The Effect of Carbonization Conditions on the Performance of Ammonia Sorbents Derived from Polyether Ether Ketone (PEEK)

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The current trace-contaminant (TC) control technology involves a packed bed of acid-impregnated granular charcoal, which is difficult to regenerate. The use of predominantly microporous monolithic carbon produced by carbonization of polyether ether ketone (PEEK) was previously proposed. In this paper, the effect of carbonization conditions on sorbent performance is reported. Although the target application will involve carbon monoliths (e.g., honeycomb structures), granular sorbents were used in this study so that their performance could be compared with the currently used reference carbon (available only in the granular form). The PEEK polymer was carbonized at temperatures 700–1,050 °C, which was followed by carbon activation to a burn-off of 20%. Activation was carried out in a flow of air at 325 °C. The carbon pore structure was characterized using nitrogen adsorption isotherm data. The PEEK-derived sorbents were tested for ammonia sorption in a laboratory packed-bed system. Sorbent regeneration was evaluated by exposing ammonia-saturated sorbents to high vacuum at room temperature for 6 hours, and subsequently re-testing their ammonia-sorption performance. All the PEEK-derived carbons were found to be highly microporous, and their surface area increased with the increasing carbonization temperature. In contrast, the initial equilibrium ammonia sorption capacity was found to decrease as the carbonization temperature increased. All sorbents showed a significant loss of sorption capacity after the first sorption-regeneration cycle, but no performance loss was observed in subsequent cycles. It was found that the presence of oxygen complexes on the carbon surface greatly enhanced ammonia sorption on carbon. In addition, PEEK-derived sorbents were shown to exhibit favorable sorption-regeneration characteristics, as compared with the acid-treated activated carbon.

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Nomenclature

BET	=	Brunauer, Emmett, and Teller (method of specific surface area determination)
$C_{NH3}{}^i$	=	ammonia-sorption capacity (mg NH_3 per g sorbent) after *i*-th vacuum-regeneration
CF	=	carbon fiber
CH_2O	=	formaldehyde
DFT	=	Density Functional Theory
DR	=	Dubinin-Radushkevich analysis
d	=	particle size
d_p	=	pore size
EVA	=	Extravehicular Activity
FTIR	=	Fourier Transform Infrared (spectroscopy, analysis, analyzer, etc.)
MFC	=	mass-flow controller
NH_3	=	ammonia
PEEK	=	polyether ether ketone
PLSS	=	Portable Life Support System
PVDC	=	polyvinylidene chloride
SA_{BET}	=	BET (Brunauer, Emmett, and Teller) surface area (m^2/g)
SMAC	=	spacecraft maximum allowable concentration
TC	=	trace contaminant
T_{carb}	=	maximum carbonization temperature (°C)
V_{micro}	=	micropore volume (cm^3/g)
V_{meso}	=	mesopore volume (cm^3/g)
V_{macro}	=	macropore volume (cm^3/g)
V, V_p	=	(total) pore volume (cm^3/g)
w	=	pore width (nm)
$\tau_{20\%BO}$	=	time needed for carbon to reach 20% burn-off (weight loss) during air activation at 325 °C (h)
τ_{hold}	=	hold time at the highest carbonization temperature (min)
*	=	Superscript * indicates values (of specific surface area, pore volume, etc.) expressed per gram of polymer-derived carbon, i.e. excluding the weight of the carbon fiber used as reinforcement.
% micro	=	V_{micro}/V_p *x 100%* percent microporosity (%)

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, the effect of PEEK carbonization conditions on sorbent performance is reported. Although the target application in the Portable Life Support System (PLSS) will involve carbon monoliths (e.g., honeycomb structures), granular sorbents were used in this work so that their performance could be compared with the currently used acid-impregnated carbon (available only in the granular form). The objectives of this study were: (1) to determine the effect of carbonization conditions on ammonia-sorption capacity and sorbent vacuum regeneration, if any; and (2) to examine the variation of the pore-structure characteristics, such as the BET surface area and the percentage of microporosity, that are associated with different carbonization conditions.

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 monolithic carbon 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) good thermal management (high thermal conductivity and low adsorption/desorption thermal effects associated with physisorption); and (e) good resistance to dusty environments. 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, it was reviewed by Paul and Jennings,[8] and it was 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] Acetaldehyde is of some concern too as it may degrade the operation of the CO_2-removal unit. This study, however, was 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,[2,3,5–7,10–21] and performance data on the PEEK-derived carbon sorbents were recently reported.[1] 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, which is not the case with the PEEK precursor.

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 TC 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, i.e. by 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. The use of PEEK/CF granular carbons rather than monoliths offered the advantage of making direct comparisons with Ammonasorb II, which is available only in the granular form. Ammonasorb II is an activated carbon which is made from coconut shells, and it is impregnated with phosphoric acid to enhance ammonia sorption. Ammonasorb II is commercially available from Calgon, and it has been used as the state-of-the-art TC sorbent by NASA.

B. PEEK/CF Carbonization and Activation
Conventional laboratory procedures were used in the preparation of granular PEEK/CF carbon, i.e. carbonization followed by carbon activation. The PEEK/CF precursor, obtained from cut PEEK/CF filaments, was carbonized in a tube furnace, and the resultant char was then subjected to air activation, also in a tube furnace. The following carbonization conditions were used: (1) heating in a flow of nitrogen from room temperature to ~500 °C at 10 K/min; (2) heating in a flow of nitrogen from ~500 °C to the final carbonization temperature at 5 K/min; (3) unless specified otherwise, no hold at the final temperature was implemented. The following final carbonizations temperatures were used: 735 °C, 830 °C, 927 °C, and 1,021 °C. The resultant carbons were subsequently activated in a flow of air at 325 °C to 20% ± 1% burn-off (weight loss), and then tested for ammonia sorption using a fixed-bed system. All carbon samples tested were ground to a 20 x 45 mesh size (particle size d = 0.355–0.850 mm) prior to ammonia-sorption experiments.

