbent has significance in gas-separation and storage applications, where large temperature gradients can be established during adsorption and desorption cycles. These temperature gradients can increase the process cycle time and hence reduce the overall efficiency of the separation process. Therefore, the increased thermal conductivity of CFCMS gives it a distinct advantage over existing activated carbons.

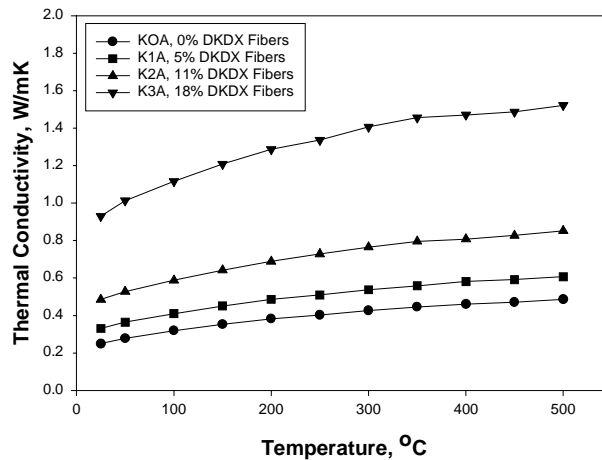


Fig. 8. Thermal conductivity of typical CFCMS samples.

In addition to being thermally conductive, the CFCMS monoliths are, by virtue of their continuous carbon skeleton, electrically conductive. This feature offers the potential of a separation system based on electrically induced desorption [1,2].

#### 4.3 Micropore Characterization Data

Micropore structure data determined from nitrogen adsorption isotherms on steam activated CFCMS with bulk densities in the range of 0.15 to 0.30 g/cm<sup>3</sup> are reported in Table 1. Similar data for higher-density CFCMS samples (0.4 to 0.8 g/cm<sup>3</sup>) activated with CO<sub>2</sub> are reported in Table 2.

Table 1. Micropore characterization data for steam activated CFCMS at different burn-off levels

Burn-off (%)	BET surface area (m <sup>2</sup> /g)	Micropore pore volume [t-method] (cm <sup>3</sup> /g)	Mean DA micropore radius (nm)
9	512	0.21	0.68
18	1152	0.40	0.71
27	1962	0.65	0.75
36	1367	0.41	0.79

Table 2. Micropore characterization data for CO<sub>2</sub> activated CFCMS at different burn-off levels

Burn-off (%)	BET surface area (m <sup>2</sup> /g)	DR micropore pore volume (cm <sup>3</sup> /g)	Mean DR micropore radius (nm)
18	961	0.36	1.60
38	1608	0.60	2.00
56	2552	0.88	2.61
66	2660	0.92	2.73

The data in Tables 1 and 2 clearly demonstrate that CFCMS can be activated to high BET surface areas and micropore volumes and that for a given burn-off the surface area and micropore volume are larger for the CO<sub>2</sub>-activated CFCMS. Moreover, these data suggest an ability to tailor the microstructure of CFCMS and thus its adsorbent characteristics.

#### 4.4 Adsorption and Separation Data

High-pressure adsorption isotherms for CO<sub>2</sub> and CH<sub>4</sub> are given for two samples of activated CFCMS in Fig. 9. The data in Fig. 9 suggest that CFCMS might provide an effective medium for the separation of CO<sub>2</sub> from gas mixtures containing CO<sub>2</sub> and CH<sub>4</sub>.



