The Effect of Trace-Contaminant Sorbent Monolith Geometry on Sorbent Performance

Marek A. Wójtowicz,[1] Joseph E. Cosgrove,[2] Michael A. Serio,[3] and Andrew E. Carlson[4]
Advanced Fuel Research, Inc., 87 Church Street, East Hartford, CT 06108, USA

and

Cinda Chullen[5]
NASA Johnson Space Center, 2010 NASA Parkway, Houston, TX 77058, USA

The current trace-contaminant (TC) control technology in the Exploration Portable Life Support System (xPLSS) involves a packed bed of acid impregnated granular charcoal, which is difficult to regenerate and is considered a consumable. The preferred implementation of TC control is pressure-swing adsorption (PSA) using a regenerable sorbent, where TCs are adsorbed in adsorption steps followed by regeneration by exposure to space vacuum (desorption steps). The adsorption-desorption steps are repeated cyclically in parallel beds, which ensures continuous TC removal. The use of sorbent monoliths is advantageous due to the low pressure drop and low fan-power requirement. TC-sorption capacity is an important sorbent property, which, in conjunction with the gas residence time within the sorbent, strongly affects sorbent performance. Sorbent-monolith geometry plays an important role through the complex mass-transfer and sorption/desorption kinetic phenomena that occur within the sorbent structure. In this paper, results are presented on the development of vacuum-regenerable TC sorbents for use in the xPLSS, with the effects of sorbent-monolith geometry studied in sorption-desorption experiments. The sorbents were derived from 3D-printed polymer honeycomb monoliths that were carbonized and oxidized to develop porosity, and also to enhance the TC-sorption capacity by the creation of carbon-oxygen surface complexes. Results are presented on the following aspects of sorbent-monolith geometry: (1) monolith size (volume); and (2) channel cross-sectional shape and size. The use of predominantly microporous carbon monoliths is associated with the following benefits: high sorption capacity; low pressure drop; rapid vacuum desorption; high mechanical strength and resistance to attrition; good thermal management (high

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

thermal conductivity and low thermal effects associated with physisorption/desorption); good resistance to dusty environments; low toxicity and flammability.

Nomenclature

AC	=	activated carbon
BO	=	burn-off, i.e. percent weight loss during activation (%)
C	=	gas concentration (mol/m^3)
CF	=	carbon fiber
D	=	monolith diameter (mm, cm); also, diffusion coefficient (m^2/s)
d_p	=	pore size (nm)
EVA	=	Extravehicular Activity
F_{gas}	=	gas flow rate (cm^3/min)
$FTIR$	=	Fourier Transform Infrared (spectroscopy, analysis, analyzer, etc.)
L	=	sorbent-monolith length (mm, cm)
m	=	sorbent-monolith mass (g)
M_i	=	molecular weight of species i (g/mol)
NH_3	=	ammonia
P	=	pressure (atm)
$PEEK$	=	polyether ether ketone
$PLSS$	=	Portable Life Support System
$PVDC$	=	polyvinylidene chloride
R	=	gas constant (L atm mol^{-1} K^{-1})
RCA	=	Rapid-Cycle Amine (swing bed)
$SMAC$	=	spacecraft maximum allowable concentration (ppm, mg/m^3)
t	=	time (s)
T	=	temperature (K)
TC	=	trace contaminant
$TCCS$	=	trace contaminant control system
V	=	sorbent volume (cm^3)
V_p	=	total pore volume (cm^3/g)
x	=	distance (m)
$xPLSS$	=	Exploration Portable Life Support System
ε	=	sorbent-monolith voidage (-)
λ	=	the average distance traveled by gas molecules by molecular diffusion
v_i	=	diffusion volume of diffusing species i (m^3/mol)
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 component 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, the effect of sorbent-monolith geometry on sorbent performance is examined. Specifically, the following aspects of the monolith geometry are considered: (1) monolith size (volume); and (2) channel cross-sectional shape and size.