C. Pore-Structure Characterization
An automated gas-sorption system Quantachrome ASiQwin was used for collecting and processing nitrogen-isotherm data for carbon sorbents. Unless stated otherwise, each sample was outgassed under vacuum at 300 ºC for at least 3 hours prior to adsorption-isotherm measurements. Nitrogen-adsorption isotherms were determined at 77 K, and these data were used to perform the following analyses: (a) Brunauer, Emmett, and Teller (BET) surface area; (b) pore volume; (c) Dubinin-Radushkevich (DR) micropore surface area and micropore volume; and (d) pore-size distribution using the Density Functional Theory (DFT).

D. Sorbent Testing

Ammonia sorption capacities were determined from breakthrough curves (ammonia concentration in the effluent versus time) measured using a packed-bed apparatus shown in Figure 1. The testing was performed in two stages: (a) ammonia sorption, where the gas stream was passed through the sorbent at atmospheric pressure; and (b) ammonia desorption (sorbent regeneration), where the sorbent was exposed to high vacuum ($\sim 10^{-6}$ Torr) for 6 hours. The test cell containing the TC sorbent was placed in a temperature-controlled enclosure (not shown in Figure 1). Ammonia and carbon dioxide concentration determination was carried out using an FTIR analyzer downstream of the reactor. The inlet gas composition was similar to that typical for the PLSS: $\sim$20 ppm ammonia, $\sim$ 1.0 vol.% CO_2, 29 vol.% O_2, and balance nitrogen. No formaldehyde and no water were present in the inlet gas in the tests reported in this paper. The presence of water is known to enhance the sorption capacity of both acid-impregnated activated carbon and PEEK/CF-derived sorbents,[1] but it was decided not to combine the effects of moisture and sorbent carbonization temperature in this study. A more detailed description of this laboratory facility, experimental procedures, and selected previous results can be found in references.[1-3,5] The gas flow rate used in this work was 1.0 L/min, the sample weight was 200 mg, the fixed-bed diameter was 5.5 mm, and the bed height was 25 mm in the case of PEEK/CF carbon and 16–17 mm in the case of Ammonasorb II. The above difference in the bed heights was a result of different densities of the PEEK/CF carbon and Ammonasorb II.
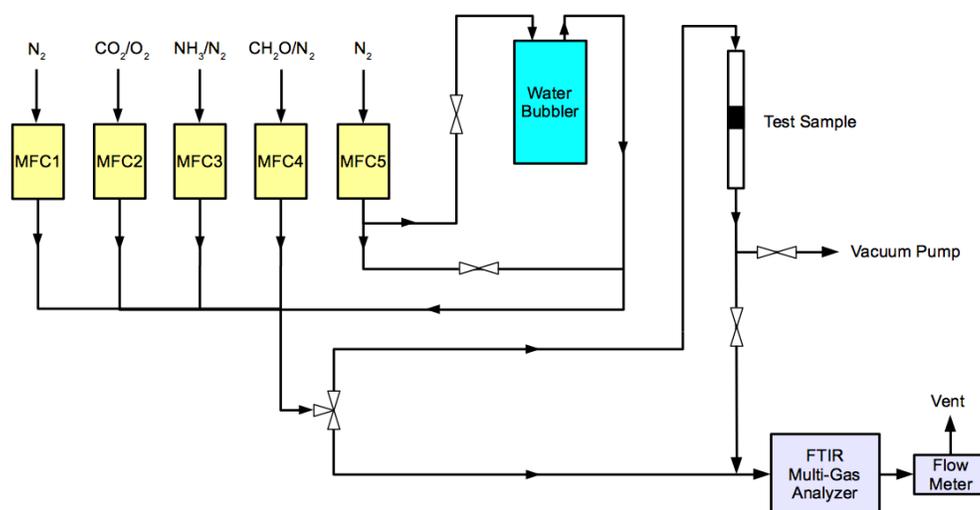

Figure 1. Sorption/desorption capacity test apparatus. MFC1 through MFC5 are mass-flow controllers, and CH₂O is formaldehyde, which was not used in this study.

III.   Results and Discussion

A. Pore-Structure Characterization

Results of pore-structure characterization obtained from nitrogen-adsorption isotherms are shown in Table 1. It can be seen that the porosity of all the sorbents, except for the PEEK/CF material carbonized at 735 °C, is dominated by microporosity (66–92% of total porosity). The proportion of micropores increases with carbonization temperature, and so does the specific surface area. The data for the 735 °C PEEK/CF carbon show unusually low specific surface area and, for this reason, the measurement was repeated for this carbon sample. The replicate measurement confirmed the BET surface area close to 215 m²/g, as shown in Table 1, but the total pore volume was found to be somewhat lower in the second measurement than in the first one.

It should be noted that the values of surface area and the specific pore volume shown in Table 1 are expressed per gram of carbon sorbent, which contains both PEEK-derived carbon and about 26 wt% of the carbon-fiber reinforcement. (The original carbon-fiber content increases from $\sim$10 wt% to $\sim$26 wt% upon carbonization and activation, assuming that carbon fiber does not undergo devolatilization and activation.) For example, as shown in Table 1, the BET surface area, total pore volume, and micropore volume of sample 120519a, carbonized at 1,021 °C, were found to be $SA_{BET} = 660$ m²/g, $V_p = 0.329$ cm³/g, and $V_{micro} = 0.231$ cm³/g, respectively. Accounting

for the presence of carbon fibers, the surface area, total pore volume, and micropore volume of the PEEK-carbon (exclusive of the carbon fiber) can be calculated by multiplying the above values by $1/(1 - 0.26) = 1.35$ to obtain the following values expressed per gram of PEEK carbon: $SA^*_{BET} = 891$ m²/g, $V^*_p = 0.444$ cm³/g, and $V^*_{micro} = 0.312$ cm³/g, respectively.

