

Pressure-Swing Adsorption of Trace Contaminants Using Carbon Sorbent Monoliths

Marek A. Wójtowicz,¹ Joseph E. Cosgrove,² Michael A. Serio,³ and Andrew E. Carlson⁴
Advanced Fuel Research, Inc., 87 Church Street, East Hartford, CT 06108, USA

John M. Hostetler⁵ and Nicolas J. Espinosa⁶
Jacobs Technology, 2222 Bay Area Blvd, Houston, TX 77058

and

Cinda Chullen⁷
NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058

The current trace-contaminant (TC) control technology involves a packed bed of acid-impregnated granular charcoal, which is difficult to regenerate, and this sorbent is at present considered a consumable. The preferred implementation of TC control is pressure-swing adsorption (PSA) using a regenerable sorbent, where TCs are adsorbed on the sorbent in adsorption steps, which are followed by sorbent regeneration by exposure to space vacuum (desorption steps). The adsorption-desorption steps are repeated cyclically in parallel beds, which ensures continuous TC removal. A similar approach has been used in carbon-dioxide control, with a cycle time of a few minutes, and it is desirable to adopt the same time scale in TC control. In addition, the use of sorbent monoliths is advantageous due to the low pressure drop and low fan-power requirement. In this paper, results are presented on the development of vacuum-regenerable TC sorbents for use in the Exploration Portable Life Support System (xPLSS). The sorbents were derived from 3D-printed polymer monoliths (e.g., honeycomb structures), which were then carbonized and oxidized in order to develop porosity, and also to enhance the TC-sorption capacity. Results are presented on the following aspects of carbon-sorbent development: (1) monolith fabrication; and (2) sorbent-performance in terms of TC-sorption and vacuum-regeneration. The use of predominantly microporous carbon monoliths is associated with the following benefits: (a) high trace contaminant sorption capacity; (b) low pressure drop; (c) rapid vacuum (pressure-swing) desorption due to thin monolith walls and low pressure drop; (d) high mechanical strength [2,3] and resistance to attrition; (e) good thermal management (high thermal conductivity and low adsorption/desorption thermal effects associated with physisorption); (f) good resistance to dusty environments; (g) non-toxic, non-flammable sorbents made of high-purity carbon; and (h) the flexibility to 3D-print/fabricate sorbent monoliths with optimized

1 Vice President, Clean Energy & Carbon Materials, Advanced Fuel Research, Inc., 87 Church Street, Suite 308, East Hartford, CT 06108

2 Senior Engineer, Advanced Fuel Research, Inc., 87 Church Street, Suite 308, East Hartford, CT 06108

3 President, Advanced Fuel Research, Inc., 87 Church Street, Suite 308, East Hartford, CT 06108

4 Senior Engineer, Advanced Fuel Research, Inc., 87 Church Street, Suite 308, East Hartford, CT 06108

5 Trace Contamination Control Cartridge Component Owner, Jacobs Technology, 2222 Bay Area Blvd, Houston, TX 77058

6 Deputy Component Manger – Ventilation and Thermal Loops, Jacobs Technology, 2222 Bay Area Blvd, Houston, TX 77058

7 Project Engineer, EVA Technology Development, NASA Johnson Space Center, 2101 NASA Parkway/EC5, Houston, TX 77058

Disclaimer: Trade names and trademarks are used in this report for identification only. Their usage does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

channel geometries (e.g., based on CFD modeling) that ensure uniform flow distribution throughout the sorbent (e.g., via variable/graded pressure-drop characteristics).

Nomenclature

<i>BET</i>	=	Brunauer, Emmett, and Teller (method of specific surface area determination)
<i>CF</i>	=	carbon fiber
CH_2O	=	formaldehyde
CH_4SH	=	methyl mercaptan
<i>d</i>	=	monolith-channel size (mm)
<i>D</i>	=	monolith diameter (mm, cm)
d_p	=	pore size (nm)
<i>EVA</i>	=	Extravehicular Activity
F_{gas}	=	gas flow rate (L/min)
<i>FTIR</i>	=	Fourier Transform Infrared (spectroscopy, analysis, analyzer, etc.)
<i>L</i>	=	sorbent-monolith length (mm, cm)
$\dot{m}_{\text{CH}_2\text{O-lab}}$	=	formaldehyde mass flow rate in a laboratory experiment ($\mu\text{g min}^{-1}$, $\mu\text{g min}^{-1} \text{g}^{-1}$)
$M_{\text{CH}_2\text{O}}$	=	formaldehyde molecular weight (g/mol)
<i>MFC</i>	=	mass-flow controller
<i>N</i>	=	number of channels in a monolith
NH_3	=	ammonia
<i>P</i>	=	pressure (atm)
<i>PEEK</i>	=	polyether ether ketone
<i>PVDC</i>	=	polyvinylidene chloride
<i>R</i>	=	gas constant ($\text{L atm mol}^{-1} \text{K}^{-1}$)
<i>RCA</i>	=	Rapid-Cycle Amine (swing bed)
S_{BET}	=	BET (Brunauer, Emmett, and Teller) surface area (m^2/g)
<i>SMAC</i>	=	spacecraft maximum allowable concentration (ppm, mg/m^3)
<i>T</i>	=	temperature (K)
<i>TC</i>	=	trace contaminant
<i>TCCS</i>	=	Trace Contaminant Control System
V_{micro}	=	micropore volume (cm^3/g)
V_p	=	total pore volume (cm^3/g)
<i>xPLSS</i>	=	Exploration Portable Life Support System
$y_{\text{CH}_2\text{O}}$	=	volume fraction of formaldehyde in the inlet gas (-)
δ_w	=	monolith-channel wall thickness (mm)
δ_{ow}	=	monolith outer wall thickness (mm)
ϵ	=	sorbent-monolith voidage (-)
ρ	=	sorbent -monolith density (g/cm^3)
τ	=	gas residence time within the sorbent monolith (ms)

I. Introduction

REGENERABLE life support systems are a critically important part of NASA's space-exploration projects. Trace-contaminant (TC) removal plays a key role in such life support systems, ensuring high quality air for the crew during Extravehicular Activities (EVAs) and also on board spacecraft. The use of predominantly microporous monolithic carbon produced by carbonization of polyether ether ketone (PEEK) was previously proposed for TC sorption.¹ In this paper, pressure-swing performance of PEEK-derived carbon TC sorbent monoliths is reported in terms of rapid adsorption-desorption cycling, with a cycle half-time of 5 minutes. The objectives of this study were: (1) to demonstrate the effectiveness of monolithic carbon sorbents with respect to ammonia, formaldehyde, and methyl mercaptan removal at concentrations close to the 7-day Spacecraft Maximum Allowable Concentrations, SMACs: 3 ppm ammonia, 0.1 ppm formaldehyde, and 0.2 ppm methyl mercaptan; (2) to evaluate the monolithic carbon sorbents with respect to multipollutant TC control, including ammonia, formaldehyde, methyl mercaptan, and carbon monoxide.

According to the proposed concept,¹⁻⁷ the starting materials for the sorbent-fabrication process are polymer-based precursors that produce microporous carbon upon carbonization and subsequent activation (pore size $d_p < 2$ nm). The use of the predominantly microporous carbon monoliths is associated with the following benefits: (a) high trace contaminant sorption capacity; (b) low pressure drop; (c) rapid vacuum (pressure-swing) desorption due to thin monolith walls and low pressure drop; (d) high mechanical strength¹ and resistance to attrition; (e) good thermal management (high thermal conductivity and low adsorption/desorption thermal effects associated with physisorption); (f) good resistance to dusty environments; (g) non-toxic, non-flammable¹ sorbents made of high-purity carbon; and (h) the flexibility to 3D-print/fabricate sorbent monoliths with optimized channel geometries (e.g., based on CFD modeling) that ensure uniform flow distribution throughout the sorbent (e.g., via variable/graded pressure-drop characteristics). Advantages (b) through (e) above are in contrast to the currently used EVA air-revitalization systems, which involve oversized, non-regenerable packed beds of activated carbon (AC) for TC control.

