Evaluation of Traditional and Vacuum-Regenerable Sorbents Exposed to a Multi-Gas Contaminant Mixture in the Trace Contaminant Control Unit

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The efficient removal of trace contaminants generated by crewmember's metabolic processes from the ventilation loop of the Exploration Portable Life Support System (xPLSS) is critical for the health and safety of astronauts. Currently, acid-impregnated activated carbon (Ammonasorb II), a non-regenerable sorbent, is used in the Trace Contaminant Control (TCC) system. This limits the TCC operational service life and can add significant logistical hurdles to spacecraft missions. New regenerable sorbents, such as XploSafe's nanoporous silica-based sorbent, can considerably expand the operational capabilities of the TCC. To evaluate potential sorbents, XploSafe developed a TCC test-bed apparatus, which is used to directly compare the trace contaminant removal capabilities of regenerable and non-regenerable sorbents under operational conditions. The tested sorbents are placed inside a model TCC cartridge and exposed to a recirculating closed-loop system at a sub-atmospheric pressure of 4.3 psia and flow rate of 6 ACFM. A multi-gas stream of nine priority NASA contaminants (including ammonia, methyl mercaptan, and formaldehyde) is injected into the recirculation loop at established source rates. Contaminant concentrations inside the recirculation loop are monitored in real time using a combination of sensors and by periodically sampling a fixed volume of the circulating gas stream. The sampled gas is analyzed by a thermal desorption unit connected to a gas chromatograph–mass spectrometer to precisely quantify the analytes within the sample. Ammonasorb II and XploSafe sorbent are individually exposed to a trace contaminant multi-gas stream for over 150 and 24 hours, respectively. In addition, a vacuum regeneration cycle is incorporated with a pressure swing at a set time interval to evaluate the effectiveness of the XploSafe sorbent with regeneration. The results show that sorbents can be evaluated under realistic conditions. With regeneration, XploSafe's sorbent could significantly increase extravehicular activity.

Nomenclature

3D	=	three-dimensional
ABS	=	acrylonitrile butadiene styrene
ACFM	=	actual cubic feet per minute
atm	=	atmosphere
CH_2O	=	formaldehyde
CH_3SH	=	methanethiol
CO	=	carbon monoxide

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

CO_2 = carbon dioxide
EVA = Extravehicular Activity
g = gram
GC = gas chromatography
h = hour
H_2O = water
H_3PO_4 = phosphoric acid
L = liter
lpm = liters per minute
m^2 = square meter
mg = milligram
min = minute
mL = milliliter
mm = millimeter
MS = mass spectrometry
ng = nanogram
NH_3 = ammonia
PFPH = pentafluorophenylhydrazine
ppm = parts per million
RH = relative humidity
SMAC = Spacecraft Maximum Allowable Concentration
TCC = Trace Contamination Control
TD = thermal desorption
wt = weight
xEMU = Exploration Extravehicular Mobility Unit
xPLSS = Exploration Portable Life Support System

I. Introduction

The Exploration Portable Life Support System (xPLSS) is a critical component of the Exploration Extravehicular Mobility Unit (xEMU), a new-generation spacesuit that protects astronauts in open space.[1,2] The Trace Contamination Control (TCC) System removes contaminants from the xPLSS ventilation system.[3,4] The primary trace contaminants that threaten the health of astronauts include ammonia, carbon monoxide, formaldehyde, and methanethiol, in addition to numerous other contaminants that must be captured.[3,5–7] Contaminant concentrations must be kept below the Spacecraft Maximum Allowable Concentration (SMAC) limits.[5,8] Currently, Ammonasorb II, a non-regenerable phosphoric acid-impregnated carbon sorbent, is used to remove contaminants. The sorbent has a limited lifetime of 150 hours, which presents replacement costs and logistical concerns. TCC solutions for long-duration space missions that can potentially replace the non-regenerable activated carbon-based technology are scarce. One example of a regenerable sorbent includes a redesigned adsorption guard bed containing a novel high-temperature catalytic oxidizer.[9] Microlith® substrate technology[6,10] consists of metal meshes coated with functionalized sorbent nanomaterials. This system could maintain the ammonia and formaldehyde concentrations at the outlet of the Rapid Cycle Amine (RCA) system below the 7-day SMAC limits. Another solution includes regenerable carbon-based sorbent monoliths integrated with the RCA swing bed.[7,11] However, both sorbents were primarily evaluated for ammonia removal under atmospheric pressure and need to be examined for all the listed contaminants under xEMU conditions.

Sorbent development requires a combination of new materials and extensive testing at realistic xEMU conditions. Testing sorbents with a multi-gas stream of NASA-priority contaminants at the established generation rates[5] requires special equipment and measurement instrumentation. XploSafe has developed a TCC test-bed apparatus[12,13] that is capable of directly comparing the trace contaminant removal capabilities of both regenerable and non-regenerable sorbents under operational xPLSS conditions.[12,13] In addition, XploSafe previously reported a new regenerable nanoporous silica sorbent for TCC applications.[14] Here, the nanoporous silica sorbent was pelletized to create sorbent in the bead form. In this study, sub-atmospheric tests with a multi-gas stream of NASA-priority contaminants at the established generation rates within the xEMU[5] are reported. In addition, Ammonasorb II and the regenerable nanoporous silica sorbent developed by XploSafe[14] were tested under identical conditions. Importantly, the first vacuum regeneration tests under realistic TCC conditions were performed with the XploSafe sorbent beads. A

successful regenerable sorbent can advance the xPLSS via its incorporation into the CO_2/H_2O removal system (such as RCA beds).

II. Background

The primary performance parameters of the TCC system are summarized by NASA.[5] The testing of new sorbents under these conditions is challenging. In particular, the TCC system should contain a ventilation loop with a pressure of 4.3 psia and a maximum pressure drop across the unit of 0.3 in-H_2O. The gas flow rate through the loop should be 170 lpm (6 ACFM) at a temperature between 1.7°C (35°F) and 51.7°C (125°F). Finally, the unit should operate in an environment with a relative humidity (RH) ranging from a –29.2 to 65°F dewpoint at 68°F (1–90 percent RH). Under these conditions, the unit must be able to remove trace contaminants to ensure that personal exposures remain below the 7-day SMAC limits.[5,8] XploSafe has previously developed a test bed for evaluating TCC prototypes and sorbent performance that mimics the TCC operational conditions.[12,13] The test rig emulates the actual spacesuit volume using stainless-steel tanks and maintains a sub-atmospheric pressure of 4.3 psia during recirculation. It also controls the temperature and relative humidity of the gas stream within the NASA-specified limits. The sorbent holder geometry of the testing apparatus allows the evaluation of the sorbent bed currently used in the TCC system, and the testing apparatus regeneration module is utilized to perform vacuum regeneration cycles with controlled durations.