Table 1. Pore-structure characteristics for the samples used in this study. T_{carb} is the maximum carbonization temperature, τ_{hold} is the hold time at T_{carb}, $\tau_{20\%BO}$ is the time needed for carbon to reach ~20% burn-off during air activation at 325 °C, V_p is the total pore volume, V_{micro} is the micropore volume (from the DR analysis), V_{meso} is the mesopore volume, V_{macro} is the macropore volume, and *% micro* is the percentage of micropore volume. The surface area and pore volume expressed per gram of total sorbent (PEEK carbon plus CF).

Sample ID	T_{carb} (°C)	τ_{hold} (min)	$\tau_{20\%BO}$ (h)	Surface Area (m²/g)			V_p (cm³/g)	V_{micro} (cm³/g)	V_{meso} (cm³/g)	V_{macro} (cm³/g)	% micro (%)
				BET	DR	DFT					
120319a	735	0	30.3	212	206	168	0.2525	0.073	0.1693	0.0102	28.9
				217	251	166	0.1641	0.089	0.0706	0.0045	54.2
012220a	737	60	54	409	412	403	0.2168	0.147	0.0639	0.0059	67.8
120619a	830	0	102.0	434	434	408	0.2328	0.154	0.076	0.0028	66.2
120419a	927	0	185.5	585	593	524	0.3040	0.211	0.0888	0.0042	69.4
120519a	1021	0	283.5	660	651	530	0.3290	0.231	0.0940	0.0040	70.2
120519a-SC†	1021	0	283.5	700	705	589	0.3425	0.251	0.0892	0.0023	73.3
Amm. (300 °C)*	N/A	0	N/A	784	941	747	0.3643	0.334	0.0269	0.0034	91.7
Amm. (150 °C)**	N/A	0	N/A	779	791	718	0.3604	0.281	0.0664	0.0130	78.0

† Sample 120519a after thermal removal of surface oxides by heating in a flow of nitrogen to 900 °C, with a hold time of 30 min at 900 °C
*Ammonasorb II outgassed in vacuum at 300 °C prior to pore-structure analysis
**Ammonasorb II outgassed in vacuum at 150 °C prior to pore-structure analysis

Two nitrogen-adsorption measurements were carried out for Ammonasorb II using two sample outgassing temperatures prior to measurements: 150 °C and 300 °C. This was done because of the concern that some species with which the carbon was impregnated, mostly phosphoric acid, could partly evolve during vacuum outgassing. Data in Table 1 indeed show that nitrogen access to some microporosity might have been blocked by the species impregnated onto the carbon in the case of the sample outgassed at 150 °C. This resulted in the lower values of DR surface area (micropores), micropore volume, and the percentage of microporosity, as compared with the Ammonasorb sample outgassed at 300 °C.

As expected, all PEEK/CF carbon sorbents were found to possess significant amounts of microporosity, i.e. pores smaller than 2 nm (20 Å), which is clearly seen in the pore-size distribution plots (Figure 2). The PEEK/CF sample carbonized at the lowest temperature (735 °C) also shows a large quantity of mesopores (pore widths, w, in the range 2–50 nm). This is most likely due to the presence of large disordered domains present within the carbon structure, in contrast to the more severely heat-treated samples (830 °C and 1,021 °C), which have developed a significant amount of graphitic domains.

B. Ammonia Sorption and Sorbent Regeneration
Ammonia-sorption data for PEEK/CF sorbents that are presented below are expressed on a per-gram-of-total sorbent-weight basis. Since the reinforcing carbon-fiber part of the sorbent is believed to play a negligible role in ammonia sorption, the sorption capacity per gram of PEEK carbon, i.e. excluding CF, is about 1.35 times higher, reflecting the initial ~10 wt% CF content in the PEEK/CF polymer, ~60 wt% carbonization yield, and ~20 wt% burn-off during activation.

Results of ammonia-sorption measurements are presented in Table 2 and Figure 3. It was found that Ammonasorb II showed the highest initial equilibrium sorption capacity (22.6 mg NH_3 / g sorbent) among all the sorbents tested. The PEEK/CF sorbent carbonized at the lowest temperature (735 °C) exhibited the second highest