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 strength[1] 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[1] sorbents made of high-

purity carbon; and (h) the flexibility to 3D-print/fabricate sorbent monoliths with optimized channel geometries that ensure uniform flow distribution throughout the sorbent. 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 was reviewed by Paul and Jennings,[8] who concluded that carbon was the most suitable TC sorbent for the Portable Life Support System (PLSS) application. Several approaches to carbon regeneration have been attempted (reverse airflow, steam regeneration, and vacuum regeneration), but the challenges of excessive regeneration temperature and of long desorption time scales remain 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 contrast, vacuum regeneration of TC sorbent monoliths was demonstrated to take place on the time scale of several minutes.[1,9] 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.[10] 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 CO_2-removal unit, the Rapid Cycle Amine (RCA) swing bed. This study is concerned only with ammonia sorption and sorbent regeneration by exposure to vacuum.

In our previous work, polyvinylidene chloride (PVDC) was extensively used as carbon-sorbent precursor,[2,3,5–7,11–22] and performance data on the PEEK-derived sorbents were recently reported.[1,9,23] 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 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 also with the mechanical strength.[1] It can be assumed that the carbon-fiber reinforcement has 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 is 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. Unless stated otherwise, activation was carried out in a flow of air at 325 °C to reach a weight loss (burn-off) of ~20%..

Details of sorbent-monolith preparation were previously reported.[9]

B. Sorbent Testing
TC sorption capacities were determined from breakthrough curves (TC concentration in the effluent versus time) measured using a fixed-bed apparatus described in Ref. 9. In rapid cycling adorption-desorption tests, 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 (~0.3–1 Torr). This was pressure-swing operation, with a half-cycle time of five minutes. The experimental time scale of

~500 minutes was chosen for the rapid adsorption-desorption tests on the basis of the typical EVA duration, which is 8 hours. Longer-duration testing is planned in the future. A more detailed description of sorption and desorption testing procedures can be found in Ref. 9. The inlet gas composition was similar to that typical for the Exploration Portable Life Support System (xPLSS): 3 ppm or 20 ppm ammonia, 1.0 vol.% CO_2, 29 vol.% O_2, and a balance of nitrogen. Dry gas was used in all the experiments reported in this paper to reduce the spectral interference between water and other species in the FTIR analyzer used for gas analysis. In a separate study, it was found that the presence of water at relative humidity 10–80% led to greatly enhanced ammonia sorption capacity.[3,6] The gas flow rates used in this study ranged from 0.52 L/min to 1.0 L/min, and, unless stated otherwise, the sorbent-monolith dimensions were: diameter, D = 17 mm; length: L = 3.6 mm or 1.8 mm; 0.5-mm square channels with a wall thickness of ~0.25 mm, which corresponds to a voidage of ~0.44. 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. Selected sorbent-performance test experiments were performed in duplicates with good data reproducibility.

III. Results and Discussion

A. The Effect of Sorbent-Monolith Size

Sorbent performance is strongly influenced by the gas residence time within the sorbent.[10,24] The gas residence time, τ, is related to sorbent volume, V, and gas flow rate, $Fgas$, as follows:

$$\tau = \frac{\epsilon V}{F_{gas}} \tag{1}$$

Thus, for a given gas flow rate, and sorbent voidage, ε, the residence time is proportional to sorbent-monolith size (volume). Since the effect of sorbent-monolith volume on sorbent performance is indirect, i.e. being a result of gas residence time variation, the effect of sorbent volume can be determined from the variation of residence time, e.g., by studying sorbent performance as a function of flow rate, which is used to control residence time.
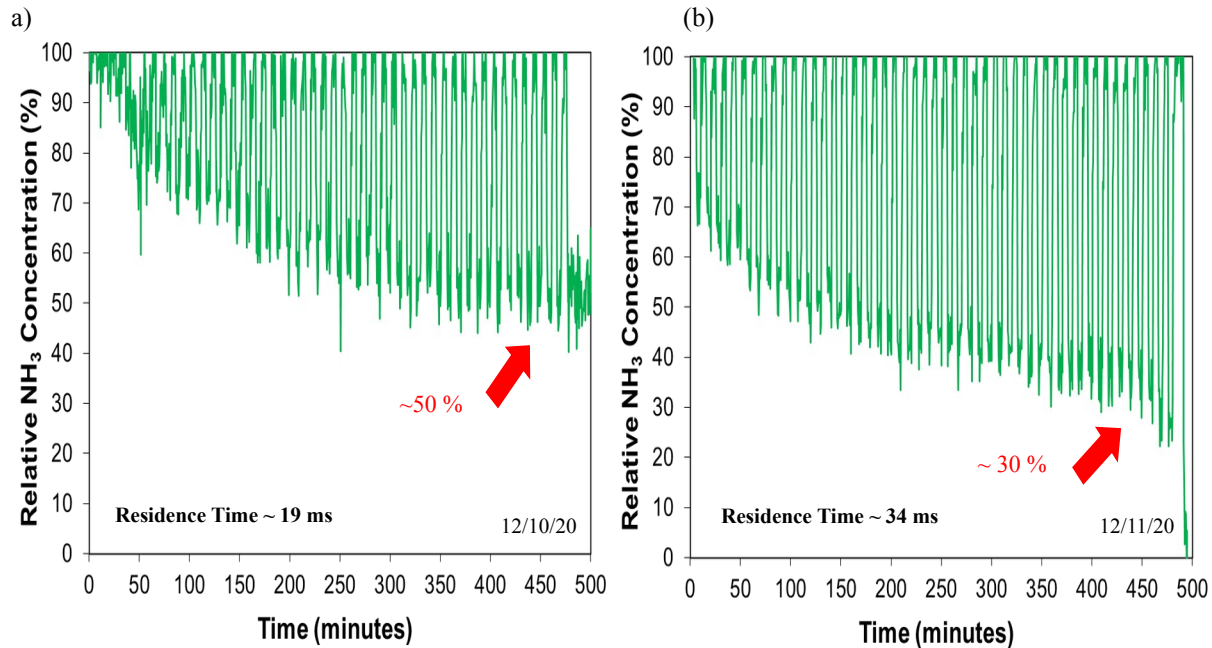
Figure 1. The effect of residence time on ammonia-sorption performance during rapid adsorption-desorption cycling experiments at a half-cycle of 5 minutes and an ammonia inlet concentration of 3.5 ppm: (a) a residence time of 19 milliseconds; and (b) a residence time of 34 milliseconds; 0.5-mm square-channel PEEK/CF-derived sorbent-monolith; D = 17 mm; L = 3.5 mm; carbonization temperature, T_c = 1,000 °C.

The minimum residence time required to obtain a high or near-optimal capture efficiency is believed to be 250 ms[10] on the basis of data reported in Ref. 24. Since capture efficiency is a function of sorbent properties, however, such as sorption capacity, a characteristic dimension, i.e. particle size for granular sorbents and channel-wall thickness for sorbent monoliths, adsorbate concentration, temperature, and other operating conditions, it is recommended that the dependence of TC-capture efficiency on the residence time be determined experimentally for specific sorbent types, adsorbates, and conditions. In fact, for the sorbent monoliths used in this work, it was found that good ammonia-capture efficiency could occur at residence times significantly lower than 250 ms (Figure 1 and Figure 2). The dependence of ammonia-removal efficiency on residence time is shown in Figure 1 and Figure 2.
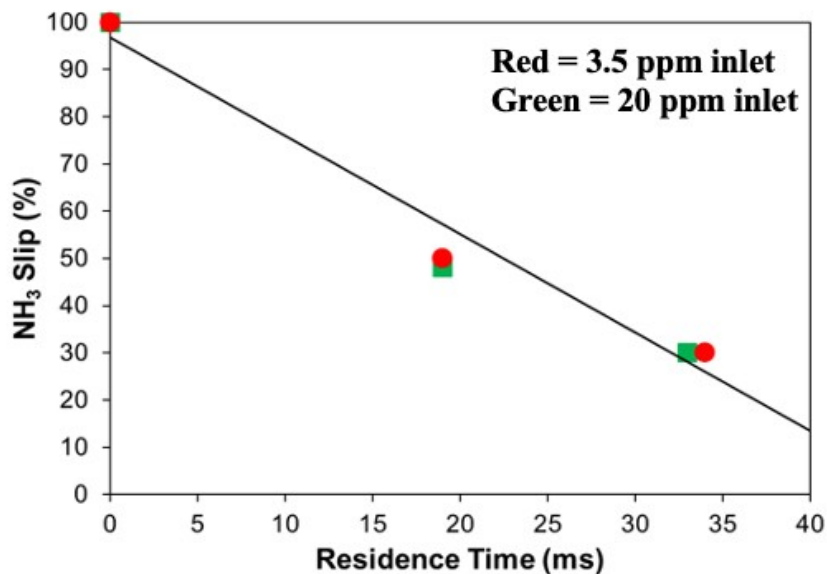
Figure 2. The effect of residence time and the ammonia inlet concentration on ammonia-sorption performance during rapid adsorption-desorption cycling experiments at a half-cycle time of 5 minutes.