Two sorbents are evaluated in this work. The first sorbent is Ammonasorb II (Calgon Carbon), and the second is sorbent beads manufactured from XploSafe's nanoporous silica, a regenerable sorbent that was found to be effective against the primary contaminants expected in the TCC.[14] Ammonasorb II is provided as irregularly shaped granules and was sieved between 6 and 8 mesh using stainless-steel ASTM-E11 rated mechanical sieves. It is made from coconut shell carbon treated with H_3PO_4 and has been chosen as the TCC sorbent after extensive testing for ammonia control, which is considered the primary contaminant in the xEMU.[15,16] XploSafe's nanoporous silica sorbent consists of hexagonal arrays of tubular pores with diameters between 2 and 5 nm. The relatively small diameter and high curvature of the pores of the nanoporous silica allow this material to not only strongly bind a large range of different analytes but also to be regenerable through vacuum desorption. The material has high capacities for an extensive array of chemical classes, including organophosphates, nitrogenated organics, chlorohydrocarbons, ketones, aldehydes, aromatics, and organic acids.[17]

III. TCC Testing Apparatus

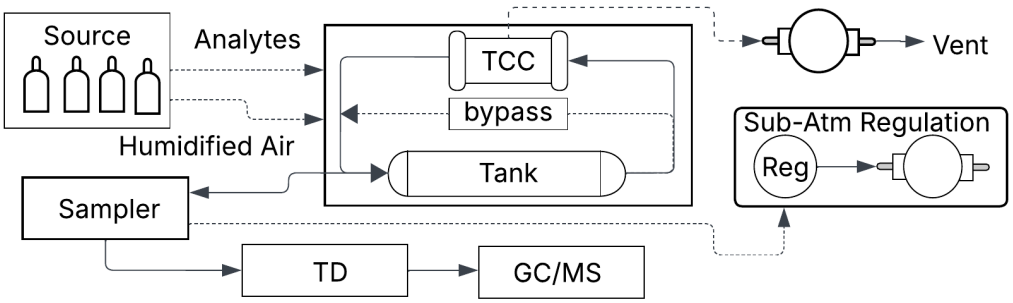

Figure 1. A block diagram of the TCC test bed mimicking the environment within the xPLSS. The recirculated TCC flow occurs continuously in the non-regeneration mode and directed through the bypass only during vacuum regeneration. The continuous, non-interrupted flow is designated by a solid line, while the flow denoted by a dashed line changes in the regeneration mode depending on the cycle time. The flow to the TD instrument only occurs during the sampling phase.

The main components of the testing apparatus include a sub-atmospheric recirculating loop with a sorbent holder, an analyte source, an automatic gas sampler, and a sub-atmospheric gas regeneration module. The previous investigations focused on the construction, testing capabilities, and prototyping of the TCC sorbent holder using 3D printing.[12,13] In this study, a sub-atmospheric automatic sampler and new stainless-steel holder for a replaceable

sorbent cartridge were designed to allow direct comparison between different materials. The sub-atmospheric automatic sampler was a significant addition and is described in more detail below. The holder (labeled as "TCC" in Figure 1) consists of a stainless-steel KF-160 vacuum nipple to allow sustaining pressure swings from sub-atmospheric pressure to 1 atm and an exchangeable internal sample holder for the sorbent. The tank volume was increased to approximately 56 L to model the ~2 ft^3 internal volume for the TCC loop,[18] a sub-atmospheric automatic gas sampler was added, and a standard sorbent container was incorporated.

A. TCC Test Bed

The TCC test bed is shown in Figure 2. The unit can maintain a sub-atmosphere pressure of 220 Torr (4.3 psia) with a recirculation flow rate of 6 ACFM and full gas sampling capabilities.[5] The system consists of two stainless-steel tanks with a total volume of approximately 56 L to match the xPLSS volume of ~2 ft^3, a Micronel blower (U100HL-024KA-4) to maintain the required airflow, a heat exchanger to maintain a constant gas temperature, and a TSI flow meter (5300 series). The gas flow can be directed through the TCC or through a bypass by four pneumatic valves. The pathways are (1) the TCC pathway that includes a stainless steel holder for a removable sorbent cartridge, and (2) the bypass loop pathway that allows the steady-state to be reached before the TCC sorbent is exposed, for assessment of background concentrations, and for injection of analytes into the loop for quantification. The bypass loop ensures the system's performance and background before starting the injection of contaminants into the TCC pathway. This loop also facilitates the changing of the TCC sorbent without breaking the recirculation loop and supports the regeneration subsystem. On the bottom tank, a safety release valve and pressure gauge are installed. The top tank contains a relative humidity/temperature sensor (Omega RH–USB) and is placed in the return flow from the loop. In both recirculation modes (TCC flow and bypass), the temperature, relative humidity, and gas pressure are also monitored using the TSI mass flow meter. Two piezoelectric pressure gauges are connected directly across the TCC unit to monitor the pressure drop and provide pressure feedback for the regeneration process. The TCC pressure drop is measured more accurately using the differential pressure gauge on the TSI flow meter. Finally, two Alcatel 2012A dual-stage mechanical pumps provide vacuum for initial evacuation, pressure regulation, and regeneration. The first pump evacuates both the TCC and bypass loops from atmospheric to sub-atmospheric pressure and performs sorbent regeneration during vacuum regeneration. The pressure regulation vacuum pump maintains the sub-atmosphere pressure inside the system and has a gas load equal to that of the flow (200 mL/min) through the injection valve during testing.

The blower speed required to maintain the necessary airflow in the loop increases the circulating gas temperature by approximately 5°C within 30 minutes of operation. Thus, a laminar flow element was utilized to cool the circulating gas after exiting the blower. The element consists of many small channels or tubes bunched together within the element and is cooled using a short coil of copper tubing wrapped around its exterior. An external chiller is used to flow a temperature-regulated water/ethylene glycol mixture through the coil. This setup is sufficient to maintain the gas temperature in the tank within 0.4°C of ambiance.

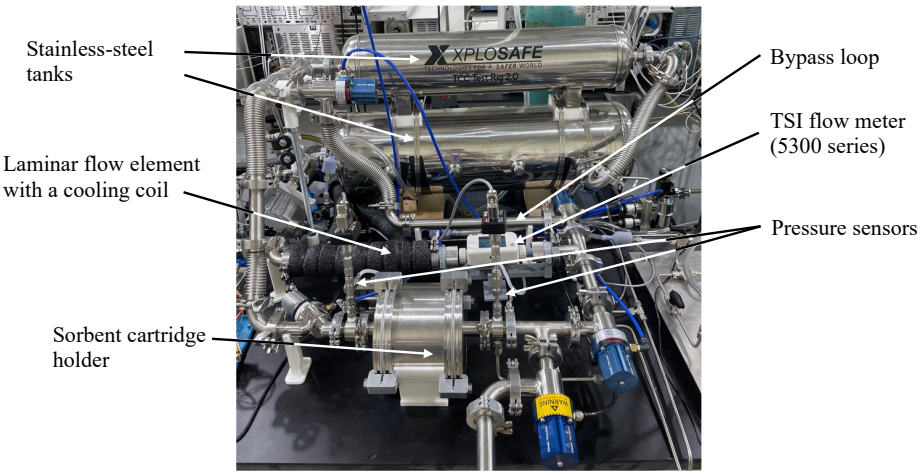

Figure 2. TCC gas recirculation loop with two stainless-steel tanks simulating the TCC volume in the xPLSS, air blower, laminar flow element, mass flow meter, and stainless-steel container for the removable sorbent cartridge.