A breakthrough apparatus [1] was used to evaluate the suitability of CFCMS for this separation. A typical breakthrough plot for a CO<sub>2</sub>/CH<sub>4</sub> mixture is shown in Fig. 10. The specimen was initially heated by the passage of a low-voltage electric current through the

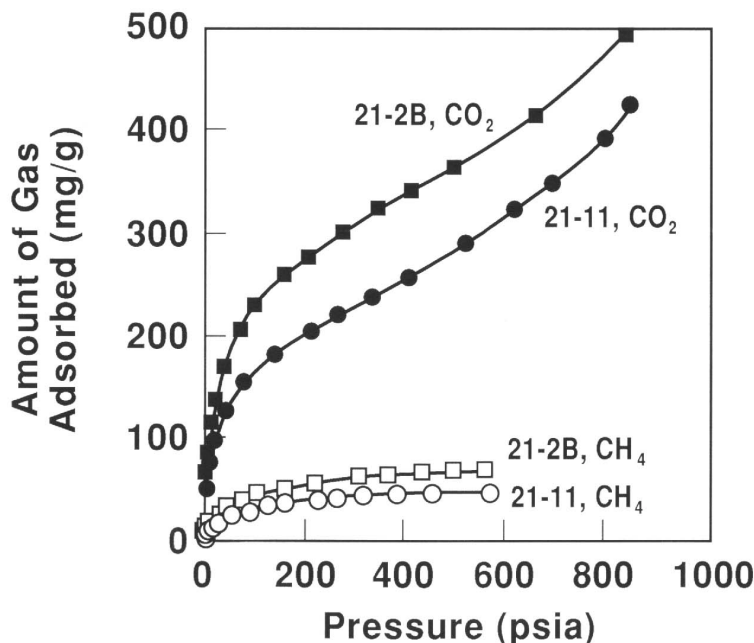


Fig. 9. High-pressure isotherms at 25°C of CO<sub>2</sub> and CH<sub>4</sub> for CFCMS monoliths.

material and the desorbed gases were driven out by a He purge. The input gas was then switched to a 2:1 mixture of CO<sub>2</sub>/CH<sub>4</sub> at a flow rate of 0.33 slpm. The outlet stream He concentration is seen to decrease to zero, and the CH<sub>4</sub> concentration increases rapidly (i.e., CH<sub>4</sub> breakthrough occurs). Adsorption of CO<sub>2</sub> occurs and therefore the concentration of CO<sub>2</sub> in the outlet gas stream remains low for a period of some 5 or 6 min, whereupon CO<sub>2</sub> breakthrough occurs. Adsorption capacity depends on the adsorbate temperature and partial pressure, but at ambient temperature and about 5 to 7 psig, the adsorption capacity of CFCMS is about 10 L of CO<sub>2</sub> per liter (bulk volume) of the CFCMS. The sample can be regenerated quickly and without any apparent temperature rise [1] by the passage of a low-voltage electric current.

The electrical regeneration of the CFCMS monolith is also illustrated in the H<sub>2</sub>/H<sub>2</sub>S breakthrough plot in Fig. 10. The breakthrough of the Ar and H<sub>2</sub> (not shown in Fig. 10) is almost instantaneous. However, the H<sub>2</sub>S is adsorbed on the CFCMS and does not break through for 18 min (Fig. 10). When the CFCMS is totally saturated with H<sub>2</sub>S (at about 42 minutes) the feed gas flow is stopped and an electrical voltage is applied to the sample. The H<sub>2</sub>S is immediately desorbed from the CFCMS, as indicated by the rapid rise in H<sub>2</sub>S concentration in the outlet gas stream. Complete desorption occurs over a period of 18 min, at which time the sample is completely regenerated.