The data are expressed in terms of ammonia slip, which is the percentage of the inlet ammonia that passes through the sorbent without getting removed. Thus, high ammonia slip corresponds to low ammonia-capture efficiency, and vice versa, as ammonia slip = 100% – capture efficiency. Data in Figure 2 show that ammonia slip decreases, i.e. ammonia-capture efficiency increases, as residence time, or sorbent volume at the same gas flow, increases. Data presented in Figure 2 were obtained from pressure-swing experimental data shown in Figure 1, where relative ammonia concentration is plotted as a function of time. The relative ammonia concentration of 100% corresponds to inlet ammonia concentration, in this case ~3.5 ppm, which is measured in the sorbent-regeneration (desorption) step, when the inlet gas is directed to the gas analyzer through a line by-passing the sorbent. The relative ammonia concentration values lower than 100% were measured at the sorbent outlet during the adsorption step. It can be seen that the ammonia-capture efficiency is higher, i.e. the ammonia outlet concentration is lower, in the experiment in which the gas residence time within the sorbent is higher (34 ms versus 19 ms). This corresponds to the conditions of higher sorbent-monolith volume and length or, alternatively, lower gas flow rate.

In reference to Figure 1, it should be noted that since the measurements were performed using sorbents initially fully saturated with ammonia, it took several adsorption-desorption cycles for the sorbents to reach near-steady state performance in terms of the outlet ammonia concentration measured by the gas analyzer. Furthermore, Trace Contaminant Control System (TCCS) design calculations similar to those described by Paul *et al.*[10] were used to show that a long-term ammonia-removal efficiency of ~50% would be sufficient to make sure that the astronaut breathes oxygen with ammonia under 7- day SMAC (2 mg/m^3) in the space suit.[9]

B. The Effect of Sorbent-Monolith Channel Cross-Sectional Shape and Size

Most of the work carried out in this project involved sorbent monoliths with square channels, and a limited number of experiments were performed using hexagonal and round channels. Equilibrium sorption measurements, i.e. breakthrough curves, for sorbent monoliths with different channel geometries are shown in Figure 3. Data for the following sorbent-monoliths are presented: (1) sample SQC-10-03a (a 1-mm square-channel monolith); (2) sample RC-08 (0.8-mm round-channel monolith); and (3) sample RC-10 (1-mm round-channel monolith). The above samples were processed under similar conditions, and the sorption capacity for these samples was found to be similar (~15 mg NH_3/g sorbent). It can be seen, however, that the shape of the breakthrough curve for sorbent SQC-10-03a is inferior, exhibiting a more pronounced tail and only providing a relatively brief period of efficient, albeit not complete, removal of ammonia. It is also observed that as the cross-sectional area of the channels increases, the time to breakthrough decreases. It should be noted that of the three monolith designs included in Figure 3, the one with 0.8 mm diameter channels, RC-08, has the shortest effective gas residence time (25 ms versus 39 ms for RC-10 and 34 ms for SQC-10-03a), but still the best performance. Thus, the differences observed in Figure 3 are due to the effect of channel size and geometry, and not due to the differences in residence time.

Under the conditions used in this work, the gas flow within sorbent-monolith channels is laminar. Therefore, with little or no lateral mixing, the gas-wall contact probability is limited by the ammonia diffusion time scale, as discussed below. In the case of the square channels, there may be the added effect of stagnation in the corner regions of the channels, further reducing the contact probability.

Figure 3. Ammonia breakthrough curves for a 1-mm square-channel monolith, SQC-10-03a, a 1-mm round-channel monolith, RC-10, and a 0.8-mm round-channel monolith, RC-08. The inlet ammonia concentration was ~20 ppm.