B. Analyte Source

The analyte source system of the TCC test rig can produce single or multi-component analyte vapor streams at preset concentrations and relative humidity levels.[13] In this system, each individual trace contaminant is introduced from a pre-calibrated gas cylinder through individual calibrated mass flow controllers respectively. A humidified carrier gas is generated using a gas washing bottle with a coarse frit to disperse the gas without further dilution. A relative humidity of 55 percent can be maintained in the injected gas mixture at atmospheric pressure. The relative humidity and temperature in the recirculation loop are continually monitored inside the tank using the attached Omega RH–USB temperature/humidity probe and immediately after the blower using the TSI flow meter (5300 series). Equation (1) expresses the source rate as a function of the injection rate of each analyte into the TCC system. Note that a day is defined as 8 hours, consistent with the definitions of the source rates provided by NASA.[19]

$$Source\ rate\ \left(\frac{\mathrm{mg}}{\mathrm{day}}\right) = Injection\ rate\ \left(\frac{mL}{min}\right) \times Gas\ concentration\ \left(\frac{ng}{mL}\right) \times \frac{mg}{10^6 ng} \times \frac{60\ min}{h} \times \frac{8\ h}{day} \qquad (1)$$

In this equation, the *Injection Rate* is set to 200 mL/min. *Gas concentration* is the concentration before the injection flow controller into the TCC loop, but after the separate flow controller for each gas source, which is computed via Equation (2).

$$Gas\ concentration\ \left(\frac{ng}{mL}\right) = Cylinder\ concentration \left(\frac{ng}{mL}\right) \times Cylinder\ flow\ \left(\frac{mL}{min}\right) \div Total\ mixure\ flow\ \left(\frac{mL}{min}\right) \qquad (2)$$

The total flow from the cylinders into the mixture is 250 mL/min, with 200 mL/min entering the TCC loop and 50 mL/min being vented. The extra flow allows a positive pressure to be maintained before the injection mass flow controller. Once the nine simultaneous equations (one for each gas) are solved, the flow rate of the humidified gas stream can be determined. The optimized flows in Table 1 are computed using the above-mentioned procedure. Note that the injection rates are three times greater than the previously computed values[13] as the source rates have been reinterpreted as 8 hours per day instead of 24 hours per day.[19] The larger 8-hour day rates represent a more rigorous test. Other sources from NASA suggest a 24-hour day.[20]

Table 1. Calculated flow rates of select TCC analytes required to match the NASA source rates.

Contaminant	Cylinder (ppm)	Flow rate (mL/min)	Injection rate ng/min
Acetone	50	4.0	402
Acetaldehyde	100	9.3	1381
Ammonia	10000	29.8	166667
1-Butanol	50	8.6	1042
Ethanol	500	12.5	9396
Formaldehyde	50	17.8	875
Furan	50	5.4	625
Methanol	500	3.9	2125
Methyl mercaptan	50	20.4	1729
Humidified carrier		138	

During operation, the TCC unit must limit the concentrations of the trace contaminants inside the TCC loop under the 7-day SMAC limits[5] for at least 150 hours or 18 extravehicular activities (EVAs). The sorbent capacities of XploSafe's nanoporous silica (OSU-6) and Ammonasorb II sorbents, determined by conducting breakthrough experiments, are listed in Table 2.[14] The breakthrough times were computed using Equation (3). These breakthroughs are the time required to reach 80 percent, which is a conservative estimate based on the point where the initial breakthrough is experimentally observed in the small flow-through scale tests conducted for Ammonasorb II and nanoporous silica powder (OSU-6).[14] The sorbent mass for XploSafe's nanoporous silica beads was based on the effective amount of OSU-6. XploSafe's nanoporous silica beads are designed for use in a cyclic regenerative system and thus exhibit shorter breakthrough times with respect to Ammonasorb II, which cannot be vacuum regenerated.

$$Time\ (h) = \frac{(0.80) \times sorbent\ mass\ (g) \times sorbent\ \ capacity\ \left(\frac{mg}{g}\right)}{Injection\ rate\ \left(\frac{ng}{min}\right)} \times \left(\frac{h}{60\ min}\right) \times 10^6 \qquad (3)$$

It should be noted the breakthroughs are based on the sorbent capacities determined by performing single-gas exposure experiments. As discussed later, the lack of timely breakthroughs for formaldehyde and acetaldehyde is hypothesized to be due to surface reactions of absorbed ammonia, which is present in relatively high concentrations, with these reactive compounds.

Table 2. Experimentally measured sorption capacities for Ammonasorb II and nanopores silicon powder (OSU-6). The breakthrough times are estimated for both Ammonasorb II and the nanoporous silica beads (see text).

Contaminant	Sorption capacity (mg/g)		Projected breakthrough (h)	
	OSU-6	Ammonasorb II	Nanoporous Silica beads	Ammonasorb II
Acetone	2.0	0.46	1061	1907
Acetaldehyde	0.040	0.028	6	13
Ammonia	1.4	16	2	160
1-Butanol	9.0	> 12	1843	14400
Ethanol	7.2	11.6	163	2058
Formaldehyde	0.0042	0.0027	1	5
Furan	0.002	0.098	< 1	720
Methanol	1.0	2.6	100	2039
Methyl mercaptan	0.004	> 1	< 1	916

C. Automatic Gas Sampler

The sub-atmospheric environment in the TCC test system is maintained by an Alcatel 2012A dual-stage mechanical pump and controlled by sub-atmospheric pressure regulators. As shown in Figure 1, the sub-atmospheric regulator is situated after the gas sampler and electrochemical sensors. Thus, excess carrier gas provided by the injection valve flows through the sampler system before being removed by the pump. In use, the automatic gas sampler collects a fixed sampling volume of the gas from the TCC recirculation loop to determine the contaminant concentrations by thermal desorption (TD)-gas chromatography (GC)/mass spectrometry (MS) and the attached electrochemical sensors. The volume of 50 mL was determined to be significant to quantify the contaminants while being sufficiently small not to affect the TCC concentrations. This volume is periodically transferred to commercially available Carbopack X tubes for the TD-GC/MS analysis of all contaminants except for ammonia and formaldehyde. Methyl mercaptan is monitored both by an electrochemical sensor (SolidsenS CLE-3611-400 with an external LMP91000-based potentiostat, 0.1−10 ppm range) and TD-GC/MS. For formaldehyde, an electrochemical sensor (Sensirion SFA30-D-T, 1−5000 ppb range) is used. In addition, the sample volume is transferred to a pentafluorophenylhydrazine (PFPH)-functionalized Tenax TA TD tube for TD-GC/MS analysis via a formaldehyde−PFPH derivative.[21] Finally, ammonia is measured using a Gravity SEN0469 electrochemical sensor (1−100 ppm range). The formaldehyde and methyl mercaptan sensors showed minimal interference with respect to the other gases. However, the ammonia sensor could be permanently damaged by methyl mercaptan, and accordingly, is replaced after each full run. The placement of the electrochemical sensor after the sampling volume and before the sub-atmospheric regulation allowed these sensors to be easily replaced without disrupting a run.

