NASA/TM—20210026041

Analytical Methods and Testbeds for Characterizing Adsorbents and Catalysts for Atmosphere Revitalization of Crewed Spacecraft

Monje, Oscar (Amentum Services, Cocoa Beach, FL, United States)
Finn, J. Riley (Bionetics Corporation Cocoa Beach, FL, United States)
Perry, Jay L. (NASA Marshall Space Flight Center Huntsville, AL, United States)
Kayatin, Matthew J. (NASA Marshall Space Flight Center Huntsville, AL, United States)

September 2021

NASA STI Program . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program plays a key part in helping NASA maintain this important role.

The NASA STI Program operates under the auspices of the Agency Chief Information Officer. It collects, organizes, provides for archiving, and disseminates NASA's STI. The NASA STI Program provides access to the NASA Technical Report Server—Registered (NTRS Reg) and NASA Technical Report Server— Public (NTRS) thus providing one of the largest collections of aeronautical and space science STI in the world. Results are published in both non-NASA channels and by NASA in the NASA STI Report
Series, which includes the following report types:

- TECHNICAL PUBLICATION. Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA counter-part of peer-reviewed formal professional papers, but has less stringent limitations on manuscript length and extent of graphic presentations.
- TECHNICAL MEMORANDUM. Scientific and technical findings that are preliminary or of specialized interest, e.g., "quick-release" reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.
- CONTRACTOR REPORT. Scientific and technical findings by NASA-sponsored contractors and grantees.
- CONFERENCE PUBLICATION. Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or co-sponsored by NASA.
- SPECIAL PUBLICATION. Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.
- TECHNICAL TRANSLATION. English-language translations of foreign scientific and technical material pertinent to NASA's mission.

For more information about the NASA STI program, see the following:

- Access the NASA STI program home page at http://www.sti.nasa.gov
- E-mail your question to help@sti.nasa.gov
- Fax your question to the NASA STI Information Desk at 757-864-6500
- Telephone the NASA STI Information Desk at
  757-864-9658
- Write to:
  NASA STI Program
  Mail Stop 148
  NASA Langley Research Center
  Hampton, VA 23681-2199

Level of Review: This material has been technically reviewed by technical management.

Available from

NASA STI Program
Mail Stop 148
NASA Langley Research Center
Hampton, VA 23681-2199

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
703-605-6000

This report is available in electronic form at http://www.sti.nasa.gov/ and http://ntrs.nasa.gov/

Analytical Methods and Testbeds for Characterizing Adsorbents and Catalysts for Atmosphere Revitalization of Crewed Spacecraft

Monje, Oscar (Amentum Services, Cocoa Beach, FL, United States)
Finn, J. Riley (Bionetics Corporation Cocoa Beach, FL, United States)
Perry, Jay L. (NASA Marshall Space Flight Center Huntsville, AL, United States)
Kayatin, Matthew (NASA Marshall Space Flight Center Huntsville, AL, United States)
National Aeronautics and Space Administration
Kennedy Space Center, Florida 32899

Summary

Spacecraft environmental control and life support systems (ECLSS) include a number of air revitalization (AR) technologies to provide breathable air and a comfortable living environment to the crew. Crew health and comfort is ensured by controlling human produced CO_2 (1 kg person^{-1} day^{-1}) and water vapor (~2 kg person^{-1} day^{-1}), and by removing trace contaminants (TCs) from cabin air. These life support functions on-board the International Space Station (ISS) are carried out by the Carbon Dioxide Removal Assembly (CDRA), the Water Processor Assembly (WPA), and the trace contaminant control system (TCCS).

During the development of the TCCS, new analytical and theoretical methods were developed in the 1970s for characterizing adsorption and desorption characteristics of activated carbons for the purpose of designing suitable AR technologies required for controlling airborne trace contaminants within spacecraft cabins during long exploration missions. The TCCS removes harmful volatile organic compounds and other trace contaminants from the circulating air. It consists of a granular activated carbon (GAC) bed for the removal of high molecular weight contaminants and ammonia followed by a heated catalytic bed for low molecular weight hydrocarbons. The high temperature catalytic oxidizer (HTCO) of the TCCS, which operates at 400°C and requires 120W average power, removes low molecular weight compounds such as carbon monoxide (CO), formaldehyde (CH_2O), and methane (CH_4), that pass through the GAC bed.

The Air Revitalization Laboratory at the Kennedy Space Center (KSC) was established to develop new analytical methods for evaluating emerging ECLSS technologies for use in future AR architectures. General properties of adsorbents and catalysts are required for trace contaminant control system design calculations and vendor-supplied data are seldom available at relevant process conditions of interest to spacecraft cabin applications. To address this shortcoming, appropriate testbeds were developed to measure the desired properties of AR technologies being considered for use in ECLS architectures. Generally, the testbeds developed at KSC challenge the test media (activated carbon, impregnated activated carbon, catalysts, zeolites, solid amines, or pleated filters) with simulated spacecraft gas streams containing representative mixtures of trace contaminants (volatile organic compounds, ammonia, CO, CO_2, or siloxanes) at the flow rates, temperatures, and relative humidity that will be encountered within manned spacecraft.

Work performed at KSC funded by NASA's Advanced Exploration (AES) Program has included: Identifying candidate sorbents to replace commercially obsolete impregnated carbons for NH_3 control within the TCCS, characterizing their adsorptive capacities using simulated spacecraft gas streams, and ranking their appropriateness in various AR applications; evaluating novel low temperature catalysts for controlling CO and formaldehyde by traditional and photocatalytic methods for trace contaminant control;

development of analytical methods to assess regenerable solid amine performance for CO_2 control via pressure swing adsorption.

The Air Revitalization lab was also funded to study trace contaminant control by other NASA programs. These include: screening of candidate sorbents for the design of new Charcoal HEPA Integrated Particle Scrubber (CHIPS) filters for removing siloxanes from cabin air; characterizing the performance of an impregnated activated carbon at low humidity for use in ORION ECLS; screening of sorbents for protecting the Sabatier 2.0 catalyst from $DMSO_2$, siloxanes, NH_3, and solid amine byproducts.

Contents

Nomenclature

AR = air revitalization
BS = Barnebey-Sutcliffe
BMP = BMP Russian acronym - microimpurity adsorption device on Zvezda (Perry TP 2017)
CBA = Charcoal Bed Assembly
CDRA = Carbon Dioxide Removal Assembly
CHIPS = Charcoal HEPA Integrated Particle Scrubber
DMSD = dimethylsilanediol
ECLS = Environmental Control and Life Support
FTIR = Fourier transform infrared
FF-PCO = Fast Flow PCO
GAC = granular activated carbon
GHSV = gas hourly space velocity (hr^{-1})
HVLA = high velocity, low aspect ratio
HTCO = High Temperature Catalytic Oxidizer
ISS = International Space Station
LSMC = Lockheed Missiles and Space Company
MFC = mass flow controller
ppm = parts per million
RH = relative humidity
PSA = pressure swing adsorption
PCO = photochemical oxidation
OGA = Oxygen Generation Assembly
SLPM = standard liter per minute
SMAC = Spacecraft Maximum Allowable Concentration
TCCS = Trace Contaminant Control System
VOC = volatile organic compound
WPA = Water Processor Assembly

1.0 Introduction

A primary goal of spacecraft ECLS is to provide a safe, habitable environment for astronauts in spacecraft or surface habitats. In particular, critical ECLS life support subsystems include trace chemical contaminant control, carbon dioxide partial pressure control, and humidity control, as well as systems that provide particulate filtration, generate oxygen, and process a variety of wastewater streams. Trace contaminants in portable life support systems, spacecraft, and surface habitats are produced by crew metabolism and by off-gassing from hardware and payloads (Perry, 1998). Air revitalization systems employing air filtration and adsorption technologies are used to maintain the buildup of trace contaminants in the cabin air of these habitats below toxicological Spacecraft Maximum Allowable Concentrations, (SMAC) which ensures crew health and performance. Spacecraft life support system design considerations identify the key compounds that drive the trace contaminant control system flow rates and process conditions (Perry, 1994; Perry and Kayatin, 2015; Richards et al., 2015). Development of the trace contaminant control system (TCCS) for the ISS established ammonia, dichloromethane, methane, and carbon monoxide as the key design-driving compounds. For example, ammonia, due to its high metabolic production rate, drives the TCCS flow rate. Similarly, dichloromethane, being difficult to remove using adsorbent media, drives the size of the activated carbon bed. Finally, the oxidation efficacy of methane sets the HTCO process operating temperature.

The Air Revitalization Laboratory was established in 2006 at the Kennedy Space Center for the purpose of characterizing candidate sorbents and catalysts for use in future AR technologies for controlling trace contaminants in spacecraft. General properties of adsorbents and catalysts are required for trace contaminant control system design calculations and vendor-supplied data are seldom guaranteed to be applicable for design purposes due to disparate process conditions. For example, filters in spacecraft cabin air are typically subject to low volatile organic compound (VOC) concentration levels (e.g. < 1 ppm and up to 5 ppm), while the current standard tests per ASHRAE 145.1 (ANSI/ASHRAE, 2008) are performed at relatively high challenge concentrations (c.a. 1–100 ppm level). The approach herein was to develop the necessary test apparatus to measure the desired properties of sorbents and catalysts being considered for use in ECLS architectures. Generally, the testbeds challenge the test media (activated carbon, impregnated activated carbon, catalysts, zeolites, solid amines, or pleated filters) with simulated spacecraft gas streams containing representative mixtures of trace contaminants (VOCs, ammonia, CO, CO_2, and/or siloxanes) at the flow rates, temperatures, and relative humidity that will be encountered within manned spacecraft.

The testbeds were assembled as needed using components for gas mixture generation, humidification, flow metering, and for measuring trace contaminant concentrations. An open loop configuration developed for measuring breakthrough curves, single pass trace contaminant removal, and maximum removal capacities of sorbents and catalysts (Monje et al., 2007ab; Monje et al., 2008; Monje et al., 2009; Monje et al., 2014). A closed loop configuration was developed to measure Polanyi adsorption potentials and steady state adsorptive capacities of activated carbons and impregnated activated carbons (Monje et al., 2016; Monje and Surma, 2017). An automated testbed was developed for creating dynamic loading/regeneration cycles for measuring the performance of technologies employing regenerable sorbents (13X, 5A, or SA9T) (Monje et al., 2009; Monje et al., 2010 a,b; Nolek and Monje, 2011; Monje et al., 2011). Another testbed was developed for evaluating photochemical oxidation catalysts using a separate solar simulator subsystem (Monje, 2012).

1.1 Trace Contaminant Control within the ISS ECLS Architecture

ECLS systems aboard manned spacecraft are designed to provide a safe, habitable environment within the hostile environment of space. In particular, crew health and comfort requires active removal of human produced CO_2 (1 kg person^{-1} day^{-1}), water vapor (1.8-2.5 kg person^{-1} day^{-1}), and trace contaminants (TCs) from cabin air (Perry, 2009) Challenges faced in the design of such systems include minimizing mass, volume, and power, while maximizing their safety, reliability, and performance. CO_2 removal and water management are carried out by ECLS subsystems that interface with AR technologies.

Future ECLS life support technologies for crewed exploration beyond low earth orbit intend to improve on the ISS-derived technologies for water recovery and management, particulate removal, atmosphere revitalization, loop-closure, and environmental monitoring (Fig 1; Perry et al, 2016a).

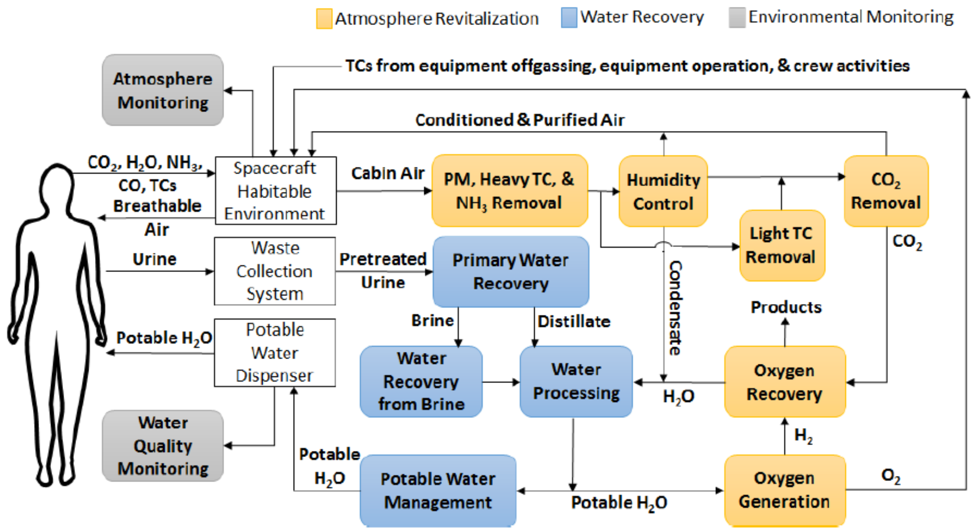

Figure 1. A simplified LSS block diagram for exploration missions. *Subsystems provide functionality for atmosphere revitalization; water recovery, purification, and management; and environmental monitoring.*

Trace contaminants are removed from ISS cabin atmosphere by the Russian Micropurification Unit (БМП or BMP) located in the Zvezda Service Module and by the trace contaminant control system (TCCS), the primary unit of which is located in the U.S. Destiny Lab Module (Perry TM 2005). The BMP utilizes a series of activated carbon beds to adsorb high molecular weight compounds on the upstream expendable bed and lighter VOCs on two downstream regenerable beds. The TCCS employs adsorption, thermal catalytic oxidation, and chemical adsorption processes. The TCCS contains an expendable packed bed of granular activated carbon (Barbebey-Sutcliffe Type 3032), charcoal bed assembly (CBA), to remove VOCs and siloxanes. BS Type 3032 is impregnated with 10 wt.% phosphoric acid to remove NH_3. The CBA is sized to maintain NH_3 and dichloromethane below their SMAC for the duration of the bed's lifetime rating at nominal process flow rate. Methane, CO, and any low molecular weight VOCs not effectively removed by physical adsorption are oxidized by the downstream catalytic oxidizer. This arrangement also serves to protect the catalyst from poisons and masking agents. Acid gases produced by the catalytic oxidizer are removed by a LiOH expendable bed.

1.2 Challenges and Lessons Learned

The TCCS is regarded as one of the most reliable ECLS subsystems, exhibiting a consistent performance record over its operating lifetime on the ISS. With the exception of a pressure delta rise across the Sorbent Bed Assembly, believed to result from physical changes in the granular lithium hydroxide media, no substantial failures have occurred (Aguilera and Perry, 2011).

Despite this track record, the TCCS, like all sorbent or media-based unit processes, is subject to the inevitable obsolescence risk driven by economic forces over time. To meet this challenge, periodic market surveys followed by characterization and testing of candidate materials are required to identify suitable replacements for utilization within future exploration missions. These surveys also serve to incorporate the latest advances in media manufacturing and quality control by selection of new materials which may increase TCCS performance or extend lifetime ratings of existing subsystem designs.

The ISS has proven an invaluable platform for identifying factors that influence TCCS performance over an extended mission duration. These challenges include the presence of persistent or recalcitrant compounds leaked from payloads and hardware, which demonstrate the limits of the process, but also the behavior in the face of unforeseen emerging contaminants found in spacecraft. Such contaminants may be the result of a number of factors including material aging over program lifetime, increased dwell time as the cabin volume is augmented, and unforeseen synergistic reactions between other hardware and processes.