The importance of channel size for effective ammonia sorption within the monolith can be explained on the basis of theoretical derivations based on Fick's second law and the Brownian motion. Fick's second law, which is equivalent to the diffusion equation, can be written in one dimension as follows:

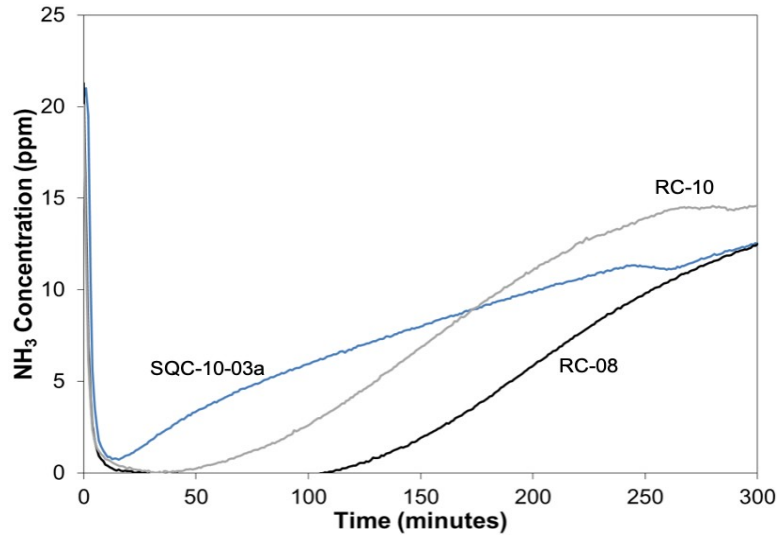$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{2}$$

where C is the concentration, e.g., expressed in (mol/m³), t is time (s), D is the diffusion coefficient (m²/s), and x is the distance (m). Eq. (2) expresses how concentration of a diffusing species changes in time. It can be shown that the solution of Eq. (2) is:

$$C(x, t) = \frac{C_0}{\sqrt{4\pi Dt}} \exp\left(\frac{-x^2}{4Dt}\right) \tag{3}$$

where $C(x, t)$ is the concentration of the diffusing species at position x and time t, and C_0 is the concentration of the diffusing species at position x = 0 at time t = 0. This is a normal distribution with the mean $\mu = 0$ and the variance $\sigma^2 = 2Dt$.

Einstein used Eq. (3) to derive an expression for the average displacement (λ) a particle, or a gas molecule, travels along the x-axis in time t:[25]

$$\lambda = \sqrt{2Dt} \tag{4}$$

which means that the mean displacement is proportional to the square root of time. In other words, the time required for a diffusing species to travel a distance λ is given by the following expression:

$$t = \frac{\lambda^2}{2D} \tag{5}$$

The above result shows that reducing the channel dimension in a laminar flow by a factor of two should reduce the average time needed for the diffusing species to reach the wall by a factor of four. This should greatly improve the adsorption of ammonia within the sorbent monolith if the gas residence time is a limiting factor.

The diffusion coefficient of ammonia in nitrogen, and also in oxygen, can be determined as follows:[26]

$$D_{AB} = \frac{10^{-3}T^{1.75}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{\frac{1}{2}}}{P\left[v_A^{1/3}+v_B^{1/3}\right]^2} \qquad (cm^2/s) \tag{6}$$

where M_A and M_B are the molecular weights of the diffusing species (g/mol); T is temperature (K); and v_A and v_B are the diffusion volumes of species A and B, respectively (m^3/mol). The diffusion volumes of the species of interest are: v_{NH3} = 14.9 (m^3/mol), v_{N2} = 17.9 (m^3/mol), and v_{O2} = 16.6 (m^3/mol). Using the above information, the following values of diffusion coefficients are calculated:

D_{NH3-N2} = 0.249 cm^2/s   at P = 1.0 atm and T = 21 °C = 294 K (lab-test conditions)

D_{NH3-O2} = 0.851 cm^2/s   at P = 0.293 atm = 4.30 psia and T = 21 °C = 294 K

(xPLSS operating conditions)

As expected, the diffusion coefficient at a lower pressure, which is characteristic of the actual xPLSS operation, is significantly higher than the diffusion coefficient at atmospheric pressure, which is the condition used in our laboratory-scale experiments.

Using Eq. (5), the mean residence time for the SQC-10-03a sorbent f (τ = 0.034 s), and the diffusion coefficient D_{NH3-N2} = 0.249 cm^2/s, both relevant to our laboratory experimental conditions, one arrives at the average distance traveled by ammonia molecules in the direction perpendicular to the gas flow:

$$\lambda = \sqrt{2D_{NH3-N2}\tau} = 0.13 \text{ cm} = 1.3 \text{ mm}$$

The above distance is similar to the channel dimensions in SQC-10-03a (1 mm x 1 mm), which means that ammonia diffusion within monolith channels may adversely affect sorbent performance. It is expected that reducing the channel size, e.g., by a factor of two (0.5 mm x 0.5 mm), will significantly increase the probability of ammonia molecules reaching monolith-channel walls. This should result in improved ammonia sorption on the time scale of the gas residence time in the monolith.

In view of the above considerations, more work was carried out using sorbent monoliths with channel dimensions smaller than 1 mm. Data presented in Figure 4 show that reducing the size of square monolith channels from 1 mm (sorbent SQC-10-03a) to 0.5 mm (sorbent SQC-05-a) results in a tremendous improvement of the breakthrough curve, with the time to breakthrough now exceeding even the corresponding value for the RC-08 sorbent. This is so, even though the
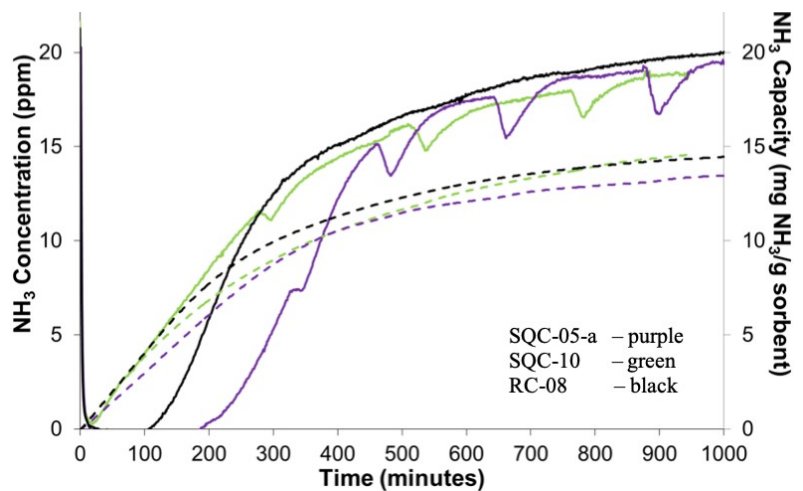
Figure 4. Ammonia breakthrough curves for a 1-mm square-channel monolith, SQC-10 (green), a 0.5-mm square-channel monolith, SQC-05-a (purple), and a 0.8-mm round-channel monolith, RC-08 (black). The inlet ammonia concentration was ~20 ppm. Breakthrough curves (ammonia outlet concentration versus time) are plotted as solid lines, and ammonia-capacity curves are shown as dashed lines. The occasional irregularities in the breakthrough curves are due to slight temperature variation during experiments.

sorption capacities of all the sorbents shown in Figure 4 are similar. It should be noted that the most desirable sorbent characteristics are a long time to breakthrough and a large sorption capacity. (For the sake of easier comparison, some data from Figure 3 were included in Figure 4.)

In addition to square-channel monoliths, a limited number of experiments were performed using hexagonal channels. 3D-printed PEEK/CF monoliths with 0.75-mm square and hexagonal channels (2 x apothem = 0.75 mm) are shown in Figure 5. The wall thickness was 0.25 mm in both cases. The PEEK/CF monoliths were carbonized at 800 °C, and activated in a flow of air at 325 °C until a weight loss of ~20% was reached. Results of rapid ammonia adsorption-desorption cycling experiments are shown in Figure 6. The vacuum used was ~0.3 Torr, and a half-cycle time was 5 minutes.
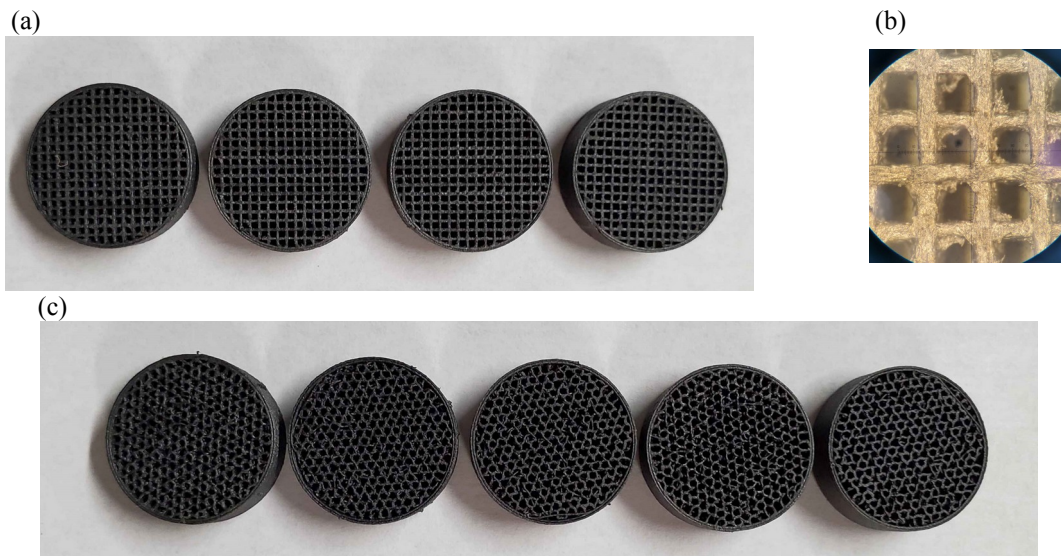
Figure 5. 3D-printed PEEK/Cf monoliths with (a) 0.75-mm square channels; (b) microscopic image of the 0.75-mm square channels; and (c) 0.75-mm hexagonal channels.

Since all the measurements were performed using sorbents initially fully saturated with ammonia, it took several adsorption-desorption cycles for the sorbents to reach near-steady state performance in terms of the outlet ammonia concentration measured by the gas analyzer (Figure 6). The fluctuations in the lowest ammonia concentration shown in Figure 6 are caused by slight changes in temperature (±2 °C). Adsorption and desorption are strongly temperature-dependent, and temperature fluctuations even as small as ±2°C produce noticeable differences in ammonia sorption. Data in Figure 6a and Figure 6b show that, under the conditions used in these experiments, there is little or no effect of channel shape (hexagonal versus square channels) on sorbent performance. The comparison of sorbent performance for 0.5-mm square channel monoliths (Figure 6c) and 0.75-mm square channel monoliths (Figure 6b) shows that the effect of channel cross-sectional size is small, if any, presumably because both channel sizes are small enough for gas diffusion not to limit the gas-wall contact. It should be noted that, unlike breakthrough-curve measurements, which characterize only TC adsorption, rapid adsorption-desorption cycling experiments capture the effects of both TC adsorption and TC desorption (sorbent vacuum-regeneration). The analysis presented above shows that adsorption is hindered by increasing the channel dimensions, but it is likely that desorption is improved with the larger channel dimensions because readsorption of the desorbed TCs is less likely to take place within larger channels. These opposing effects are, in general, difficult to separate on the basis of pressure-swing data.

(a)

(b)