sorption capacity (17.6 mg NH$_3$ / g sorbent). This came as a surprise as the latter sorbent was found to have a very low BET surface area (212 m^2/g), whereas Ammonasorb II had the highest (784 m^2/g). This means that the surface area, i.e. the pore structure, alone is not necessarily a good predictor of sorbent performance as surface chemistry evidently matters a lot too. This is presumably why the acid-treated Ammonasorb is initially more effective than high-purity PEEK carbons, although this advantage is quickly lost after the first sorbent regeneration, as will be shown later.
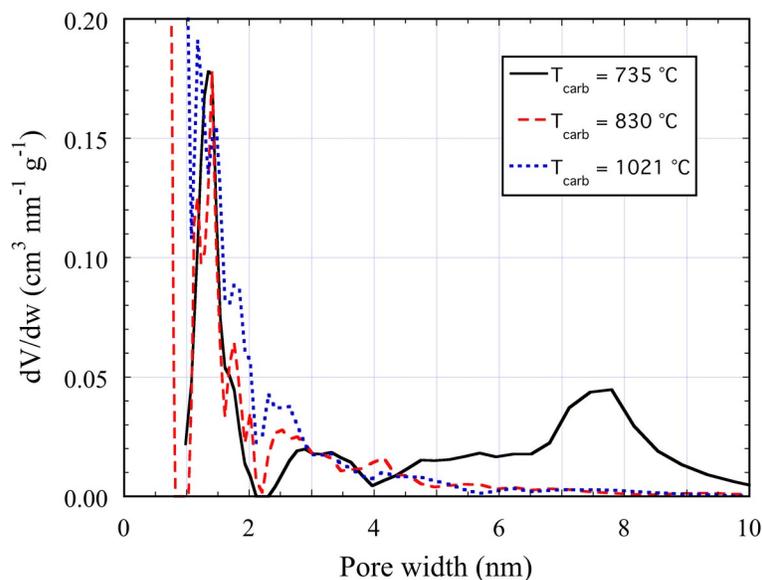
Figure 2. Pore-size distribution of PEEK/CF carbonized at 735 °C, 800 °C, and 1021 °C activated at 325 °C to ~20 wt% burn-off. The data are derived from nitrogen isotherms at 77 K using the Functional Density Theory (DFT).

Table 2. Equilibrium ammonia sorption capacities for PEEK/CF carbon sorbents and for Ammonasorb II. C^0_{NH3} is the ammonia-sorption capacity of the freshly prepared sorbent (i.e. prior to vacuum regeneration). C^1_{NH3}, C^2_{NH3}, C^3_{NH3}, C^4_{NH3}, and C^5_{NH3} are sorption capacities after the first, second, third, fourth, and fifth vacuum regeneration, respectively. *Capacity Loss* is the maximum percentage loss of ammonia-sorption capacity in subsequent sorption-desorption cycles with respect to the initial value, C^0_{NH3}. Ammonia-sorption capacity is expressed in mg NH$_3$ per sorbent weight, which includes the weight of the PEEK carbon and the weight of the carbon-fiber reinforcement (CF).

Sample ID	T_{carb} (°C)	τ_{hold} (min)	Equilibrium Ammonia Sorption Capacity, C_{NH3} (mg NH$_3$ / g)						Capacity Loss (%)
			C^0_{NH3}	C^1_{NH3}	C^2_{NH3}	C^3_{NH3}	C^4_{NH3}	C^5_{NH3}	
120319a	735	0	17.6	5.2					70.4
012220a	737	60	19.4	5.4	7.4				
120619a	830	0	14.7	6.4	6.4	5.2	6.6	5.3**	64.6
120419a	927	0	10.8	5.2					51.4
120519a	1,021	0	9.9	4.9					50.3
120519b-SC†	1,021	0	0.37						
Amm.*	N/A	N/A	22.6	8.4	6.5	6.4	6.6		71.5

*Ammonasorb II
**The sample was compressed to occupy the fixed-bed volume similar to that for Ammonasorb.
†Sample 120519a after thermal removal of surface oxides by heating in a flow of nitrogen to 900 °C, with no hold time at 900 °C
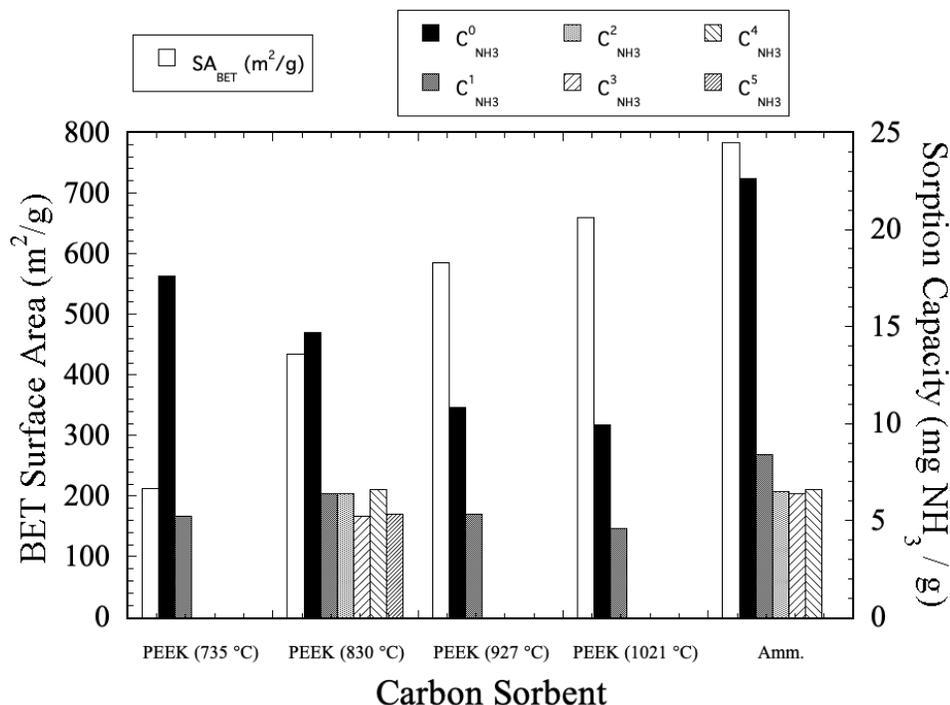
Figure 3. BET surface area and ammonia-sorption capacity for PEEK/CF sorbents and Ammonasorb II.
C^0_{NH3} **is the ammonia-sorption capacity of the freshly prepared sorbent (i.e. prior to vacuum regeneration).**
C^1_{NH3}**,** C^2_{NH3}**,** C^3_{NH3}**,** C^4_{NH3}**, and** C^5_{NH3} **are sorption capacities after the first, second, third, fourth, and fifth**
vacuum regeneration, respectively.

