

# **Carbon-Based Regenerable Sorbents for the Combined Carbon Dioxide and Ammonia Removal for the Primary Life Support System (PLSS)**

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**Results are presented on the development of reversible sorbents for the combined carbon dioxide and trace-contaminant (TC) removal for use in Extravehicular Activities (EVAs). Since ammonia is the most important TC to be captured, data on TC sorption presented in this paper are limited to ammonia, with results relevant to other TCs to be reported at a later time. The currently available life support systems use separate units for carbon dioxide, trace contaminants, and moisture control, and the long-term objective is to replace the above three modules with a single one. Furthermore, the current TC-control technology involves the use of a packed bed of acid-impregnated granular charcoal, which is non-regenerable, and the carbon-based sorbent under development in this project can be regenerated by exposure to vacuum at room temperature. The objective of this study was to demonstrate the feasibility of using carbon sorbents for the reversible, concurrent sorption of carbon dioxide and ammonia. Several carbon sorbents were fabricated and tested, and multiple adsorption/vacuum-regeneration cycles were demonstrated at room temperature, and also a carbon surface conditioning technique that enhances the combined carbon dioxide and ammonia sorption without impairing sorbent regeneration.**

## **Nomenclature**

<i>A</i>	=	adsorption capacity (g CO <sub>2</sub> per 100 g sorbent; mg NH <sub>3</sub> per g sorbent)
<i>AFR</i>	=	Advanced Fuel Research, Inc. (AFR)
<i>AS</i>	=	Allied Signal (currently Honeywell)
<i>BET SA</i>	=	BET (Brunauer, Emmett, and Teller) surface area (m <sup>2</sup> /g)
<i>EDX</i>	=	Energy-Dispersive X-ray (spectroscopy)
<i>EVA</i>	=	Extravehicular Activity
<i>FTIR</i>	=	Fourier Transform Infrared (spectroscopy)
<i>G</i>	=	Goodfellow
<i>MFC</i>	=	mass-flow controller
<i>MGA</i>	=	multi-gas analyzer

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<i>PLSS</i>	=	Portable Life Support System
<i>PVDC</i>	=	polyvinylidene chloride
<i>RH</i>	=	relative humidity
<i>SEM</i>	=	Scanning Electron Microscopy
<i>TC</i>	=	trace contaminant
<i>TO</i>	=	thermal oxidation
<i>UTAS</i>	=	UTC Aerospace Systems
$V_{micro}$	=	micropore volume (cm <sup>3</sup> /g)
<i>VI</i>	=	vacuum impregnation

## I. Introduction

THE NASA objective of expanding the human experience into the far reaches of space will require the development of regenerable life support systems. Carbon dioxide (CO<sub>2</sub>), water-vapor (H<sub>2</sub>O), and trace-contaminant (TC) removal plays a key role in such systems ensuring high quality air for the crew during Extravehicular Activities (EVAs) and also on board spacecraft. CO<sub>2</sub>, trace-contaminant, and water-vapor control is currently performed in three separate units, out of which only CO<sub>2</sub> and H<sub>2</sub>O control units are regenerable. Thus, it would be greatly beneficial if a single, regenerable sorbent could be developed, thus integrating the removal of the above species in a single module. The development of such a sorbent, and air-revitalization system, is the main objective of this project, but the subject of this paper is limited to the combined CO<sub>2</sub> and TC removal, with water-vapor results to be reported in a future publication. Also, since ammonia is the main trace contaminant of concern, ammonia was the only TC used in this proof-of-concept study. The objective of this work was to demonstrate the technical feasibility of using a vacuum-regenerable, microporous, high-purity carbon sorbent for simultaneous CO<sub>2</sub> and ammonia capture.

A regenerable CO<sub>2</sub> removal system for use on board spacecraft, or in the Portable Life Support System (PLSS), which is part of any Extravehicular Activity (EVA) suit, will need to minimize power, weight, and volume. For example, the advanced PLSS will need to use a minimum of power due to the limited on-the-back power supply (fuel cell or battery). As part of a planetary exploration suit, the mass of the system certainly should not exceed the 4.5 lb of the non-regenerable lithium oxide (LiOH) system used in the Apollo program. Finally, the entire PLSS needs to be small enough to be maneuvered by an individual astronaut, thus putting a premium on maximizing sorbent density.

The currently available polymer-supported amine based CO<sub>2</sub>-removal system<sup>1,2</sup> developed at UTC Aerospace Systems (UTAS), formerly Hamilton Sundstrand Space Systems International, Inc., offers a viable alternative to LiOH, and is in fact used as a benchmark for future CO<sub>2</sub>-removal systems. The amine-based sorbent (SA9T) is efficient and reliable, but it has the following drawbacks: (1) poor heat transfer within the packed bed of polymer particles; (2) substantial pressure drop across the bed of granular sorbent; and (3) complex behavior with respect to ammonia (offgassing<sup>3</sup> versus removal<sup>4</sup>) and limited control of other trace contaminants<sup>5</sup>.

CO<sub>2</sub> absorption in liquid amines residing within the porous polymer support<sup>1,2</sup> occurs with a release of heat, whereas the desorption process that is associated with sorbent regeneration involves heat absorption from the environment. Thus, it is often convenient to use several adjacent CO<sub>2</sub>-removal units operated in a swing fashion (absorption/desorption) to help manage the thermal effects. Research at UTAS has shown that enhanced heat transfer between the CO<sub>2</sub> adsorbing and desorbing beds will increase the cyclic CO<sub>2</sub> removal capacity of the solid amine systems. The exothermic nature of the absorption tends to increase the temperature of the absorbing bed and decrease the temperature of the desorbing bed. This change in temperature directly opposes the equilibrium capacity isotherms. These isotherms indicate that higher absorption can be achieved with lower temperature and more efficient regeneration accomplished at higher temperatures. The UTAS method for achieving this enhanced heat transfer has relied on a passive conduction path using open cell aluminum foam, with sorbent particles encapsulated within the foam voids. UTAS testing has shown that this aluminum foam can increase cyclic CO<sub>2</sub> removal capacity by 35% compared to the same sorbent operated in an adiabatic system.