1.2.1 Media Obsolescence

Sufficient time has passed since the TCCS was designed by Lockheed Missiles and Space Company (LMSC) in the 1970s. As such, the activated carbon used presently, Barnebey Sutcliffe Type-3032, has become commercially obsolescent and is no longer available for purchase or manufacture. While this may not seem surprising, given the time period since the initial activated carbon downselect, the CBA media has already been replaced twice before. The original TCCS media selected was Barnebey-Cheney Type BD, an untreated activated carbon. Due to its obsolescence, the Type BD carbon was no longer commercialy available when Barnebey-Cheney was purchased by Sutcliffe Waterlink of the United Kingdom. As a result, Barnebey Sutcliffe Type-AC, an aftermarket 12% phosphoric acid treated activated carbon, was deemed to be the replacement carbon for Type BD and it too had become commercially obsolescent. Therefore, commercial market surveys followed by in-house characterization and testing are required periodically to continue to be able to respond to NASA mission demands for ECLS design and delivery.

1.2.2 Low Offgassing Sources

Low offgassing sources can still result in significant amounts of trace contaminants being released onto ISS cabin air (Perry et al., 2016b). Light aldehydes (e.g. formaldehyde) are pervasive cabin contaminants due to their offgassing from adhesives, packaging materials and acoustic foams. Although the offgassing rate of formaldehyde (4.4 x10^{-6} mg/kg-day) is low compared to ethanol (7.8 x10^{-3} mg/kg-day), its presence impacts TCCS removal flow capacity because the capacity of activated carbon to remove formaldehyde is low compared to ethanol. Thus, efforts to limit accumulation of formaldehyde offgassing sources on board the ISS or improved methods for formaldehyde removal may be necessary to avoid overwhelming the onboard trace contaminant control capability. A similar strategy is needed for controlling emissions of volatile methyl siloxanes, which has increased due to the use of personal hygiene products containing these compounds.

1.2.3 Emerging Contaminants

Degradation of volatile methyl siloxanes onboard ISS results in the formation of silanols and formaldehyde via hydrolysis reactions. One problematic byproduct silanol is dimethylsilanediol (DMSD) and affects the performance and process economics other ISS systems, including the Water Processor Assembly (WPA) and other downstream hardware (Richards et al., 2015; Carter et al., 2015). To mitigate its impact, Charcoal HEPA Integrated Particle Scrubber (CHIPS) filters were developed and installed on

ISS to aid the TCCS in additional volatile siloxane removal from cabin air before they can affect other ISS systems (Carter et al., 2016).

1.3 Previous Work

Trace contaminant generation rates produced by metabolic processes and material offgassing in crewed spacecraft are often mitigated using activated carbon adsorption as a primary control strategy. For a fixed bed dimension, lifetime is determined by the adsorptive capacity of the media for various VOCs found in spacecraft. Therefore, accurate measurements of adsorption isotherms are needed for sizing suitable trace contaminant removal systems and/or predicting their operational lifetime. In the 1970's, a rapid screening method based on the Polanyi adsorption potential theory was developed by the LMSC for predicting the adsorption equilibrium capacities of activated carbons using commonly available adsorbent and adsorbate properties (Robell et al., 1970).

The Polanyi sorption approach describes the energy relations involved in transferring contaminant molecules from the gaseous phase to the adsorbed state (pore-filling) within micropore volumes of activated carbons and assumes a fixed volume of sorption space close to the sorbent surface (Monje et al., 2016; Monje and Surma, 2017). Polanyi divided the adsorption process into two steps: 1) the free energy change from the gaseous to the saturated liquid state and 2) the free energy change in passing from the liquid state to the adsorbed state. He found that the free-energy change for the first step, the adsorption potential, could describe the whole process. Polanyi also found that the adsorption potential was a function of the volume of the adsorbed phase, and that the shape of this function did not change with temperature (Lewis, 1950). In fact, a key advantage of Polanyi's approach is the utility of process temperature as an adjustable parameter in which varied test temperatures can be compensated for.

Constructing Polyani adsorption potential plots for various candidate sorbents is advantageous to the TCCS designer by allowing for accurate and reliable adsorption bed sizing and predictive bed lifetime estimates from limited datasets. This approach saves not only time but also costs associated with iterative full-scale component fabrication and testing. Design conservatism can be integrated by utilizing statistically adjusted contaminant loads and by including a 10-20% margin for co-adsorption effects on equilibrium capacity loading. The rigorous bed sizing and design process is well described by Perry (1998). This method was used to characterize the adsorptive capacities of activated carbons for VOC and NH_3 to be used within the TCCS (Leban et al.,1991).

1.4 Current Work

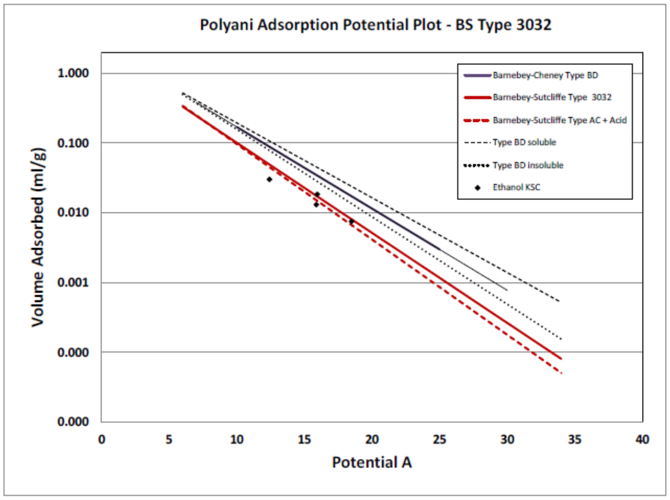

Figure 2. *Polanyi adsorption potential plots for ethanol adsorption by Barnebey-Sutcliffe Type 3032. The KSC data was validated with data of Robbell et al 1970.*

A closed loop testbed for measuring Polanyi plots was constructed. These measurements were validated by reproducing Polanyi plots of ethanol adsorption by Barnebey-Sutcliffe Type 3032 activated carbon collected by LMSC (Figure 2; Monje et al., 2016). Barnebey-Sutcliffe Type 3032 is a commercially obsolete acid-treated carbon used within the ISS TCCS. Figure 2 shows the comparison between historical LMSC and KSC generated datasets via a Polanyi adsorption potential plot. The wet and dry ethanol adsorption capacity data collected using the present method, denoted as "Ethanol KSC" in Fig. 2, fall along the adsorption potential curves reported by LMSC for Barnebey Sutcliffe Type 3032 and the aftermarket acid-treated Type AC carbons. This agreement provides high confidence that the test methodology and the analytical approach for determining the adsorption potential plots are valid and consistent between the two studies.

An open loop testbed was also developed for screening sorbents for high capacities of NH_3 removal under ISS environmental conditions. In this testbed, NH_3 gas was supplied from a K-bottle, diluted with N_2, humidified, and pre- and post-sorbent gas concentrations were measured with an FTIR spectrometer. The initial measurements in this testbed were validated by reproducing NH_3 removal capacity of a 5 ppm NH_3 gas stream by BS Type 3032 at 40% RH and 23°C. A second open loop testbed was developed for screening sorbents for removal of volatile siloxanes from spacecraft cabin air. This testbed utilized a gas generator to supply siloxanes via heated lines to a gas chromatograph. Finally, an open loop testbed was developed for screening photocatalysts used for trace contaminant removal of spacecraft simulated gas streams. This tesbed utilized a gas generator to generate ethanol, acetaldehyde, and acetone gas streams and a solar simulator to provide ultraviolet radiation to a photocatalyst. The data produced by this testbed was validated using trace contaminant removal rates reported in relevant photocatalytic literature.

1.5 Lessons Learned during Tesbed Design

The following lessons were learned during the development of the testbeds presented here:

- The performance and data obtained in new testbeds were evaluated using published measurements of trace contaminant removal. For example, a new open loop test bed was deemed valid when it was able to reproduce published values of NH_3 removal capacity of BS Type 3032 at 40% humidity and 23°C measured by LMSC. A similar validation approach was used to validate data produced by a closed loop testbed; Polanyi plots for ethanol were used to validate the methodology used for measuring Polanyi potential plots of new sorbents.
- Testbeds were designed using a modular approach, whereby similar subsystems for humidification, gas generation and VOC measurement were utilized. New testbeds were assembled using common fittings, flow measurement, gas generation equipment, and trace contaminant concentration

measurement equipment used in previous testbeds. This modular design approach reduces the development time for new testbeds because the operation of the components in each testbed has been previously validated.

- Rapid protocols were developed to reduce the time for conducting characterization of new candidate sorbents and catalysts. The duration of the analytical methods was shortened by using crushed sorbents, which essentially cuts down the time for saturating a sample from days or weeks to hours. However, the validity of the data obtained using these rapid methods has been evaluated by conducting longer tests using uncrushed sorbents in an effort to gauge if the rapid test methods can produce meaningful data for use in future air revitalization designs.
- The analytical methods used in the design of new testbeds were reviewed by a safety review panel so that the operation of the testbeds is safe and conforms to norms imposed by NASA KSC safety, PVS certification, and identifies the appropriate PPE and monitoring equipment. This approach has resulted in faster approval of new methodologies employing potentially harmful chemicals (i.e. CO, formaldehyde, NH_3) or sources of ultraviolet radiation.
- Under COVID, new protocols for the laboratory were developed so that pertinent social distancing, PPE and masks, as well as proper ventilation is provided. These protocols were instrumental for allowing the Air Revitalization Lab to be allowed to conduct mission critical work while KSC operated at Phase 3 during the pandemic.

2.0 Analytical Methods

2.1 General Approach

The approach used has been to assemble the necessary testbeds to characterize the adsorptive properties and trace contaminant removal capacities of candidate sorbents and catalysts. Adsorptive and removal capacities were measured under ISS environmental conditions. These capacities were used to rank commercial sorbents and catalysts for replacing commercially obsolete sorbents (BS type 3032) and for developing new trace contaminant control technologies. The new candidate sorbents evaluated at KSC include activated carbons (Chemsorb 1000, Calgon 208C, Calgon 207C, Cabot Norit RB2, Cabot Norit GCA48) for trace contaminant removal, impregnated activated carbons (Ammonasorb II, Chemsorb 1425) and pleated filters (Serionix AM390, Camfil NXPP B2) for NH_3 removal, and catalysts (Carulite 300, Sofnocat 423, HS Pt1) for removal of carbon monoxide and formaldehyde. Similarly, new testbeds were developed for measuring CO_2 and trace contaminant removal capacities from zeolites (13X and 5A) and solid amines (SA9T) used in pressure swing adsorption (PSA) systems. In addition, testbeds were developed for examining the trace contaminant removal rates by photochemical oxidation technologies using ultraviolet sources.

Generally, the testbeds were assembled as needed using analytical equipment (e.g. gas chromatography or Fourier transform spectrometry) for measuring changes in trace contaminant concentrations from simulated spacecraft gas streams in contact with sorbents or catalysts held in custom-built sample holders. The gas streams (i.e. low concentrations 5-50 ppm) created using gas generation equipment (e.g. gas generators or K-bottles). Rapid assessment at low concentrations of trace contaminants was achieved by crushing sorbents to utilize smaller amounts (40-60 mg) so that maximum adsorptive capacities could be determined in experiments taking 8-24 hrs to complete (Figure 3). In addition, a testbed for determining Polanyi potential plots was also developed for assessing sorbent performances.

2.2 Analytical Equipment

2.2.1 Sample Holders

Four sample holders were designed to hold crushed/uncrushed sorbents, pleated filter materials, and photocatalysts. These sample holders are modular so that they can be used in any testbed interchangeably.

2.2.1.1 Sorbent Tubes

Thermal desorption tubes (Scientific Instrument Services, Ringoes, NJ) with an inner diameter of 4 mm were used to measure adsorptive capacities of candidate sorbents. Small diameter tubes and small sample sizes are used to reduce the duration of adsorptive capacity measurements while maintaining low velocity high aspect ratio conditions. To achieve this, large granules are crushed to less than 3 mm using a mortar and pestle and dust is removed (Figure 3). Using two glass wool plugs to hold the sample in place, 40-60 mg of crushed sorbent is loaded into each desorption tube and height measured to ensure an aspect ratio between 3-5. Next, the tubes are loaded into a thermal desorption conditioning system (SIS Model # CS-1) where dry nitrogen at 100 °C is used to remove any moisture adsorbed during storage. A final mass is recorded to determine the amount of dry sorbent and tubes are capped and stored in a desiccant chamber until use (Finn et al., 2020).

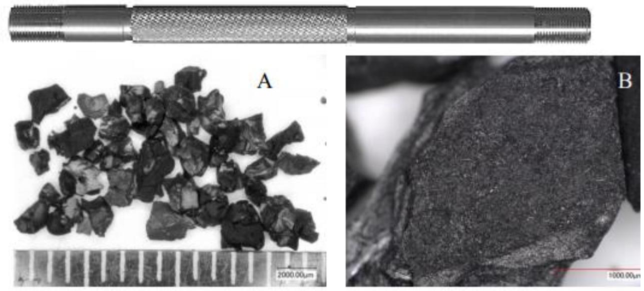

Figure 3. *Crushed sorbent Chemsorb 1000 samples (40-60 mg) are dried and held in a thermal desorption tube while being challenged with simulated spacecraft gas streams. The 1-2 mm particles (A) retain the microporous structure of the sorbent (B).*

2.2.1.2 Adsorbent Beds

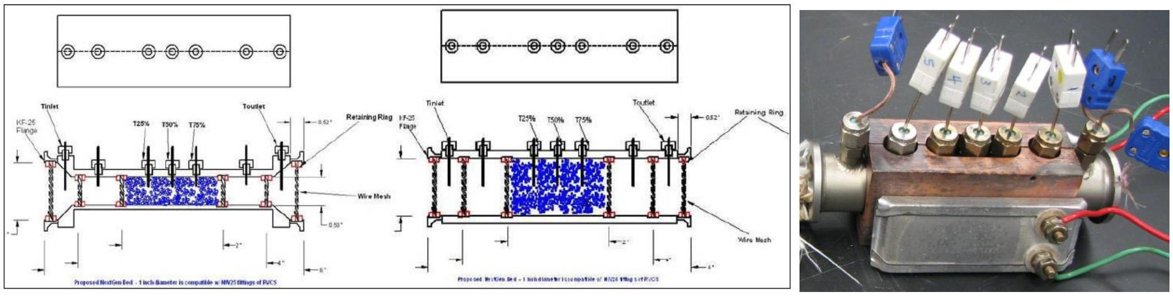

Figure 4. *Adsorbent beds were designed to expose uncrushed adsorbents. A heated adsorbent bed can be used to thermally regenerate sorbents (e.g. zeolites 13X and 5A).*

Sorbent beds (1/2 inch and 1 inch diameter; Figure 4) were designed for working with zeolites (13X and 5A), solid amines (SA9T), and uncrushed sorbents. The beds can be packed with 1-10g samples held between two wire mesh screens fixed into grooves by retaining rings (Figure 4). The beds have a high metal:sorbent mass ratio (~4-5 on a mass basis) and are insulated to try to attain isothermal conditions within the adsorbent. The beds can be instrumented with inlet/outlet temperature sensors, as well as three sensors located at 25%, 50%, and 75% along the length of the bed. The flow rate for the tests is chosen to match the contact times used in trace contaminant technologies onboard spacecraft (e.g. 1.6 L min^{-1} for the ½-inch diameter bed gives a contact time of 0.25 s). The sorbent beds can be used with any testbed and can be heated when used in PSA systems.