Data in Table 1, Table 2, and Figure 3 show that the specific surface area increases as the carbonization temperature increases, whereas the initial equilibrium ammonia sorption capacity is reduced with increasing carbonization temperature. It can also be seen that the initial sorption capacity is reduced by 50–72% after the first sorbent regeneration. It is interesting to note that the highest reduction in sorbent performance was observed for Ammonasorb and the PEEK/CF sorbent carbonized at 735 °C, which are the carbons that showed the highest initial sorption capacities. Although it is understandable that the acid-impregnated Ammonasorb lost a high proportion of its original active sites due to the mostly irreversible adsorption of ammonia on strongly acidic sites, it is unclear why the 735 °C PEEK/CF carbon behaved in the same way. It is hypothesized that some acidic moieties exist within the thermally decomposing PEEK polymer during carbonization, and that these acidic species still exist at 735 °C, but their amount is significantly reduced at higher carbonization temperatures. The partial vacuum-regenerability of Ammonasorb can be explained by the fact that not all Ammonasorb sites are occupied by strongly acidic functional groups. In addition, high-vacuum conditions and long regeneration times were used (10^{-6} Torr for 6 hours), and it is likely that much worse regeneration performance would be observed under less favorable conditions. In contrast, excellent dynamic response of PEEK/CF-derived sorbents was previously demonstrated on a time scale of a few minutes at a relatively poor vacuum of ~0.35 Torr.[1]

The available data, although still somewhat limited, also show that little or no further reduction in sorption capacity takes place after subsequent ammonia sorption-desorption cycles (see Table 2 and Figure 3). This behavior is consistent with the data previously reported for carbons derived from polyvinylidene chloride (PVDC).[3] It is also interesting to note that the equilibrium sorption capacity for different PEEK/CF sorbents, and also for Ammonasorb, seem to settle in the range 4.9–7.4 mg NH_3 / g sorbent after multiple sorption-desorption cycles. More data are needed, however, to establish the long-term performance characteristics of these carbon sorbents.

Sorbent evaluation would be incomplete without the examination of sorption and desorption kinetics. In general, a steep (sharp) breakthrough curve, i.e. the one with little or no tail, is desirable because a high percentage of the total sorption capacity can be utilized before breakthrough occurs. In contrast, a flat breakthrough curve, i.e. the one with a long tail, results in sorbent underutilization as the breakthrough takes place when a large proportion of the sorbent remains unsaturated.

The dynamic behavior of the sorption process is captured by breakthrough curves, and fast sorption kinetics favor steep breakthrough curves. Breakthrough curves for the carbons used in the present study are shown in Figure 4. It can be seen that much of the initial equilibrium sorption capacity for Ammonasorb and the 735 °C PEEK/CF carbon is contributed by the long tails. It can be questioned whether sorbents with breakthrough curves having such long tails will provide effective TC removal on time scales of several minutes that are envisioned for PLSS operation. (The CO_2-removal unit in the PLSS operates under rapid cycling conditions, with a cycle time of a few minutes, and it is desirable for the TCCS to operate in a similar fashion.) In contrast to Ammonasorb and the 735 °C PEEK/CF carbon, the PEEK/CF sorbents carbonized at higher temperatures exhibit steeper breakthrough curves, which are more desirable for better sorbent utilization in rapid-cycling systems.

It should be noted that breakthrough curves and sorption-capacity curves, such as those shown in Figure 4a and Figure 4b, respectively, represent the same information because sorption-capacity curves are obtained by integrating the area between breakthrough curves and the line indicating ammonia input concentration (~20 ppm). For this reason, additional sorption data presented below are discussed only in terms of breakthrough curves, and the corresponding sorption capacities can be found in Table 2. The sorption capacities shown in Figure 4b have the same slopes up to their breakthrough points (~100 minutes in most cases) because the above-described integral is the same for all the sorbents at the early stages of adsorption.

The irregular shifts in the effluent concentration seen in Figure 4a (Ammonasorb and the PEEK/CF sorbent carbonized at 830 °C), and also in some breakthrough curves discussed below, are believed to be experimental artifacts most likely related to imperfect temperature control. They can be disregarded, and they do not affect data processing and interpretation.

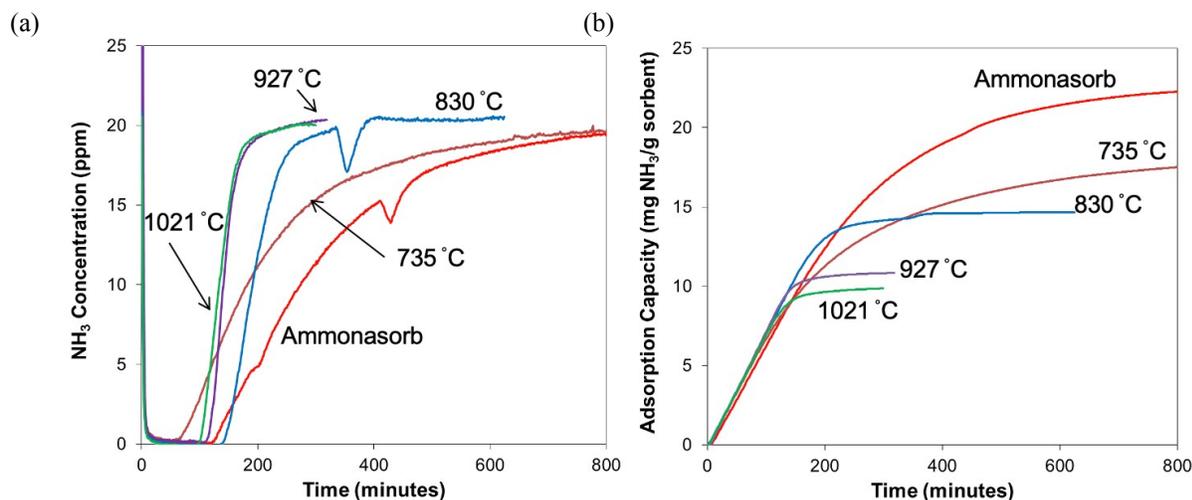(a)   (b)