Trace-contaminant removal in spacecraft environments has a long history, and it was reviewed by Paul and Jennings,⁸ who concluded that carbon was the most suitable TC sorbent for the PLSS application. Several approaches to carbon regeneration have been attempted (reverse airflow, steam regeneration, and vacuum regeneration), but the challenge of excessive regeneration temperature, and of long desorption time scales, remains to be resolved. For this reason, the current state of the art is still based on a non-regenerable activated carbon impregnated with phosphoric acid, which has a high ammonia-sorption capacity, but is not meant to be regenerated. In general, the trace contaminants of current interest are ammonia and formaldehyde as they are the only ones that are likely to exceed the spacecraft maximum allowable concentration (SMAC) limits within the space suit.⁹ Methyl mercaptan is also of some concern, even though it is unclear whether its concentration can be kept below the SMAC because the generation rate of methyl mercaptan has not been quantified yet. Acetaldehyde is another TC of interest as it may degrade the operation of the CO₂-removal unit, the Rapid Cycle Amine (RCA) swing bed. This study, however, was concerned only with ammonia, formaldehyde, methyl mercaptan, and carbon monoxide sorption and sorbent regeneration by exposure to vacuum.

In our previous work, polyvinylidene chloride (PVDC) was extensively used as carbon-sorbent precursor,^{2,3,5-7,10-21} and performance data on the PEEK-derived carbon sorbents were recently reported.^{1,22} The use of PEEK is advantageous in terms of sorbent fabrication as the carbonization of PVDC is associated with the release of large amounts of hydrogen chloride during carbonization. In contrast, no corrosive gases are released during PEEK carbonization, and the carbon product yield is also higher than in the case of PVDC.

The approach to TC sorption used in this work is based mostly on physisorption, although surface chemistry still plays a role. The pore sizes are close to molecular dimensions, which ensures sufficiently strong van der Waals forces to obtain high TC-sorption capacities. Also, the high purity of the carbon derived from polymer precursors makes it possible to keep the carbon surface acidity low, which facilitates the reversible ammonia sorption. The fact that the underlying principle for our sorbents is physisorption, rather than chemisorption, makes vacuum and thermal regeneration fast and reversible. In contrast, most commercial activated carbons contain only modest amounts of microporosity, and this is why their sorption-capacity is relatively low, unless enhanced by acid-treatment, which facilitates the chemisorption of ammonia on acidic sites.

II. Materials and Experimental Procedures

A. Carbon Sorbents

A commercially available PEEK filament reinforced with about ~10 wt% carbon fiber (CF) was obtained from 3DXTECH, and this material served as a precursor for ammonia sorbents. The use of the carbon-fiber reinforcement is associated with some fabrication benefits, notably with the improved shape retention during carbonization and mechanical strength.¹ It was assumed in this study that the carbon fiber had low porosity and surface area, and also low oxidation reactivity, as compared with the PEEK-carbon. Thus, the carbon-fiber component of the PEEK/CF composite was considered an inert material with respect to ammonia sorption and pore-structure characterization.

Sorbent-monolith fabrication involved the following steps:

1. Fabrication of a polymer precursor in a desired monolithic shape using high-resolution 3D printing;
2. Oxidative treatment of the polymer monolith (pre-oxidation);
3. Polymer-monolith carbonization to produce a carbon monolith;
4. Carbon-monolith activation via gasification to produce an activated carbon monolith.

Step 2 was added to the original monolith-fabrication procedure on the basis of recent results that showed that the use of this step greatly improves monolith shape retention during softening and melting stages of carbonization

(step 3). As a consequence, the need to use elaborate support structures during carbonization, which was standard practice in our previous work,¹ was eliminated. In what follows, the sorbent monolith fabrication steps are briefly described.

3D Printing – An Intamsys Funmat HT 3D printer was used in this project. This model was designed specifically for higher-temperature polymer materials, such as PEEK and PEEK/CF.

Figure 1 displays a drawing of a typical monolith that is to be 3D printed using the PEEK/CF filament. In this case, the design is for a 0.5-mm square channel monolith, with an 18-mm diameter, 6-mm height, a channel-wall thickness of 0.25 mm, and a 0.5-mm outer wall thickness. This geometry was used as a baseline design in this work, and, unless specified otherwise, the above monolith dimensions were used in the experiments described in this paper. A square-channel geometry is quite typical for monoliths.²³ Since in the case of low TC concentrations, long adsorption time scales were expected during breakthrough-curve measurements (several days), smaller PEEK/CF monoliths were also fabricated, with a monolith height of 3 mm rather than the standard 6 mm, to reduce the experimental time scale during sorbent testing.

Pre-oxidation – This technique involves PEEK oxidative treatment at temperatures below the PEEK melting point. This treatment is performed prior to carbonization in a tube furnace. It was previously shown that this step successfully preserved the original PEEK/CF monolith shape during carbonization, without the need for supporting structures.¹ This greatly simplifies the fabrication process. Unless indicated otherwise, pre-oxidation was carried out in a flow of air at 340 °C for 3 hours in a tube furnace.

PEEK/CF Carbonization and Activation – Conventional laboratory procedures were used in the preparation of PEEK/CF carbon monolith sorbents, i.e. carbonization followed by carbon activation. The PEEK/CF monolith, fabricated by 3D printing, was carbonized in a tube furnace, and the resultant char was then subjected to air activation, also in a tube furnace. The following carbonization steps were used sequentially: (1) heating in a flow of nitrogen from room temperature to ~500 °C at 10 °C/min; and (2) heating in a flow of nitrogen from ~500 °C to the final carbonization temperature at 5 °C/min. Unless specified otherwise, no hold at the final temperature was implemented. In this work, the following final carbonizations temperatures were used: 800 °C, and 900 °C. The resultant carbon monoliths were subsequently activated in a flow of air at 325 °C to ~20% burn-off (weight loss, determined by weighing the sample before and after activation), and then tested for TC sorption using a fixed-bed system. The final sorbent monoliths (after carbonization and activation) had the following dimensions and properties: diameter, $D = 17$ mm; length, $L = 3.6$ mm (nominal) and 1.8 mm; 0.5-mm square channels; channel-wall thickness, $\delta_w \approx 0.25$ mm; outer wall thickness, $\delta_{ow} \approx 0.5$ mm; voidage, $\epsilon = 0.444$; density, $\rho \approx 0.55$ g/cm³; BET surface area, $S_{BET} \approx 585$ m²/g; total pore volume, $V_p \approx 0.304$ cm³/g; micropore volume, $V_{micro} \approx 0.211$ cm³/g; percent microporosity: 69.4 %.

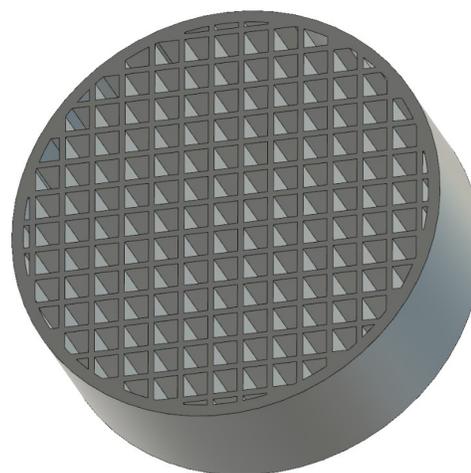


Figure 1. Conceptual design of a 3D-printed monolith with square channels (not to scale). Channel size, $d = 0.5$ mm; monolith diameter, $D = 18$ mm; monolith length, $L = 6$ mm; number of channels, $N \approx 403$; voidage, $\epsilon = 0.444$; wall thickness, $\delta_w = 0.25$ mm; outer wall thickness, $\delta_{ow} = 0.50$ mm. After thermal processing, the carbonized structure dimensions are reduced ($D \approx 17$ mm, $L \approx 3.6$ mm).

B. Sorbent Testing

TC sorption capacities were determined from breakthrough curves (TC concentration in the effluent versus time) measured using a fixed-bed apparatus shown in Figure 2. The testing was performed in two stages: (a) TC sorption, where the gas stream was passed through the sorbent at atmospheric pressure; and (b) TC vacuum desorption (sorbent regeneration), where the sorbent was exposed to vacuum. Two types of desorption regimes were used: (1) exposure to high or low vacuum ($\sim 10^{-6}$ Torr or ~ 0.3 –1 Torr, respectively) by removing the sorbent from the test rig and placing it in a vacuum chamber for up to a few hours; and (2) pressure-swing operation with a cycle half-time of five minutes (low vacuum, i.e. ~ 0.3 Torr). Sorption and desorption testing is described below.

The test cell containing the TC sorbent was placed in a temperature-controlled enclosure (not shown in Figure 2). TC concentration determination was carried out using an FTIR analyzer downstream of the reactor. The inlet gas

composition was similar to that typical for the xPLSS: ~ 3 ppm ammonia, ~ 0.1 ppm formaldehyde, ~ 0.2 ppm methyl mercaptan, ~ 1.0 vol.% CO_2 , 29 vol.% O_2 , and a balance of nitrogen. The apparatus shown in Figure 2 includes a Perma Pure MH series Nafion humidifier (24" length) for introducing moisture in the test gas. At normal room temperature (21 °C), and at flow rates of up to about 1.0 L/min, the humidifier can increase the relative humidity of the carrier gas to 80-90%. Lower levels are obtained by dilution downstream of the humidifier. No water was present in the inlet gas in the tests reported in this paper. The presence of water is known to enhance the sorption capacity of the PEEK/CF-derived sorbents.¹ The gas flow rates used in this work were 0.52 L/min and 1.0 L/min, and, unless stated otherwise, the sorbent-monolith dimensions were: diameter, $D = 17$ mm; length: $L = 3.6$ mm and 1.8 mm; 0.5-mm square channel monoliths with a wall thickness of ~ 0.25 mm, which corresponds to a voidage of ~ 0.444 . The nominal experimental conditions (0.52 L/min; $D = 17$ mm, and $L = 3.6$ mm) correspond to a gas residence time within the sorbent monolith of ~ 39 ms, which is identical to the gas residence time envisaged for the full-scale TC sorbent monolith.

Two FTIR analyzers were used for gas analysis, both of them On-Line Technologies model 2010 Multi-Gas Analyzers. One of them employed a liquid nitrogen-cooled, mercury-cadmium-telluride (MCT) detector, with a bandpass of 500–6500 cm^{-1} and a spectral resolution of 0.5 cm^{-1} , and a multi-pass gas cell with a 2-liter sampling volume and an effective path length of 5.1 m. The other instrument was a newer, ultra-sensitive version of the same model, with a 0.2-liter multi-pass gas cell. The latter instrument was optimized for measurements in the mid-infrared region, for high sensitivity to formaldehyde and methyl mercaptan. Furthermore, this FTIR instrument was equipped with a thermoelectrically cooled detector,

which was convenient for long-term continuous operation. Selected sorbent-performance test experiments were performed in duplicates with good data reproducibility.

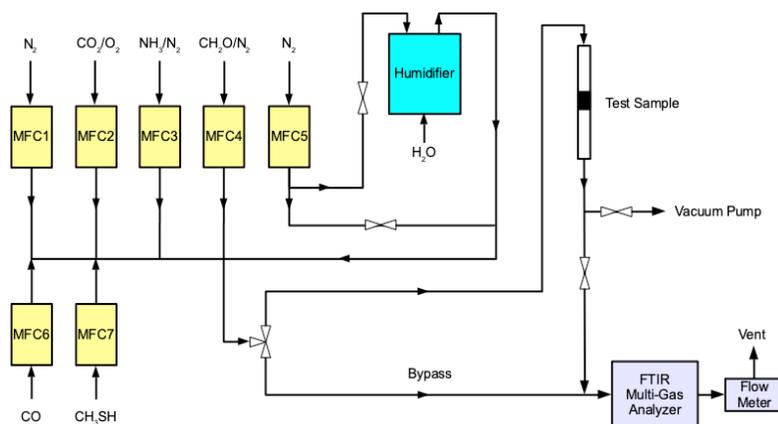


Figure 2. Sorption/desorption capacity test apparatus. MFC1 through MFC7 are mass-flow controllers, CH_2O is formaldehyde, and CH_3SH is methyl mercaptan.

III. Results and Discussion

A. TC Sorption and Sorbent Regeneration

Data in Figure 3 show ammonia breakthrough and sorption capacity curves for a 0.5-mm square-channel sorbent monolith that had been regenerated in high vacuum for 6 hours prior to testing. It can be seen that, under the conditions used in this experiment, ammonia is completely removed from the gas stream for about 250 minutes, and that the equilibrium sorption capacity is close to 4.0 mg NH_3/g carbon. Since the sorption capacity is strongly dependent on

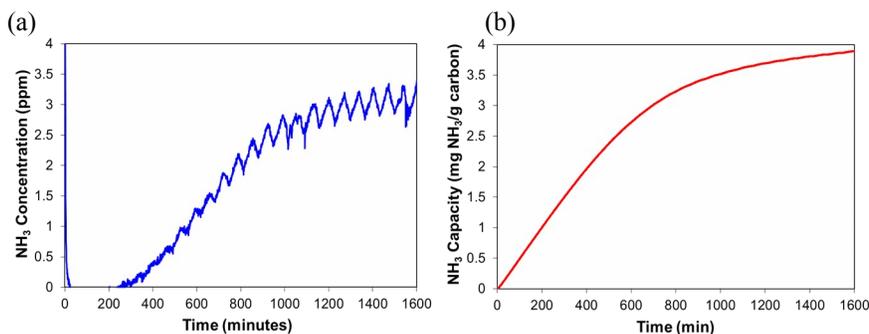


Figure 3. Ammonia breakthrough curve (a) and sorption-capacity curve (b) under dry-gas conditions. Sorbent carbonized at 800 °C: 0.50-mm square-channel monolith, 17-mm diameter, 3.5-mm height, 0.25-mm wall thickness, 0.472 g regenerated in high vacuum for 6 hours (vacuum applied from one side of the sorbent); ammonia inlet concentration: ~ 3.35 ppm; total gas flow rate: ~ 1.0 L/min.

adsorbate partial pressure, the sorption capacity at 3 ppm is expected to be much lower than the sorption capacity at higher ammonia concentrations. Thus, due to the above fundamental equilibrium property of adsorption isotherms, the ammonia-sorption capacity of PEEK/FC carbon sorbents at 20 ppm was previously found to be higher than that shown in Figure 3 for ammonia concentration of 3 ppm, i.e. ~ 20 mg NH_3/g carbon at 20 ppm ammonia^{1, 22} versus ~ 4 mg NH_3/g carbon at ~ 3 ppm ammonia (Figure 3). The fluctuations in the ammonia concentration seen in Figure 3a result from temperature fluctuations within the laboratory, and they reflect the generally high sensitivity of gas adsorption to temperature. For a sorbent monolith fabricated at a different carbonization temperature (900°C), the ammonia sorption capacity was found to be even higher than that shown in Figure 3, i.e. about 6 mg NH_3/g sorbent. The formaldehyde and methyl-mercaptan sorption capacities were found to be even more impressive: >8 mg $\text{CH}_2\text{O}/\text{g}$ and > 50 mg $\text{CH}_3\text{SH}/\text{g}$ at concentrations close to 7-day SMAC limits, as shown in Figure 4. Data presented in Figure 4 were collected for more than 20 days at a gas residence time within the sorbent much lower than in a full-scale application ($\tau_{\text{lab}} \approx 9.4$ ms $\ll \tau_{\text{full-scale}} \approx 39$ ms). It can be seen that the sorbent is far from being saturated after such a long exposure to CH_2O and CH_3S , which demonstrates the enormous sorption capacity with respect to formaldehyde and methyl mercaptan. This indicates that, unlike with ammonia, sorbent regeneration in the case of these two species may be unnecessary as the expected TC-sorbent life time is ~ 150 8-hour EVAs. This point is addressed in some detail below.

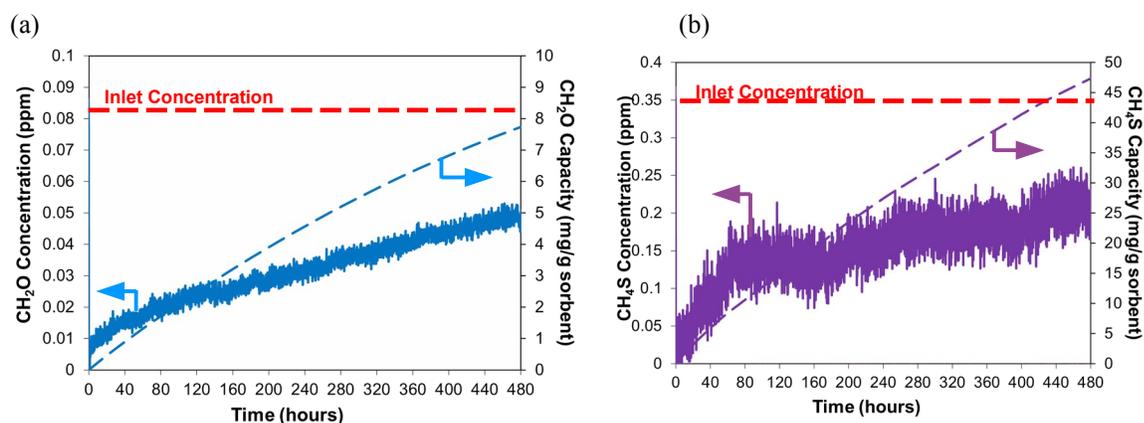


Figure 4. The formaldehyde (a) and methyl -mercaptan (b) breakthrough and sorption-capacity curves for a carbon sorbent derived from a 3D-printed PEEK/CF monolith carbonized at 900°C and activated in a flow of air at 325°C to a burn-off of ~ 20 wt% (0.5-mm square-channel monolith, with a wall thickness of ~ 0.25 mm, a diameter of ~ 17 mm, a height of ~ 1.75 mm, and a weight of 0.235 g). The gas flow rate through the sorbent was 1 L/min (gas residence time, $\tau \approx 9.4$ ms).

To evaluate the dynamic behavior of sorbent monoliths under Pressure-Swing Adsorption (PSA) conditions, rapid ammonia sorption-desorption cycling was performed, which mimics the expected xPLSS operation. 5-minute half-cycles were used, the ammonia inlet concentration was 3.35 ppm, and the gas flow rate was 1.0 L/min. Testing was carried out using a PEEK/CF carbon sorbent monolith with the following properties: 0.5-mm square channels, 17-mm diameter, 3.5-mm height, 0.25-mm wall thickness, a sorbent weight of 0.472 g.

In the first experiment, high-vacuum regeneration in a vacuum chamber (pumped using a turbomolecular pump system) was used (10^{-6} Torr), and the sample-transfer period between the sorption and desorption steps was approximately 1.0–1.5 minutes. Vacuum was applied to one side of the sorbent during regeneration. Data in Figure 5a show how the initially fully saturated sorbent improves its performance, as evidenced by the gradual reduction in the outlet ammonia concentration over several cycles to reach a near steady-state condition at ~ 0.5 – 0.6 ppm. It should be borne in mind that the above measured ammonia concentration is higher than the actual concentration at the sorbent outlet. This is so because of the lag in the measured concentration value, which is caused by the time needed to purge the analyzer 2-liter gas cell after a step change in ammonia concentration. To put it differently, the analyzer response time is too long for the accurate measurement of rapidly changing ammonia levels. It is nonetheless clear that the feasibility of using the PEEK/CF carbon sorbent monoliths to control ammonia at the 7-day SMAC level is demonstrated at a cycle time of a few minutes. Data in Figure 5b show a breakthrough curve determined immediately after the final desorption half-cycle. It can be seen that almost half of the sorption capacity

is recovered despite the repeated exposure to ammonia after each desorption step (sorption capacity ≈ 1.7 mg NH_3/g).

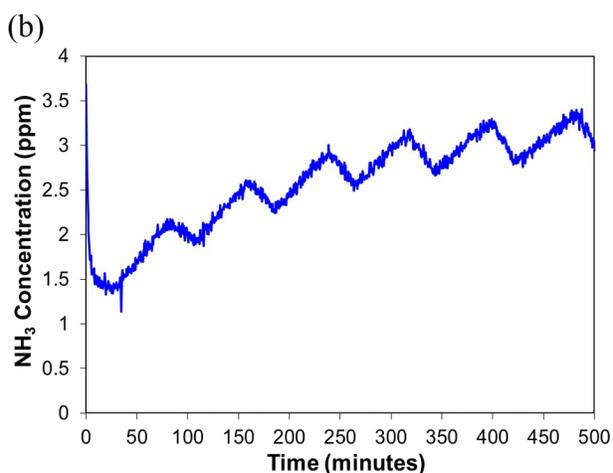
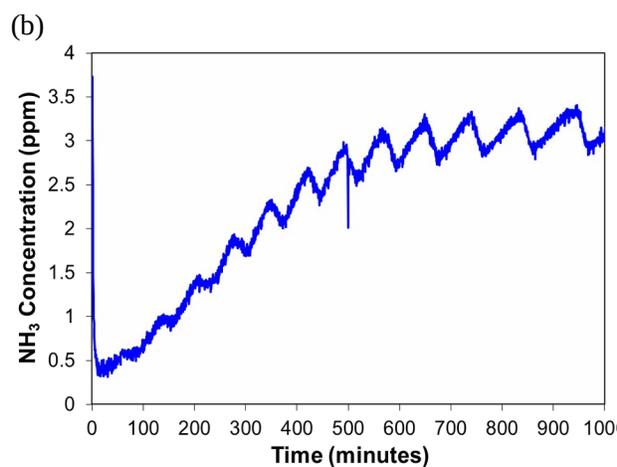
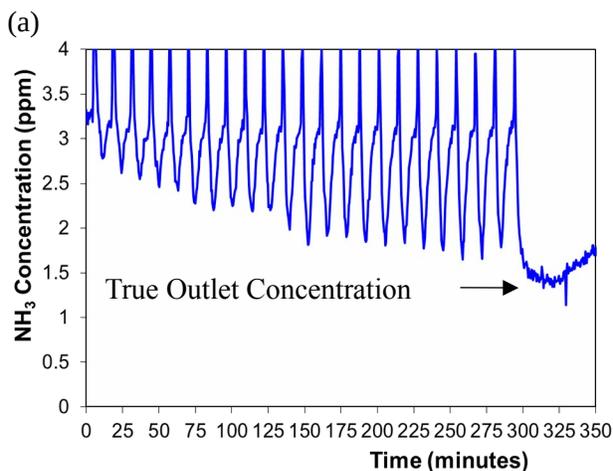
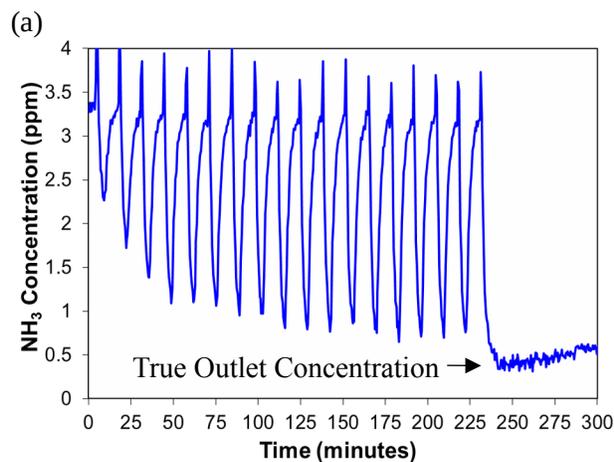


Figure 5. Rapid ammonia sorption-desorption cycling measurements with sorbent regeneration at high vacuum (10^{-6} Torr); gas analysis using the analyzer with a 2-liter gas cell: (a) ammonia concentration at sorbent outlet over multiple cycles; and (b) ammonia breakthrough curve determined after the final desorption half-cycle. Sorbent: 0.50-mm square-channel monolith, 17-mm diameter, 3.5-mm height, 0.25-mm wall thickness, 0.472 g (vacuum applied from one side of the sorbent); ammonia inlet concentration: ~ 3.35 ppm; total gas flow rate: ~ 1.0 L/min.

Figure 6. Rapid ammonia sorption-desorption cycling measurements with sorbent regeneration at low vacuum (1 Torr); gas analysis using the analyzer with a 2-liter gas cell: (a) ammonia concentration at sorbent outlet over multiple cycles; and (b) ammonia breakthrough curve determined after the final desorption half-cycle. Sorbent: 0.50-mm square-channel monolith, 17-mm diameter, 3.5-mm height, 0.25-mm wall thickness, 0.472 g (vacuum applied from one side of the sorbent); ammonia inlet concentration: ~ 3.35 ppm; total gas flow rate: ~ 1.0 L/min.

The above experiment was repeated in the same manner, except that regeneration was now performed at 1 Torr, using only the vacuum chamber roughing pump (rotary pump). The sorbent, and the operating conditions, were otherwise the same. The low-vacuum desorption is obviously a more challenging environment for ammonia removal, as compared with high-vacuum regeneration discussed above. As a consequence, the ammonia concentration dropped to only ~ 1.5 – 2.0 ppm under these conditions, and the approach to a steady state appeared

to be slower (see Figure 6a). Not surprisingly, the ammonia breakthrough curve determined immediately after the last desorption half-cycle showed less sorbent capacity than in the case of high-vacuum regeneration (~ 0.64 mg NH_3/g versus ~ 1.7 mg NH_3/g), as shown in Figure 6b. Data shown in Figure 5 and Figure 6 demonstrate a strong dependence of sorbent performance on vacuum quality in the regeneration step.

To further investigate the effect of regeneration conditions on TC sorbent performance, additional experiments were carried out using various conditions in the vacuum chamber. Both absolute pressure and sorbent-regeneration time were varied, vacuum was applied from one side of the sorbent, and results are shown in Figure 7. It can be seen that the sorbent performance, here measured as ammonia-sorption capacity and time to breakthrough, increases with improving regeneration conditions, i.e. with better vacuum and longer regeneration time. Results of the dynamic ammonia sorption-desorption experiments shown in Figure 5a and Figure 6a are consistent with this conclusion, and so does our previously published work on PVDC-derived carbon sorbents.³

The culmination of the sorbent-monolith testing effort was a long run involving simultaneous removal of ammonia, formaldehyde, and methyl mercaptan using a rapid adsorption-desorption cycle testing protocol, with a half-cycle of 5 minutes and a residence time close to the one characteristic of the xPLSS, i.e. $\tau \approx 40$ ms. This run involved about 14 days of continuous operation, and the vacuum-regeneration pressure was chosen to be that of a rotary-vane pump (~ 0.3 Torr) so that the testing conditions were quite challenging for the sorbent, thus making the results rather conservative. Results are shown in Figure 8 through Figure 10, where the TC slip is defined as TC concentration at the sorbent outlet, expressed in terms of the percentage of the TC inlet concentration. The data show that the sorbent monolith performs well over about 330 hours (~ 14 days), i.e. 2,000 rapid adsorption-desorption cycles, at the relevant residence time ($\tau \approx 40$ ms), and with modest-quality vacuum used for regeneration (0.3 Torr). Furthermore, data in Figure 8 show that ammonia removal efficiency, initially close to 100%, decreases gradually with time to reach about 70% at the end of this long test. TCCS-design calculations similar to those described by Paul *et al.*⁹ indicate that a long-term ammonia-removal efficiency greater than $\sim 50\%$ would be sufficient to make sure the astronaut breathes oxygen with ammonia under 7-day SMAC ($2 \text{ mg}/\text{m}^3$) in the space suit. This relatively high TC-removal efficiency is needed because of the high ammonia generation rate within the suit ($80 \text{ mg}/\text{day}$). In contrast, a much lower TC-removal efficiency would be sufficient in the case of formaldehyde ($\sim 3\%$) because of the much lower formaldehyde-generation rate ($0.42 \text{ mg}/\text{day}$). The above considerations, and data shown in Figure 8 and Figure 9, show that the currently available sorbent monoliths have the rapid-cycle performance that is adequate for ensuring that ammonia and formaldehyde concentration within the space suit stay below SMAC levels for many EVAs.

Data in Figure 9 show that the efficiency of formaldehyde removal, initially at 100%, stays at or above 60% throughout the entire test, which is more than adequate to keep formaldehyde concentration within the space suite below the 7-day SMAC. The question to address is how many equivalent EVAs, or hours, our sorbent would be expected to last for and provide adequate formaldehyde removal on the basis of laboratory data shown in Figure 9. It should be noted that the time the sorbent is on-line in our laboratory experiment is not identical to the time of operation in the actual, full-scale space suit. Although the residence times for both cases are identical, which means that the TC-removal efficiency should be comparable, the sorbent used in our lab experiment is subjected to a much higher formaldehyde mass flow per gram sorbent than would be the case in the full-scale system. Thus, there is a need to convert the lab-experiment time scale to the number of equivalent EVAs, taking into account differences in the formaldehyde mass flow rate and sorbent mass.

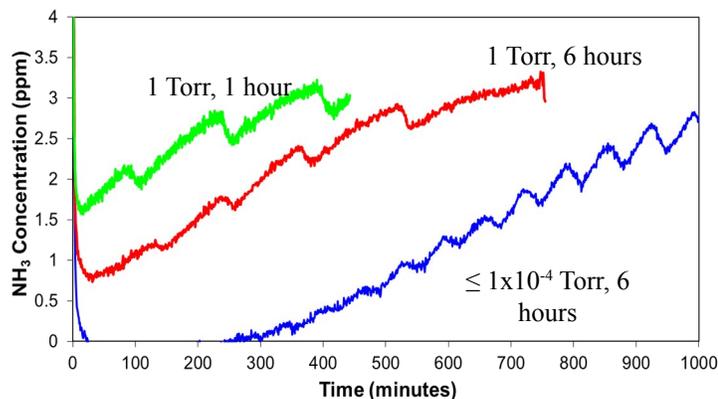


Figure 7. Ammonia breakthrough curves for a PEEK/CF carbon sorbent monolith regenerated under different conditions. Sorbent: 0.50-mm square-channel monolith, 17-mm diameter, 3.5-mm height, 0.25-mm wall thickness, 0.472 g; ammonia inlet concentration: ~ 3 ppm; total gas flow rate: ~ 1.0 L/min.

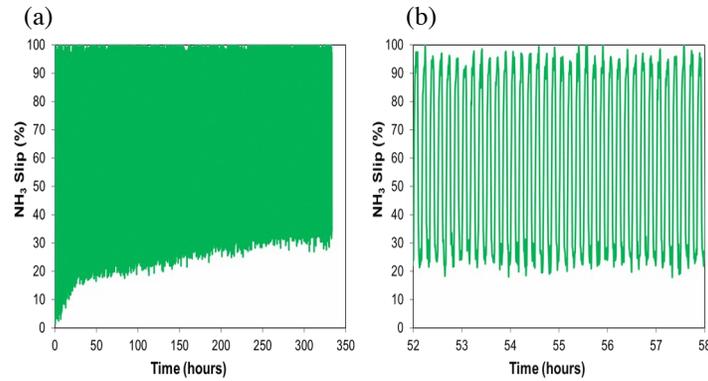


Figure 8. Ammonia-sorption performance, (a), during a rapid adsorption-desorption cycling experiment with a half-cycle of 5 minutes (sorbent derived from a 3D-printed PEEK/CF monolith carbonized at 900 °C and activated in a flow of air at 325 °C to a burn-off of ~20 wt%; 0.5-mm square-channel monolith, with a wall thickness of ~0.25 mm, a diameter of ~17 mm, a height of ~3.5 mm, and a weight of 0.466 g). The gas flow rate through the sorbent was 0.52 L/min, and the ammonia inlet concentration was ~5.5 ppm. The sorbent was regenerated by exposure to vacuum created by a roughing pump (~0.3 Torr). The plot on the right, (b), shows part of the large data set shown in the left plot, (a).

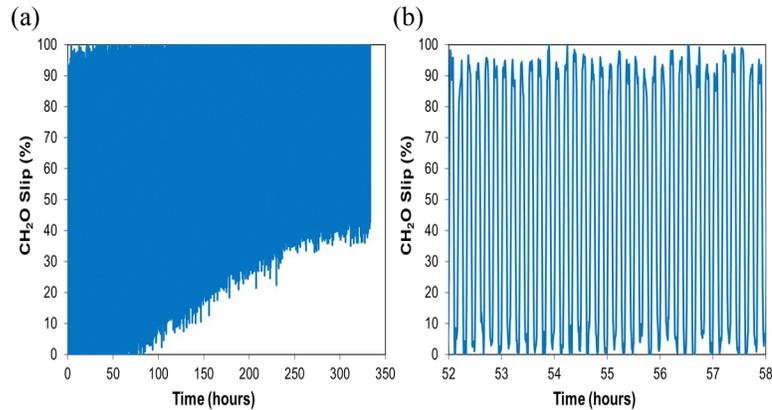


Figure 9. Formaldehyde-sorption performance, (a), during a rapid adsorption-desorption cycling experiment with a half-cycle of 5 minutes (sorbent derived from a 3D-printed PEEK/CF monolith carbonized at 900 °C and activated in a flow of air at 325 °C to a burn-off of ~20 wt%; 0.5-mm square-channel monolith, with a wall thickness of ~0.25 mm, a diameter of ~17 mm, a height of ~3.5 mm, and a weight of 0.466 g). The gas flow rate through the sorbent was 0.52 L/min, and the formaldehyde inlet concentration was ~0.095 ppm. The sorbent was regenerated by exposure to vacuum created by a roughing pump (~0.3 Torr). The plot on the right, (b), shows part of the large data set shown in the left plot, (a).

The sorbent geometry in the full-scale system is as follows: the diameter $D = 5.3'' = 13.5$ cm, the monolith length: $L = 0.7'' = 1.8$ cm, which gives the sorbent volume of $V = 257.6$ cm³. Using the carbon monolith density of $\rho \approx 0.55$ g/cm³, one can calculate the expected sorbent mass in the full-scale system: $m = \rho V = 141.7$ g. This amount of the sorbent will be subjected to a mass flow of formaldehyde that is close to the rate of formaldehyde generation, i.e. 0.42 mg/day. The above generation rate is taken from NASA-published data at <https://ntrs.nasa.gov/api/citations/20190033446/downloads/20190033446.pdf>, according to which all the TC generation rates are expressed in mg/day. There is a question whether these generation rates are meant to be expressed in mg/24 hours or in mg/8-hour EVA. The ammonia generation rate is given as 80 mg/day, which, if *mg/day* means *mg/8-h EVA*, is identical to the generation rate of 80 mg/8-h EVA given in the paper by Paul *et al.* (2010).⁹ This strongly favors the interpretation of *mg/day* as *mg/8-h EVA* rather than *mg/24 hours*. On the other hand, if one interprets the formaldehyde generation rate of 0.42 mg/day as 0.42 mg/24 hours, then one obtains a formaldehyde generation rate of 0.14 mg/8-h EVA, which is very close to the value of 0.13 mg/8-h EVA quoted by Paul *et al.* (2010).⁹ The above ambiguity in unit interpretation most likely originates from the fact that some TCs are

generated mostly metabolically, in which case mg/8-h EVA seems appropriate, whereas other TCs may originate mostly from equipment outgassing, in which case their generation is continuous, i.e. 24 hours a day, rather than limited to an 8-hour EVA time frame. Be it as it may, we decided to carry out calculations for both cases, with slight preference given to the interpretation that *mg/day* really means *mg/8-h EVA* because this assumption leads to a more conservative conversion of time on-line in a lab experiment to the number of equivalent EVAs for the xPLSS. Thus, if the nominal formaldehyde generation rate of *0.42 mg/day* is understood as *0.42 mg/8-h EVA*, then the generation rate per minute is $0.42/8/60 = 0.000875$ mg/min. Normalizing with respect to sorbent mass in the full-scale TCCS, one obtains the formaldehyde mass flow rate per gram sorbent equal to $0.000875/141.7 = 0.00000618$ mg/(g min) = $0.00618 \mu\text{g CH}_2\text{O}/(\text{g sorbent min})$. This is a relatively small formaldehyde inlet duty as compared with our lab experiment, for which the corresponding formaldehyde flow is calculated as follows:

$$\dot{m}_{\text{CH}_2\text{O-lab}} = M_{\text{CH}_2\text{O}} \frac{P y_{\text{CH}_2\text{O}} F_{\text{gas}}}{RT} \quad (1)$$

where $M_{\text{CH}_2\text{O}}$ is the formaldehyde molecular weight, P is the pressure, $y_{\text{CH}_2\text{O}}$ is the volume fraction of formaldehyde in the inlet gas, F_{gas} is the gas flow rate (L/min), R is the gas constant, and T is temperature, in degrees Kelvin. Substituting numerical values into Eq. (1), one obtains:

$$\dot{m}_{\text{CH}_2\text{O-lab}} = 30 \frac{1 \times 0.095 \cdot 10^{-6} \times 0.52}{0.082 \times 293} = 6.168 \cdot 10^{-8} \text{ g/min} = 0.06168 \mu\text{g/min}$$

The above flow rate per gram sorbent is $0.06168/0.466 = 0.132 \mu\text{g}/(\text{g min})$. One can now calculate the equivalent number of 8-hour EVAs expected in the full-scale space suit on the basis of the number of hours in a lab experiment, e.g. the time scale for the data shown in Figure 9, as (lab-experiment time[h]) $\times 0.132/0.00618/8 = (\text{lab-experiment time [h]}) \times 2.67$ [EVAs]. (It can be easily shown that the corresponding factor for converting lab-experiment time to equivalent EVAs is ~ 147 in the case where $0.42 \text{ mg CH}_2\text{O/day}$ is understood to be $0.42 \text{ mg CH}_2\text{O}/24 \text{ hours}$.) Thus, 330 hours of sorbent testing under the lab conditions used in our experiment are equivalent to more than 850 EVAs in the full scale system. This is clearly more than adequate to satisfy the NASA requirement of a 150 EVA sorbent life time with formaldehyde-removal efficiency, and the formaldehyde-removal efficiency is demonstrated to be greater or equal $\sim 60\%$. Since calculations based on work by Paul et al.⁹ show that a removal efficiency greater or equal to $\sim 3\%$ is needed for formaldehyde concentration within the space suit to stay below the 7-day SMAC, it is fair to conclude that the sorbent-monolith performance is adequate from the point of view of formaldehyde removal for at least 850 EVAs. Clearly, this meets the NASA 150-EVA-sorbent-life requirement.

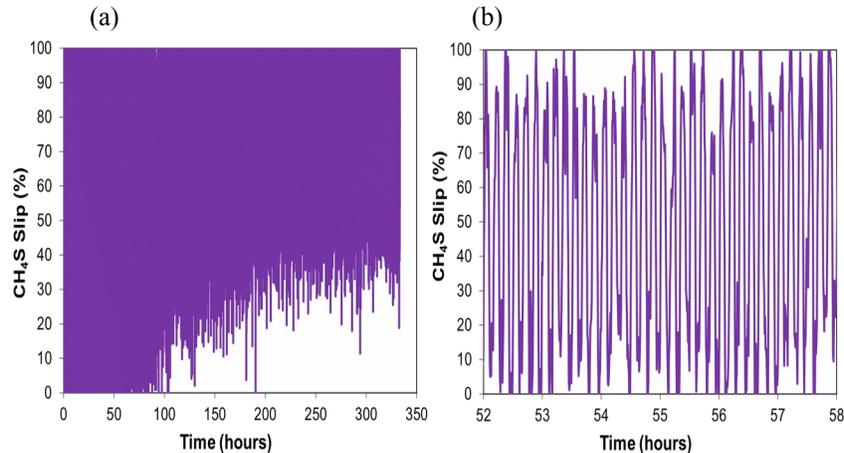


Figure 10. Methyl mercaptan sorption performance, (a), during a rapid adsorption-desorption cycling experiment with a half-cycle of 5 minutes (sorbent derived from a 3D-printed PEEK/CF monolith carbonized at $900 \text{ }^\circ\text{C}$ and activated in a flow of air at $325 \text{ }^\circ\text{C}$ to a burn-off of $\sim 20 \text{ wt}\%$; 0.5-mm square-channel monolith, with a wall thickness of $\sim 0.25 \text{ mm}$, a diameter of $\sim 17 \text{ mm}$, a height of $\sim 3.5 \text{ mm}$, and a weight of 0.466 g). The gas flow rate through the sorbent was 0.52 L/min , and the methyl -mercaptan inlet concentration was $\sim 0.4 \text{ ppm}$. The sorbent was regenerated by exposure to vacuum created by a roughing pump ($\sim 0.3 \text{ Torr}$). The plot on the right, (b), shows part of the large data set shown in the left plot, (a).

Data in Figure 10 show that the efficiency of methyl-mercaptan removal, initially at 100%, stays at or above ~65% throughout the entire test. It should be noted in Figure 10 that methyl-mercaptan analysis in the gas stream is associated with a higher noise as compared with ammonia and formaldehyde measurements (Figure 8 and Figure 9, respectively). Since the methyl-mercaptan generation rate is currently unknown, it is impossible to ascertain whether the 65% TC-removal efficiency is adequate to ensure the astronaut's comfort. One can hypothesize that it is indeed the case as the methyl-mercaptan generation rate, an important factor in minimum TC-removal efficiency determination, is expected to be relatively low, as compared to ammonia, and perhaps close to the generation rate of formaldehyde. If this were indeed the case, it could be shown, through similar calculations as in the case of formaldehyde, that the sorbent monoliths developed in this study would be effective with respect to methyl-mercaptan control for hundreds equivalent EVAs in the full-scale xPLSS. This assertion will be critically addressed in future research, when it is expected that methyl-mercaptan generation rate will be published by NASA.

A single experiment involving carbon-monoxide sorption on a 0.75-mm square-channel PEEK/CF carbon monolith (0.394 g) was carried out. A flow of 1.0 L/min gas containing 56 ppm of carbon monoxide was directed first through a bypass line, and then through the sorbent. Results of carbon monoxide concentration measurements showed that no detectable adsorption of carbon monoxide could be observed. This result is hardly surprising as we are not aware of any cases of successful CO removal by adsorption on carbon reported in the literature, even though numerous attempts have been made as the subject is important in other fields, e.g., in the efforts directed towards reducing the harmful effects of tobacco smoking.

IV. Conclusions

Pressure-swing adsorption of trace contaminants was investigated in a laboratory-scale fixed-bed testing system. Carbon-sorbent monoliths derived from the PEEK polymer were used, and rapid-cycle adsorption-desorption operation was carried out at a half-cycle of 5 minutes. Experimental data led to the following conclusions:

1. Activated carbon monoliths derived from the PEEK/CF polymer precursor were shown to have excellent ammonia adsorption and vacuum-regeneration properties at ammonia 7-day SMAC (3 ppm) in the presence of formaldehyde, methyl mercaptan, carbon dioxide, and oxygen, all at concentrations relevant to Exploration Portable Life Support (xPLSS) operation.
2. The carbon monoliths exhibited outstanding formaldehyde and methyl-mercaptan sorption performance at concentrations close to 7-day SMAC levels (0.1 ppm formaldehyde and 0.2 ppm methyl mercaptan).
3. Demonstrated fast sorbent monolith response and compatibility with rapid-cycle pressure swing adsorption (PSA) operation (at a 5-minute half-cycle time and 0.3-Torr regeneration pressure) over about 2,000 adsorption-desorption cycles (~330 hours of continuous operation).
4. Sorbent performance with respect to ammonia sorption was found to be strongly dependent on the quality of vacuum in the regeneration step, and also on regeneration time.
5. Little or no carbon-monoxide sorption was observed on activated carbon sorbent monoliths.

Acknowledgments

Financial support for the project was provided by NASA SBIR program under Contract No. 80NSSC20C0553. The authors wish to express their appreciation for the guidance and helpful discussions with Cinda Chullen and John Hostetler, the Contracting Officer's Technical Representatives at NASA Johnson Space Center. A high-sensitivity FTIR multigas analyzer was provided for the project by Max Analytical Technologies of East Windsor, CT, with Dr. Marty Spartz contributing invaluable help with instrument set-up, its customization, and calibration. Nitrogen adsorption isotherm analyses of carbon samples were performed by Dr. Indrek Külaots of Brown University. Helpful discussions and consulting input were provided by Professor Eric Suuberg of Brown University. The above contributions are gratefully acknowledged.

References

¹ Wójtowicz, M. A., Cosgrove, J. E., Serio, M. A., Carlson, A., and Chullen, C., "Monolithic trace-contaminant sorbents fabricated from 3D-printed polymer precursors," *Proc. 49th International Conference on Environmental Systems (ICES)*, Boston, MA, Paper No. ICES-2019-286, 2019

² Wójtowicz, M. A., Cosgrove, J. E., Serio, M. A., Manthina, V., Singh, P., and Chullen, C., "Carbon-Based Regenerable Sorbents for the Combined Carbon Dioxide and Ammonia Removal for the Primary Life Support System (PLSS)," *Proc. 44th International Conference on Environmental Systems (ICES)*, Tucson, Arizona, ICES-2014-241, 2014

- ³ Wójtowicz, M., Cosgrove, J., Serio, M., and Jennings, M., “Reversible Ammonia Sorption on Carbon for the Primary Life Support System (PLSS),” *Proc. 42nd International Conference on Environmental Systems*, American Institute of Aeronautics and Astronautics, San Diego, California, AIAA-2012-3437, 2012
- ⁴ Wójtowicz, M. A., Cosgrove, J. E., Serio, M. A., Nalette, T., Guerrero, S. V., Papale, W., and Wilburn, M. S., “Development of Trace Contaminant Control Prototypes for the Portable Life Support System (PLSS),” *Proc. 47th Int. Conf. on Environmental Systems*, ICES, Charleston, SC, ICES-2017-270, 2017
- ⁵ Wójtowicz, M. A., Cosgrove, J. E., Serio, M. A., and Wilburn, M. S., “Adsorption of ammonia on regenerable carbon sorbents,” *Proc. 45th International Conference on Environmental Systems (ICES)*, Bellevue, WA, Paper No. ICES-2015-179, 2015
- ⁶ Wójtowicz, M. A., Cosgrove, J. E., Serio, M. A., and Wilburn, M. S., “Co-adsorption of Ammonia and Formaldehyde on Regenerable Carbon Sorbents for the Primary Life Support System (PLSS),” *Proc. 46th International Conference on Environmental Systems (ICES)*, Vienna, Austria, Paper No. ICES-2016-345, 2016
- ⁷ Wójtowicz, M., Florczak, E., Kroo, E., Rubenstein, E., Serio, M. A., and Filburn, T., “Monolithic sorbents for carbon dioxide removal,” *Proc. 36th Int. Conf. on Environmental Systems (ICES)*, SAE International, Norfolk, VA, 2006-01-2193, 2006
- ⁸ Paul, H. L., and Jennings, M. A., “Results of the trace contaminant control trade study for space suit life support development,” *Proc. 39th Int. Conf. on Environmental Systems*, SAE International, Savannah, Georgia, Paper No. 2009-01-2370, 2009
- ⁹ Paul, H. L., Jennings, M. A., and Waguespack, G. M., “Requirements and sizing investigation for Constellation space suit Portable Life Support System Trace Contaminant Control,” *Proc. 40th Int. Conf. on Environmental Systems*, AIAA, Barcelona, Spain, Paper No. AIAA 2010-6065, 2010
- ¹⁰ Wójtowicz, M. A., Cosgrove, J. E., and Serio, M. A., “Carbon sorbent for reversible ammonia sorption, US Pat. No. 9,073,039,” US Pat. No. 9,073,039, 2015
- ¹¹ Wójtowicz, M. A., Rubenstein, E. P., Serio, M. A., and Cosgrove, J. E., “High-strength porous carbon and its multifunctional applications,” US Pat. No. 8,615,812, 2013
- ¹² Wójtowicz, M. A., Markowitz, B. L., and Serio, M. A., “Microporosity development in carbons for gas-storage applications,” *Proc. EUROCARBON '98: Science and Technology of Carbon*, AKK & GFEC, Strasbourg, France, 589–590, 1998
- ¹³ Wójtowicz, M. A., Markowitz, B. L., Smith, W. W., and Serio, M. A., “Microporous carbon adsorbents for hydrogen storage,” *Proc. Third International Conference on Materials Engineering for Resources (ICMR '98)*, Akita, Japan, 416–429, 1998
- ¹⁴ Wójtowicz, M. A., Markowitz, B. L., Bassilakis, R., and Serio, M. A., “Hydrogen storage carbons derived from polyvinylidene chloride,” *presented at the 1999 Hydrocarbon Resources Gordon Research Conference*, Ventura, CA, 1999
- ¹⁵ Wójtowicz, M. A., Markowitz, B. L., Smith, W. W., and Serio, M. A., “Microporous carbon adsorbents for hydrogen storage,” *Int. Journal of the Society of Materials Engineering for Resources*, 7(2), 253–266, 1999
- ¹⁶ Wójtowicz, M. A., Smith, W. W., Serio, M. A., Simons, G. A., and Fuller, W. D., “Microporous carbons for gas-storage applications,” *Proc. Twenty-Third Biennial Conference on Carbon*, Pennsylvania State University, 342–343, 1997
- ¹⁷ Simons, G. A., and Wójtowicz, M. A., “A model for microporosity development during char activation,” *Proc. Twenty-Third Biennial Conference on Carbon*, Pennsylvania State University, 328–329, 1997
- ¹⁸ Simons, G. A., and Wójtowicz, M. A., “Modeling the evolution of microporosity and surface area during char activation,” *Proc. 9th Int. Conf. on Coal Science*, A. Ziegler, K. H. Van Heek, J. Klein, and W. Wanzl, eds., DGMK, Hamburg, Germany, 1783–1786, 1997
- ¹⁹ Simons, G. A., and Wójtowicz, M. A., “Modeling the evolution of microporosity in a char-activation process involving alternating chemisorption-desorption cycles,” *Proc. EUROCARBON '98: Science and Technology of Carbon*, AKK & GFEC, Strasbourg, France, 273–274, 1998
- ²⁰ Wójtowicz, M. A., Bassilakis, R., Leffler, M., Serio, M. A., and Fuller, W. D., “Adsorption of hydrogen on activated carbons derived from polyvinylidene chloride,” *Proc. First World Conf. on Carbon EUROCARBON 2000*, Berlin, Germany, 407–408, 2000
- ²¹ Wójtowicz, M. A., Rubenstein, E., and Serio, M. A., “Carbon-based sorbent for gas storage, and method for preparation thereof,” US Pat. No. 8,231,712, 2012
- ²² Wójtowicz, M. A., Cosgrove, J. E., Serio, M. A., Carlson, A. E., Espinosa, N. J., Hostetler, J. M., and Chullen, C., “The Effect of Carbonization Conditions on the Performance of Ammonia Sorbents Derived from Polyether Ether Ketone (PEEK),” 2020 International Conference on Environmental Systems, 2020
- ²³ Cybulski, A., and Mouljin, J. A., “Monoliths in Heterogeneous Catalysis,” *Catalysis Reviews*, 36(2), 179–270, 1994