2.2.1.3 Pleated Filters

Figure 5. *The pleated filter sample holder contains a disc of known area and mass within a sealed housing while it is challenged with simulated spacecraft gas streams.*

Pleated panel filters offer a new commercial form factor for controlling VOCs in spacecraft cabin air. They differ from conventional commercial granular activated carbons because they have a lower pressure drop across the filter. A pleated filter sample holder was developed for evaluating the removal capacities of commercial pleated panel filters (Camfil GigaPleat NXPP B2, Serionix AM390) for NH_3 removal (Monje and Finn, 2019).

A disc sample holder holds the filter discs (6 and 15.5 mm diameter) between two o-rings to force air flow to pass perpendicular to the filter (Figure 5). The disc holder is within a sealed housing that passes simulated spacecraft gas streams through the filter disc. Trace contaminant removal is expressed on a per area basis or on a filter disc mass basis.

The disc sample holder contains up to 360 ml of dead air space below the filter disc, which would normally be filled with N_2 when the air flow is tested prior to supplying the challenge concentrations of trace contaminants. This dead air space could influence the shape of the breakthrough curve during the first 3-5 minutes after the challenge concentration is applied at 1-1.1 liter/min flow rates. Thus, a bleed valve installed in the chamber below the filter disc allows the challenge concentration to purge the 360 ml volume below the filter disc for 30-40 seconds, which is slower than the time constant for adsorption into the filter material. Once the chamber volume is purged, then the challenge concentration can be applied to flow through the filter disc.

2.2.1.3 Fast Flow Photochemical Oxidation (FF-PCO) Bed

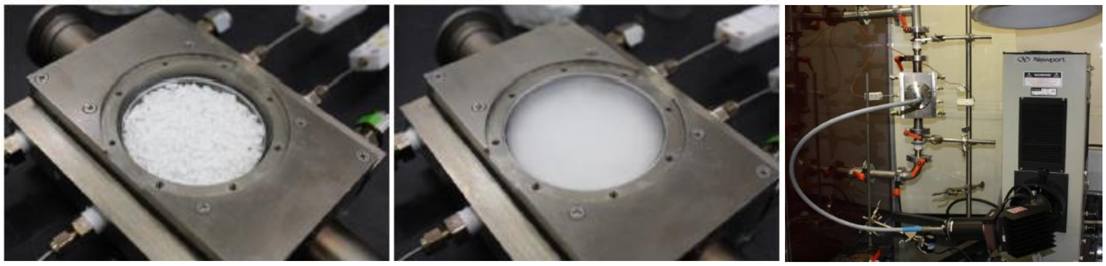

Figure 6. *The FF-PCO bed has a modular design for irradiating the catalyst within the bed with ultraviolet radiation (UV-C, UV-B, or UV-A). The FF-PCO bed is shown being irradiated by UV radiation from a Xenon arc lamp through a fiber optic.*

The FF-PCO bed has a modular design for irradiating the catalyst within the bed with ultraviolet radiation (UV-C, UV-B, or UV-A) from a Xenon arc lamp, an UVA LED, or with UV-C/UV-A from conventional germicidal/black light lamps. The catalyst is held within a cylindrical volume that can be irradiated from 2 sides through quartz windows (Figure 6). The FF-PCO bed can hold a total volume of catalyst of 38 ml (31.7 cm^2 by 1.2 cm height) and an illuminated volume of 27.5 ml (22.9 cm^2 by 1.2 cm height). The path for air flow is perpendicular to the path for irradiation. This modularity ensures that catalyst responses to spectral quality can be evaluated using identical conditions (catalyst mass, flow, humidity, inlet temperature) (Monje, 2012).

2.2.2 Gas Generation

Simulated spacecraft gastreams are generated by mixing trace contaminants with zero air (Sabio Model 2020, Portable zero air generator) or high purity N_2 provided from K-bottles. The Air Revitalization Lab utilizes a Kintek Gas Standard Generator (491M-B) to generate continuous gas streams containing trace VOCs. Two additional modules (491M-PM) are connected in series and run at varying temperatures to generate mixtures at different concentrations (Figure 7). Heated gas lines are used to prevent siloxanes or dimethyl sulfone to precipitate inside the tubing from the Kin-Tek gas generator.

Gases can also be supplied via high concentration K-bottles. The K-bottles are fitted with PVS approved gas regulators and a mass flow controller to supply a constant flow. Gas from K-bottles of 1400 ppm ammonia, 200 ppm CO, or 100 ppm formaldehyde are diluted with nitrogen and injected to testbeds at low flow rates to achieve simulated spacecraft concentrations of 0.5-60 ppm. These streams can then be humidified using a Miller-Nelson humidifier to generate humid streams between 0-90% RH.

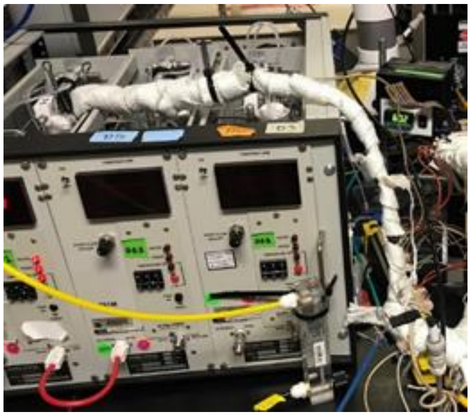

Figure 7. *A Kintek gas standard generator (491-MB) is used to generate known concentrations of trace contaminants.*

2.2.3 VOC Detection

Simulated gas streams are generated using the gas generation system and flow rates and temperature is adjusted to achieve desired concentrations of each component. These simulated trace VOC streams are then routed through sorbent beds at flow rates of 0.4-1.5 LPM to determine adsorption capacities using either an FTIR or a gas chromatograph.

2.2.3.1 FTIR Spectrometer

Fourier Transform Infrared Spectroscopy (FTIR) utilizes the unique adsorption and emission bands of different compounds to determine the composition of a sample. Simulated gas streams are pumped through a Fourier transform infrared spectrometer (Gasmet DX4040) to analyze their composition. The DX4040 model is rugged, portable and designed for on-site measurements of various organic and inorganic compounds at low concentrations in ambient air (>0.5 ppm for most trace contaminants found in spacecraft). Analysis results of up to 25 pre-calibrated compounds is possible simultaneously, which reduces calibration time and minimizes drift (Figure 8). There are no consumable parts that would need to be replaced on regular basis. In addition, due to FTIR technology, the calibrations remain very stable and span calibrations are not needed. In addition, cross-references (i.e. interferences with other gases) are automatically compensated in the analysis algorithm during the calculation of the results.

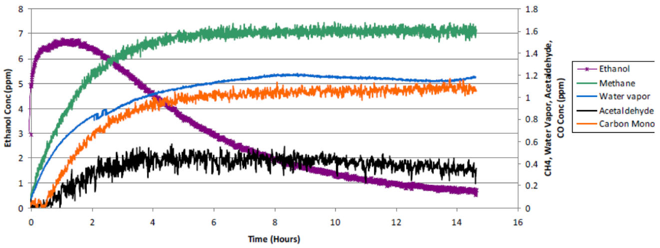

Figure 8. *The ability of the Gasmet DX4040 FTIR to measure several gases at the same time is useful for monitoring intermediates formed during photocatalytic degradation of ethanol into methane, water vapor, acetaldehyde and carbon monoxide.*

2.2.3.2 Gas Chromatograph

A SRI 8610C Gas Chromatograph equipped with a flame ionization detector (FID) is used to measure removal rates for compounds such as siloxanes which cannot be measured by FTIR (Figure 9). The GC uses a hydrogen generator and helium as a carrier gas. PeakSimple software is used to control GC functions such as temperature and sample rate, as well as an external Valco Flow-through Flowpath Selector valve which directs either pre or post-sorbent flow to the GC sample loop.

The peak area measured at each elution time is calibrated for each contaminant using the permeation rate measured for each Kin-Tek permeation tube. This value is then divided by the flow rate to give a concentration in grams per milliliter. Multiplying this concentration by the volume of the GC sample loop gives the mass of contaminant per sample.

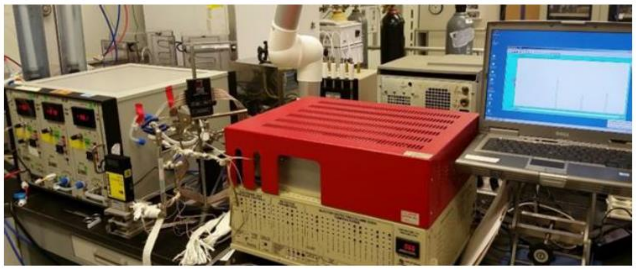

Figure 9. *The SRI portable gas chromatograph is shown attached to the Kintek gas generator during measurement of the adsorptive capacity of Cabot Norit GCA48 for siloxanes.*

2.2.3.3 Gas Stream Humidity Control

A Miller-Nelson HCS-401 flow controller was used for supplying humid air to the simulated spacecraft gas streams used in the KSC testbeds (Figure 10). The unit is supplied with tap water and N_2 and generates humid streams up to 95% RH at flow rates of 0-50 SLPM. Generally, the humid stream is mixed with a dry VOC stream, to provide the final RH of the airstream as measured by the FTIR.

Figure 10. *A Miller-Nelson HCS-401 humidifier is used to generate humid gas streams.*

3.0 Testbeds

3.1 Open Loop Testbed

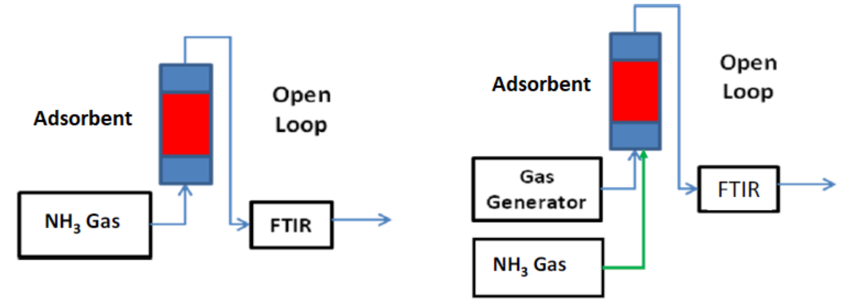

Figure 11. *Breakthrough curves for single components (e.g. NH_3) or multiple components (e.g. VOCs + NH_3) are measured in Open Loop testbeds.*

Open Loop testbeds (Figure 11) are used for determining breakthrough curves of single or multiple components. The basic setup includes a source of trace contaminants, an adsorbent bed, and analytical instrumentation for measuring concentration versus time. In Open Loop testbeds, the trace contaminant concentration seen by the adsorbent remains constant throughout the duration of the breakthrough curves.

3.1.1 Overview

The adsorptive capacity of an adsorbent bed for a given trace contaminant is determined from plots of gas stream composition versus time. Adsorption of a trace contaminant through an adsorbent bed is a transient process. As a gas stream containing a trace contaminant enters an adsorbent bed, the solute is adsorbed in the mass transfer zone (MTZ) by filling the available sites within the first few layers of the bed. As the adsorbent sites become saturated the solute is continually being adsorbed down the length of the bed and the gas stream emerging from the bed has no solute (Figure 12 A). Eventually, the bed no longer adsorbs solute efficiently and the concentration of unadsorbed solute rises when breakthrough occurs. An example of a breakthrough curve shows the challenge concentration entering the bed (Figure 12 B, green) and the Solute concentration exiting the bed (Figure 12 B, red). In this example, breakthrough occurs after 4 hours and maximal capacity is reached after 9 hours. The adsorptive capacity (measured in g of solute per g of adsorbent) is determined by integrating the breakthrough curves (analytically, numerically, or graphically).

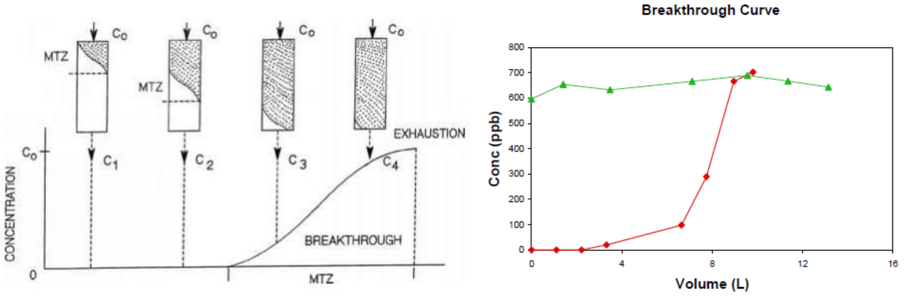

Figure 12. *A) The concentration versus time plot reflects the mass of solute removed by an adsorbent bed. B) Maximal capacity occurs when the solute concentration entering the bed equals the concentration exiting the bed.*

3.1.2 System Schematic

A detailed diagram of an Open Loop testbed for measuring NH_3 removal (Figure 13) shows how NH_3 is added to dry N_2, humidified, mixed with VOCs generated by a Kintek gas generator, and supplied to an adsorbent bed. The testbed includes a bypass loop that is used to adjust the simulated gas stream composition and flow rate before it is used to challenge an adsorbent held in a sorbent tube. This same testbed can be reconfigured to measure CO removal by a catalyst by simply changing the gas from NH_3 to CO and replacing the adsorbent in the sorbent tube by a catalyst.

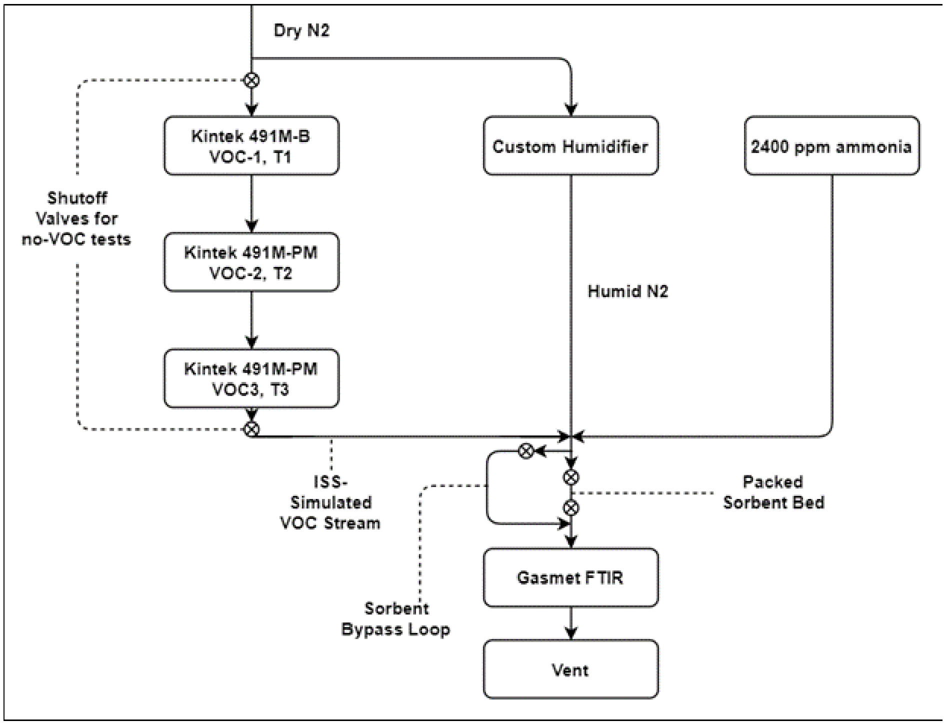

Figure 13. Diagram of open-loop sorbent testbed. *Dry Nitrogen is humidified to 40%RH and mixed with ammonia, acetone, ethanol, and toluene. Additional Kintek oven modules were set to different temperatures to achieve desired concentration of each VOC. This stream flows through a packed sorbent bed and analyzed with a FTIR spectrometer until concentrations reach steady state.*

3.2 Closed Loop Testbed

In a Closed Loop testbed, the trace contaminant concentration seen by the adsorbent is constantly changing. The basic setup includes a sealed mixing chamber with a constant volume, where trace contaminants are introduced at the start of the experimental run, an adsorbent bed, and analytical instrumentation for measuring concentration versus time (Figure 14). The mixing chamber has a recirculating fan. This setup makes it possible to study 1) low emission rates because as time passes, the concentration in the constant volume increases, and 2) removal rates in a recirculating multiple-pass mode. The closed system has been used to measure Polanyi potential plots, as well as to study the formation of intermediates during PCO reactions.