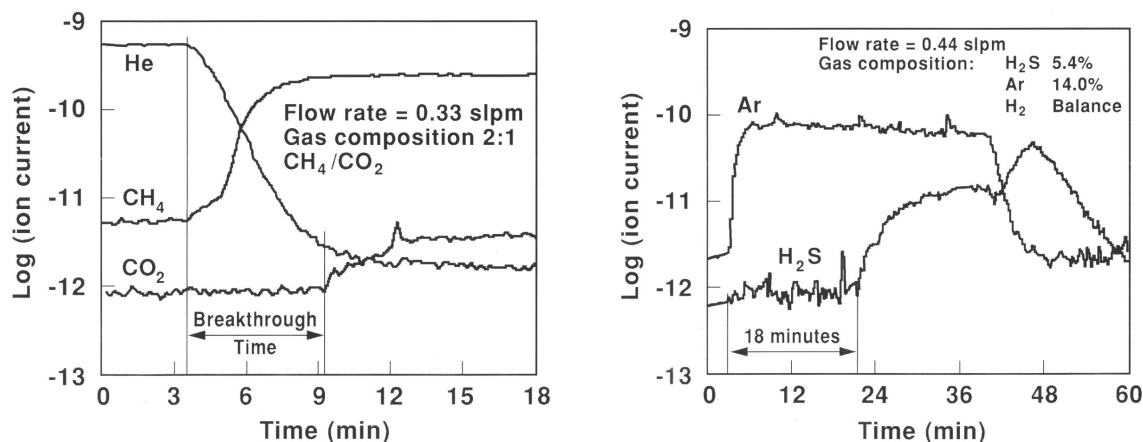


Fig. 10. A typical room temperature CO<sub>2</sub>/CH<sub>4</sub> breakthrough plot (left) for a CFCMS sample with 9% burn-off and a typical H<sub>2</sub>S breakthrough plot for a CFCMS monolith with 18% burnoff.

The combination of CFCMS adsorbent monoliths and the passage of a low voltage electrical current provides the basis for a new unit operation separation system wherein the regeneration of the adsorbent CFCMS is achieved by electrical swing rather than by pressure or thermal swing.

#### 4.5 Electrical Swing Adsorption

Figure 11 shows three adsorption/desorption cycles. In the first and second cycles (A and B in Fig. 11), desorption is caused by the combined effect of an applied voltage (1 v DC) and a He purge gas. In the third cycle (C in Fig. 11), desorption is caused only by the application of a He purge gas. It is evident from A, B, and C in Fig. 11 that desorption of the adsorbed CO<sub>2</sub> (regeneration) can be rapidly induced by the application of a direct current voltage. This is the basis of the ESA process. Bonding the fibers together with a carbon derived from a phenolic resin creates a continuous electrical circuit. The attractive forces, static electrical forces, or perhaps van der Waals forces between the carbon and the adsorbate are disrupted or perhaps reversed in polarity by the electric current. As a result, the adsorbed gases are released or repulsed from the micropore surfaces and desorption occurs.

In the ORNL tests, most of the adsorbed gas is released in the first few seconds of current flow, followed by a slower, probably diffusion-controlled release of the balance of the gas. There is no indication of gross thermal heating of the mass of carbon during the initial rapid desorption phase. Current must be allowed to flow for several minutes to cause heating of the mass of carbon. Any ohmic heating during this phase is obviously offset by the cooling on desorption of the gas. To a first approximation, the energy requirement for desorption of a gas from CFCMS is equal to the heat of adsorption of that gas. ORNL researchers have suggested that the kinetics of desorption are such that it may be desirable in an operating system to limit the desorption phase to the initial rapid desorption. This would minimize cycle time but would have some impact on individual

cycle adsorption capacity. In an adsorption-desorption cycle, the CFCMS would be saturated with CO<sub>2</sub> during the adsorption phase and approximately 80% of the CO<sub>2</sub> would be desorbed during the desorption phase, and then the cycle would be repeated. Such an approach would maximize the kinetics of the desorption phase and would minimize any ohmic heating of the CFCMS. On desorption of most (90 to 95%) of an adsorbed gas, continued electrical current flow causes heating of the monolith. This is shown in Fig. 12 where, in the absence of an adsorbed gas, the carbon is readily heated. However, as discussed previously [1], when an adsorbed gas is present on the CFCMS, the temperature is not observed to rise until virtually all of the adsorbed gas is desorbed.