Automatic gas sampling is performed at a preset time interval and initiated by the TD-GC/MS start sequence. A diagram of the sampler and the placement of the electrochemical sensors is shown in Figure 3. The sampler consists of six electronically controlled valves (labeled 1 through 6) controlled by an Arduino board, three manual valves (labeled 7 through 9), and one mechanical pump to return the sampler volume to the sub-atmospheric pressure after the content is transferred to a TD sorption tube for measurement. When samples are not being transferred, the sample volume is connected to the TCC system. A timing sequence showing the positions of the open and closed valves during a sampling event is presented in Figure 4. The top pulse (Load Sample Command) is supplied from the TD instrument and is used to trigger the sample transfer. During the high-to-low transition, the sample volume is isolated, and the TCC flow is redirected through the bypass. Next, the sample is pressurized to 20 psi using an external helium source. Once pressurized, the sample column is transferred by a flow of helium into a thermal desorption tube within the thermal desorber. At a predetermined time (indicated by the low-to-high transition of the Load Sample Command pulse), the TD-GC/MS unit starts to process to analyze the sorbent tube and inject its contents into the GC/MS system. At the same time, the sampler turns off the helium flow to the TD-GC/MS line and opens a valve to an independent sub-atmospheric pumping system to return the sampling chamber to sub-atmospheric pressure. Once the sub-atmospheric pressure is reached inside the chamber, the sample volume is once again connected to the TCC loop.

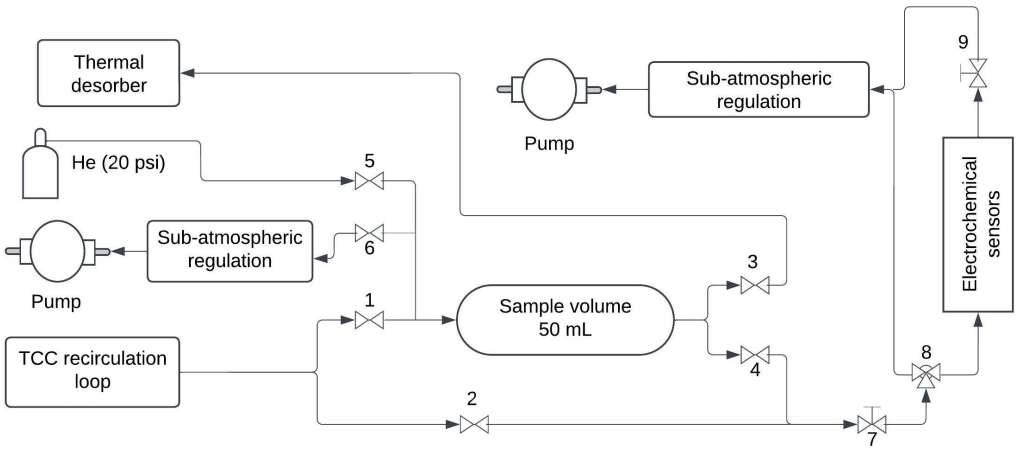

Figure 3. Schematic diagram of the automatic gas sampler connected to the TCC recirculation loop.

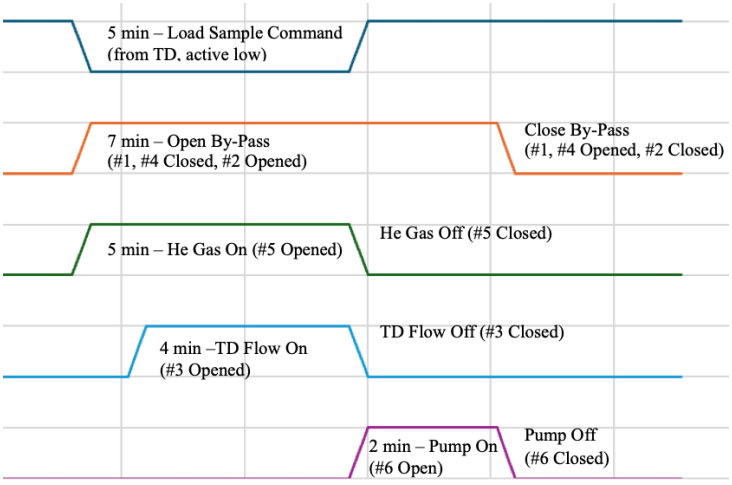

Figure 4. Timing sequence showing the open and closed positions of the automatic valves during a sampling event initiated by the TD-GC/MS instrument. The top pulse (Load Sample Command) is from the TD instrument.

D. Sorbents and Sorbent Holder

In this work, a new cylindrical holder for the removable sorbent cartridge was designed to allow direct comparisons between different sorbents. The holder consists of a stainless-steel tube with an inner diameter of 150 mm and length of 106 mm (Kurt Lesker QF160-600-N nipple) that can sustain pressure swings from sub-atmospheric pressure to 1 atm. Within the cylinder, an exchangeable internal sorbent holder is placed. Figure 5A shows one of the two sorbent holders filled with Ammonasorb II. This holder can support a total sorbent volume of approximately 230 mL to simulate the current TCC sorbent volume (dimensions: Ø122×19.7 mm).[20] 3D materials printed from ABS filament using a RAISE 3D Pro3 printer were found to be compatible with the pressure requirements and produced no detectable outgassing.[13] Figure 5B shows a larger sorbent holder (460 mL) filled with XploSafe's nanoporous silica beads. Figures 6A and B are the front views of the assembled sorbent holders filled with Ammonasorb II and nanoporous silica beads, respectively. Figures 5 and 6 also show the stainless-steel mesh (#80) pieces that are permanently attached to both sorbent holder sides using an epoxy paste (Loctite EA Aero 9321). The holder fits tightly into the stainless-steel holder in the TCC loop. A wrapping of Teflon tape along the edge provides a tight seal between the sorbent holder and stainless steel cartridge holder.

Two different sorbents were evaluated. Ammonasorb II is a transitional sorbent, which has been well-studied for non-regenerative use in the TCC system.[15,16] It was purchased from Calgon Carbon and sieved between 6 and 8 mesh

to a particle size range of 2.36–3.35 mm using ASTM E-11 rated stainless steel test sieves manufactured by Advantech/WS Tyler. The obtained Ammonasorb II material was dried in a vacuum oven at 75°C for 24 hours at a base pressure of approximately 10^{-2} Torr. After cooling to 24°C inside the oven, the sorbent was immediately transferred to the sorbent holder (Figure 5), sealed with six metallic screws, and placed inside the stainless-steel sorbent cartridge holder of the TCC loop under atmospheric pressure. The Ammonasorb II sorbent mass inside the 230-mL TCC-sized holder was 126 g.