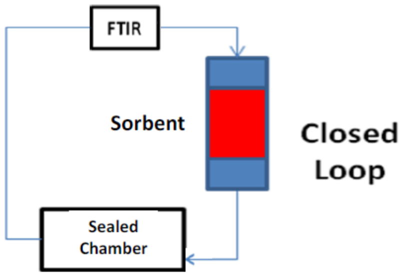

Figure 14. *A Closed Loop Testbed is composed of a sealed constant volume. The trace contaminant concentration seen by the sorbent is constantly changing.*

3.2.1 Polanyi Potential Plots

The methodology for measuring Polanyi potentials was developed and verified using the Closed Loop System (Figure 14). The Polanyi adsorption potential accounts for temperature, thus adsorption capacity data acquired at a single temperature can be used to predict performance at different temperatures. This method reduces the need for time-consuming efforts to acquire a full range of equilibrium isotherm data, typically obtained from breakthrough experiments in an Open Loop testbed. This approach saves not only time but also costs associated with acquiring data for a complete set adsorption isotherm curves. The slopes of the Polanyi potential plots determine the performance for VOC removal.

3.2.2 Polanyi Potential Method

The adsorptive capacity, q, is determined under closed loop dynamic test conditions whereby the sorbent is exposed to an initial contaminant concentration, C_{init} (ppmv), in a sealed chamber and allowed to adsorb until an equilibrium concentration, C_e (ppmv), is reached (Figure 15). The testbed and methodology for obtaining the Polanyi potential plots is described in Section 3.2.3 (Monje and Surma, 2017). Briefly, the potential plot relates the adsorption capacity, q, with the adsorption potential, A. The adsorption capacity is defined by Eq. 1 and the adsorption potential is defined by Eq. 2.

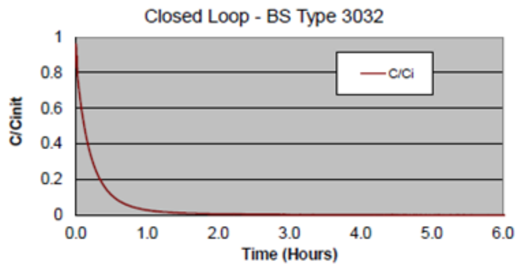

Figure 15. *The Closed Loop Testbed is composed of a sealed constant volume. The trace contaminant concentration seen by the sorbent is constantly changing.*

$$q = \alpha e-\beta A \qquad (1)$$

$$A = (T / V_m) \log^{10} (Ps/P) \qquad (2)$$

In Eq. 1, empirical constants (α and β) are determined from the adsorption potential plot. In Eq. 2, T is the sorbent temperature (K), V_m is the molar volume at the normal boiling point (ml/mol), Ps is the contaminant vapor pressure (atm) at T, and P is the contaminant partial pressure (atm) obtained from the equilibrium concentration. The adsorption potential is calculated from the molar volume, the vapor pressure, and the equilibrium concentration (Robell et al., 1970). The Polanyi adsorption potential theory has been applied to the study of activated carbon adsorption for VOCs (Nirmalakhandan, 1993; Brown, 1995).

3.2.3 System Schematic

The closed loop dynamic test system consists of a 16-liter mixing volume, which includes the 0.4-liter cell of a Gasmet DX-4040 Fourier transform infrared radiation (FTIR) spectrometer (Figure 16). The system also includes a fan to mix the test gases within the mixing chamber, a diaphragm pump to recirculate the test gases from the mixing chamber through the sorbent, and a bypass line with valving to divert the test gases through tube containing the adsorbent. A sample (4 mm diameter x 20 mm long; 40-60 mg dry sorbent) is placed in a thermal desorption tube and fed with a single VOC concentration in the mixing chamber volume. The sealed mixing chamber is loaded with a single VOC using an adsorbent tube injection system (Supelco ATIS) that flash vaporizes a 5 – 10 µl liquid VOC (ethanol, acetone, dichloromethane, or toluene) sample into a continuous flow of an inert gas which carries the sample into the mixing chamber (Monje et al., 2016).

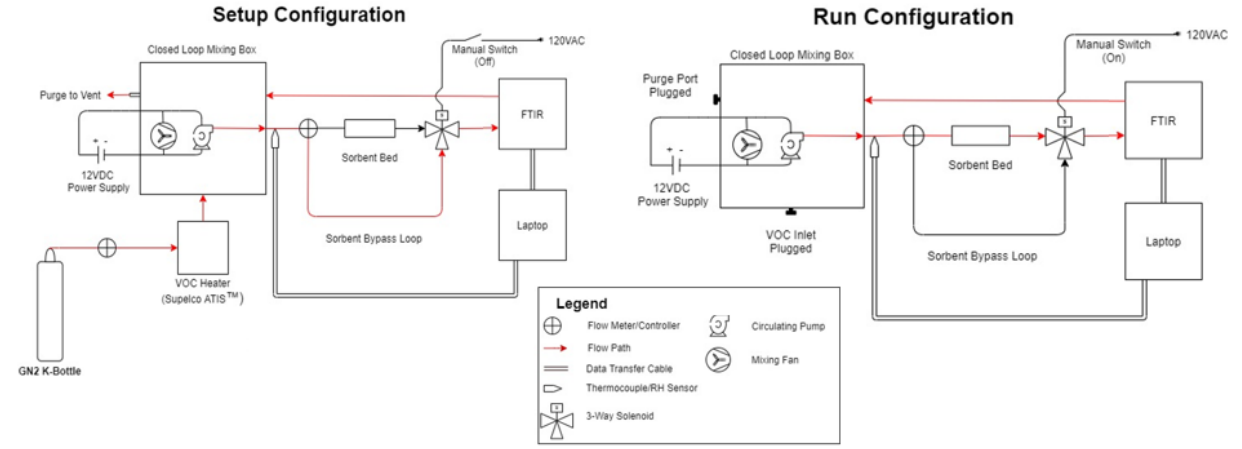

Figure 16 – Polanyi Potential Closed Loop testbed. *A) The closed loop chamber is filled by syringing 5-15 µliters of trace contaminant (50-200 ppm) via a heated injection system (ATIS) when the sorbent is bypassed. B) when loaded, a three-way solenoid valve recirculates the trace contaminant through the sorbent. The experiment ends when the trace contaminant concentration in the closed loop chamber reaches steady state.*

Once loaded, the VOC circulates through the adsorbent in the desorption tube and returns to the mixing volume until the equilibrium concentration is reached. The initial concentration (C_{init}) is recorded before circulating the VOC mixture through the adsorbent sample. The change in concentration in the mixing volume is measured every 20 seconds using the FTIR until an equilibrium concentration (C_e) is reached. When the ratio C_e/C_{init} becomes constant, the chamber concentration (C_e) is in equilibrium with the contaminant concentration in the adsorbed phase in the activated carbon. The Polanyi adsorption potential and the equilibrium adsorptive capacity, q, (ml/g) are derived based on data acquired when C_e is achieved after several C_{init} concentrations are introduced into the mixing chamber (e.g. 50, 120, and 250 ppm). This approach is similar to that used by Leban et al. (1991), except that they used much higher C_{init} concentrations and their system was very well-sealed. The closed mixing chamber system used for the present evaluation was found to leak, thus a correction was applied to the adsorption data recorded.

The saturation capacity for ethanol was determined using the closed loop dynamic test at ambient temperature and pressure. The chamber was filled with ~250 ppmv ethanol, which was removed by 40 mg

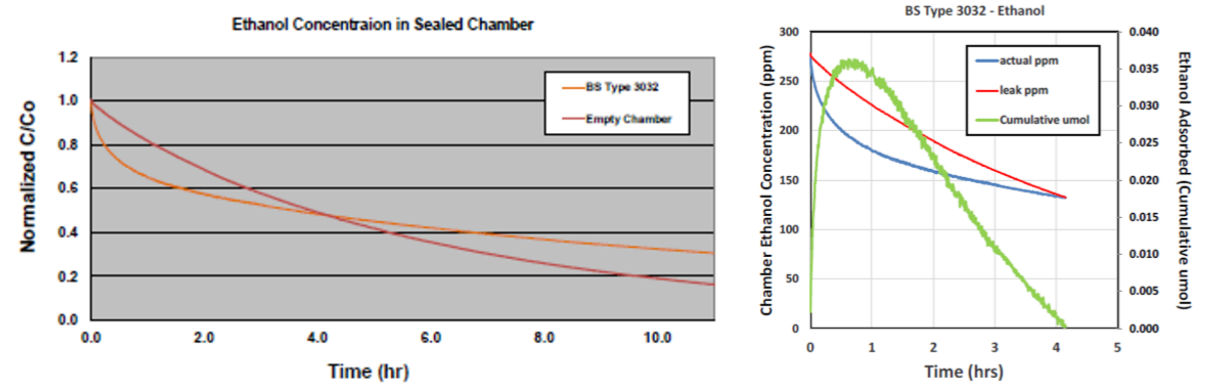

Figure 17. *A) The ethanol concentration in the chamber decreases faster than the chamber leak rate (red line) when the sorbent is present (orange line). B) The concentration difference between the chamber leak rate and the sorbent removal rate is used to calculate the amount of ethanol removed by the sorbent (green line).*

of Barnebey Sutcliffe Type 3032 activated carbon held in the sorbent tube. The ratio of chamber concentration, C, to C_{init} was plotted as a function of time as shown by Fig. 4. When the ratio becomes constant, the chamber concentration, C_e, is in equilibrium with the contaminant concentration in the adsorbed phase in the activated carbon sorbent. The Polanyi adsorption potential and the equilibrium adsorptive capacity, q, (mg/g) is derived based on data acquired at this condition.

The method for accounting for leakage is presented by the following discussion. The concentration of trace contaminants (e.g. ethanol) introduced into the chamber is reduced at a constant chamber leak rate as shown by Figure 17 (A, red line). The concentration decreases faster when a sorbent is in the chamber because the sorbent adsorbs the trace contaminant as it flows past the sorbent at 1 L/min. The sorbent reaches equilibrium when the chamber leak rate exceeds the sorbent removal rate.

The amount of ethanol removed from the chamber decreases with time as illustrated by the blue line in Figure 17 B. This cumulative amount is composed of the amount leaking from the chamber (red line) and the amount removed by the sorbent (green line). The total amount of ethanol (in µmol) removed by the sorbent is obtained from the area under the green curve and is used to calculate the equilibrium capacity, q, in mol/kg or ml/g.

3.3 Regenerable VOC Testbed

3.3.1 Overview

The dynamic performance of zeolites (13X and 5A) or solid amines (SA9T) was tested at NASA's KSC in the Regenerable VOC Control System (RVCS), a sub-scale testbed. The RVCS consists of the following subsystems: CO_2 mixing, humidifier, gas generator, and instrumented filter bed with vacuum regeneration from both sides of the bed, automated sampling of pre- and post-filter gas streams, gas chromatograph for quantifying VOCs, and an infrared gas analyzer for CO_2 measurements (Figure 18). A detailed description of the RVCS is found in Nolek and Monje (2011) and in Monje et al. (2009). The RVCS is capable of measuring VOC, CO_2, and water vapor breakthrough curves (static tests) and exposing the bed to programmed Pressure Swing Adsorption (PSA) cycles (dynamic tests). This study presents results for static and dynamic adsorption tests performed to determine the performance of Zeolite 13X during dynamic conditions found within air revitalization systems.

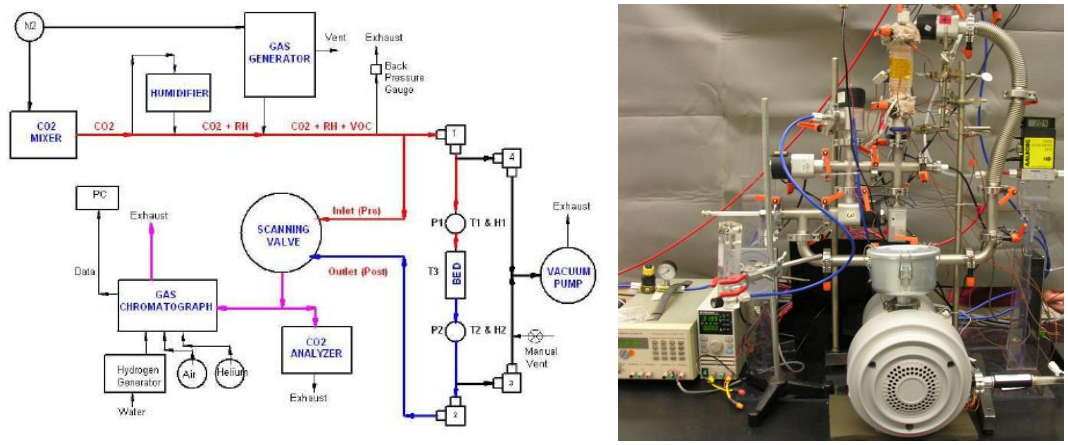

Figure 18. *RVCS subsystems, 4 valves, inlet (red) and outlet gas (blue), and sampling (pink) flows. Simulated spacecraft gas streams are produced by a gas generator, a* CO_2 *K-bottle, and a humidifier. VOCs are measured by a GC and* CO_2 *by an FTIR. A vacuum pump or a heater is used to regenerate the zeolites.*

Static Tests. These tests consisted of loading samples of Zeolite 13X with simulated spacecraft gas streams for up to 2 hrs long. During a typical breakthrough curve measurement (static adsorption) test, the sorbent bed is challenged with a simulated spacecraft gas stream containing 6000 ppm CO_2, 1-5 ppm VOC

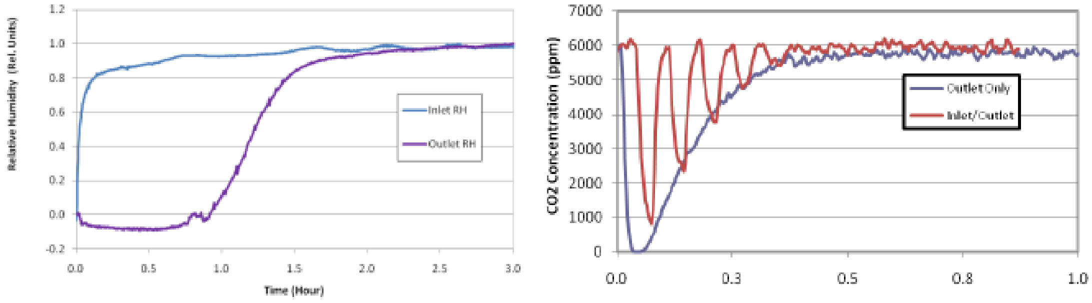

Figure 19. *Breakthrough curves of* H_2O *vapor (Left) and* CO_2 *(right) in Zeolite 13X measured in the Regenerable VOC Control System.*

and/or humid air (~52% RH) at ~23 ºC and ambient pressure (101.3kPa) for at least 1 ½ hours. The VOC, CO_2 and water vapor of the simulated gas stream were adjusted to the desired levels and allowed to equilibrate at the given flow rate. The bed was then exposed to the gas stream and changes in bed temperature, as well as in inlet and outlet pressure, humidity, and temperature were recorded every 10 seconds until water vapor and CO_2 adsorption loading ended.