Figure 4. Breakthrough (a) and adsorption capacity (b) curves measured for Ammonasorb II and PEEK/CF granular carbon samples (measurements performed using fresh, i.e. not regenerated sorbent samples).

As mentioned above, the loss of initial equilibrium capacity was found to be most dramatic (~70%) in the case of Ammonasorb II and the 735 °C PEEK/CF carbon. These two carbons also happened to show long tails in their breakthrough curves (Figure 4a), which will most likely adversely affect their performance in the PLSS. It is instructive to examine the shape of the breakthrough curves for these two sorbents after the first vacuum regeneration, and compare them to the corresponding breakthrough curves for the high-temperature PEEK/CF sorbents. The relevant data are shown in Figure 5. It can be seen that although the sorption capacity of Ammonasorb II is relatively large, a significant proportion of it is still due to the long tail. The performance of the 735 °C PEEK/CF carbon also dropped substantially after sorbent regeneration, and it is fair to say that most of its capacity is now contributed by the tail. In contrast, the high-temperature PEEK/CF carbons have nice steep breakthrough curves, even though the capacities are now 50–65% lower than the initial values.

Data in Table 2, Figure 4, and Figure 5 indicate that the PEEK/CF sorbent carbonized at 830 °C may offer the combination of the relatively high sorption capacity (5.2–14.7 mg NH_3 / g), a modest capacity loss after the first sorption-regeneration cycle (< 65%), and the favorable sorption kinetics (steep breakthrough curves). It should be understood, however, that additional factors may influence the final sorbent selection, such as the hold time at the

carbonization temperature, the degree of burn-off during activation, desorption kinetics (especially during rapid cycling), and mechanical strength. Nonetheless, there are already good reasons to examine ammonia-sorption behavior of the 830 °C PEEK/CF sorbent over several cycles, and the relevant data are shown in Figure 6.
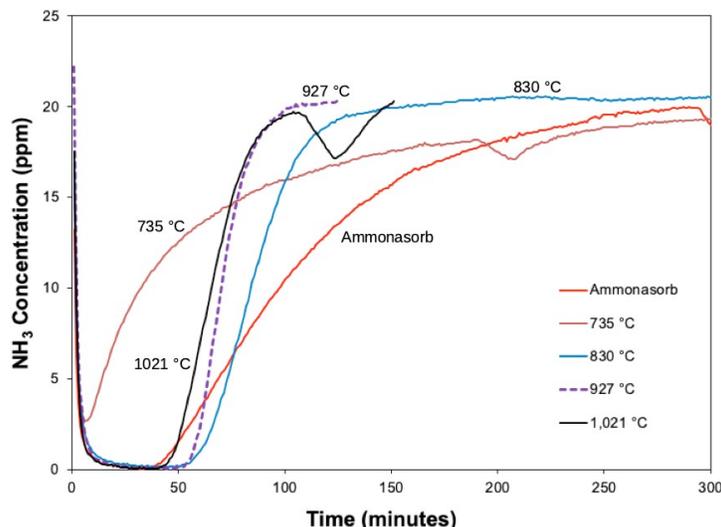

Figure 5. Breakthrough curves measured for Ammonasorb II and PEEK/CF granular carbon samples carbonized at the temperatures indicated after the first vacuum regeneration.
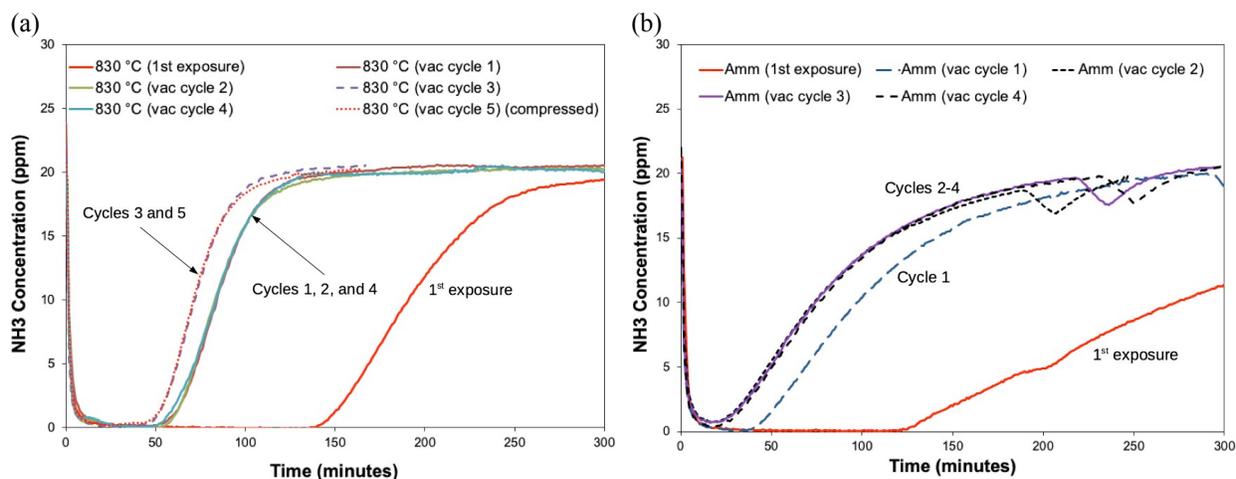

Figure 6. Ammonia breakthrough curves after several sorption-desorption cycles for: (a) the PEEK/CF granular sorbent carbonized at 830 °C; and (b) Ammonasorb II.