It is clear from the above considerations that there exists a strong need to make space suit air revitalization systems regenerable, to further reduce their weight, size, and power requirement, and to integrate CO<sub>2</sub>, TC, and eventually also water-vapor removal in a single unit.

To meet the above need, additional research on regenerable sorbents was performed at Advanced Fuel Research, Inc. (AFR). This research sought: (1) to develop a regenerable, physisorption-based CO<sub>2</sub> carbon sorbent; (2) to integrate the removal of CO<sub>2</sub> and trace contaminants, notably ammonia, within a single sorbent unit; (3) to improve the thermal management of sorbent beds; and (4) to lower the pressure drop across the sorbent unit (reduce the

power requirement). This was done through the use of microporous monolithic carbon derived from polyvinylidene chloride (PVDC). The specific advantages include: (a) improved heat-transfer and reduced heat of adsorption within the sorbent; (b) reduced pressure drop; (c) ability to handle dusty environments (unlike granular sorbents, honeycomb monoliths do not get plugged easily); (d) simultaneous removal of CO<sub>2</sub>, trace contaminants, and water vapor; (e) proprietary carbon-surface treatment to enhance sorption; and (f) fully regenerable operation, including trace-contaminant sorption. The latter feature is in contrast to the EVA air-revitalization systems used in the past: (i) single use lithium hydroxide (LiOH) cartridges for CO<sub>2</sub> control; (ii) metal oxide cartridges, which are difficult to regenerate; and (iii) single-use, non-regenerable activated carbon (AC) for TC control.

In previous projects<sup>6,7,8,9</sup>, we demonstrated that it is possible to make carbon monoliths from PVDC and accomplish between 50% and two orders of magnitude reduction in pressure drop with respect to granular sorbent through the use of monolithic carbon. Reversible and effective ammonia sorption was already demonstrated in our previous project<sup>9,10,11</sup>. The focus of the present work was the development of improved, multifunctional PVDC-based carbon sorbents in the granular form, which made sorbent preparation and testing easier and faster. Work on sorbent-performance optimization, multifunctional sorbent monolith development, and sorption/desorption of water and TCs other than ammonia will be performed in the future.

The approach to CO<sub>2</sub>/TC sorption used in this project is based mostly on physisorption on highly microporous carbon derived from PVDC (pores dimensions  $d_p < 20$  Å). The pore sizes are close to molecular dimensions, which ensures sufficiently strong van der Waals forces to obtain impressive sorption capacities. In contrast, most commercial activated carbons contain only a small or modest percentage of microporosity, and this is why their sorption-capacity performance is poor. The fact that the underlying principle for our sorbents is physisorption, rather than chemisorption, or absorption by a liquid agent, makes vacuum or thermal regeneration fast and reversible. Also, the high purity of the carbon derived from a polymer precursor makes it possible to keep the carbon surface acidity low and thus facilitate the reversibility of ammonia sorption.

## II. Materials and Experimental Procedures

### A. PVDC Precursor Selection

Polyvinylidene chloride (PVDC) was extensively and successfully used in our previous work. Upon carbonization, and optional activation, it produced high-purity carbon with large surface area and angstrom-size pores with a narrow distribution. With surface conditioning, this carbon proved to be a superb ammonia sorbent with excellent room temperature vacuum regeneration capabilities<sup>9,10,11</sup>. We noted significant differences in performance, however, among carbons produced from PVDC provided by different suppliers. For this reason, three different PVDC precursor formulations were procured for the present project from different suppliers to see which of them is most suitable for the combined CO<sub>2</sub>/NH<sub>3</sub> sorption and regeneration. Samples of PVDC from the following suppliers were studied in this project: Goodfellow and Allied Signal (currently Honeywell).

In addition to the two above-mentioned types of PVDC, it was decided to include third-party PVDC-based carbons similar to the ones that had proved effective in CO<sub>2</sub> capture from coal-fired power plant combustion flue gas<sup>12</sup>. Although the above application is different from air-revitalization in NASA spacecraft systems (15 vol% CO<sub>2</sub> versus 1% vol% CO<sub>2</sub> and thermal versus vacuum regeneration, respectively), PVDC carbons for CO<sub>2</sub> capture from the flue gas may be a good starting point for developing effective air-revitalization sorbents for CO<sub>2</sub>, trace contaminants, and water. Modifications in carbon structure and surface chemistry can be made by carbon activation and post-treatment, e.g., with oxidizing agents.

### B. PVDC Carbonization and Activation

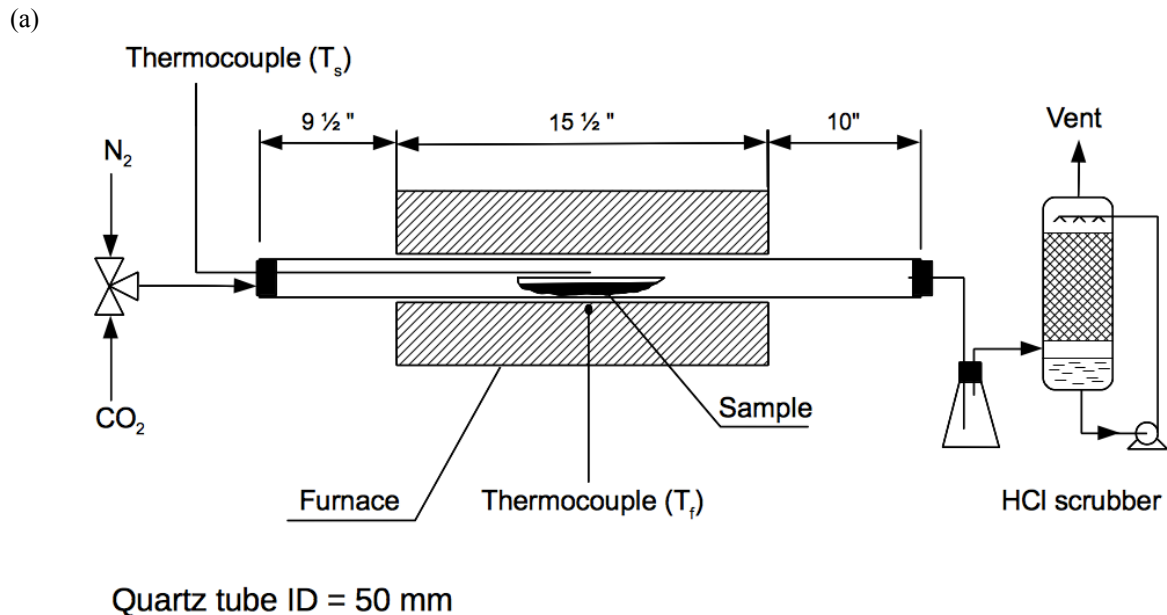
The preparation of granular carbon followed the conventional procedures described below. Carbon precursor (PVDC) was carbonized in a tube furnace and, if desired, the resultant char was then subjected to CO<sub>2</sub> activation, also in a tube furnace. Based on our prior experience, the carbonization temperature

**Table 1. The furnace heating profile used in carbonization runs (after ref. <sup>3</sup> with some modifications).**

Step No.	Temperature (°C)	Time (h:min)
0	100	0:40 or 1:56
1	165	2:10
2	165	0:30
3	180	2:30
4	180	0:30
5	200	3:20
6	200	0:30
7	248	8:00
8	548	10:00
9	900	1:10 or 2:20
10	900	0:03 or 0:15
11	20	10 min

was chosen to be 900 °C. CO<sub>2</sub> activation was performed at temperatures between 800 °C and 950 °C, with a hold time of 0.5–10 hours.

PVDC polymer was subjected to carbonization under modified reference conditions given in Table 1. Carbonization was carried out in a flow of ~2.0 scfh of nitrogen using a 50-mm ID tube furnace shown in Figure 1. The tube furnace (Thermolyne 21100) was equipped with a quartz tube 50 mm (~2 inches) in inner diameter and 35 inches in length. Temperature was measured using two K-type thermocouples, one placed within the furnace ( $T_f$ ), and the other one positioned next to the sample ( $T_s$ ), as shown in Figure 1. A temperature controller (Love model 2600) was operated using input from  $T_s$ . A smaller, 1-in diameter tube furnace was used for CO<sub>2</sub> activation. Dilute aqueous solution of sodium hydroxide was used to scrub the gaseous hydrogen chloride produced during carbonization.



**Figure 1. The PVDC-carbonization/CO<sub>2</sub>-activation tube-furnace system: (a) schematic representation; (b) the tube furnace and temperature controller; and (c) hydrogen-chloride scrubber.**

### C. Carbon Post-Treatment

Two types of sample treatment were used in this work: (1) thermal oxidation in ambient air at 250-325 °C for 2-24 hours; and (2) carbon wet impregnation with sodium or potassium hydroxide, or sodium carbonate, followed by calcination at 150-250 °C in the air. The first of these treatments was meant to improve the ammonia-sorption capacity, and it is described in references<sup>9,10,11</sup>. The purpose of the second treatment was to increase CO<sub>2</sub>-sorption capacity, and the carbon-impregnation procedure is described below.

Vacuum impregnation (VI) is a non-destructive method used to introduce dissolved salts in the porous structures of carbon. The deposition of the salts is due to the hydrodynamic action introduced by pressure changes. Compared with traditional impregnation techniques, VI can induce uniform deposition of the impregnants on internal and external surface of the porous carbons. Under high vacuum conditions, the impregnants can be deposited in the deep pores of the activated carbon. The technique was implemented as follows. 50 g of carbon particles was placed in a Petri dish, and 100 ml of 2% aqueous NaOH solution was added. The formation of foam was observed due to adsorption and release of the air in the carbon particles. The Petri dish was then placed in a vacuum impregnation system and sealed. Then, the vacuum was maintained at -25 inches Hg gauge for 3 minutes to infuse the sodium into the porous carbon particles. The formation of bubbles was observed within the solution as the solution impregnated the pores. Then the vacuum was released slowly in about a minute, and the carbon particles were stirred. The above procedure was repeated five times for effective coverage. After impregnation, the sample was placed in a covered glass dish and calcined in a furnace at 250 °C for 2 hours.

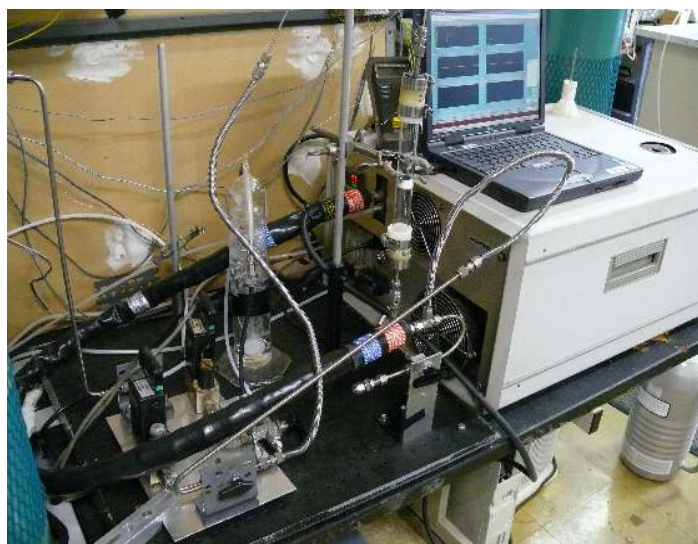
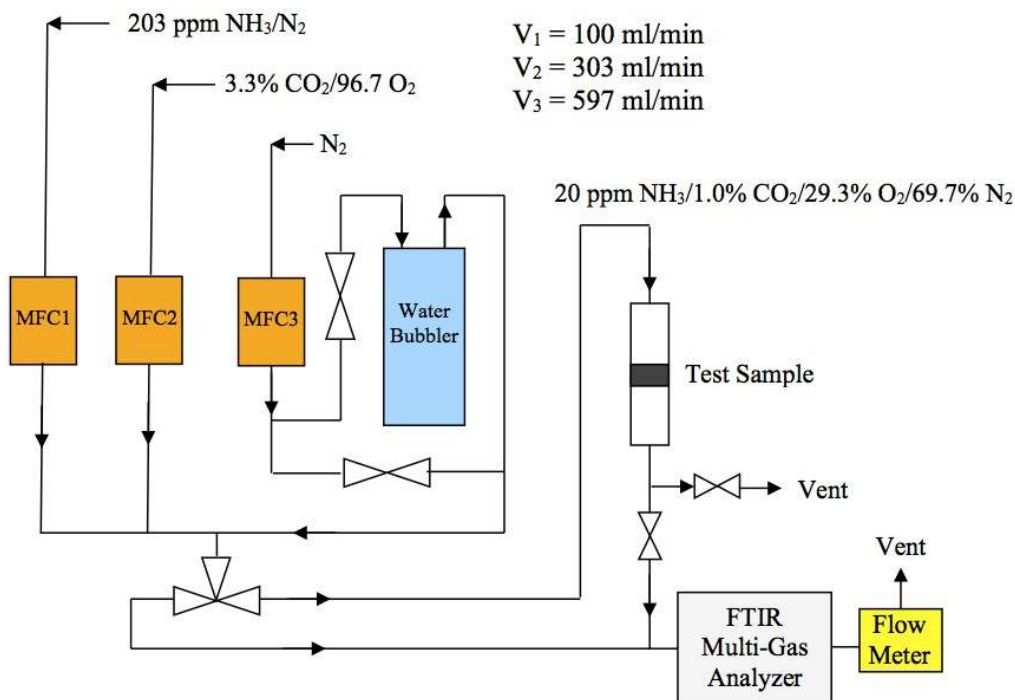
### D. Sorbent Testing

Figure 2 shows a schematic of the testing system that was used for measuring the cyclic and total (equilibrium) CO<sub>2</sub>/NH<sub>3</sub> sorption capacity of sorbents used in this study. The apparatus, shown in Figure 2, incorporates a Fourier transform infrared (FTIR) spectrometer-based On-Line Technologies model 2010 Multi-Gas Analyzer (MGA) for the CO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>O quantification. Using mass flow controllers, gas mixtures shown in the system flow chart are blended to achieve the desired concentration of CO<sub>2</sub>, NH<sub>3</sub>, O<sub>2</sub>, and N<sub>2</sub>. For humidifying the gas stream, if desired, a portion of the nitrogen stream can be re-routed through a water bubbler, using fine needle valves for adjustment. During testing, the final mixture is first routed through a sample bypass line, to establish the baseline NH<sub>3</sub> (and humidity) conditions. The gas is then re-directed through the sample “cell” for the sorbent adsorption testing. The sample cell consists of a quartz or glass tube that contains the sorbent sample. It is mounted in a vertical orientation with the gas inlet at the top of the cell so that gas flow is in a downward direction. Sorption experiments were run either using a 22-mm diameter quartz tube for CO<sub>2</sub>-sorption measurements, or using a 5 mm i.d. glass tube for ammonia-sorption determinations. The carbon sample was held in place by means of ceramic wool on both ends, and it was verified that no CO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>O sorption occurred in the empty reactor containing the ceramic wool. The reason why two different tube and sample sizes were used was the large difference in ammonia and CO<sub>2</sub> sorption capacities. As a result, when a large carbon sample size was used (0.7–5.0 g), CO<sub>2</sub> breakthrough curves could easily be determined, but ammonia breakthroughs never occurred on a time scale of many hours because the sorbent effectively removed all ammonia. When the measurements were performed in a smaller bed, using a smaller sample (0.035–1.0 g), ammonia breakthrough curves could readily be measured, but CO<sub>2</sub> adsorption peaks were too small to be reliably quantified.

The MGA shown in Figure 2 employs a liquid nitrogen-cooled, mercury-cadmium-telluride (MCT) detector with a bandpass of 500–6500 cm<sup>-1</sup> and a spectral resolution of 0.5 cm<sup>-1</sup>. The instrument employs a heated, multi-pass gas sampling cell with an effective pathlength of 5.1 m. The long effective pathlength and the high resolution of the instrument enable sub-ppm sensitivity to NH<sub>3</sub>, even in the presence of high H<sub>2</sub>O concentrations. All data were collected at 30-second intervals. The procedure was to monitor the CO<sub>2</sub>/NH<sub>3</sub> breakthrough curves (concentration versus time) and to terminate the adsorption measurement when the concentration had reached at least 90% of the cell inlet concentration (after breakthrough).

The testing was performed in two stages: (a) CO<sub>2</sub>/NH<sub>3</sub> adsorption, where the gas stream was passed through the sorbent at pressure close to atmospheric; and (b) CO<sub>2</sub>/NH<sub>3</sub> desorption, where the sorbent was exposed to a flow of nitrogen. CO<sub>2</sub>/H<sub>2</sub>O/NH<sub>3</sub> concentration determination was carried out using an FTIR analyzer downstream of the reactor. The inlet gas composition was similar to that typical for PLSS: ~20 ppm NH<sub>3</sub>, ~1.0 vol.% CO<sub>2</sub>, 29 vol.% O<sub>2</sub>, and balance nitrogen. For the CO<sub>2</sub> adsorption step, the flow rates add up to a total of 1.00 L/min, as indicated in Figure 2. This constitutes about 1/40 of the nominal flow rate expected in the full-scale PLSS. In the desorption step, the flow rates were somewhat different: the CO<sub>2</sub>/O<sub>2</sub> gas (flow No. 2) was turned off, and a flow of nitrogen was directed through mass-flow controller No. 1 instead of the NH<sub>3</sub>/N<sub>2</sub> mixture. This resulted in a total nitrogen flow rate of 697 ml/min. The total NH<sub>3</sub> adsorption step flow rate through the small-diameter tube was 0.956 L/min.

The effect of the relative humidity ( $RH$ ) of the gas stream was not systematically investigated, and it will be a subject of future work. We already reported the beneficial effect of  $RH$  on ammonia sorption in our previous paper<sup>10</sup>.



**Figure 2.** The sorption/desorption capacity test apparatus used in this study. *MFC1*, *MFC2*, and *MFC3* are mass-flow controllers, and  $V_1$ ,  $V_2$ , and  $V_3$  are volumetric flow rates of the corresponding gas streams.

### III. Results and Discussion

#### A. Carbon Characterization

A number of carbons were prepared by carbonization of PVDC, some of them were activated in a flow of  $\text{CO}_2$ , and some sorbents were also subjected to carbon post-treatment. Selected samples were characterized with respect to their surface area, pore volume, and pore-size distribution using nitrogen-adsorption isotherms at 77 K, and results

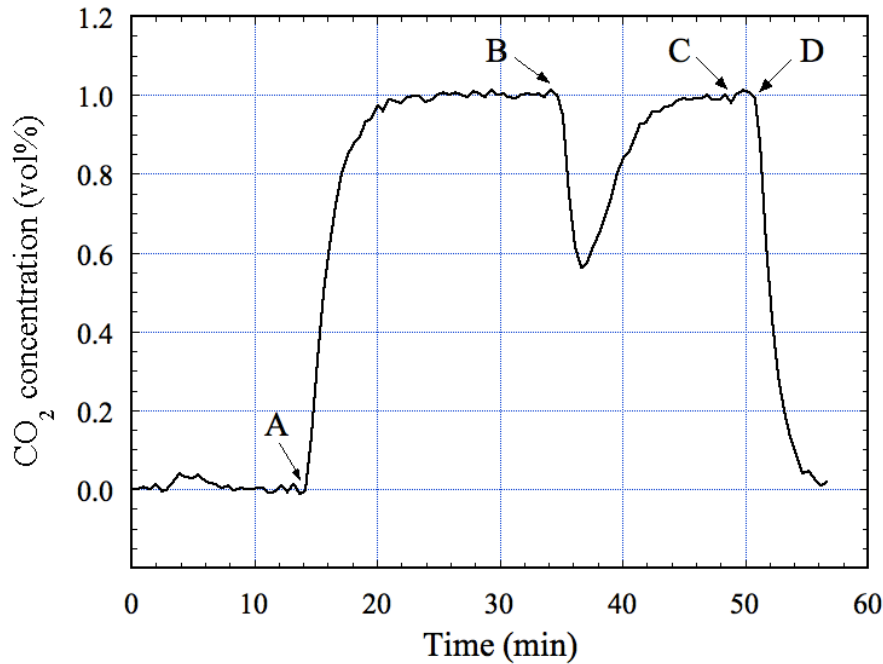
of these measurements are shown in Table 2. It can be seen that carbon impregnation with sodium hydroxide results in a tremendous reduction in surface area. It will be shown below that such carbons exhibited the highest CO<sub>2</sub>-sorption capacities, which means that CO<sub>2</sub>-sorption does not necessarily correlate with high surface area. Another point to make is that the impregnation step results in a significant drop in the available porosity, presumably due to pore blocking. In spite of that, metal-impregnated sorbents were found to perform exceedingly well (see below), which means that they would perform even better if pore blocking could be avoided. This defines one of the directions for the future quest for better sorbents, with improved, i.e. more open, pore structures.

**Table 2. Carbon BET surface area (*BET SA*) t-plot micropore volume ( $V_{micro}$ ) for selected carbon samples used in the study. *AS* denotes the Allied Signal PVDC carbon.**

No.	Sample	BET SA (m <sup>2</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)
FB477	AS, carbonized at 900 °C	824	0.358
FB480	AS, CO <sub>2</sub> activated at 825 °C for 9 h	865	0.380
FB481	AS, impregnated with 2% NaOH aq.	84	0.0387
FB481-ox	AS, oxidized in air at 325 °C for 24 h	935	0.355
A-B200-AB00	Third-party PVDC carbon	1,033	0.372

## B. Sorbent Testing

An example of CO<sub>2</sub> adsorption data is discussed below for a third-party carbon 3A050307. Data showing CO<sub>2</sub> concentration at the adsorber outlet as a function of time are shown in Figure 3, and experimental conditions used are summarized in Table 3.



**Figure 3. Carbon-dioxide concentration at the adsorber outlet as a function of time for the third-party PVDC carbon 3A050307: A - start CO<sub>2</sub> flow through bypass; B - start CO<sub>2</sub> flow through carbon sample; C - switch CO<sub>2</sub> flow to bypass; and D - turn off CO<sub>2</sub> flow.**



**Table 3. Experimental conditions used during CO<sub>2</sub>-adsorption tests involving carbon 3A050307.**

	<b>Carbon 3A050307</b>
Sample mass (g)	3.865
Carbon particle/disc diameter (mm)	approximately 7-8
Carbon particle/disc thickness (mm)	approximately 3-4
Packed-bed diameter (cm)	2.19
Packed-bed height (cm)	2.7 ± 0.3
Carbon bulk density (g/cm <sup>3</sup> )	0.38
Apparent gas residence time (s)	1.2
Gas flow rate (L/min)	0.500
Inlet CO <sub>2</sub> concentration (vol%)	1.0
Frequency of data acquisition (min <sup>-1</sup> )	0.50

The integration of the CO<sub>2</sub> adsorption peak in Figure 3 shows that 9.22 cm<sup>3</sup> of CO<sub>2</sub> gets adsorbed on the carbon in about 10 minutes, which corresponds to 0.0166 g CO<sub>2</sub>, assuming a density of CO<sub>2</sub> at 25 °C of 0.001799 g/cm<sup>3</sup> (ref. <sup>13</sup>). Normalizing with respect to carbon 3A050307 weight gives a CO<sub>2</sub>-adsorption capacity of 4.29 g CO<sub>2</sub> per kg of carbon, or 0.429 wt%. It is interesting to note that the sorption capacity obtained for the above carbon (~4 g CO<sub>2</sub> per kg carbon) is not very different from the CO<sub>2</sub>-sorption capacity estimated on the basis of crude interpolation of CO<sub>2</sub> adsorption isotherm data<sup>14</sup> for a similar carbon (~5 g CO<sub>2</sub> per kg carbon). This agreement provides confidence in the methodology used in this study. Ammonia breakthrough curves, qualitatively similar to the one shown for CO<sub>2</sub> in Figure 3, were published in our previous paper for several consecutive adsorption-desorption events<sup>10</sup>.

A summary of selected CO<sub>2</sub> and ammonia sorption tests is shown in Table 4 and Table 5, respectively, and the observations made on the basis of these data can be found in Table 6.

**Table 4. A summary of CO<sub>2</sub>-adsorption tests. [*A* is the CO<sub>2</sub>-adsorption capacity. Subscripts 1, 2, etc. refer to individual adsorption/desorption cycles. *m<sub>s</sub>* is the sample mass. *AS* denotes carbon produced from the precursor provided by Allied Signal. *G* denotes carbon produced from the precursor provided by Goodfellow, and carbons with designations starting with *A-* were provided by a third party. (*TO*) denotes thermal oxidation. Thermally oxidized samples were oxidized in air at 325 °C for 24 hours. (*CO<sub>2</sub>*) indicates that CO<sub>2</sub> only was adsorbed from the gas stream, i.e. there was no NH<sub>3</sub> present in the inlet gas. (*VI*) indicates vacuum impregnation. (*I-xxxx*) indicates impregnation with xxxx solution. Sorption experiments were performed at RH = 0%.]**

Run No.	Date	Sample	<i>m<sub>s</sub></i> (g)	<i>A</i> <sub>1</sub> (g/100 g)	<i>A</i> <sub>2</sub> (g/100 g)	<i>A</i> <sub>3</sub> (g/100 g)	<i>A</i> <sub>4</sub> (g/100 g)
S18	10/11/13	AS	2.003	0.70	0.65	0.48	
S21	10/18/13	AS (TO) (CO <sub>2</sub> )	1.933	0.34	0.39	0.32	
Base 1	10/24/13	AS (CO <sub>2</sub> ) (I-2%Na <sub>2</sub> CO <sub>3</sub> )	2.030	0.94			
S36	11/08/13	AS (CO <sub>2</sub> ) (VI) (I-2%Na <sub>2</sub> CO <sub>3</sub> )	1.983	0.72	0.72	0.73	
S27	10/31/13	AS (CO <sub>2</sub> ) (I-10%Na <sub>2</sub> CO <sub>3</sub> )	0.766	0.93			
S28	10/31/13	AS (TO) (CO <sub>2</sub> ) (I-10% Na <sub>2</sub> CO <sub>3</sub> )	0.776	0.64	0.73	0.62	
S31	11/06/13	AS (CO <sub>2</sub> ) (VI) (I-NaOH)	1.422	0.82	0.76	0.76	
S34	11/07/13	AS (CO <sub>2</sub> ) (VI) (I-KOH)	1.640	0.53			



Run No.	Date	Sample	$m_s$ (g)	$A_1$ (g/100 g)	$A_2$ (g/100 g)	$A_3$ (g/100 g)	$A_4$ (g/100 g)
S23	10/23/13	Activated AS (TO) (CO <sub>2</sub> )	0.878	0.29	0.35	0.30	
S40	11/13/13	Activated AS (CO <sub>2</sub> ) (VI) (I-NaOH)	0.600	0.62	0.63		
S42	11/14/13	Activated AS (TO) (VI) (I-NaOH)	1.201	0.30	0.33		
S16	10/09/13	G	2.031	0.41	0.49	0.47	
S22	10/23/13	G (CO <sub>2</sub> )	1.860	0.55	0.55		
S17	10/10/13	G (TO)	1.010	0.63	0.51	0.58	
S06	09/20/13	A-1296	5.680	0.42	0.54	0.55	0.56
S11	10/03/13	A-B200-AB00	5.300	0.42	0.42	0.41	0.41
S50	11/21/13	A-1686 (TO) (VI) (I-2% NaOH)	5.202	0.81	0.71	0.68	0.75
S12	10/03/13	A-B200-AA00	5.700	0.34	0.35	0.34	
S02	08/29/13	A-3A050307	3.865	0.43			

**Table 5. A summary of ammonia-adsorption tests. [ $A$  is the NH<sub>3</sub>-adsorption capacity. Subscripts 1, 2, etc. refer to individual adsorption/desorption cycles.  $m_s$  is the sample mass. *AS* denotes carbon produced from the precursor provided by Allied Signal, and carbons with designations starting with *A*- were provided by a third party. (TO) denotes thermal oxidation. Unless stated otherwise, thermally oxidized samples were oxidized in air at 325 °C for 24 hours. (VI) indicates vacuum impregnation. (I-xxxx) indicates impregnation with xxxx solution. Unless stated otherwise, sorption experiments were performed at RH = 0%.]**

Run No.	Date	Sample	$m_s$ (g)	$A_1$ (mg/g)	$A_2$ (mg/g)	$A_3$ (mg/g)
S20	10/17/13	AS	0.102	0.66	0.36	0.30
OXHON	10/14/13	AS (TO)	0.067	10.00		
S47	11/15/13	AS (TO) (I-10% Na <sub>2</sub> CO <sub>3</sub> )	0.045	6.41		
ACTHO	10/15/13	Activated AS	0.100	0.15		
OXACT	10/14/13	Activated AS (TO)	0.570	2.50		
S45	11/14/13	Activated AS (TO) (VI) (I-NaOH)	0.056	4.46	2.28	
S15	10/08/13	A-1296	1.001	0.51		
N/A	N/A	A-1296 (TO)	0.035	12.10		
S25	10/30/13	A-B200-AB00 (TO - 325 °C for 2 h)	0.131	0.50		
S26	10/31/13	A-B200-AB00 (TO - 325 °C for 4 h)	0.128	0.88		
S30	11/01/13	A-B200-AB00 (TO - 325 °C for 8 h)	0.080	2.70	1.46	
S52	11/22/13	A-1686 (TO) (VI) (I-2% NaOH); RH = 40%	0.057	9.09	3.14	3.15

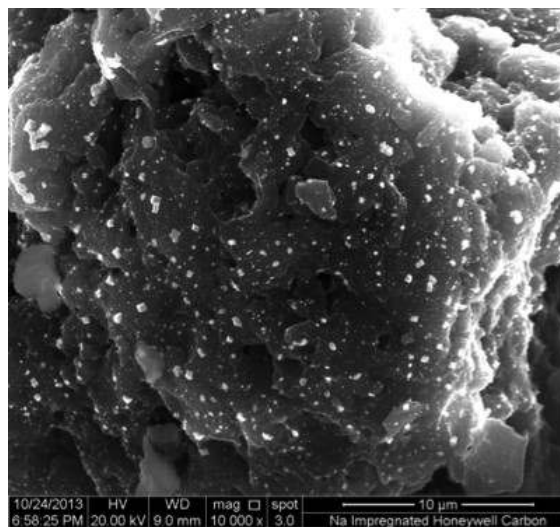
**Table 6. Main results of the CO<sub>2</sub> and ammonia sorption tests.**

<i><b>CO<sub>2</sub>-Sorption Tests</b></i>	<i><b>Ammonia-Sorption Tests</b></i>
<ol style="list-style-type: none"> <li>1. CO<sub>2</sub>-sorption capacity in the range 0.30-0.94 g CO<sub>2</sub> per 100 g of sorbent.</li> <li>2. Good cycle-to-cycle reproducibility of CO<sub>2</sub> adsorption. The amount of CO<sub>2</sub> desorbed from the carbon is equal to the amount of CO<sub>2</sub> adsorbed on the sorbent.</li> <li>3. Impregnation with sodium (Na<sub>2</sub>CO<sub>3</sub> or NaOH) leads to improved sorption capacity by a factor of 2-3.</li> <li>4. Carbon activation was not found to improve CO<sub>2</sub>-sorption capacity. Since only one sample of activated carbon was tested, the effect of carbon activation needs to be studied systematically in the future.</li> <li>5. Sorbent performance depends on carbon precursor.</li> </ol>	<ol style="list-style-type: none"> <li>6. NH<sub>3</sub>-sorption capacity in the range 0.50-12 mg NH<sub>3</sub> per g of sorbent for oxidized samples.</li> <li>7. Thermal oxidation can increase NH<sub>3</sub>-sorption capacity by about a factor of 20.</li> <li>8. The first peak is larger than subsequent peaks by a factor of ~2-3, but ammonia sorption still remains strong, consistent, and reversible in subsequent peaks. Ammonia desorption in an atmosphere of flowing nitrogen is slower than CO<sub>2</sub> desorption from the same carbon.</li> <li>9. Carbon activation was not found to improve NH<sub>3</sub>-sorption capacity. Since only one sample of activated carbon was tested, the effect of carbon activation needs to be studied systematically in the future.</li> </ol>

The comparison of ammonia sorption on thermally oxidized activated carbon and a similar carbon impregnated with NaOH (runs OXACT and S45 in Table 5) leads to a counterintuitive result. Data show that ammonia-sorption capacity for the oxidized sample is lower than for the NaOH-impregnated sample, which is opposite to what one would expect. (Sodium hydroxide, which is a strongly basic agent, should neutralize acidic sites on the carbon surface and, thus, make ammonia less adsorbable on such less acidic surface.) The reason for the above result is currently unknown, and it is hoped that future research will shed light on the complexity of surface functional groups and the role they play in ammonia and CO<sub>2</sub> sorption.

### **C. Sorbent Post-Treatment by Impregnation with Salt Solution**

A sample of about 300 ml of carbon sorbent was prepared for CO<sub>2</sub> and ammonia sorption testing in the system shown in Figure 2, and also for future testing using a twin-bed test rig. The starting material was PVDC carbon called A-1686, which was provided by a third-party collaborator in the form of 3.3 mm x 2.2 mm granules. This material was supposed to be essentially the same as A-B200-AB00. The A-1686 granules were ground using an IKA Labortechnik MF10basic hammer mill, and then sieved to the 20/40 mesh size (0.425–0.850 mm). The sample was then thermally oxidized in the air at 300 °C for 12 hours. Subsequently, the carbon was vacuum-impregnated with a 2 wt% aqueous solution of NaOH, dried at 90 °C for one hour, and then calcined at 150 °C for two hours. A Scanning Electron Microscopy (SEM) image of a carbon particle impregnated with sodium is shown in Figure 4. It can be seen that vacuum impregnation results in a non-uniform distribution of sodium on the carbon surface (white dots). It is expected that sodium distribution could be made more uniform by using a different impregnation technique, e.g., centrifugation, which will be explored in the future. Energy-dispersive X-ray (EDX) spectroscopy analysis showed the presence of 7.0 % of sodium in the calcined sorbent (see Figure 5). The sorbent was tested for CO<sub>2</sub> and NH<sub>3</sub> sorption and good results were obtained (see Table 4 and Table 5). Based on the currently available

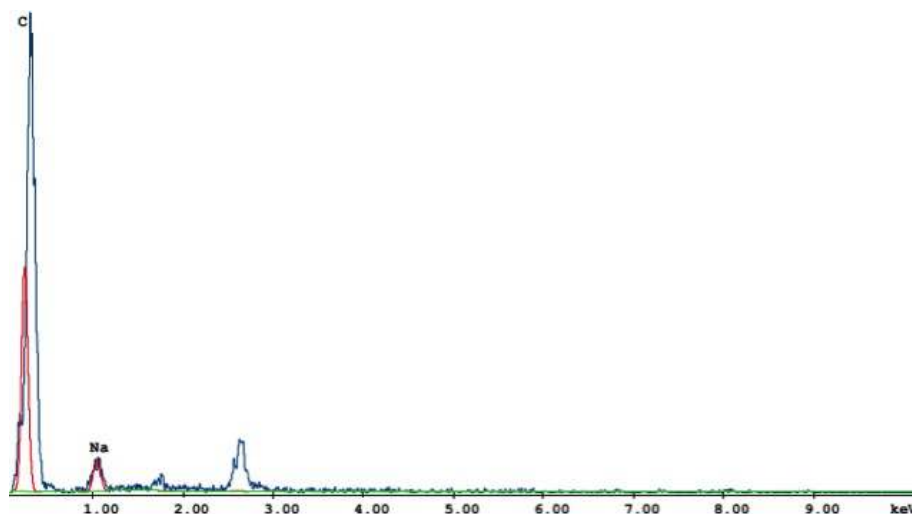


**Figure 4. SEM image of the A-1686 carbon impregnated with 2% NaOH solution.**

data, the A-1686 carbon, thermally oxidized in the air at 325 °C for 24 hours and vacuum-impregnated with 2% aqueous NaOH solution, looks quite promising. It is characterized by a CO<sub>2</sub>-sorption capacity of 0.7-0.8 g CO<sub>2</sub> per g sorbent, and an NH<sub>3</sub>-sorption capacity of approximately 3.1 mg NH<sub>3</sub> per g sorbent. A detailed parametric study and sorbent optimization will be conducted in the near future, as well as extensive sorbent testing to be performed under various conditions.

#### EDS Quantitative Results

Element	Wt%	At%
CK	92.79	96.10
NaK	7.21	3.90



**Figure 5.** EDX spectrum of the A-1686 carbon impregnated with 2% NaOH solution.

## IV. Conclusions

The technical feasibility of using microporous, PVDC-derived carbon sorbents for CO<sub>2</sub>/NH<sub>3</sub> control was demonstrated. A number of sorbent samples were prepared and tested for CO<sub>2</sub>/ammonia adsorption and desorption. Good performance with respect to CO<sub>2</sub> and ammonia sorption and regeneration was found, and this was partly due to the effective surface-treatment methods developed to enhance reversible sorption. CO<sub>2</sub>-sorption capacity was improved by a factor of two by impregnating carbon with sodium, which was followed by a calcination step performed in the air. Ammonia sorption was improved by a factor of ~20 by oxidizing carbon at 250–325 °C in the air for up to 24 hours.

CO<sub>2</sub> sorption was found to be always rapid and reversible, with well-defined adsorption/desorption peaks of equal areas, and with no degradation in sorption capacity over several cycles. PVDC-derived sorbents also showed very good ammonia-sorption capacity and, unlike the state-of-the-art sorbents, they could be repeatedly regenerated. The ammonia results were found to be consistent with our previous study<sup>9,10,11</sup>. The CO<sub>2</sub>-sorption capacity was found to be in the range 0.30–0.94 g CO<sub>2</sub> per 100 grams of sorbent, and the ammonia-sorption capacity was in the range 0.50–12 mg NH<sub>3</sub> per gram sorbent for oxidized (surface-treated) samples. At this stage of development, the carbon-based CO<sub>2</sub> sorbent has a sorption capacity 5-6 times lower than the amine-based SA9T (0.8–0.9 g CO<sub>2</sub> per g sorbent versus ~5 g CO<sub>2</sub> per g sorbent<sup>6</sup>, respectively). This difference may be reduced, however, as a result of future sorbent development and optimization. It should also be borne in mind that net benefits of the microporous carbon monoliths are likely to come from their multifunctionality (regenerable CO<sub>2</sub>, TC, and water sorption), low pressure drop, and good heat management.

The present study, as well as the results of our complementary project<sup>9,10,11</sup>, show that the following parameters are important for sorbent design and PLSS operation:

- *Carbon-surface acidity* – The absence of strongly acidic sites makes vacuum regeneration possible for ammonia. It is also likely that the low surface acidity may promote CO<sub>2</sub> sorption, with unknown

consequences for CO<sub>2</sub> regeneration. For the PVDC carbons studied so far, this seems to have not been a problem so far.

- *Surface oxidation* – Up to a factor of 20 improvement in ammonia sorption was found in the case of oxidized samples, presumably due to the slightly increased surface acidity caused by oxidation. It is surmised that the degree of acidity induced by surface oxidation is sufficient to enhance ammonia sorption, but not high enough to impair ammonia desorption. Although surface acidity was not measured in this study, there is ample evidence in the literature for the presence of acidic groups on carbon surface following surface oxidation. For example, Bansal and Goyal state that the "acidic groups are very well characterized and are formed when carbon is treated with oxygen at temperatures up to 400 °C. (...) These acidic groups render the carbon surface hydrophilic and polar in character and have been postulated to be carboxylic, lactone, and phenolic groups.<sup>15"</sup>
- *Gas humidity* – A factor of ~2.5 improvement in ammonia sorption was found with respect to dry gas for ammonia sorption<sup>9,10,11</sup>; the effect of humidity on CO<sub>2</sub> sorption was not studied in this project, but a positive effect was reported in the literature<sup>12</sup>.
- *Carbon activation conditions* (the use of CO<sub>2</sub>, steam or oxygen activation at different temperatures and hold times) – Although CO<sub>2</sub> activation was proved ineffective in this study, with respect to both CO<sub>2</sub> and ammonia sorption, this result was obtained for only one carbon. In general, activation certainly affects the carbon pore structure, which influences sorbent performance. In fact, it is possible that the modest increase in the surface area and micropore volume that occurred upon activation (see Table 2) was responsible for the similar sorption performance of activated and unactivated carbon in the present study. Our previous work showed some benefit for ammonia sorption that was associated with carbon-monolith activation<sup>9,10</sup>, and the effect of activation certainly deserves further investigation.
- *Pore structure* (surface area and pore-size distribution) – A high percentage of microporosity ( $d_p < 20 \text{ \AA}$ ) seems to enhance ammonia-sorption capacity, but mesoporosity would certainly improve sorption kinetics.
- *Carbon precursor* – PVDC from different suppliers produced carbons with different performance.
- *Carbonization conditions* – This parameter was not extensively studied in this project, and since carbonization affects the pore structure, different carbonization regimes ought to be tested (different temperatures and hold times).

### Acknowledgments

This work was supported by the NASA Johnson Space Center under SBIR Phase I contract NNX13CJ32P. Further work on this project is currently underway under Phase II NASA contract NNX14CJ09C, which was awarded in April 2014. In addition to NASA funding, financial assistance by Connecticut Innovations, Inc. under the SBIR Acceleration and Commercialization Program Grant is gratefully acknowledged. The authors also wish to thank Dr. Tim Nalette of UTAS for helpful discussions on sorbent testing and system requirements.

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