The amount of water adsorbed by the bed was calculated from the difference between inlet (pre-RH) and outlet (post-RH) relative humidity (Figure 19) multiplied by the mass flow rate. Similarly, the amount of CO_2 adsorbed by the bed was calculated from the difference between inlet (pre-bed) and outlet (post-bed) CO_2 concentrations and the mass flow rate.

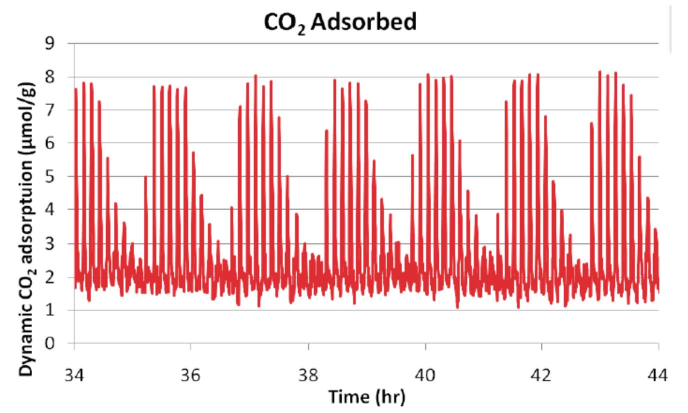

Figure 20. *Dynamic adsorption of CO_2 by a Zeolite 13X bed undergoing 8 min PSA cycles in the Regenerable VOC Control System.*

Dynamic Tests. The dynamic test consisted of loading Zeolite 13X during 8 minute PSA cycles. The PSA cycles (i.e ~8 cycles/hour; Figure 20) consisted of loading of CO_2 for 4 minutes, followed by 4 minutes of vacuum desorption at 0.2 torr. The dynamic tests are representative of the environment (e.g. flow rate and cycle time) that Zeolite 13X must operate when used in cyclic mode.

Thermal Regeneration. Zeolite 13X adsorbent was thermally regenerated by flowing dry N_2 gas in a direction counter to that used for loading the bed at 0.4 L min-1. The heating system was ramped to 50°C for 1 hr, 100°C for 1 hr, then 150°C for 1 hr, then to 200°C for 1 hr, and finally to a maximum temperature of 225°C for 2 hours (Figure 21). Careful examination of the humidity data indicates when the Zeolite 13X sorbent was completely dry. The target dew point was -50°C recommended, but the dew point reached -42°C but did not go lower. This difference in dew point indicates that the bed still holds some moisture that can reduce CO_2 adsorption.

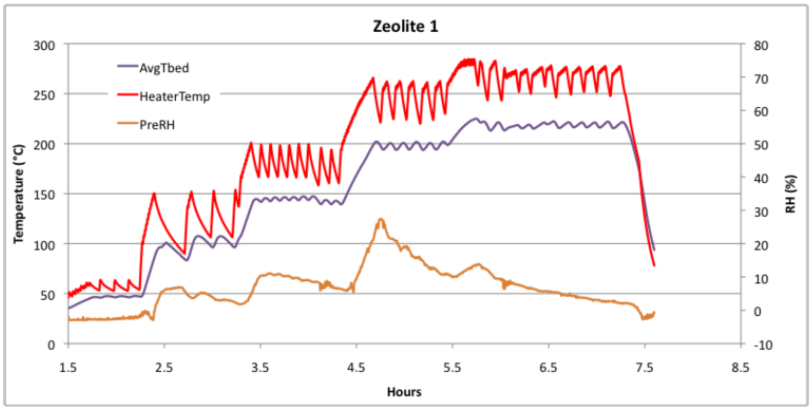

Figure 21. *Dynamic adsorption of CO_2 by a Zeolite 13X bed undergoing 8 min PSA cycles in the Regenerable VOC Control System.*

3.4 Photochemical Oxidation Testbed

3.4.1 Background

Photo-Chemical Oxidation (PCO) is a candidate technique for controlling trace amounts of volatile organic compounds (VOC) in spacecraft cabin air. The VOCs in cabin air pass through a PCO reactor illuminated with ultraviolet (UV) radiation and they are converted to carbon dioxide (CO_2) and water vapor. However, many unwanted intermediates are often produced during PCO, which may exceed the toxicity of the parent compounds. Furthermore, the catalyst in the PCO reactor may be inhibited by VOCs, leading to decreased performance, as well as the production of unwanted intermediates. The concept of a Hybrid-PCO (H-PCO) reactor uses a combination of photocatalysts, catalysts, and sorbents to effectively eliminate the production and/or release of unwanted intermediates from the reactor during the photocatalytic removal of VOCs.

PCO systems utilize a photocatalyst, lamps that illuminate the photocatalyst with UVC, UVA or visible radiation, and a reactor housing that optimizes the PCO reaction. A Hybrid-PCO reactor includes catalysts and sorbents for removing unwanted intermediates produced during the PCO process. These intermediates could be further mineralized or adsorbed and prevented from being discharged from the reactor or kept in the reactor longer so that they can eventually be removed via photocatalytic oxidation.

3.4.2 System Schematic

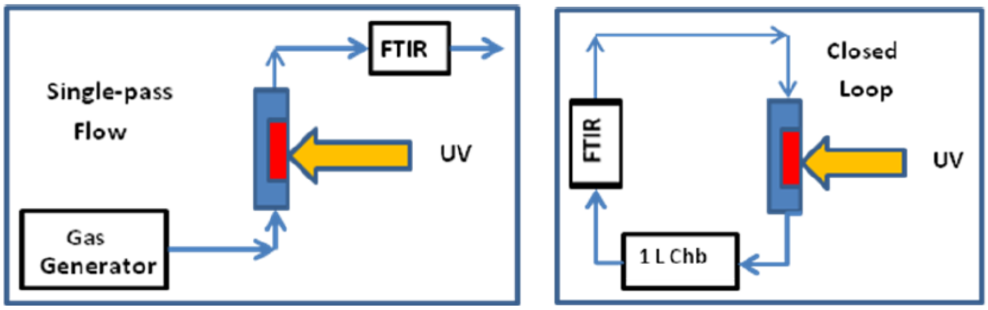

Figure 22. *PCO can be studied in a single pass (Left) or a closed loop configuration (Right).*

The FF-PCO (shown in Figure 6) gas flow can be operated in a single-pass mode and the residence time can be varied by changing the flow rate (Figure 22, Left). In this arrangement the challenge concentration over the catalyst is kept constant. A sufficient amount of catalyst is needed to be able to measure intermediates, however, this system will not be able to detect/quantify minor intermediates when the concentration of the challenge VOC is low (1-5 ppm).

The FF-PCO gas flow can be operated in a recirculating multiple-pass mode (Figure 22, Right). A 1 L chamber was added to increase the total volume of the system so that the concentration of gas phase PCO products can be increased above the limit of detection of the FTIR. The flow rate needed to operate the FTIR is 1 L/min. In this arrangement the challenge concentration over the catalyst is constantly changing kept constant. The system is airtight and VOCs produced accumulate within the 2.3 total volume of the system. This system is useful for measuring rates of intermediate production because their concentration rises linearly as they accumulate. The rate is determined from the slope of the accumulation rate.

4.0 Example Test Cases

4.1 NH_3 Removal Capacity

Two factors make NH_3 an important contaminant in spacecraft, as well as the efficiency and capacity of NH_3 sorbents used to control it (Perry et al., 1998). First, most airborne NH_3 is probably removed in the condensate water of condensing heat exchangers, but thermal control systems of future vehicles may not include the condensing heat exchanger used in the current ECLSS architecture. Second, the health effects associated with long term NH_3 exposure determines the recommended maximum allowable concentration for cabin air quality. A significant source of NH_3 in the space cabin is human metabolism (50 mg crew^{-1} day^{-1}) and the maximum allowable concentration for cabin air quality has recently been lowered by toxicology experts (SMAC 2 mg/m^3). The flow rate of the TCCS needed for ammonia removal is 5 cfm minimum, 7.5 cfm maximum. This flow rate range will accommodate the offgassing and from 4 to 6 crewmembers while providing an operational margin to achieve control to half the SMAC (Luna et al., 2008).

4.1.2 Impregnated Activated Carbon

Ammonia is difficult to remove by untreated activated carbons due to its high vapor pressure and small molecular weight. On board ISS, the TCCS removes NH_3 with a bed of B-S Type 3032 4x6 mesh granular activated carbon. B-S Type 3032 carbon is impregnated with H_3PO_4 to react with ammonia and has a total acid content of approximately 10% by weight. The acid treatment reduces the VOC loading capacity relative to an unimpregnated carbon. A replacement for BS Type 3032 is Calgon Ammonasorb II, a coconut shell carbon treated with H_3PO_4 with a quoted NH_3 capacity of 7 to 16% by weight. Molecular Products Chemsorb 1425 is another coconut-shell carbon containing about 10% phosphoric acid to target ammonia and amine compounds. Luna et al., (2010) studied the ammonia removal capacity of B-S Type 3032, Ammonasorb II, Chemsorb 1425, and others using 25 and 50 ppm NH_3 and under dry and moist (40% relative humidity) conditions. The work of Luna et al (2008) was revised in FY15 at KSC to include NH_3 removal measurements in the 1-50 ppm range (Figure 23).

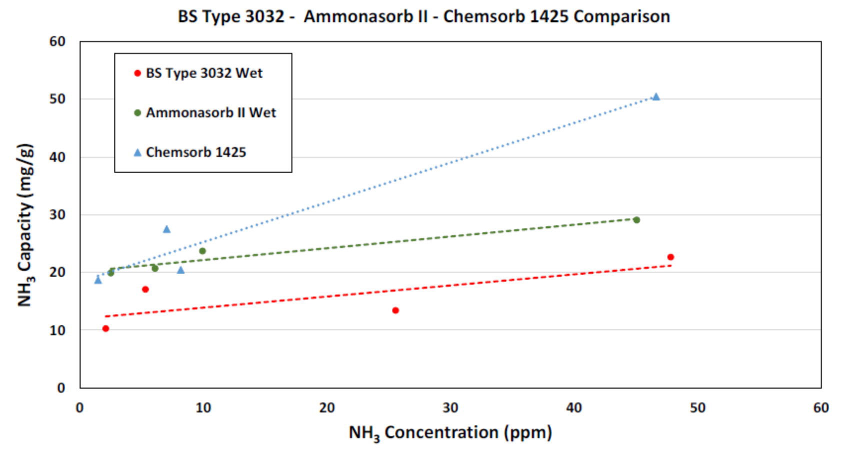

Figure 23. *Ammonia removal capacities of BS Type 3032, Ammonasorb II, and Chemsorb 1425 were measured in an open loop testbed as a function of* NH_3 *concentration: 40% RH and 23° C.*

4.1.3 Pleated Filters

Camfil Gigapleat NXPP B2 pleated filters are a form factor with a lower pressure drop than conventional packed beds (Figure 24). The efficiency of removal in ion-exchange resins depends on the humidity in the air, and a humid resin removes NH_3 from air much faster than dry resin. The resin can also swell due to water adsorption causing a volume increase of up to 50%.

Camfil B2 are composed of an ion-exchange resin that is held between two layers of scrim fabric material (Figure 25 A). The color of the scrim was observed to lighten after its ammonia removal capacity is exhausted.

Figure 24. *Camfil GigaPleat NXPP B2 pleated filter is made of cation-exchange resin sandwiched between two layers of felt. .Its pleated form factor allows a lower pressure drop than filters using packed beds.*

Figure 25 B shows that Camfil B2 has an NH_3 removal capacity of 26 mg/g at 5 ppm and rises to nearly 40 mg/g at 40-50 ppm of NH_3 (purple squares). In the presence of VOCs, the capacity of Camfil B2 for NH_3 decreased; it was 19 mg/g at 5 ppm NH_3 rising to only 27 mg/g at 45 ppm NH_3. The NH_3 removal capacity of Camfil B2 was higher than that of BS Type 3032, and comparable to the capacities of Ammonasorb II and Chemsorb 1425 at 5 ppm NH_3.

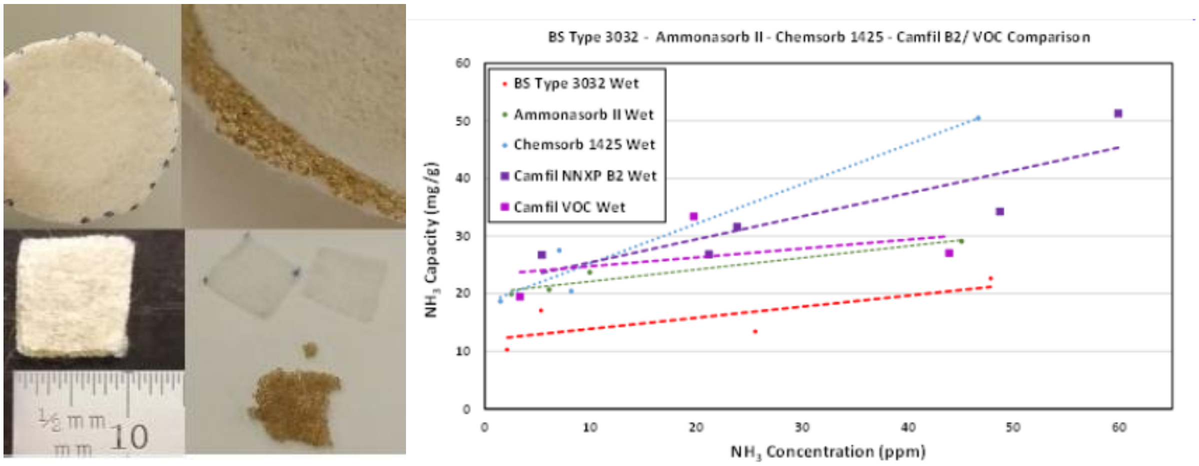

Figure 25. *A) Camfil GigaPleat NXPP B2 pleated filter is composed of resin and scrim. B) The ammonia removal capacity of Camfil B2 in the presence of VOCs was higher than that of BS Type 3032, and equal to the capacities of Ammonasorb II or Chemsorb 1425.*

4.2 Effects of Flow Rate and VOCs on NH_3 Removal

As part of an effort to address BS-3032 commercial obsolescence, two candidate replacements—Ammonasorb II and Chemsorb 1425—were tested in the presence of VOCs to examine the effects of these compounds on ammonia adsorption capacity (Monje et al., 2018). Gas streams containing acetone, ethanol, toluene and ammonia were generated to challenge each sorbent at 40% relative humidity (RH) and 23°C. These ersatz mixtures were delivered to test beds at two flow rates, a key parameter affecting mass transfer kinetics. Results were compared to previous pure component tests using only ammonia.