It can be seen in Figure 6a that the 830 °C PEEK/CF sorbent breakthrough curves for several cycles seem to be consistent, without significant deterioration in the sorption capacity beyond the first-cycle capacity loss. This is true about both equilibrium sorption capacities and the shape of the breakthrough curves. Having said that, the slope of the rising part of the breakthrough curves seems to be somewhat larger (steeper) for subsequent sorption-desorption cycles as compared with the first-exposure curve. This is likely to result in better sorbent utilization than in the case of breakthrough curves with long tails (the slowly rising breakthrough curves). The slight variation in the curves for cycles 1–5 seen in Figure 6 is most likely a result of differences in sample treatment, in the sense that some samples were vacuum-regenerated immediately after the sorption measurement, whereas other samples were stored in ambient air for a few days prior to regeneration. These differences are not deemed significant, however. Prior to the 5th cycle, the carbon sample was compressed to a bed height of approximately 17 mm to see if the volume

reduction, and thus the gas residence time reduction, would have an effect on sorption performance. (The sample weight was unchanged in this experiment.) The data of Figure 6a show no evidence of such an effect.

A similar sequence of experiments was carried out using Ammonasorb II, and the collected breakthrough curves are shown in Figure 6b. The comparison with the 830 °C PEEK/CF carbon shows a larger sorption-capacity loss after the first regeneration for Ammonasorb, the less steep breakthrough curves for this sorbent, and also the ammonia breakthrough is found to occur sooner for Ammonasorb II than for the 830 °C PEEK/CF carbon for all the cycles studied. The above observations point to the potential attractiveness of PEEK-based sorbents, as compared with Ammonasorb II, in addition to the ability to fabricate them in the monolithic form (low pressure drop, thin walls, rapid vacuum-regeneration).

In a limited number of experiments, the effect of hold time at the final carbonization temperature on ammonia-sorption capacity was studied using the 735 °C PEEK/CF carbon. The baseline carbonization condition was zero hold time, and another PEEK/CF sorbent was prepared using a 60-minute hold time at 735 °C. Results of ammonia sorption on the above two carbons are shown in Figure 7. The following observations can be made:

1. The increase in the severity of heat treatment, i.e. the increase of the hold time at the final carbonization temperature from 0 to 60 min., results in improved sorbent performance in terms of both: (a) the increased sorption capacity; and (b) the steeper breakthrough curves.
2. The breakthrough curves for the sorbent carbonized at 735 °C with a 60-minute hold time still exhibit longer tails (less steep curves) than the corresponding breakthrough curves for the PEEK/CF sorbents carbonized at higher temperatures.
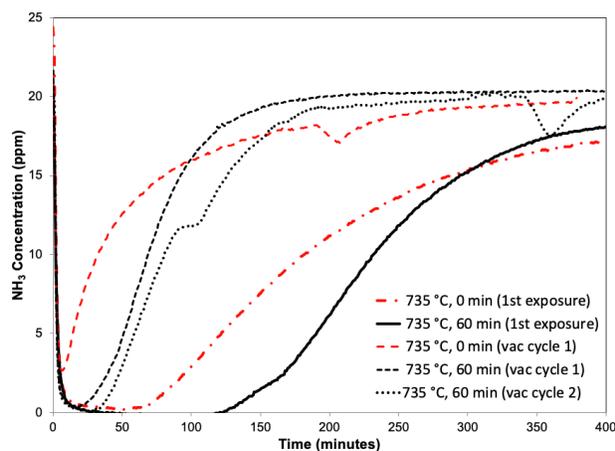

Figure 7. Ammonia breakthrough curves for the PEEK/CF sorbent carbonized at 735 °C at zero and 60-minute hold time at the final carbonization temperature.
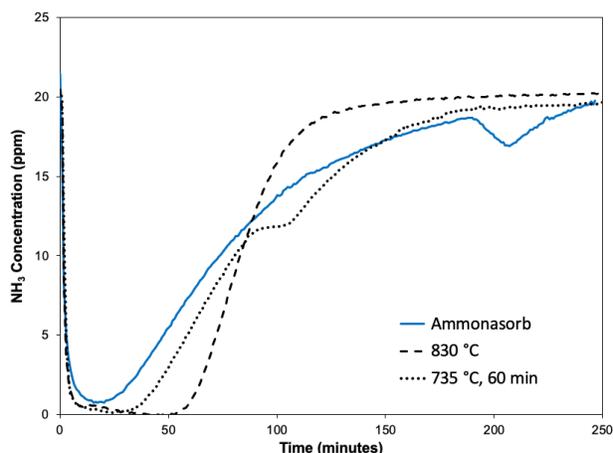

Figure 8. Ammonia breakthrough curves after the second cycle of ammonia sorption-desorption (Ammonasorb II; PEEK/CF sorbents carbonized at 830 °C and 735 °C (60 min. hold time).