The second sorbent was created by pelletizing XploSafe's previously studied nanoporous silica-based regenerable sorbent.[14] In this study, fine nanoporous silica particles (surface area: 547–599 m^2/g) were combined with 30 wt.% colloidal silica (LUDOX AM-30). The resulting paste was extruded using an automated syringe pump through an 18-gauge needle to form drops with sizes of 3.12–4.21 mm, which were collected and frozen in a liquid nitrogen bath. The drops were converted to beads by freeze-drying overnight followed by calcining at 550°C for 12 hours. The produced beads exhibited mechanical robustness and resistance to cracking/powdering, and their surface area was 237–303 m^2/g, reflecting the range of different pellet batches. A sorbent holder filled with the nanoporous silica beads is shown in Figure 6. The beads were heated to 550°C for 48 hours and cooled down to room temperature before packing inside the sorbent cartridge, which was immediately sealed and placed inside the stainless steel holder of the TCC loop under atmospheric pressure. The total bead mass in the 230-mL TCC-sized or small sorbent holder was 76 g. This mass is significantly less than that of Ammonasorb II due to the difference in material density and void volume between the beads. Figure 5B shows a larger sorbent holder (460 mL) with XploSafe's nanoporous silica beads for a larger scale regeneration testing.

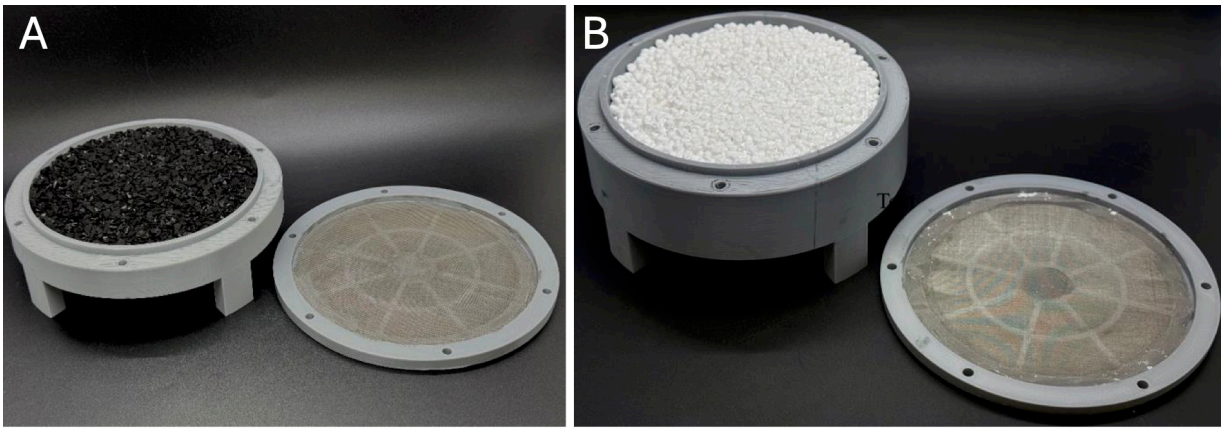

Figure 5. (A) Open TCC-sized ABS sorbent holder (230 mL) filled with 126 g of Ammonasorb II sorbent particles with sizes of 2.36–3.35 mm and (B) larger sorbent holder (460 mL) filled with 145 g nanoporous silica beads.

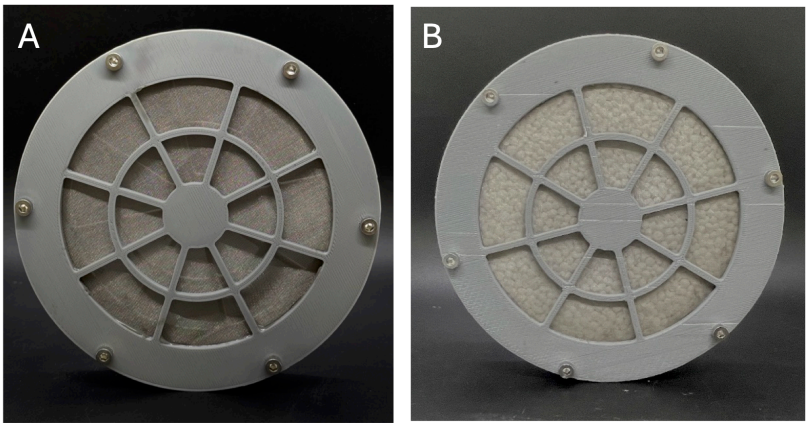

Figure 6. Front views of the assembled ABS sorbent holders filled with (A) Ammonasorb II and (B) nanoporous silica beads.

IV. Experimental Procedure

A. Sorbent Breakthrough Studies

The Ammonasorb II and nanoporous silica sorbent beads were subjected to breakthrough studies under conditions mimicking the TCC operation. Experiments were conducted at a continuous flow of humidified air with a relative humidity of 16 percent under the sub-atmospheric pressure of 220 Torr and a recirculation flow rate of 6 ACFM. Nine NASA contaminants (acetaldehyde, methanol, ethanol, furan, acetone, 1-butanol, methyl mercaptan, formaldehyde, and ammonia) were continuously supplied to the TCC recirculation loop at the injection rates specified in Table 1. The concentrations of these analytes in the loop were periodically monitored by TD-GC/MS and the gas sensors. In particular, a sample volume of 50 mL was transferred to a Carbopack X tube every 2 hours and to a PFPH-functionalized Tenax TA tube (for formaldehyde analysis) every 12 hours. The gas sensor readings, gas temperature, relative humidity, gas flow rate, pressure inside the recirculation system, and pressure drop across the sorbent cartridge were periodically logged at 5-minute intervals. For each sorbent, dosing was planned to continue for up to 180 hours or when any of the measured target analyte concentrations exceeded the 7-day SMAC limit.

Before conducting breakthrough experiments on both sorbents, humidified air was continuously recirculated through the tanks, but not through the sorbent holder, for at least 12 hours. TD-GC/MS (both Carbopack X and PFPH-functionalized Tenax TA tubes) and the gas sensors were used to verify the background of the air inside the loop before starting. The humidified air was generated using the same 138 mL/min flow rate through the water bubbler combined with zero-grade air flowing at 112 mL/min, which is the total flow rate of the analysis gases. After opening the TCC loop, a small burst of the formaldehyde sensor reading (> 1 ppm) was detected for Ammonasorb II before quickly returning to zero. No contaminants were observed via Carbopack X or the PFPH-functionalized Tenax TA sampling, which was performed after the final formaldehyde blip was detected using the sensor. After approximately 3 hours of the baseline measurement, the gas mix was introduced in the TCC loop, and sampling was started.

B. Gas Concentration Measurements

The concentrations of seven contaminants (acetaldehyde, methanol, ethanol, furan, acetone, 1-butanol, and dimethyl disulfide, which is a product of methyl mercaptan oxidation) were measured via TD-GC/MS. For this purpose, commercially available Carbopack X thermal desorption tubes were sampled with 50 mL of the gas stream at fixed time intervals (every 2 hours). Each tube was heated to 250°C for 5 minutes in the autosampler of a Markes TD-100 thermal desorber in a stream of He gas to transfer its contents into an AirToxics trap cooled down to –10°C, which served as a pre-concentrator. Subsequently, the cold trap was heated to 280 °C to desorb the analytes into the inlet of an Agilent GC6890/MS5973 unit. Analysis was conducted using a 60-m GC column (DB-624UI) in the m/z range of 35–500 amu for ethanol, furan, acetone, 1-butanol, and dimethyl disulfide, at m/z = 29 in the single-ion mode for acetaldehyde and methanol, and at m/z = 210 in the single-ion mode for formaldehyde. A typical spectrum recorded for the gas mixture without the sorbent filter is presented in Figure 7. Peak intensities were calibrated by measuring the peak areas at known analyte concentrations inside the bypass loop (without a sorbent).

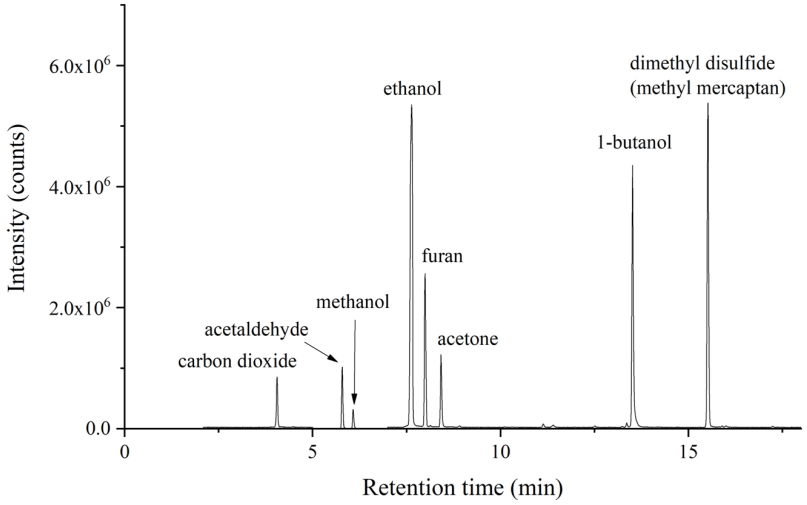

Figure 7. GC/MS spectrum recorded for seven NASA analytes in the bypass loop (without a sorbent).

V. Results and Discussion

A. Non-Regeneration Breakthrough Studies

XploSafe evaluated the breakthrough performance of Ammonasorb II and XploSafe's nanoporous silica beads exposed to the daily source rates of the nine target analytes inside the TCC recirculation loop. All the non-regenerative experiments used the small or TCC size sorbent cartridge. The measured trace contaminant concentrations in the test rig are summarized in Table 3. During Ammonasorb II testing over 180 hours, the target analyte concentrations within the TCC test rig did not exceed their 7-day SMAC limits at any time and were in the sub-ppm or low-ppm range. In particular, negligible amounts (below quantification limits) of furan, 1-butanol, methyl mercaptan, formaldehyde, and acetaldehyde were detected during the continuous 180-h run. Figure 8A shows the methanol concentration steadily increasing from 0 to 2.5 ppm within the first 90 h and then remaining stable till the completion of the experiment. The figure also shows trace concentrations of ethanol below 1 ppm, and the acetone background concentration in the recirculation system decreased from 0.3 to 0.1 ppm. Figure 8B shows the ammonia concentration slowly increased from 0 to 2 ppm after 180 h, remaining well within the NASA SMAC limit of 3 ppm. These results are consistent with the projected Ammonasorb II breakthrough times listed in Table 2, which significantly exceed 180 hours for most contaminants. No breakthroughs were detected for formaldehyde or acetaldehyde despite their relatively short, predicted breakthrough times of 5 and 13 hours, respectively. This phenomenon can be attributed to surface reactions of these two analytes with ammonia on the Ammonasorb II surface in the presence of phosphoric acid and water.[22] Consistent with these results, a significant enhancement in formaldehyde uptake was observed previously when formaldehyde was co-adsorbed with ammonia by an activated carbon-based TCC sorbent for the xPLSS in humidified air.[19] Finally, the pressure drop measured across the filled sorbent cartridge was 0.18 ± 0.06 in-H_2O, within the 0.3 in-H_2O limit specified in Ref. [20]

Table 3. Analyte concentrations measured at different stages of the TCC test run with the TCC sized sorbent cartridge without vacuum regeneration. The symbol "–" indicates that the measured concentration is below the detection limit of 0.01–0.05 ppm for most analytes.

Contaminant	Source rate (mg/day)	7-Day SMAC limit (ppm)	Measured concentrations (ppm)				
			Nanoporous silica beads			Ammonasorb II	
			0–30 min	1–3 h	20–24 h	0–24 h	150–180 h
Acetone	0.193	22	0.10	0.10	0.13	0.24	0.13
Acetaldehyde	0.663	2	–	0.9	1.8	–	–
Ammonia	80	3	0	30	64	0	2
1-Butanol	0.50	25	–	–	–	–	–
Ethanol	4.51	1000	–	0.7	5.8	–	0.69
Formaldehyde	0.42	0.1	–	–	–	–	–
Furan	0.3	0.025	0.03	0.9	1.1	–	–
Methanol	1.02	70	1.1	2.6	7.4	0.69	2.8
Methyl mercaptan	0.83	0.2	–	0.7	3.6	–	–

Using an identical TCC filter cartridge filled with 76 g of nanoporous silica beads, a breakthrough experiment was started using the same procedure and sample holder design as that for Ammonasorb II. Figure 9A shows the methanol and ethanol concentrations measured for the nanoporous silica beads without vacuum regeneration. Although the methanol and ethanol contents in the TCC recirculation loop slowly increased during the run, their values were significantly lower than the corresponding SMAC limits. Figure 9B displays the results obtained for ammonia without and with periodic vacuum regeneration (discussed below). Finally, Figure 10A shows the concentrations of ethanol while 10B shows concentrations of methyl mercaptan measured through the sorbent in both direct dosing and a periodic regeneration mode respectively; data for the two analytes without the sorbent is also provided for comparison. The breakthrough without periodic regeneration was stopped after 24 hours because several analytes (ammonia, furan, and methyl mercaptan) broke through within the first hour, exceeding their corresponding 7-day SMAC limits, consistent with the predicted values in Table 2. Ammonia broke through after 40 min and exceeded the 7-day SMAC limit of 3 ppm at 50 min (Figure 9B). The ammonia concentration in the system reached a maximum value of 64 ppm after 14 hours at an injection rate of 170 mg/min. The short breakthrough times can be attributed to the much lower capacities of the nanoporous beads as compared with Ammonasorb II (see Table 2)[14] and low mass of nanoporous silica within the beads (approximately 16 g) as compared to 126 grams for Ammonasorb II. Although the predicted breakthrough times for formaldehyde and acetaldehyde were also short (1 and 6 hours, respectively), their

concentrations never exceeded the 7-day SMAC limits over the 24-hour period, which may be related to their possible reactions with ammonia on the sorbent surface, similar to that found for the activated carbon-based Ammonasorb II sorbent.[19] Finally, no acetone or 1-butanol breakthroughs were detected, in agreement with their predicted breakthrough times in Table 1. It is important to note that these results for the nonporous silica sorbent are not unexpected given the sorbent mass and predicted breakthrough times. Possible ways of increasing the breakthrough times of the NASA contaminants using nanoporous silica beads include performing vacuum regeneration (see below), increasing the sorbent mass in the beads, and increasing the residence time across the beads. The last solution can increase the pressure drop across the bed. However, the pressure drop measured across the TCC-sized (230 mL) filled sorbent cartridge was 0.18 ± 0.06 in-H_2O, while for the larger (460 mL) cartridge it was 0.20 ± 0.06 in-H_2O, within the maximum allowable pressure drop of 0.3 in-H_2O. The effects of the sorbent bed diameter and particle size on the pressure drop are discussed in Ref.[20]

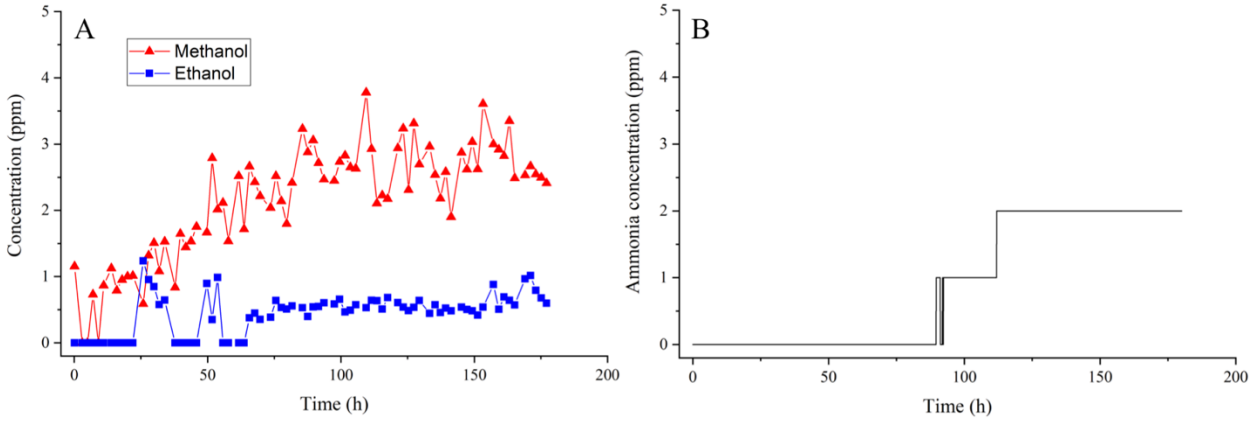

Figure 8. (A) Methanol and ethanol concentrations, two contaminants with quantifiable breakthroughs, and (B) ammonia concentration versus time in the TCC recirculation loop with Ammonasorb II in a TCC sized cartridge.

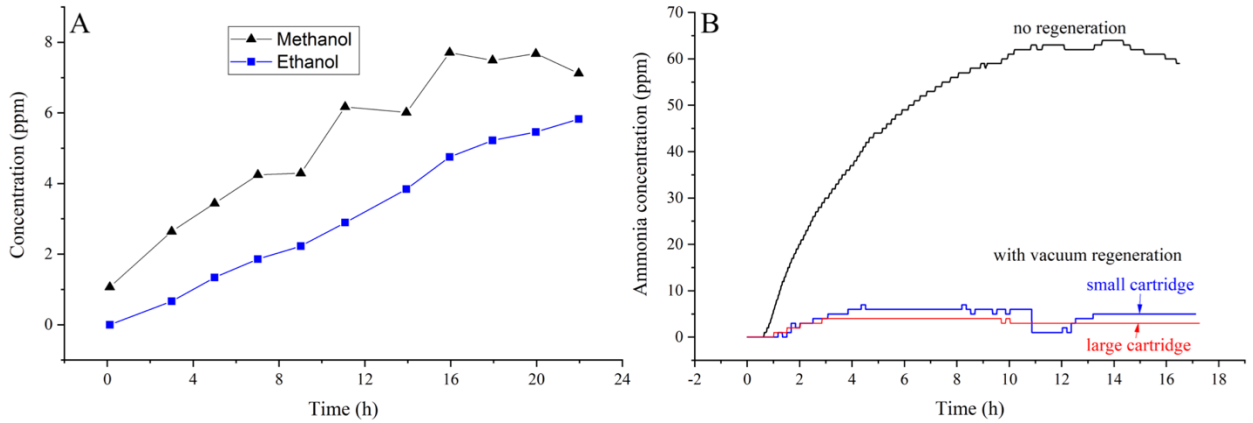

Figure 9. (A) Methanol and ethanol concentrations and (B) ammonia concentration versus time in the TCC recirculation loop with nanoporous silica beads in the small (TCC-sized) cartridge. The results obtained for ammonia in the first 18 hours of a 96-hour run for the small (TCC-sized) and large cartridges with vacuum regeneration are also plotted for comparison.

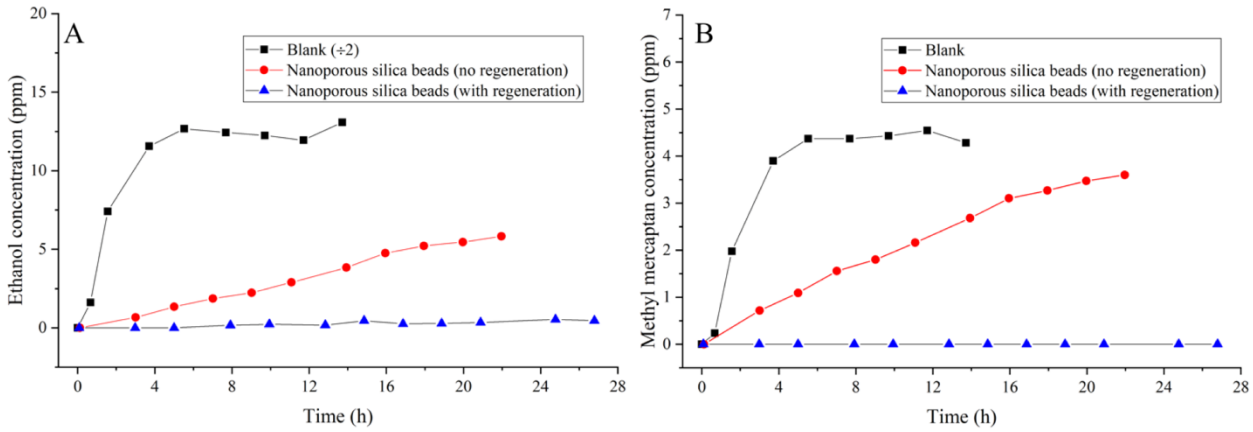

Figure 10. (A) Ethanol and (B) methyl mercaptan concentrations in the TCC recirculation loop versus time obtained without a sorbent (blank) and with the small or TCC-sized cartridge of nanoporous silica beads. The results obtained with and without vacuum regeneration are shown for comparison. The vacuum regeneration results show only the first 28 hours of a 96-hour run.

B. Regeneration Breakthrough Studies

The test system was designed to mimic not only the conditions faced by the current TCC system but also those potentially found in the RCA system to allow new sorbent systems to be evaluated. To evaluate the performance of nanoporous silica beads towards the removal of the nine NASA contaminants under vacuum regeneration conditions, the beads were subjected to periodic regeneration cycles. Although the system is capable, this paper only considered a periodic regeneration cycle consisting of 2 min of flow through the TCC with contaminants injected at the NASA source rates, followed by 2 min of sorbent pumping to a pressure below 1 Torr. In the regeneration period, the TCC system was isolated, and no contaminants were injected into the TCC recirculation loop, simulating a swing bed. All other experimental conditions were identical to those used for the non-regenerative studies. The average analyte concentrations obtained for different periods over the course of a 96-hour TCC run (12 EVA durations) with vacuum regeneration are listed in Table 4.

Figure 9B shows the ammonia concentrations measured for the non-regenerative and first 18 hours of two regenerative runs using different sorbent amounts. The small cartridge is identical to the one used during the non-regenerative experiments for the beads and Ammonasorb II. The larger 460-mL cartridge has approximately a double sorbent amount. The ammonia concentration while evaluating the small TCC-sized cartridge increased to 4 ppm within the first 16 h and then decreased a bit to go below the SMAC limit after 24 hours, potentially due to enhanced absorption as the sorbent absorbed more moisture from the injected water. Figures 10A and B show the results obtained for the first 28 hours of a 96-hour TCC run (12 EVA durations). Figure 10A displays the ethanol data, directly comparing the concentration increase without any sorbent, with the TCC-sized sorbent cartridge; and with and without regeneration. Figure 10B shows the plots of the methyl mercaptan concentration with time obtained during the non-regeneration and regeneration studies. No methyl mercaptan breakthrough occurred over the duration of the experiment. Similar to ammonia, furan also exceeded its respective SMAC limits slightly. The furan concentration varied from 0.034 to 0.046 ppm for the small cartridge. Table 5 lists the results obtained after switching to the larger cartridge with a double sorbent amount. The methanol has an initial higher value, which we attribute to the presence of residual methanol in the system after the previous run. With time, all methanol is removed from the TCC loop. These breakthrough studies show that the concentrations of all analytes (including ammonia and furan) remained below their SMAC limits over the course of the 96-hour TCC run or 12 EVA durations. These promising results strongly suggest that the proposed vacuum-regenerable TCC sorbent can be potentially integrated with the RCA swing beds into a single system for sustainable Lunar and Martian spacecraft missions that cannot require frequent sorbent replacement.

Table 4. Analyte concentrations measured using nanoporous silica beads in the smaller (230-mL) sorbent holder at different stages of the TCC test run under vacuum regeneration. The 96-hour run represents 12 EVA durations. The symbol "–" indicates that the measured concentration is below the detection limit of 0.01–0.05 ppm for most analytes.

Contaminant	7-Day SMAC limit (ppm)	Measured average concentrations (ppm)						
		0–30 min	1–8 h	9–16 h	17–24 h	25–32 h	33–48 h	49–96 h
Acetone	22	0.2	0.1	0.1	0.1	0.1	0.1	0.1
Acetaldehyde	2	–	–	–	–	–	–	–
Ammonia	3	0	4	4	3	2	1	0
1-Butanol	25	–	–	–	–	–	–	–
Ethanol	1000	–	0.1	0.3	0.4	0.4	0.4	0.4
Formaldehyde	0.1	–	–	–	–	–	–	–
Furan	0.025	–	0.034	0.041	0.046	0.042	0.039	0.040
Methanol	70	0.3	0.6	0.8	0.6	0.7	0.4	–
Methyl mercaptan	0.2	–	–	–	–	–	–	–

Table 5. Analyte concentrations measured using nanoporous silica beads in the larger (460-mL) sorbent holder at different stages of the TCC test run under vacuum regeneration. The 96-hour run represents 12 EVA durations. The symbol "–" indicates that the measured concentration is below the detection limit of 0.01–0.05 ppm for most analytes.

Contaminant	7-Day SMAC limit (ppm)	Measured average concentrations (ppm)						
		0–30 min	1–8 h	9–16 h	17–24 h	25–32 h	33–48 h	49–96 h
Acetone	22	0.6	0.4	0.3	0.3	0.4	0.3	0.3
Acetaldehyde	2	–	–	–	–	–	–	–
Ammonia	3	0	3	3	3	2	1	1
1-Butanol	25	–	–	–	–	–	–	–
Ethanol	1000	–	–	–	–	–	–	–
Formaldehyde	0.1	–	–	–	–	–	–	–
Furan	0.025	–	–	–	–	–	–	–
Methanol	70	1.7	6.1	3.9	5.8	5.1	2.5	0.8
Methyl mercaptan	0.2	–	–	–	–	–	–	–

VI. Conclusion

The primary trace contaminants that must be removed by the TCC include ammonia, formaldehyde, and methyl mercaptan. The TCC sorbent must remove all compounds that can potentially exceed the 7-day SMAC limits during an EVA. The current sorbent is non-regenerable and must be replaced; therefore, the TCC unit was moved to the hatch of the xEMU, an accessible area, to allow TCC sorbent cartridge replacement every 150 hours. XploSafe has developed a TCC test-bed apparatus[12,13] that mimics the realistic sub-atmospheric TCC operation and can inject and quantify a multi-gas stream of at least nine NASA-priority contaminants into the recirculation loop at NASA's provided source rates.[5] Two different sorbents were evaluated: Ammonasorb II and XploSafe's nanoporous silica sorbent beads. The results obtained for the currently used non-regenerable Ammonasorb II show that no significant breakthrough was observed for any of the nine analytes during Ammonasorb II evaluation on the TCC scale over a period of 180 hours. This validates the sorbent modeling for Ammonasorb II and its associated operational lifetime. XploSafe's regenerable nanoporous silica beads were also evaluated under identical conditions. Without regeneration, ammonia, furan, and methyl mercaptan exceeded their 7-day SMAC limits within the first 24 hours for nanoporous silica beads (containing approximately 16 g of OSU-6) as compared to 126 grams for Ammonasorb II. The obtained breakthrough times were in good agreement with the predicted values. Two nanoporous silica sorbent masses were investigated using a 4-min cycle (2 min flow-through, 2 min regeneration). With the small mass (76 g), almost all contaminants were maintained below their 7-day SMAC limits with the exception of ammonia, furan, and methyl mercaptan. After doubling the sorbent mass (145 g), the concentrations of all analytes in the recirculation loop were maintained below their 7-day SMAC limits for a period of 96 hours, which corresponded to a duration of 12 EVAs. Further improvements of nanoporous silica towards NASA-priority contaminants may be implemented by optimizing the cycle time and increasing the residence time across the sorbent. In addition, further sorbent bead optimization is possible by adjusting the fraction of nanoporous silica or altering the bead size in an effort to reduce the void volume

while maintaining a small pressure drop. Thus, it should be possible to replace the non-regenerable Ammonasorb II sorbent currently used in the xPLSS with a regenerable nanoporous silica sorbent, considerably reducing the overall sorbent consumption and simplifying the logistics of future space explorations. Furthermore, the increased power consumption and other logistical impacts of a regeneratable TCC system can be potentially mitigated via its incorporation into the RCA system.

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