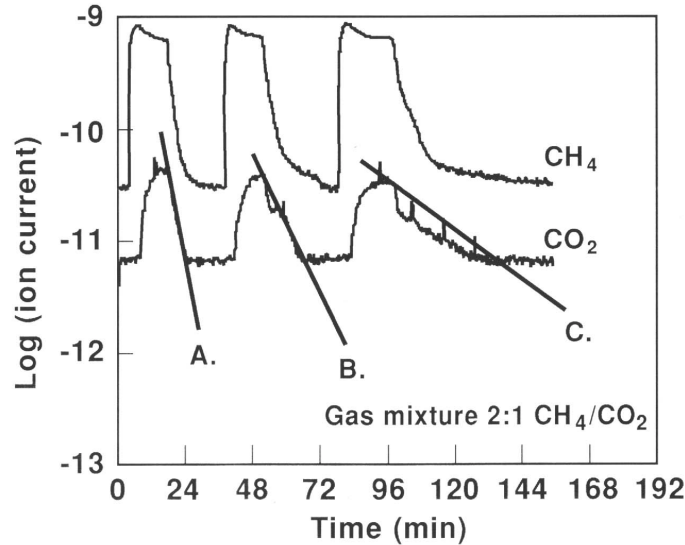


Fig. 11. CO<sub>2</sub>/CH<sub>4</sub> breakthrough plots for a CFCMS sample with 10% burn-off, showing the benefit of electrically enhanced desorption: A. 1 volt, He purge @ 0.4 slpm, B. 1 volt, He purge @ 0.06 slpm, and C. 0 volts, He purge @ 0.06 slpm.

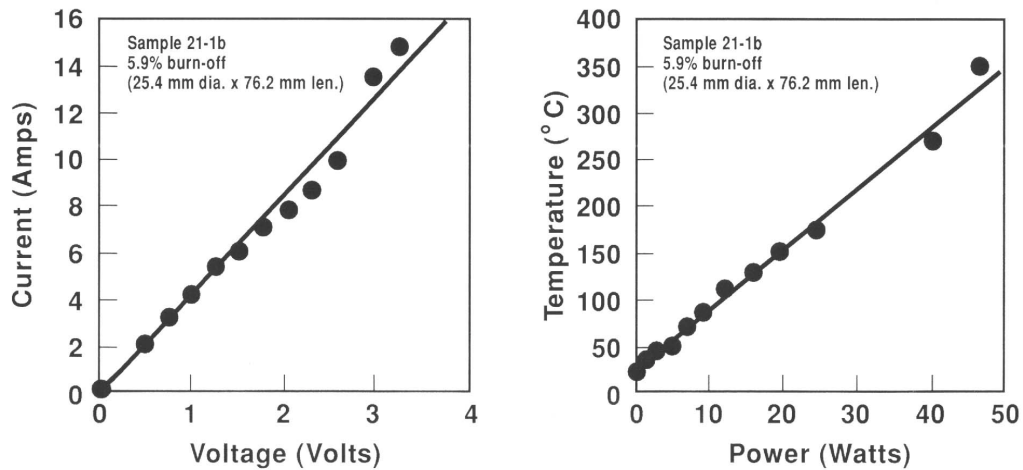


Fig. 12. The voltage-current relationship (left) and resistive heating curve (right) for a CFCMS monolith (18% burn-off, 2.5-cm diameter and 7.5-cm length).

## 4.6 ESA Test Programs

The new experimental gas flow loop and ESA test system were described in Section 3 of this paper. A more comprehensive description of the gas flow loop and ESA cell can be found elsewhere [3].

The experimental program currently being pursued in the gas flow loop/ESA system includes the separation of CO<sub>2</sub> from natural gas, the separation of CO<sub>2</sub> from gas turbine exhaust streams, the removal of impurities from H<sub>2</sub>-rich gas mixtures, and fuel and oxidant processing for fuel cell applications.

These test programs, complemented by earlier tests, are demonstrating the versatility of CFCMS over a wide range of process conditions. The CFCMS can reduce the concentration of CO<sub>2</sub> in air from its nominal value of about 350 ppm to much less than 50 ppm, and it can remove essentially all the CO<sub>2</sub> from natural gas containing about 33 % CO<sub>2</sub> by volume.

## 5. Conclusions

A novel carbon-fiber-based adsorbent monolith has been developed at ORNL. The adsorbent monolith referred to as CFCMS, shows considerable promise for the separation of gas mixtures, especially the removal of CO<sub>2</sub>. The monolithic material has numerous advantages over conventional powdered and granular activated carbons. For example, CFCMS is more robust and does not settle or suffer attrition during use. Thus, the formation of channels such as those that develop in packed granular beds cannot form. Moreover, the continuous carbon structure of the monoliths imparts improved thermal conductivity and makes the monoliths electrically conductive. The principle of an ESA system based upon the electrical conductivity of CFCMS and its gas-adsorption properties has been demonstrated. The efficacy of CFCMS for separating CO<sub>2</sub> from CH<sub>4</sub> and other gas mixtures has been demonstrated. A new ESA test apparatus has been constructed at ORNL, and a test program aimed at further developing CFCMS-ESA for gas separation is currently being pursued.

## 6. Research Needs

Although dramatic progress has been made in the development of CFCMS and the ESA process, there is a great need for R&D focused specifically on CO<sub>2</sub> separation and capture.

The operating systems that will be the focus of carbon mitigation strategies employing sequestration operate under dramatically different conditions. For example, gas turbine exhaust streams will have perhaps 3 to 10 % CO<sub>2</sub> at or near ambient pressure and at high temperatures. Both of these conditions militate against the preferred performance characteristics, but cooling and use of low-pressure drop versions of CFCMS appear to resolve this issue. Natural gas from production or storage sources is typically at very high pressure and at sufficiently low temperature that any additional cooling is not a

significant issue. These conditions are ideal for CFCMS and permit higher-density (and thus higher-pressure-drop versions of the material to be used. The wide variability of system conditions suggests the need for several variants of CFCMS, ranging primarily in macroporosity or pressure-drop requirements. Alternatively, there is simply a need for a development activity to determine the flexibility of the processing techniques to achieve a wide range of properties in CFCMS.

For CO<sub>2</sub> separation, development of modified activation procedures to render the CFCMS more or less selective for CO<sub>2</sub> is needed. This development should include system-configuration considerations such as series or parallel operation in the case of gas streams that contain other contaminants.

Although the capacity of the CFCMS for CO<sub>2</sub> is high, studies at ORNL indicate that different activation methods and degrees of activation may achieve dramatic differences in adsorption capacity. A systematic study of CFCMS to maximize its adsorptive capacity for CO<sub>2</sub> is needed. The use of statistical experimental design is a likely approach to address this issue.

The operational characteristics of different systems that may employ CFCMS for CO<sub>2</sub> separation and capture will likely impose varied operational approaches to the CFCMS-ESA system. For example, results at ORNL suggest that in some instances, it will be desirable from a kinetics perspective to limit desorption to perhaps 80% of the adsorbed gas, because there is a decline in desorption rate with time. Also, after prolonged current flow, there is some ohmic heating of the material and this would be detrimental to subsequent adsorption cycles. In other instances, particularly for streams with very low concentrations of CO<sub>2</sub>, it may be desirable to limit the time of adsorption because effectiveness of CFCMS is greatest during the initial phase of the adsorption step. Experiments to fully define the appropriate operational characteristics are needed.

A high-thermal-conductivity version of the CFCMS has been patented, but studies of its use in adsorption processes have been very limited. As noted in Section 4.2 of this paper, high thermal conductivity will be important in those systems where high thermal gradients may be established during the adsorption and desorption cycles. Studies of the efficacy of this high-thermal-conductivity material are needed.

A most important need for the development of CFCMS is the integration of CFCMS with sequestration technologies. Parameters such as the need for compression, cooling, and purity of CO<sub>2</sub>, are critical to the overall system; these needs will have a direct impact on the CFCMS-ESA system configuration.

All of the above R&D needs would be appropriately addressed in a single program directed toward the use and application of CFCMS-ESA as a CO<sub>2</sub> separation and capture method specifically for integration with carbon sequestration.

## 7. References

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