The comparison between breakthrough curves after the second vacuum-regeneration for PEEK/CF sorbents carbonized at 735 °C and 830 °C and Ammonasorb II is shown in Figure 8. It can be seen that the PEEK/CF carbonized at 830 °C is the best performer in terms of: (a) the breakthrough time; and (b) the absence of a long tail in the breakthrough curve. Even the total sorption-capacity of PEEK/CF (830 °C) is as large as that exhibited by Ammonasorb II.

The effect of the presence of oxygen complexes on the carbon surface was also investigated, following our previous finding that surface chemistry plays an important role in ammonia-carbon surface interactions.[1] Stable oxygen surface complexes are known to form during carbon exposure to oxidizing gases, including air. These complexes can be thermally removed, however, usually in the form of carbon monoxide, at elevated temperatures in a non-oxidizing atmosphere. In view of the above, it is fair to say that all the PEEK/CF carbons that were subjected to air activation at 325 °C had significant proportions of their surface covered with such complexes. In one experiment, the PEEK/CF sample carbonized at 1,020 °C, and activated in air, was subsequently thermally cleaned in a flow of nitrogen at 900 °C. It is believed that the above post-treatment removed a large amount of oxygen surface complexes, without significantly changing the carbon pore structure. The latter assertion is supported by data shown in Table 1 (sample 120519a-SC versus 120519a). Results of ammonia-sorption measurements on the PEEK/

CF (1,020 °C) sorbent before and after the above-described thermal surface cleaning are shown in Figure 9. A tremendous drop in ammonia-sorption capacity can be seen after the surface cleaning (0.37 mg NH_3/g versus 9.9 mg NH_3/g prior to surface cleaning), which means that oxygen surface complexes play an important role in ammonia sorption on carbon. In fact, the available data show that the effect of surface chemistry on ammonia sorption is stronger than the effect of pore structure.

IV. Conclusions

The effect of carbonization conditions on ammonia-sorption performance, sorbent vacuum regeneration, and the pore-structure characteristics was studied for sorbents derived from the PEEK/CF polymer precursor. Precursor carbonization was performed at 735–1,020 °C, which was followed by carbon activation in a flow of air at 325 °C to a burn-off of ~20 wt%. Granular sorbents were used in a particle-size range of 0.355–0.850 mm (20 x 45 mesh). Ammonasorb II, the currently used state-of-the-art TC sorbent, served as a reference material, and it was ground and sieved to the same particle-size range as the PEEK/CF sorbents. Ammonia-sorption experiments were carried out in a laboratory packed-bed system, with sorbent-regeneration carried out by exposure to vacuum (~10^{-6} Torr) for 6 hours. Experimental data lead to the following conclusions:

Figure 9. Ammonia breakthrough curves for the PEEK/ CF sorbent carbonized at 1,020 °C before and after thermal cleaning in a flow of nitrogen at 900 °C.

1. Ammonasorb showed the highest initial equilibrium sorption capacity (~22.6 mg NH_3/g), which is not surprising as this sorbent was produced by impregnating activated carbon with phosphoric acid. Although the sorption capacity for Ammonasorb was the highest among the sorbents studied, the breakthrough curve exhibited the longest tail, which is generally undesirable. The sorption capacity of the 735 °C PEEK/CF carbon was found to be somewhat lower than for Ammonasorb (17.6 mg NH_3/g), and a significant tail was also observed in the ammonia breakthrough curve. The PEEK/CF carbons carbonized at higher temperatures showed respectable sorption capacities (9.9–14.7 mg NH_3/g), and their breakthrough curves were found to be relatively steep, i.e. not exhibiting long tails.
2. All sorbents lost a significant proportion of their original sorption capacity after the first sorption-regeneration cycle (51%–72%), but little or no loss of capacity was found to occur in the second and subsequent cycles.
3. The proportion of micropores in the PEEK/CF sorbents was found to increase with the increasing carbonization temperature, and so did the specific surface area and the micropore volume. In contrast, the initial equilibrium ammonia sorption capacity was found to decrease with the carbonization temperature.
4. It was found that the removal of oxygen surface complexes from the carbon surface caused a factor of 27 drop in the ammonia-sorption capacity. Thus, the oxygen complexes present on the carbon surface strongly enhance ammonia sorption, with the specific surface area being of secondary importance.
5. The increase in the severity of carbon heat treatment, i.e. the increase in the carbonization temperature, and also in the hold time at the final carbonization temperature, results in improved sorbent performance in terms of both: (a) the increased sorption capacity; and (b) the steeper breakthrough curves.
6. The PEEK/CF sorbent carbonized at 830 °C was found to be the best performer in terms of: (a) the breakthrough time; and (b) the absence of a long tail in the breakthrough curve. Even the total sorption-capacity of PEEK/CF (830 °C) was as large as that exhibited by Ammonasorb II after the first sorption-regeneration cycle.
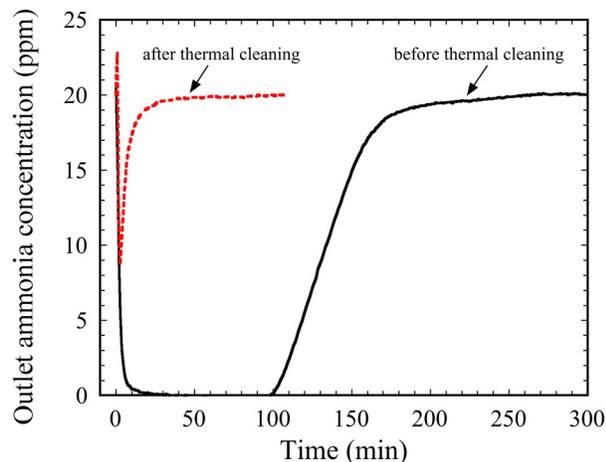
Acknowledgments

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