4.2.1 BS Type 3032

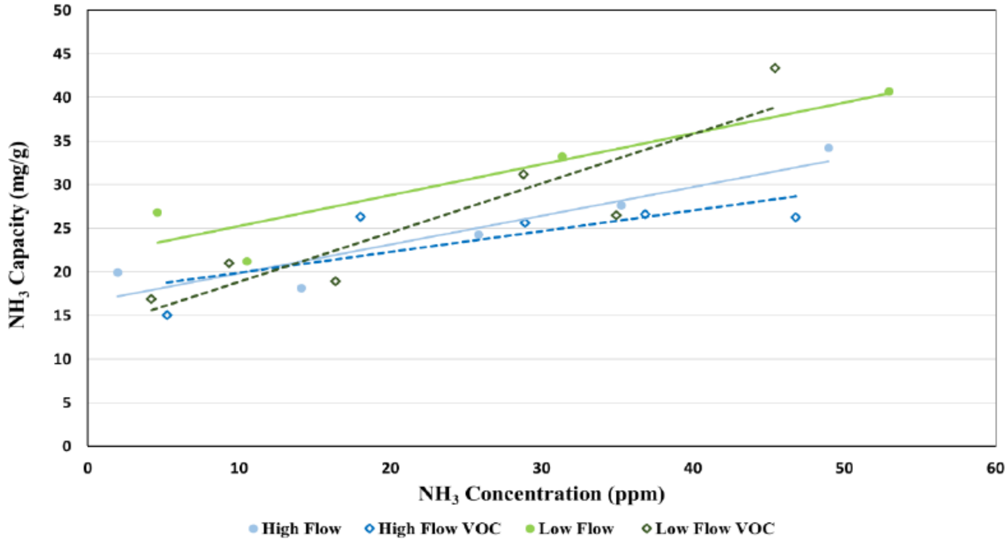

Figure 26. *BS-3032 capacities for high flow (blue) and low flow (green), with VOCs (dashed lines) and without VOCs (solid lines). The presence of VOCs for high flow runs had a greater effect at high concentrations, whereas the effect of VOCs on low flow runs was more prominent at low concentrations. Run at 40% RH and 23°C.*

Figure 26 depicts the NH_3 removal capacity of BS-3032 as a function of NH_3 inlet concentration. Low flow rates are plotted in green and high flow rates in blue, and the gas streams containing VOCs are shown as dashed lines. At high flow rates, NH_3 removal rises from ~15 mg/g at 5 ppm NH_3 to 27 mg/g at 50 ppm NH_3 (blue lines). In contrast, the NH_3 removal at low flow with no VOCs rises from ~23 mg/g at 5 ppm NH_3 to 40 mg/g at 50 ppm NH_3 (green solid line). For low flow rates with VOCs, the capacity rises from ~15 mg/g at 5 ppm to 40 mg/g at 50 ppm (green dashed line). The presence of VOCs for high flow runs reduced capacity at high concentrations, whereas the effect of VOCs on low flow runs was more prominent at low concentrations.

4.2.2 Chemsorb 1425

Figure 27 shows that removal capacity of Chemsorb 1425 as a function of NH_3 challenge concentration is also higher at high flow rates (blue lines) than at low flow rates (green lines). Ammonia removal increased from approximately 20 mg/g at low flow rates (green) to 30 mg/g for high flow rates (blue) at low ammonia concentrations. These relations were not affected by the presence of VOCs. This implies that Chemsorb 1425 has a low capacity for VOCs under these test conditions, leaving more sorption sites open for ammonia. At 50 ppm NH_3 the capacity was not affected by flow or VOCs, thus all test conditions gave capacities of approximately 50 mg/g.

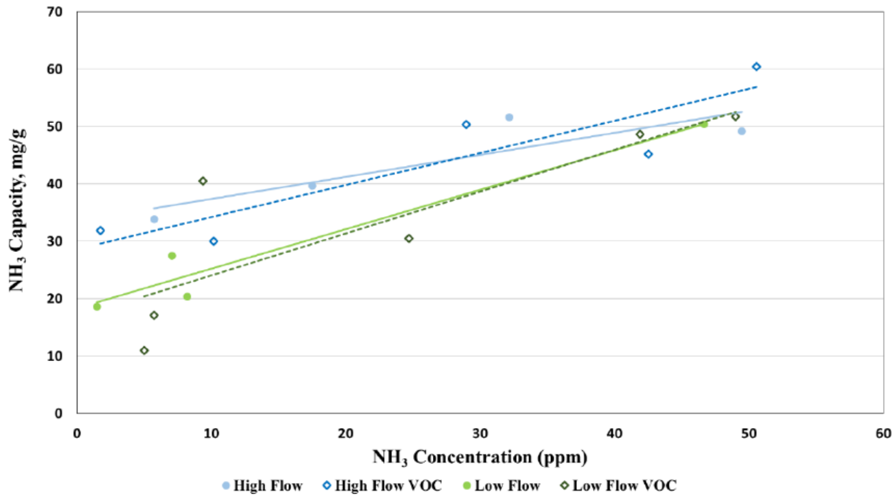

Figure 27. *Chemsorb 1425 capacities for high flow (blue) and low flow (green), with VOCs (dashed lines) and without VOCs (solid lines). At high NH_3 concentrations, neither flow nor VOCs have a large effect on capacity. At low concentrations, flow rate has the largest impact and VOC effects are miniscule. Run at 40% RH and 23°C.*

4.2.3 Ammonasorb II

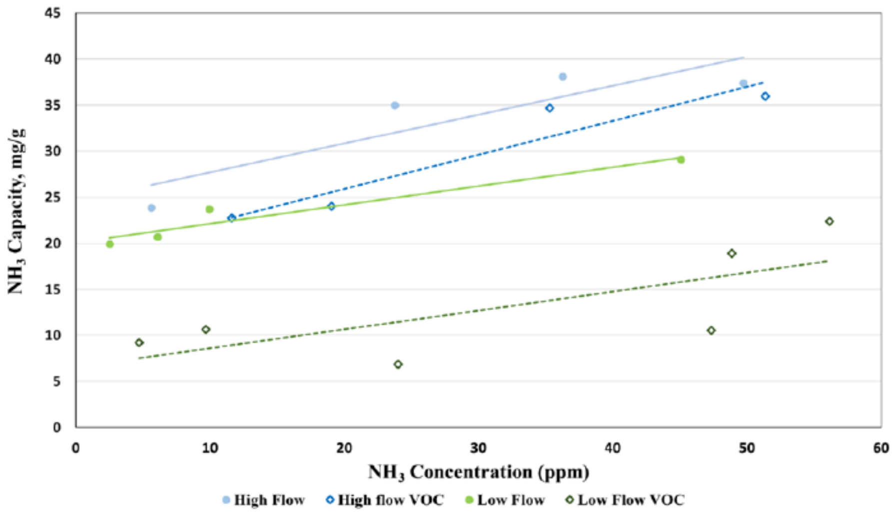

Figure 28. *Ammonasorb II capacities for high flow (blue) and low flow (green), with VOCs (dashed lines) and without VOCs (solid lines). At low flow rates, capacity is greatly reduced in the presence of VOCs. At high flows this reduction is much smaller. Run at 40% RH and 23°C.*

In contrast to BS-3032, Fig. 28 shows that the NH_3 removal capacities of Ammonasorb II at high flow rates (blue lines) are higher than at low flow rates (green lines). The presence of VOCs reduced the capacity at high flow rate by about 5 mg/g at all NH_3 concentrations. In addition, the presence of VOCs significantly reduced NH_3 removal capacity at low flow rates (green dashed line). This behavior is similar to that of BS 3032, as VOCs cause a greater reduction at low flow, except that the effect is much larger and is not diminished at high NH_3 concentrations for Ammonasorb II. This implies that Ammonasorb II adsorbs more VOCs at lower flow rates, leaving less sorption sites for ammonia.

4.3 Polanyi Potentials

4.3.1 Cabot Norit GCA48

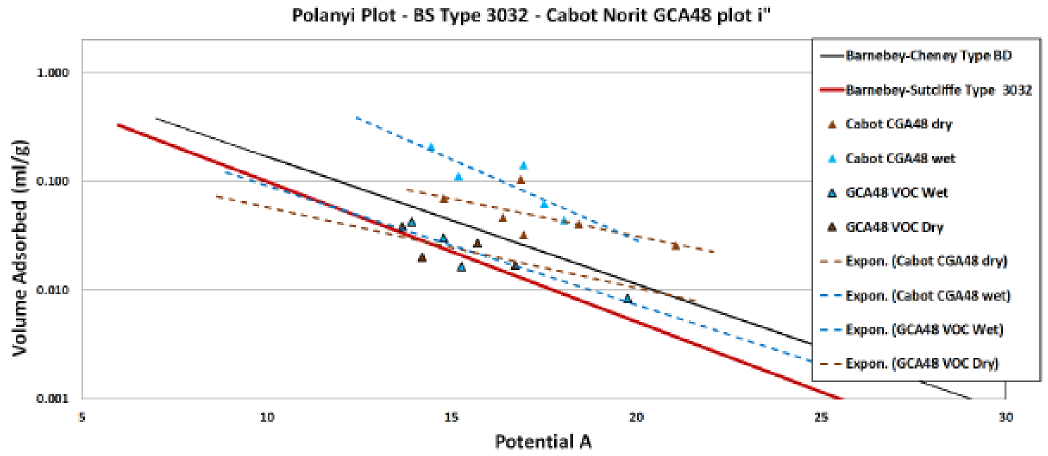

Figure 29. *Polanyi potential plots comparing Cabot Norit GCA48 to Barnebey Sutcliffe Type 3032 (red) and Barnebey Cheney Type BD (black) for VOCs.*

The Polanyi potential plots for VOC adsorption onto Cabot GCA48 untreated activated carbon is shown in Figure 29. In the presence of VOCs, the data show that Cabot GCA48 has a similar performance to Barnebey-Sutcliffe Type 3032 for ethanol and acetone. The Polanyi plots for wet or dry conditions are indistinguishable. This analysis shows that the performance of Cabot GCA48 is reduced by the presence of VOCs in the gas stream.

4.3.2 Chemsorb 1000

The Polanyi potential plots for VOC adsorption onto Chemsorb 1000 untreated activated carbon is shown in Figure 30. In the presence of VOCs, the data show that Chemsorb 1000 has a similar performance to Barnebey-Sutcliffe Type 3032 for ethanol and acetone. The Polanyi plots for wet or dry conditions are also similar. This analysis shows that the performance of Chemsorb 1000 is also reduced by the presence of VOCs in the gas stream.

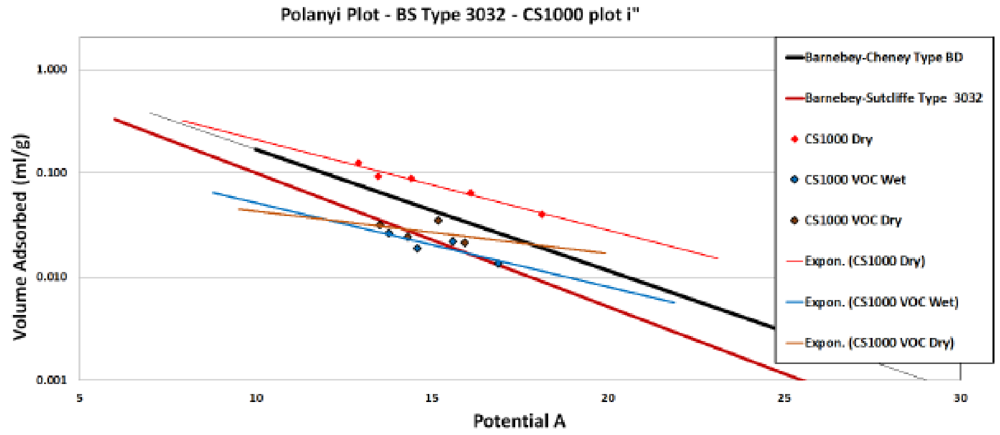

Figure 30. *Polanyi potential plots comparing Chemsorb 1000 to Barnebey Sutcliffe Type 3032 (red) and Barnebey Cheney Type BD (black) for VOCs.*

4.3.3 Applying Polanyi Potential Data to TCC Design

Acquiring adsorption capacity data and constructing Polanyi adsorption potential plots for various candidate sorbents is advantageous to the TCCS designer by allowing for accurate and reliable adsorption bed sizing as well as serving as the basis for predictive bed lifetime estimates (Perry, 1994). Bed dynamic adsorption capacity modeling techniques have been shown to be accurate within ±16% (Perry, 1998). Because the Polanyi adsorption potential as defined by Eq. 2 accounts for temperature, adsorption capacity data acquired at a single temperature can be used to predict performance at different temperatures. This negates the need for time-consuming efforts to acquire a full range of equilibrium isotherm data. This approach saves not only time but also costs associated with acquiring data for a complete set adsorption isotherm curves but also reduces the need for iterative fabrication and testing of the adsorbent bed. Design conservatism is integrated into the design process by utilizing statistically adjusted contaminant loads (mean plus σ), including a 10-20% margin for co-adsorption effects on equilibrium capacity loading, and accounting for shifts in the adsorption potential characteristic curve caused by humidity. The rigorous bed sizing and design process based on the Polanyi adsorption potential is well described by Perry (1994) and is based on Eqs. 1 and 2.8. Herein, we briefly describe that process.

First, equilibrium adsorption capacity data are acquired using the methods described by Sections II and III. These data provide both the equilibrium capacity, q, in Eq. 1 but also the equilibrium concentration, C, in Eq. 2. Second, the adsorption potential parameter, A, is determined for the test condition using Eq. 2. To calculate A, accurate and traceable physical property data at the required system temperature and pressure must be obtained from the literature for the vapor pressure, C_s, and liquid molar volume, V_m. For instances where literature data on liquid molar volume are not available, the method of Tyn and Calus (1975) is recommended for obtaining the liquid molar volume from critical properties of fluids. It should be noted that liquid molar volumes at the normal boiling point typically vary from that at room temperature by approximately 5%. The Antoine equation can be used to calculate the vapor pressure at the temperature condition. Utilizing the dataset that includes the equilibrium concentration, vapor pressure, and molar volume, values of A are determined according to Eq. 2 for each chemical contaminant of interest for the TCCS adsorbent bed design. Contaminants with a large A value will drive the sizing of the charcoal bed due to their low adsorption capacity.

Next, as a first design draft, the component with the largest adsorption potential value is used for the initial bed sizing. It follows that the adsorption capacity for this compound can then be extracted from the sorbent Polanyi adsorption potential plot. Good engineering design practice dictates that bed aspect ratios (l/d) should approximate a value of two. With this in mind, bed sizing can proceed by identifying a target bed lifetime and/or a desired TCCS performance goal (Perry and Kayatin, 2015). Bed sizing using the equilibrium capacity alone accounts for only the bed's saturation zone length. A margin must be added to account for unusable adsorption (mass transfer zone). Velocity dependent correlations have been utilized to this end (Tyn and Callus, 1975).

Ultimately an iterative calculation process described by Perry 1998 that accounts for all of the contaminants of interest for the bed design is used to refine the initial design. The bed design is then validated by testing at full scale. This approach, which has been found to be a highly economical compared to acquiring a large dataset to construct a full set of equilibrium isotherm curves, has been successfully used for designing TCCS beds for both the Spacelab and ISS programs.

4.4 Siloxane Removal Capacity

Polydimethylsiloxane (PDMS) compounds have been reported in cabin air quality samples from the beginning of crewed operations aboard the ISS. A variety of sources of PDMS compounds are found aboard ISS, including crew hygiene products, adhesives, caulks, lubricants, and various nonmetallic materials (Carter et al., 2015). Four compounds contribute to the load: hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and trimethylsilanol (TMS). Postflight analysis of activated carbon used in the Trace Contaminant Control System (TCCS) has indicated that the dominant compounds were D4 and D5 siloxanes. The total siloxane concentration in the ISS cabin atmosphere is typically between 2 mg/m^3 and 4 mg/m^3 (Perry, 1998).

4.4.1 CHIPS sorbent selection

The degradation of PDMS has been implicated in the accumulation of dimethylsilanediol (DMSD) in humidity condensate and in the ISS WPA product water observed in 2010 (Carter et al., 2015, Carter et al., 2016). Although DMSD is not a crew health hazard at the levels observed in the product water, it can degrade the WPA catalytic reactor's effectiveness and cause early replacement of Multi-filtration Beds. In 2015, eleven adsorbent media were evaluated at KSC using a testing scheme designed to shorten the time for down selecting the most promising sorbent candidates for future filter development. The sorbents with the highest siloxane removal capacity for L2 and D3 siloxanes were the activated carbon Cabot Norit GCA 48, ACC 50720 carbon cloth, and Ambersorb 4652 resin (Richards et al., 2015).

A Siloxane Scrubber Filter was designed using Cabot Norit GCA 48 activated carbon (4×8 mesh), because the activated carbon cloth has a low density and the resin has very small particle size and high pressure drop compared to the large particles of GCA 48 (Carter et al., 2016). The impact of these differences on filter design were addressed when scaling the sorption results obtained in the adsorbent media testbed. A further consideration is that the measured sorbent capacities measured at KSC were 40% lower because the concentration of siloxanes in the ISS cabin atmosphere is lower than was used during the testing. Four Node 1 scrubbers were installed in May 2015 (Carter et al., 2016). These scrubbers provided an immediate, but temporary, decrease in ISS cabin siloxane concentrations based on the Air Quality Monitor (AQM) measurements, which includes detection of D3, D4, D5, and TMS. D4 siloxane was removed effectively to its detection limit of 0.05 mg/m^3, D5 siloxane and D3 siloxane were also reduced to less than 1.5 mg/m^3 and 1 mg/m^3, respectively. Trimethylsilanol gradually increased as it has the lowest affinity for the GCA 48 and slowly saturated the adsorbent. Despite the excellent performance of the Node 1 scrubbers the DMSD concentration in the condensate was not decreased and eventually the capacity of the GCA 48 was exhausted.

4.4.2 Siloxane Removal Properties of Activated Carbons

The adsorptive capacities for a dry mixture containing ~ 3 ppm of D3, D4, and D5 was measured (GCA48, Figure 31). The adsorptive capacities of GCA 48 for the single components were much higher than for the D3, D4, and D5 mixture (GCA48-S, Figure 31). The sorptive capacity for D3 in the mixture was lower than the adsorptive capacity for D3 in the presence of humidity and L2 measured in FY15 (GCA48 KSC). When adjusted for a 3 ppm challenge concentration, GCA 48 adsorbs 4, 7 and 2 times more D3, D4, and D5 when the siloxane is supplied alone than when in a mixture. In addition, the adsorptive capacity for D3 (69 mg/g) is lower in the mixture than when supplied with L2 and water (171 mg/g).

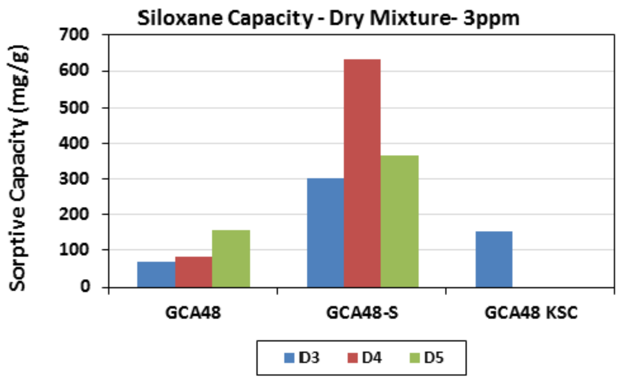

Figure 31. *Comparison of adsorptive capacities for a dry mixture of D3, D4 and D5 by GCA 48. GCA48-S denotes capacity during exposures to single compounds. GCA48 KSC denotes D3 capacity measured in presence of water vapor and L2.*

The adsorptive capacities of other candidate sorbents were also compared to that of GCA 48 (Fig 32; top). The adsorptive capacities of Cabot Norit GCA 48, Barnabey Sutcliffe Type 3032 (BS 3032), Calgon 207C and Calgon 208C were measured using a dry mixture of D3, D4, and D5 (Figure 32). The siloxane removal capacities of candidate sorbents was measured with a dry challenge mixture of D3, D4, and D5, each with concentration of 2-2.8 ppm. The sorbents (~65mg) were held in a 4 mm sorbent tube and exposed to the siloxane mixture at a flow rate of 0.3 L/min at 23°C.

The measured capacities were adjusted to 3 ppm using the concentration at which they were measured. Generally, BS 3032 and 207C had smaller adsorptive capacities of D3 than GCA 48. However, 208C had similar D3 capacities, ~10% higher capacity for D4 and ~40% higher capacity for D5 than that of GCA48 (Figure 32; bottom). These results indicate that siloxane adsorption of a dry mixture of D3, D4 and D5 can affect the adsorptive capacities of the sorbents. Clearly, B-S Type 3032 has the smallest (~ 60% less) siloxane capacity. The data (Figure 32; top) show that the activated carbons 207C, 208C, and GCA 48 have much higher capacities than BS Type 3032 for D5 than for D4 and D3. In addition, these data suggest that Calgon 208C may be a replacement for GCA 48 since it has a 10% higher capacity for D4 and a 40% higher capacity for D5. These increases in capacity could represent a longer time between filter replacements.

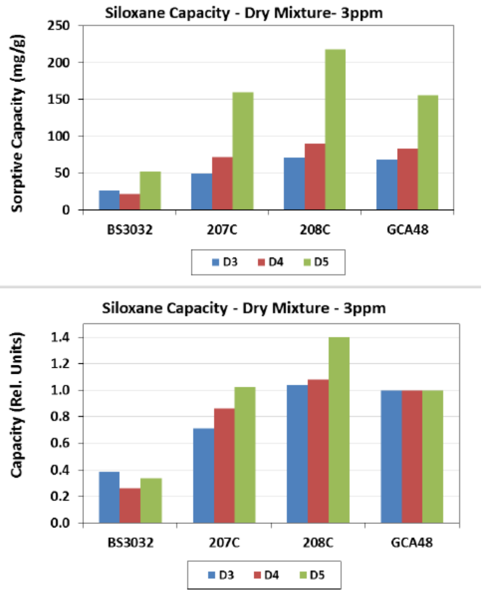

Figure 32. *(Top) Comparison of adsorptive capacities (mg/g) for a dry mixture of 3 ppm of D3, D4 and D5 by GCA 48, BS 3032, 207C, and 208 C. (Bottom) Comparison in relative units with respect to CGA 48.*

5.0 Rapid Method for Sorbent Screening

5.1 Introduction

The trace contaminant control subassembly (TCCS) on board the International Space Station (ISS) utilizes a granular impregnated activated carbon (GAC) bed to remove high molecular weight volatile organic contaminants and ammonia (NH_3) (Perry, 1991). The acid-impregnated GAC (i.e. Barnebey-Sutcliffe Type-3032) used in the TCCS is a commercial product that has become obsolete and is no longer available for purchase or manufacture. Therefore, it is necessary to identify and characterize suitable replacements to support air revitalization functions of present and future spacecraft environmental control and life support (ECLS) systems. General performance characteristics of candidate adsorbents are required for new TCCS designs and vendor-supplied data are seldom available at relevant process conditions encountered in a crewed spacecraft cabin.

Direct testing of GAC using typical spacecraft cabin air or indoor air contaminant concentrations (<1-6 ppm) requires very long test times on the order of days to weeks to complete. Rapid testing is needed to reduce expense and to increase throughput of sorbent evaluation experiments. Thus, most testing from indoor air applications is done at elevated concentrations. Rapid tests with challenge concentrations ~100 ppm are short (a few hours), but since adsorptive capacity depends on the challenge concentration, the sorbent capacities obtained at high concentrations are not representative of capacities expected at spacecraft cabin air concentrations.

A rapid protocol was developed to shorten the duration of the analytical methods for screening sorbents for siloxane removal by using crushed sorbents, which essentially cuts down the time for saturating a sample from days or weeks to hours (Richards et al., 2015). Commercial sorbent particles (e.g. 4×8) are large so they are crushed to produce ~50 mg samples held in 4 mm diameter desorption tubes for analysis. The sorbent particles were crushed so that the particles could be packed more efficiently to avoid effects from channeling of the gas stream past the sorbent (Figure 33).

Figure 33. Comparison of uncrushed (Left) and crushed (Right) B-S Type 3032. *The sorbent was crushed and the remaining dust removed prior to packing and drying in a 4 mm sorbent tube.*

This rapid method utilizing crushed sorbents was used to compare and rank the adsorptive capacities of three impregnated GAC (Ammonasorb II, Chemsorb 1425, and B-S Type 3032) for moist gas streams containing 2 to 50 ppm NH_3 (Monje et al., 2018). The method was reliable and shortened the duration of low concentration experiments from weeks to a few days. A second study comparing the same impregnated GACs explored the effect of flow velocity on their adsorptive capacities for NH_3 (Finn et al., 2020). Sorbent capacities were tested at low (0.5-0.7 L min^{-1}) and high (1.1-1.3 L min^{-1}) flow rates, which corresponded to flow velocities of 80 cm/s and 165 cm/s, respectively. The GACs showed a higher removal capacity at high compared to low flow rates, which differs from what is expected for chemisorption, where higher capacities are expected due to greater contact time at lower flow rates.

The present study was conducted to evaluate the validity of the data obtained using this rapid method by comparing adsorption capacities from crushed sorbents with uncrushed sorbents. The tests were conducted with three impregnated GACs (NH_3 removal by Ammonasorb II, Chemsorb 1425, and Chemsorb 1410) and two untreated GACs (ethanol removal by Chemsorb 1000 and Norit GCA48) in an effort to gauge if the rapid test methods can produce meaningful data for use in future air revitalization designs.

5.2 Methods

5.2.1 Sorbent Containment Method

For crushed carbon tests, thermal desorption tubes (Part #786003, Scientific Instrument Services (SIS), Ringoes, NJ) with an inner diameter of 4 mm were used as the containment to test each sorbent. Small diameter tubes were used to reduce test duration while maintaining low velocity and high aspect ratio conditions (Monje et al., 2018; Finn et al., 2020). To achieve this, large granules were crushed to less than 3 mm using a mortar and pestle and dust was removed. Using two glass wool plugs to hold the sample in place, 50-60 mg of dust free, crushed sorbent was loaded into each desorption tube and the height measured to ensure an aspect ratio between three and five. Next, the tubes were loaded into a thermal desorption conditioning system (Model # CS-1, SIS, Ringoes, NJ) where dry nitrogen at 100 °C for two hours was used to remove any moisture adsorbed during storage. The sorbent mass was determined after drying.

A 12.7 mm (1/2 inch) diameter sorbent bed (Figure 34) was designed for working with uncrushed sorbents. The bed can be packed with 1-5 g samples held between two wire mesh screens fixed into grooves by retaining rings (Figure 34). The bed has a high metal-to-sorbent mass ratio (~4-5 on a mass basis) and is insulated to maintain isothermal conditions within the adsorbent. The flow rate for the tests is chosen to match the contact times used in trace contaminant technologies onboard spacecraft (e.g. 1.6 L min^{-1} for the 12.7-mm diameter bed gives a contact time of 0.25 s). To prepare uncrushed sorbents, carbon is packed into a 9.52 mm (3/8-inch) tube plugged with glass wool and dried for three hours with dry nitrogen at 23 °C. A final mass was recorded to determine the amount of dry crushed and uncrushed sorbents. The tubes were capped and stored in a desiccant chamber until use.

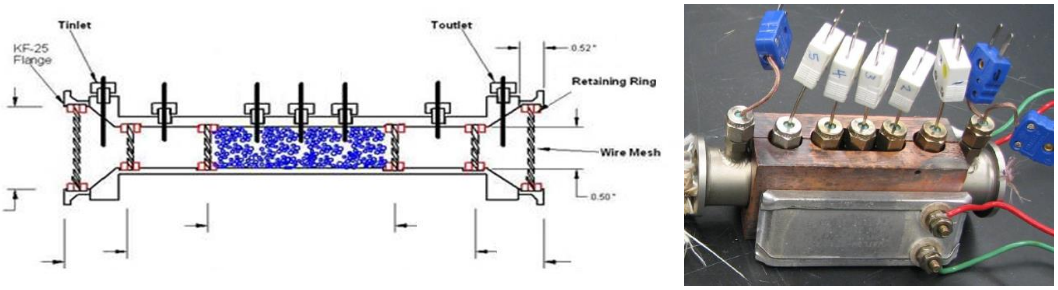

Figure 34. Adsorbent bed used to expose uncrushed adsorbents to simulated gas streams. *The 12.7-mm diameter bed was loaded with 4×8 sorbent to a bed length of 25.4 mm (1 inch) to give a L/D ratio = 2.*

5.2.2 NH_3 or Ethanol Challenge

The open-loop sorbent test bed used in this study is depicted in Figure 35. For ethanol testing, a Gas Standard Generator (Model 491M-B, Kin-Tek Analytical, La Marque, TX) was used to generate a continuous stream of 19.7 ± 1.3 ppm ethanol. For NH_3 testing, the Kintek oven was bypassed and a compressed gas bottle delivered a low flow of 1,400 ppm ammonia, which was mixed with the humid gas stream to achieve a concentration of 50.1 ± 2.5 ppm.

These NH_3 or ethanol streams were then combined with humid N_2 to reach ISS relative humidity of approximately 39.5 ± 0.8% relative humidity (RH).

Once mixed, the humid VOC stream was directed through a sorbent bypass loop containing an empty tube filled with glass wool and into a Model DX4040 Fourier transform infrared (FTIR) spectrometer (Gasmet Technologies, Finland) to analyze its composition.

Gas generator flow rates and permeation oven temperature were adjusted to achieve the desired ethanol concentration. This stream was then routed through the sorbent tubes at rates 0.4-1.3 L min^{-1} at a flow temperature of 22.9 ± 0.3 °C.

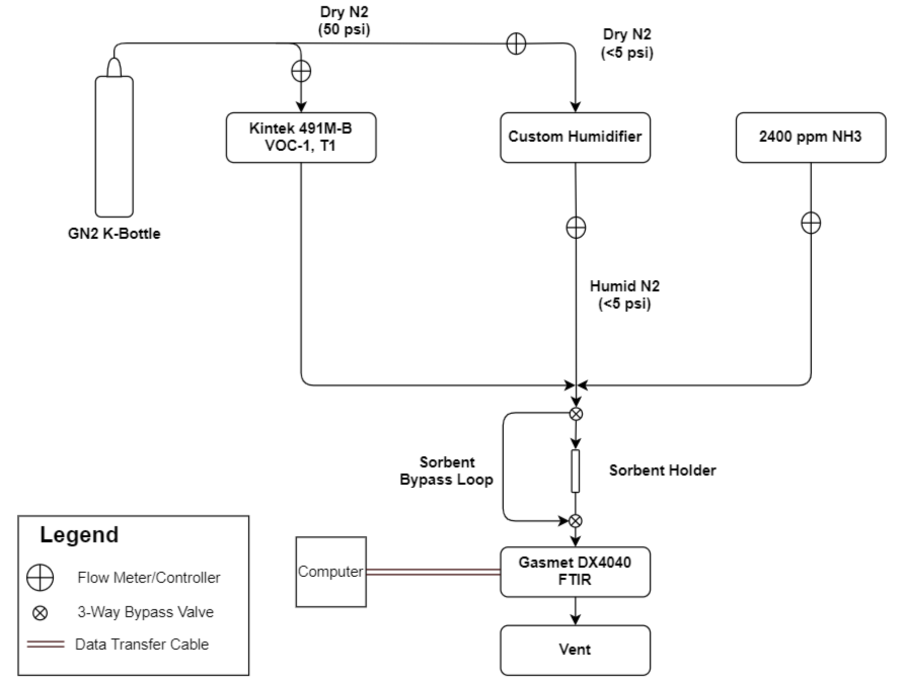

Figure 35. Diagram of open-loop sorbent testbed. *Dry Nitrogen is humidified to 40% RH and mixed with ammonia or ethanol. This simulated spacecraft gas stream flows through a packed sorbent bed and is analyzed via FTIR spectrometry until inlet concentration equals outlet concentrations.*

5.2.3 Adsorptive Capacity Calculations

The adsorptive capacity of an adsorbent bed for a given trace contaminant is determined from plots of gas stream composition versus time. NH_3 or ethanol concentration was measured every 20 seconds by the FTIR after the gas stream passed through the sorbent, and the run was completed when NH_3 or ethanol concentrations reached a steady state. The amount of ammonia or ethanol removed was found by solving for the area between the breakthrough curve and the challenge concentration, C_0, the concentration before passing through the adsorbent. This value is calculated using the following Riemann sum: $\sum(C_0-C)\times Q\times\Delta t$, where C is the concentration at the time of sampling, C_0 is the challenge concentration, Q is the flow rate, and Δt is the time between each sample. These values are summed over the duration of the run to determine the total amount of ammonia or ethanol removed and this value divided by the mass of sorbent used to give a capacity in mg adsorbed per gram of sorbent.

5.2.4 Sorbent Properties and Test Conditions

The untreated GACs remove ethanol via physisorption, and the impregnated GACs remove NH_3 by chemisorption (Erkey, 2011). Physisorption is an exothermic process whereby a solute molecule adheres to a surface without the formation of a chemical bond, usually by van der Waals forces or electrostatic attraction. Low molecular weight or polar gases such as hydrogen chloride (HCl), sulfur dioxide (SO_2), formaldehyde (CH_2O), and NH_3 are not removed by physisorption and typically require chemisorption for removal. Treated activated carbons are impregnated with a chemical agent such as phosphoric acid (H_3PO_4) that reacts with those gases, converting them to solids or salts within the carbon and removes them from the air stream. This process occurs via neutralization and adsorption capacity is exhausted when the available impregnated acid is consumed.

The properties of the coconut shell sorbents used in this study are listed in Table 1. Carbon Tetrachloride Activity (ASTM D3467) measures the pore volume of the GAC by the adsorption of a saturated organic vapor and reflects the degree of activation in each sorbent. Another property distinguishing these GACs is the internal surface area per gram of sorbent that can become filled by sorbates.

Table 1. Properties of GACs used in this study.

Sorbent	Manufacturer	Mesh Size	Acid Treatment	(%wt) CCl_4 Activity	$(m^2\,g^{-1})$ Surface Area[6]
Ammonasorb II	Calgon Carbon	6 × 12	Impregnated	60	659[7]
Chemsorb 1425	Molecular Products	4 × 8	Impregnated	60-80	1,000
Chemsorb 1410	Molecular Products	4 × 8	Impregnated	60-80	1,000
Chemsorb 1000	Molecular Products	4 × 8	Untreated	60-80	1,000
Norit GCA 48	Cabot	4 × 8	Untreated	60	1,200

The adsorptive capacities of the GACs were determined at similar relative humidity, air temperature and solute concentration. However, the crushed sorbents were contained in a 4 mm diameter desorption tube and the uncrushed sorbents were contained in a 12.7 mm diameter bed (Figure 34). These geometries determined the sorbent mass, bed volume, bed depth, and Length/Diameter ratio that resulted in the range of retention times listed in Table 2. Generally, the crushed sorbent had a 35% smaller packing density than the uncrushed sorbent. The tests with crushed sorbents took 6-8 hours to complete compared to 5-7 days to complete the uncrushed tests. Due to the large differences in retention time, gas hourly space velocity (GHSV; ratio of flow rate and reactor volume) was calculated to compare changes in adsorption capacity in these sorbent beds.

Table 2. Differences in Sorbent Bed Geometry, Retention Time, and Experiment Duration.

Particle Size	Bed Inlet Area	Sorbent Mass	Bed Volume	Bed Depth	L/D	Retention Time	Experiment Duration
Crushed	0.13 cm^2	50 - 60 mg	0.21 ml	0.017 m	4.3	0.2 – 0.5 s	6-8 hours
Uncrushed	1.27 cm^2	1.2 - 1.4 g	3.21 ml	0.025 m	2.0	0.01 – 0.03 s	5-7 days

5.3 Results and Discussion

The effect of crushing sorbent particles for reducing sample size and thus the duration of sorbent testing was evaluated by comparing available adsorption capacity measurements made with uncrushed particles. Conducting these tests with ~1.4 g of uncrushed sorbent is not trivial because they take up to a week at contaminant concentrations ranging from 20-50 ppm. These tests take even longer when the contaminant concentrations are ~5 ppm. The complexity lies in delivering a constant humid contaminant concentration at a constant flow rate for >150 hrs and using analytical instrumentation to measure contaminant and water vapor concentrations that will not drift significantly during the test duration. These comparisons were made with untreated and impregnated GACs challenged with humid ~20 ppm ethanol and ~50 ppm NH_3, respectively. The untreated GACs remove ethanol via physisorption, while the impregnated GACs remove NH_3 via chemisorption. This approach was used because in spacecraft air revitalization control architectures, both ethanol and NH_3 are present, albeit at lower concentrations, and an impregnated GAC is exposed to both contaminants simultaneously.

5.3.1 Impregnated GACs

The adsorptive capacities for NH_3 measured in impregnated GACs are shown in Table 3. Generally, the adsorptive capacities in crushed sorbents were higher (126% in Ammonasorb II, 262% in Chemsorb 1425, and 140% in Chemsorb 1410) than in uncrushed sorbents when measured at high flow rates (i.e. 1,300 ml min^{-1}). Another difference was that increasing flow rate led to higher capacities in the crushed sorbents while increased flow rate reduced capacity in the uncrushed sorbents. The reason for decreased capacity with increasing flow rate is decreased contact time between NH_3 and the impregnated acid (Schaefer, 99; Amid et al., 2019; Vohra, 2020). This reduction in capacity was also observed in uncrushed sorbents (e.g. Ammonasorb II measurements by Amid et al., and in Chemsorb 1410).

Table 3. Effect of Particle Size on Sorbent Capacity, GHSV, and Linear Velocity of Impregnated GAC.

Sorbent	Particles	(ml min^{-1}) Flow Rate	(ppm) [NH_3]	(mg g^{-1}) Capacity	(hr^{-1}) GHSV	(m s^{-1}) Velocity
Ammonasorb II	Uncrushed (dry)[7]	498	50.0	30.0	199,136	0.26
	Uncrushed (dry)[7]	250	50.0	65.3	100,000	0.13
	Uncrushed	400	51.4	29.5	7,459	0.05
	Crushed	440	45.1	29.1	123,579	0.58
	Crushed	1,300	49.7	37.4	365,120	1.58
Chemsorb 1425	Uncrushed	1,250	48.0	23.1	23,309	0.16
	Crushed	600	49.0	51.7	168,517	0.80
	Crushed	1,300	50.6	60.5	365,120	1.72
Chemsorb 1410	Uncrushed	425	49.4	24.7	7,925	0.06
	Uncrushed	1,350	51.7	20.8	25,174	0.18
	Uncrushed	1,950	53.7	18.1	36,363	0.26
	Crushed	1,300	52.9	29.1	365,120	1.72

5.3.2 Untreated GACs

The adsorptive capacities for ethanol measured in untreated GACs are shown in Table 4. The treated GACs behaved similarly to the impregnated GACs, whereby crushing resulted in higher capacities of adsorption. These observations contradict the notion that in untreated GACs, a higher GHSV implies that the contact time between the VOC in the flow and the surface of the sorbent is decreased, that reduces the mass transfer coefficient and a lower capacity is expected (Vohra et al., 2020).

Table 4. Effect of Particle Size on Sorbent Capacity, GHSV, and Linear Velocity of Untreated GAC.

Sorbent	Particles	(ml min^{-1}) Flow Rate	(ppm) [Ethanol]	(mg g^{-1}) Capacity	(hr^{-1}) GHSV	(m s^{-1}) Velocity
Chemsorb 1000	Uncrushed	1,100	21.0	14.6	20,512	0.14
	Crushed	1,100	20.3	33.1	308,948	1.46
Norit GCA 48	Uncrushed	1,275	19.6	20.3	23,776	0.17
	Crushed	450	19.2	26.2	126,388	0.60
	Crushed	1,100	17.9	23.5	308,948	1.46

5.4 Conclusions

The results in Tables 3 and 4 show that the crushed sorbents were tested with an L/D = 4, lower packing density, and a much larger GHSV (~16X) than the uncrushed sorbent. They also suggest that crushing probably 'opens up' additional surface area for VOC removal that is not available in the uncrushed sorbents and may affect kinetics of adsorption in a flow through method where mass transfer coefficients matter (Monje et al., 2021).

The uncrushed observations at different flow rates with Chemsorb 1410 indicate that increased GHSV may reduce capacity due to lower mass transfer, which is a different mechanism from what is observed with crushed sorbents. A potential cause for the observed results is that the crushed sorbents were dried at 100 °C for two hours while the uncrushed sorbents were dried at 23 °C for three hours. Data for Ammonasorb II shows that drying at higher temperatures leads to increased capacities vs unbaked sorbent due to removal of moisture within the sorbent (Amid et al., 2017).

The results presented here suggest that using crushed sorbents to reduce the duration of adsorptive capacity measurements at low concentrations may introduce biasing due to increased surface area that is not normally available for adsorption.

5.5 Future Work

This study shows that crushing the sorbents may be artificially increasing the surface area available for sorbate removal compared to uncrushed sorbents. The work of Amid et al. (2017) suggests that small particles can be used directly without crushing, even at L/D ratios lower than two. Future comparisons between crushed and uncrushed sorbents should be made at similar packing densities and GHSV to minimize differences in sorbent geometry. These modifications in sorbent geometry should be explored at a suitable range of flow velocities so that the expected decrease in adsorptive capacities as flow rate increased should be observed. The effect of drying temperature (100 °C for crushed and 23 °C for uncrushed sorbents in this study) must also be explored because drying temperature was found to affect adsorptive capacity (Amid et al., 2017). These improvements are needed for this rapid method to be useful in future comparisons of future candidate sorbents

References

Aguilera , T., and Perry, J.L. 2011. Root cause assessment of pressure drop rise of a packed bed of lithium hydroxide in the International Space Station Trace Contaminant Control System. SAE Int. J. Aerospace 4:291-298.

Ansi/AHRAE Standard 170-2008. Ventilation of Health Care Facilities. 2008.

Amid, H., Maze, B., Flickinger, M. C., and Pourdeyhimi, B. Dynamic adsorption of ammonia: apparatus, testing conditions, and adsorption capacities. Meas. Sci. Technol. V28:1-7, 2017.

Brunauer, S., Emmett, P. H. and Teller, E. Adsorption of gases in multimolecular layers. Journal of the American Chemical Society 60:309-19, 1938.

Carter, L., Perry, J.L., Kayatin, M.J., Wilson, M., Gentry, G.J., Bowman, E., Monje, O., Rector, T., and Steele, J. 2015. Process Development for Removal of Siloxanes from ISS Atmosphere. ICES 2015-074.

Carter, L., Kayatin M., Perry J., Agui J., Green R., Gentry G., Bowman E., Wilson M, Rector T. 2016. Design and Delivery of a Filter for Removal of Siloxanes from the ISS Atmosphere. ICES-2016-15.

Erkey, C. Chapter 4 - Thermodynamics and Dynamics of Adsorption of Metal Complexes on Surfaces from Supercritical Solutions. In Supercritical Fluid Science and Technology, Volume 1, Pages 41-77, 2011.

Finn, J.R., Monje, O., Kayatin, M. H., and Perry, J. L. 2020. Effect of Flow Velocity and VOCs on Ammonia Adsorption in Acid Impregnated Activated Carbon Sorbents. ICES-2020-393.

Leban, M.I., Kawasaki, E.H., Connie, G.P. 1991. Performance characterization of activated carbon and oxidation catalyst for gaseous trace contaminant control. SAE 911548.

Lewis, W.K., Gilliland, E.R., Chertow, B., Cadoganz, W.P. 1950. Pure gas isotherms. *Ind. Eng. Chem.* 42:1326-1332.

Luna, B., Podolske J., Ehresmann D., Howard J., Salas L.J., Mulloth L., and J.L. Perry. 2008. Evaluation of Commercial Off-the-Shelf Ammonia Sorbents and Carbon Monoxide Oxidation Catalysts. ICES 2008-01-2097.

Luna, B., Somi, G., Winchester, J. P., Grose, J., Mulloth, L., and Perry, J. L., 2010. Evaluation of Commercial Off-the-Shelf Sorbents and Catalysts for Control of Ammonia and Carbon Monoxide," AIAA 2010-6062.

Monje, O., and Finn, J.R. 2019. Testbed for Characterizing the Adsorptive Capacities of Pleated Panel Filters. ICES-2019-266.

Monje, O., Kayatin, M. H., and Perry, J. L. 2018. Characterization of Sorbents for Controlling Ammonia in Spacecraft Cabin Air. ICES-2018-253.

Monje O., J Surma. 2017. Polanyi evaluation of adsorptive capacities of commercial activated carbons, ICES-2017-291.

Monje, O., Surma, J.M., Kayatin, M.J., and Perry, J.L. 2016. Measuring Polanyi Potentials for Chemsorb® 1000 and Chemsorb® 3800. ICES 2016-321.

Monje, O. 2012. Solar Simulator Tesbed: Demonstration of a Solar Photocatalytic Oxidation System. Paper AIAA-2012-3426.

Nolek, S.D., and Monje, O. 2011. Regenerable VOC Control System (RVCS) for Characterizing properties of Sorbents used in Separation Technologies. