

PASSIVE CO₂ REMOVAL USING A CARBON FIBER

COMPOSITE MOLECULAR SIEVE

TIMOTHY D. BURCHELL AND RODDIE R. JUDKINS

DEC 08 1995

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831 USA

OSTI

Abstract - Manufacture and characterization of a carbon fiber composite molecular sieve (CFCMS), and its efficacy as a CO₂ gas adsorbent are reported. The CFCMS consists of an isotropic pitch derived carbon fiber and a phenolic resin derived carbon binder. Activation (selective gasification) of the CFCMS creates microporosity in the carbon fibers, yielding high micropore volumes ($>0.5 \text{ cm}^3/\text{g}$) and BET surface areas ($>1000 \text{ m}^2/\text{g}$). Moreover, the CFCMS material is a rigid, strong, monolith with an open structure that allows the free-flow of fluids through the material. This combination of properties provides an adsorbent material that has several distinct advantages over granular adsorbents in gas separation systems such as pressure swing adsorption (PSA) units. The results of our initial evaluations of the CO₂ adsorption capacity and kinetics of CFCMS are reported. The room temperature CO₂ adsorption capacity of CFCMS is $>120 \text{ mg}$ of CO₂ per g of CFCMS. A proposed project is described that targets the development, over a three-year period, of a demonstration separation system based on CFCMS for the removal of CO₂ from a flue gas slip stream at a coal-fired power plant. The proposed program would be conducted jointly with industrial and utility partners.

I. INTRODUCTION

Several options currently exist to reduce CO₂ emissions. Most activity and success have resulted by increasing efficiency in power generation and use, substitution of nonfossil energy sources such as nuclear energy for fossil sources, and the substitution of natural gas for coal [1]. All of these techniques have the attractive feature of limiting the amount of CO₂ produced. However, all have technical or societal limitations. Very substantial efficiency gains are predicted and are being realized in advanced coal-fueled power generation technologies such as pressurized fluidized bed combustors, integrated coal gasification combined cycles, and advanced steam cycles. Although improving the efficiency of fossil fuel use is probably the least expensive path to reducing CO₂ emissions, the practical efficiency limits for these technologies appear to be on the order of 50-55% on a higher heating value basis. Natural gas has a much lower carbon emission factor than does coal, i.e. moles of CO₂ emitted per unit of energy produced is much lower (about 60% as much) for natural gas than for coal. Natural gas systems are also considerably more efficient than corresponding coal systems, because of the increased energy usage of coal-handling compared to

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

natural gas and the requirement for pollution abatement equipment such as electrostatic precipitators for coal systems. Two major limitations exist for the substitution of natural gas for coal vis-a-vis reduction of carbon dioxide emissions. Resources of natural gas are much smaller than those of coal, and leakage of natural gas from production and transport may partially offset its advantage because methane has about thirty times the greenhouse effect of CO_2 . Nonfossil energy sources are currently poor competitors for new power generating capacity, although nuclear power certainly contributes significantly to overall power generation.

The strategy addressed here is to capture the CO_2 and concentrate it for utilization or disposal. Capture methods include growing forests to recycle carbon back into the biomass reservoir. This approach requires tremendous land area to be forested to offset a significant amount of total emissions. For example, offsetting the emissions of a 500 MWe coal-fired power plant operating at about 34% efficiency would require about 500 square miles of forest to be grown, assuming the forest fixes 2 tons of carbon per acre per year over the lifetime of the plant [2]. Other techniques proposed for the capture or removal of CO_2 include physical adsorption and chemical absorption (mostly by amine scrubbing), cycle modifications, and membrane separation. Scrubbing with monoethanolamine is the only (presently) commercially demonstrated process for scrubbing CO_2 from low pressure flue gas. However, it has several disadvantages; costs are high (perhaps \$39 to \$41/ton of CO_2); efficiency losses are great [perhaps a 35% (relative) reduction]; other acid gases must be removed prior to amine stripping, etc. [3,4]. Membrane systems are held in high regard, and inorganic, particularly ceramic, membranes offer the potential for high temperature, thus energy saving, removal. However, the deployment of these systems appears to lie several years in the future, at best. Thus, a passive and inexpensive approach to the issue of carbon dioxide capture is indicated. At Oak Ridge National Laboratory (ORNL), we are pursuing the development of a novel adsorbent called the carbon fiber composite molecular sieve (CFCMS) for a variety of gas separation and gas storage applications. Among these applications is the capture of CO_2 from coal fired generation plant exhaust streams.

The CFCMS is a monolithic activated carbon composed of petroleum pitch-derived carbon fiber and a phenolic resin-derived binder. This material is the subject of an invention by researchers at ORNL and the University of Kentucky Center for Applied Energy Research (UKCAER). Routinely, fiber microporosity with surface areas $> 1000 \text{ m}^2/\text{g}$ are obtained using pitch fibers. The CFCMS offers a highly adsorbent material with very little resistance to bulk gas flow. Experiments discussed herein suggest the CFCMS has a high affinity for CO_2 coupled with rapid adsorption and desorption compared to zeolites and conventional granular activated carbons. The monolithic CFCMS also allows certain equipment variations not possible with granular materials. It can be molded to almost any shape, i.e., shape is constrained only by the ability to fabricate molds, which appears to be minimal. The CFCMS can be machined by skilled operators using conventional tooling. These features permit the activated carbon to be formed to a desired shape to suit the process equipment constraints as opposed to the conventional filling of vertically oriented vessels with granular carbon. Granular carbon systems are also subject to attrition due to abrasive wear in service, and channeling of the gas being processed as a result of inhomogeneous packing in the beds. Use of the CFCMS would permit the employment of, for example, horizontally oriented vessels with controlled flow of the gas to be adsorbed through the adsorbent without risk of channeling and bypass flows. In use, we envision the system operation to be a sequence of adsorbing CO_2 by flowing it through the CFCMS, desorbing the CO_2 by thermal or pressure swings (for example), and compression of the desorbed gas as an interim containment method pending determination by others as to the desired storage or sequestration option [5].

An exploratory project is under way to demonstrate the efficacy of the CFCMS as a CO_2 capture material. A summary of the experiments conducted to date, the results of these experiments, analysis of the data vis-a-vis indications for successful CO_2 removal, and description of a plan for continued development, scale-up, and demonstration of this technology are presented in the following sections.

2. EXPERIMENTAL

The carbon fiber composite molecular sieve (CFCMS) material used in this study was fabricated using a process initially developed by the U. S. Department of Energy (USDOE) for the production of thermal insulators for NASA space missions [6]. The CFCMS synthesis route is illustrated in Fig.1. Isotropic pitch derived carbon fibers are mixed with powdered phenolic resin to form a water slurry. the slurry is transferred to a molding tank and the water drawn through a porous screen under vacuum. The resultant green artifact is dried, cured at 60°C in air, and stripped from the mold screen. The composite is cured at ~150°C in air prior to carbonization at 650°C in an inert gas. The final synthesis stage involves activation of the composite in steam or CO₂ in the temperature range 800-950°C.

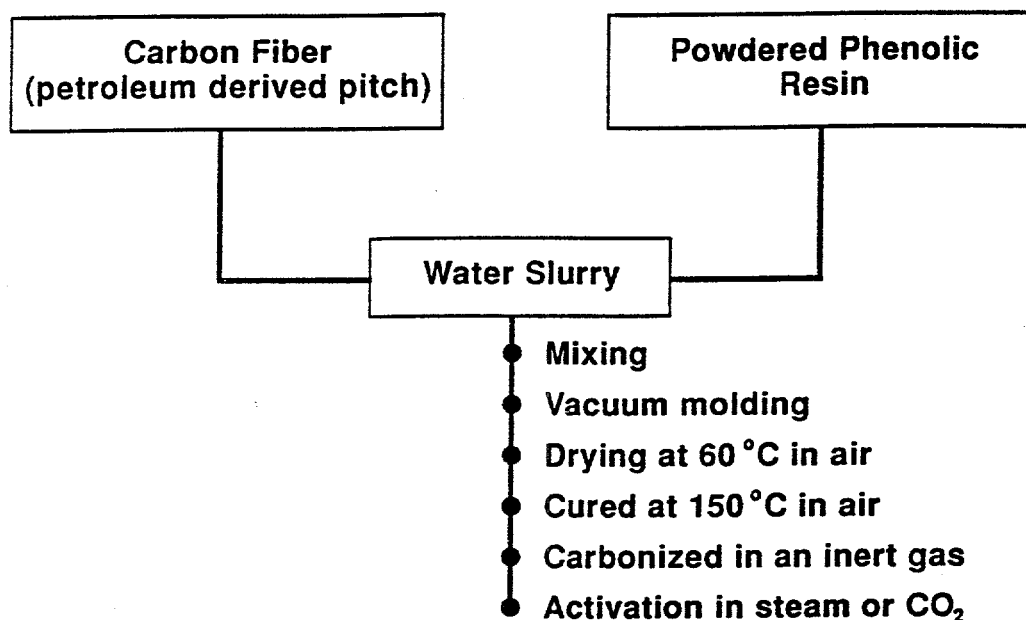


Fig. 1. The CFCMS synthesis route.

Porosity characterization was performed using nitrogen adsorption and mercury intrusion. Nitrogen adsorption isotherms were measured at 77 K using our Autosorb-1 instrument. Micropore size analysis used a variety of methods, including the Brunauer, Emmett, and Teller (BET) [7] method for surface area and the Dubinin-Redushkevich (DR) [8] method for micropore volume and micropore size. Additional micropore size estimates were obtained using the Hovarth-Kawazoe (HK) and Dubinin-Astakhov (DA) methods. Mesopore (2-50 nm) and macropore (>50 nm) size data were obtained using a Micromeritics Autopore II mercury intrusion apparatus over the pressure range vacuum (~10 μ m Hg) to 90,000 psia. Equilibration times of 10 and 60 seconds were used for the low and high pressure measurements, respectively.

CO₂ adsorption measurements were performed on a Mettler thermal microbalance. Three separate studies were undertaken. First, the CO₂ adsorption capacities of a series of CFCMS samples activated under different conditions were measured. CO₂ adsorption capacity was determined by placing a sample in the microbalance, evacuating and heating to 300°C to thoroughly outgas the sample. The balance chamber was then back-filled with CO₂ and the temperature swung from 25 to 100°C while recording the mass lost, and subsequently gained upon cooling to 25°C. Our second study utilized the CFCMS sample with the largest CO₂ capacity. The sample was outgassed at 300°C in vacuo on the balance and allowed to come to equilibrium at 25°C in flowing He. The balance chamber was then purged with CO₂ and the specimen mass gain recorded. Finally, the CO₂ adsorption as a function of CO₂ partial pressure at 25°C was determined by controlling the flow rates of both He and CO₂ following specimen outgassing at 300°C in He.

3. RESULTS AND DISCUSSION

Pore characterization

Typical bulk densities of our CFCMS material after carbonization are 0.3-0.4 g/cm³. The material comprises short carbon fibers of nominal length 400 μ m and diameter 10-20 μ m bonded to one another at their contact points. Mercury intrusion analysis indicated that the macro-voids between the fibers are typically in the size range 10-1000 μ m, an observation confirmed by SEM analysis [9]. The resultant open structure allows free flow of fluids through the material and ready access to the carbon fiber surface and microporosity.

Details of the CFCMS samples, their activation conditions, and analysis of their microporosity, are given in Table 1. The BET surface areas ranged from 281 to 1461 m²/g, and the mean micropore size (DR method) varied from 0.58 to 1.34 nm. Micropore volumes were in the range 0.1-0.73 cm³/g. The large surface area and micropore volumes are associated with porosity that develops in the carbon fibers during the activation (selective gasification) process. Moreover, the size range of the microporosity suggest the material should be capable of selectively adsorbing gases on the basis of molecular size and shape.

Table 1. Activation conditions and micropore characterization data.

Spec. Ident.	Activation Conditions				Micropore Analysis Data				
	Temp (°C)	Time (mins)	Agent	Burn-off (%)	BET Area (m ² /g)	Micropore Width (nm)			DR Pore Vol (cm ³ /g)
						HK	DA	DR	
160	800	30	H ₂ O	7	394	0.48	1.3	0.58	0.20
161A	950	10	CO ₂	6	292	0.48	1.8	1.21	0.13
161B	950	10	CO ₂	6	281	0.47	1.9	1.34	0.10
166	800	180	H ₂ O	17	762	0.48	1.48	0.75	0.39
167	800	360	H ₂ O	28	891	0.49	1.5	0.76	0.49
170	950	180	CO ₂	32	1132 1038	0.47	1.6	0.78 0.76	0.48
46	850	90	H ₂ O	28	1461	0.62	1.3	0.67	0.73

Carbon Dioxide Adsorption Studies

Six CFCMS samples and one granular coconut shell carbon (Fisher Scientific Co. 5-685-A, 6-14 mesh), were studied to determine their CO₂ adsorption capacities (Table 2). CFCMS sample 170 exhibited the largest CO₂ uptake (>10 mg of CO₂ per 100 mg of CFCMS). In comparison, the coconut shell carbon adsorbed 8.3 mg per 100 mg of sample. The CO₂ adsorption capacity of CFCMS is related to the micropore volume as shown in Fig. 2. The wt.% of CO₂ adsorbed increases with sample micropore volume, reaching peak adsorption capacity at micropore volumes ~0.5 cc/g. Figure 3 shows the CO₂ uptake as a function of the micropore size (DR method). The optimum pore size appears to be ~0.8 nm. Significantly, samples 161 and 160 showed the lowest CO₂ uptakes (6.9 and 7.8 wt.% respectively), yet possessed the largest and smallest mean micropore sizes (1.21 and 0.58 nm) respectively, suggesting a strong sensitivity of CO₂ adsorption to the mean micropore size.

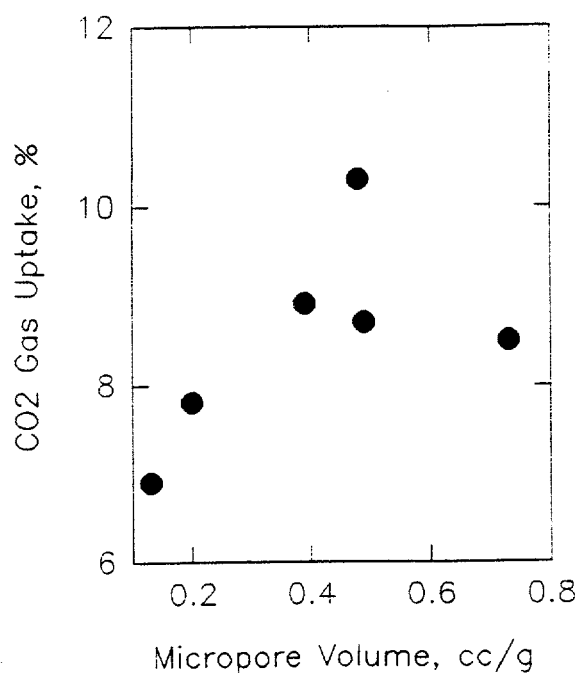


Fig. 2. The relationship between CO₂ uptake and micropore volume for CFCMS.

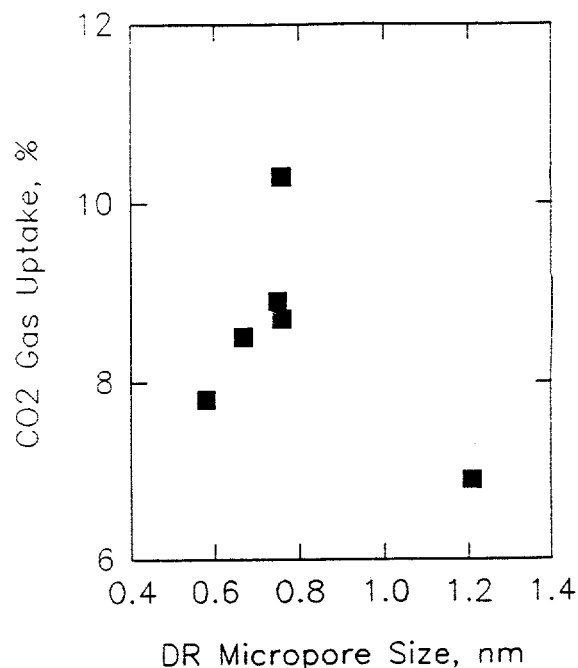


Fig. 3. The relationship between CO₂ uptake and mean micropore size for CFCMS.

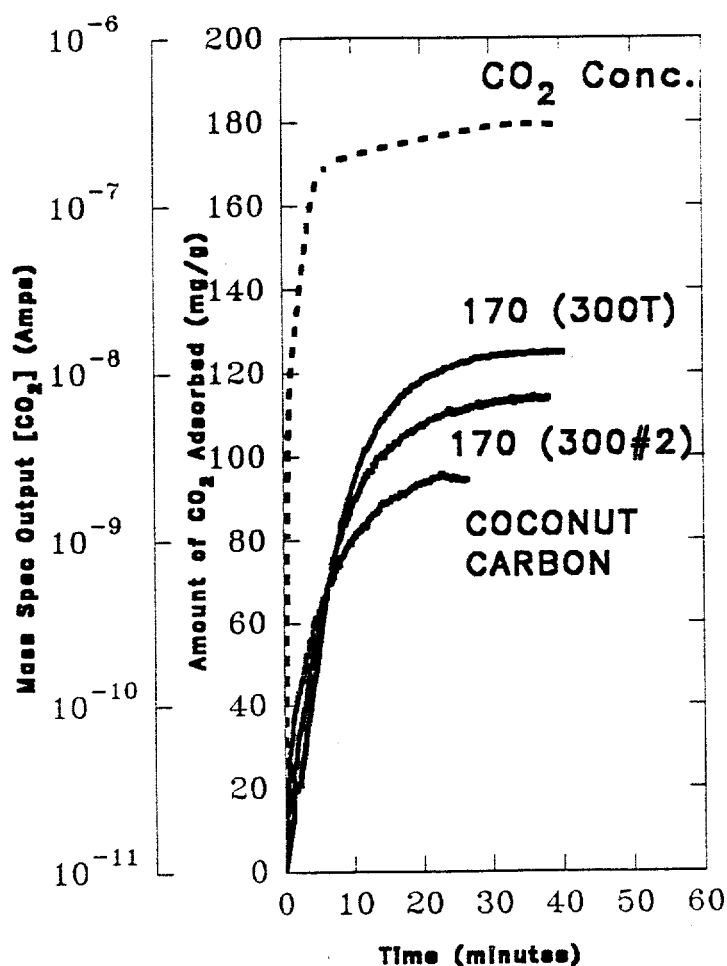


Fig. 4. CO₂ adsorption rates for CFCMS and coconut shell carbon at 25°C and 1 atm.

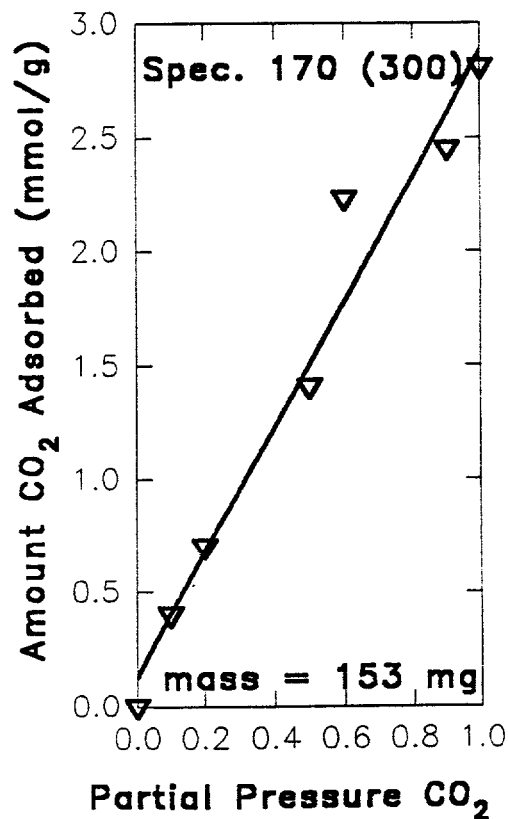


Fig. 5. Amount of CO₂ adsorbed as a function of CO₂ partial pressure (CO₂/He @ 25°C and 1 atm.).

Table 2. CO₂ uptake data and micropore data

Spec. Ident.	CO ₂ Uptake data				Micropore Analysis Data				
	Sample Mass (mg)	Wt% CO ₂ Uptake	Vol CO ₂ Ads. (cm ³)	Spec. CO ₂ Ads. Capacity (cm ³ /g)	BET Surf. Area (m ² /g)	Micropore Width (nm)			DR Pore Vol (cm ³ /g)
						HK	DA	DR	
160	89.50	7.8	3.95	44	394	0.48	1.3	0.58	0.20
161	72.45	6.9	2.53	35	292	0.48	1.8	1.21	0.13
166	89.95	8.9	4.05	45	762	0.48	1.5	0.75	0.39
167	92.27	8.7	4.04	44	891	0.49	1.5	0.76	0.49
170	74.89	10.3	3.9	52	1132	0.47	1.6	0.76	0.48
46	73.88	8.5	3.2	43	1461	0.62	1.3	0.67	0.73
Coconut shell carbon	90.22	8.3	3.8	42	168	0.5	1.6	-	-

CO₂ adsorption curves for two samples of CFCMS 170, and the coconut shell carbon are shown in Fig. 4. In Fig. 4, initially the CO₂ gas concentration is zero (pure He). The CO₂ gas concentration increases rapidly, approaching saturation (pure CO₂) after approximately five minutes. The increase in CO₂ concentration is accompanied by a rapid adsorption of CO₂. The CFCMS samples 170 (300 #2) and 170 (300 T) adsorbed 112 and 125 mg of CO₂ per g of sample, respectively, compared to 95 mg of CO₂ per g of sample for the coconut shell carbon. Moreover, the CFCMS samples reached an uptake of 90 mg/g in ~10 minutes compared with ~16 minutes for the coconut shell derived carbon. The superior adsorption kinetics of the CFCMS materials are ascribed to the small diameter of the carbonfibers (10-20 μ m) compared to the 2-3 mm size of the coconut shell carbon granules. The diffusion paths for the CO₂ to an adsorption site are, therefore, substantially shorter in the case of the CFCMS. In our final CO₂ adsorption study, adsorption was monitored as a function of the CO₂ partial pressure in a CO₂/He mixture at 25°C and 1 atm. Our data for sample CFCMS 170 (300) are summarized in Fig. 5. The amount of CO₂ adsorbed increased linearly with CO₂ concentration reaching a maximum of 2.8 mmol/g (124 mg/g) of CO₂ at saturation in pure CO₂ at 25°C and 1 atm.

A Development Plan for Passive CO₂ Removal

The goal of the Passive CO₂ Removal Project is to develop an essentially passive system for CO₂ capture from the flue gases of a pulverized coal power plant, in sufficient quantity to reduce CO₂ emissions by 30-50%. This represents a direct approach to the CO₂ greenhouse gas issue as opposed to the indirect approach of reducing these emissions as a result of efficiency gains. We have set a goal of a 30-50% reduction in CO₂ emissions, because, typically, the advanced coal technologies such as integrated coal gasification combined cycle (IGCC) and pressurized fluidized-bed combustion (PFBC) offer efficiency gains over conventional pulverized coal power plants that will result in about the same relative reductions in net CO₂ emissions [5,10]. Combining the direct and indirect approaches would, of course, result in even more substantial reductions. However, the bulk of electric power production from coal will continue to be pulverized coal power plants for the foreseeable future, and thus the focus of any effective CO₂ emissions reduction scheme must address these plants. We will attempt to obtain funding for the project and then implement a plan culminating in the development of a passive CO₂ removal or capture device within three years of receipt of initial funding. We have begun discussions with the USDOE, Office of Fossil Energy, relative to this activity. At this time, the potential for funding is indeterminant. The objective of this development is to scale, in successive increments, to a skid mounted

unit that can accommodate a relevant flow of flue gas from a commercial coal-fired power plant by way of a "slip stream." Our strategy will be to team with appropriate adsorbent materials suppliers, separations systems suppliers, and an electric utility company to achieve this objective.

To date, fabrication of the carbon fiber composite molecular sieve has been limited by slurry molding equipment at ORNL, which is capable of producing preforms that will yield about 1 kg of CFCMS after drying, carbonization, and activation. Installation of new and larger slurry molding equipment was completed in June 1995. The new equipment provides the capability of producing preforms that will yield > 10 kg of the CFCMS product. We are collaborating with several industrial firms who manufacture and use activated carbons and pressure swing adsorption systems. The CFCMS has been provided to these firms for evaluation for gas separation, including CO₂ separation, and storage. One of these firms, a major gas separations supplier, is presently evaluating the CFCMS specifically for CO₂ separations. Based on the results of these independent evaluations, modifications to the fabrication and activation processes will be made to optimize the CFCMS and separations system(s) for CO₂ capture from flue gases from a pulverized coal power plant.

This is an ambitious schedule, but we believe it can be accomplished to the state suggested above, i.e., the completion of a skid-mounted demonstration unit ready for installation at a coal fired power plant, within three years. This schedule does consider all of the relatively formidable issues we have identified such as scale up of the fabrication and activation processes, demonstration of the efficacy of the adsorbent in removal of CO₂ from a simulated flue gas stream containing about 15% CO₂, incorporation of the material into operating test units to obtain system scale-up information, and various systems issues such as providing the driving force for flow of the flue gas through the CFCMS CO₂ removal unit. The role of ORNL in this activity will be to establish the research and development team(s); produce the test quantities of CFCMS; perform CO₂ capture tests in simulated flue gas environments; and establish, in concert with our industrial and utility partners the specification and protocol for producing the final version of the CFCMS for use in the demonstration unit. We will then work with the partners to develop a plan for the demonstration phase of the project. Although accomplishment of the project will require dedicated funding, we expect to obtain sufficient information under our base development activity sponsored by the DOE Office of Fossil Energy Advanced Research & Technology Development Materials Program to provide the basis for obtaining funds.

In summary, the project will include the following elements:

- Preparation of a comprehensive three-year project plan that will further define the R&D required to achieve the objective of a skid-mounted demonstration unit.
- Identification of industrial and utility partners to scale up and define the parameters for the CO₂ capture demonstration.
- Completion of the laboratory R&D to produce a CFCMS with the requisite properties for capture of CO₂.
- Demonstration of the efficacy of the CFCMS in the capture of CO₂ from a simulated flue gas stream.
- Demonstration of the capability of the ORNL/UKCAER process for fabrication and activation of the CFCMS at demonstration scale.
- Complete construction of the skid-mounted unit for demonstration in a slip stream at a coal-fired power plant.

4. CONCLUSIONS

A porous monolithic activated carbon material (CFCMS) has been developed that is strong, rigid, and which overcomes problems associated with operations using granular adsorbents. The open structure of CFCMS results in a permeable material which offers little resistance to the free-flow of fluids. The new CFCMS material has a strong affinity for CO₂, adsorbing > 120 mg of CO₂ per g of material. The CFCMS material has a higher CO₂ adsorption capacity and greater adsorption rate than a granular coconut shell carbon.

CO₂ gas capture and mitigation options have been briefly reviewed and the need for a passive and inexpensive approach to the issue of carbon dioxide capture was highlighted. The combination of conventional pressure or thermal swing adsorption apparatus, and our new CFCMS material, may provide the desired approach to CO₂ capture from coal fired generation plant exhaust streams. A plan for the development of a passive CO₂ removal system has been described. The recommended approach is the formation of a partnership with a manufacturer of gas separation plants, and, in collaboration with a power generating utility, the operation of a skid mounted CO₂ separation system on an exhaust slip stream. If successful, the efficacy of CFCMS for passive CO removal would thus be demonstrated.

REFERENCES

1. B. St. John, in *Proc. Second U.S./Japan Workshop on Global Change Research: Environmental Response Technologies (Mitigation and Adaptation)*, Conf. 930285, p. 71 (1993).
2. F. Pearce, *New Sci.* Oct. 1988, p. 15.
3. A. M. Wolsky, in *Proc. Second U.S./Japan Workshop on Global Change Research: Environmental Response Technologies (Mitigation and Adaptation)*, Conf. 930285, p. 75 (1993).
4. K. Blok et al., Eds. *Proceedings of the First International Conference of Carbon Dioxide Removal*, Amsterdam, The Netherlands, Pub. Pergamon Press, New York (1992).
5. R. R. Judkins and W. Fulkerson, *Energy and Fuels* 7, p. 14 (1993).
6. G. C. Wei and JM Robbins, *Ceramic Bulletin* 64, p. 691 (1985).
7. S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.* 60, p. 309 (1938).
8. R. C. Bansel, J-B. Donnet, and F. Stoeckli, *Activate Carbon*, Pub. Marcel Dekker, Inc., New York (1988).
9. T. D. Burchell, "Carbon Fiber Composite Molecular Sieves," in *Proc. 8th annual Conf. on Fossil Energy Materials*, Conf. 9405143, ORNL/FMP-94/1, pp. 63-70 (1994).
10. K. K. Pillai, "Presurized Fluidized Bed Combustion," *Electricity Efficient End-Use and New Generation Technologies, and Their Planning Implications*: Lund University Press, Lund Sweden, pp. 555-593 (1989).

ACKNOWLEDGEMENTS

Research sponsored by the U.S. Department of Energy, Office of Fossil Energy, Advanced Research and Technology Development Materials Program [DOE/FE AA 15 10 10 0, Work Breakdown Structure Element ORNL-3(E)] under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. The authors wish to thank Mike Rogers for technical assistance with pore characterization and CO₂ adsorption studies.