(c)
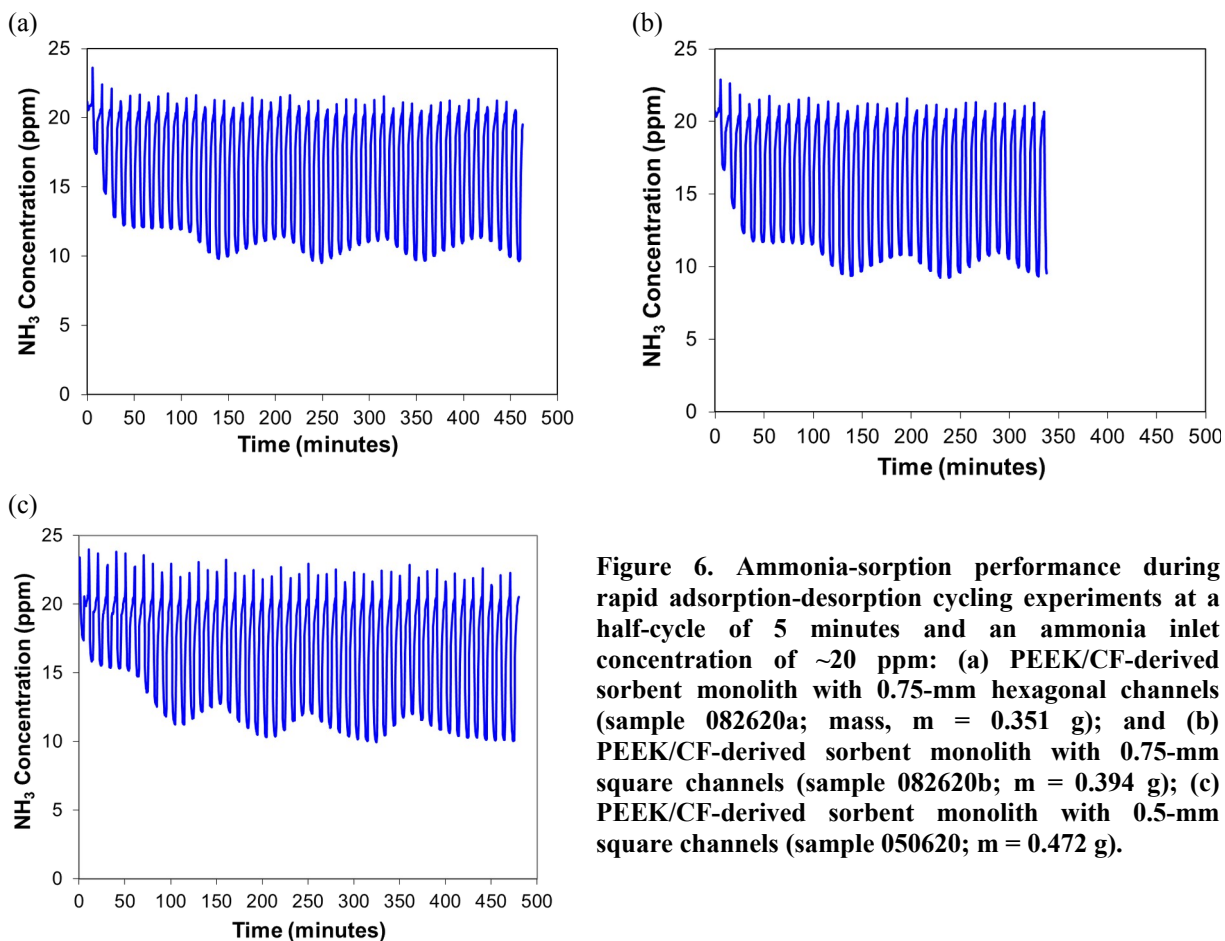
Figure 6. Ammonia-sorption performance during rapid adsorption-desorption cycling experiments at a half-cycle of 5 minutes and an ammonia inlet concentration of ~20 ppm: (a) PEEK/CF-derived sorbent monolith with 0.75-mm hexagonal channels (sample 082620a; mass, m = 0.351 g); and (b) PEEK/CF-derived sorbent monolith with 0.75-mm square channels (sample 082620b; m = 0.394 g); (c) PEEK/CF-derived sorbent monolith with 0.5-mm square channels (sample 050620; m = 0.472 g).

IV. Conclusions

The effects of TC sorbent-monolith size and geometry were investigated in a laboratory-scale fixed-bed testing system. Carbon-sorbent monoliths derived from the PEEK polymer reinforced with carbon fiber were used. TC-breakthrough data were collected, and rapid-cycle adsorption-desorption operation was also carried out at a half-cycle time of 5 minutes. Experimental data led to the following conclusions:

1. Sorbent performance in terms of TC capture efficiency was found to be strongly dependent on gas residence time within the sorbent monolith, which is directly proportional to monolith volume and length. The capture efficiency was found to increase as residence time (monolith volume and length) increases.
2. Experimental data, as well as theoretical calculations, show that sorbent-monolith performance may be limited by TC diffusion within the monolith channels. Under the conditions used in this work, the limiting channel dimension seems to be close to 1 mm. Thus, sorbent monoliths with channel dimensions smaller than 1 mm are recommended.
3. No evidence was found for the strong effect of channel cross-sectional shape (square versus round and hexagonal channels).

Acknowledgments

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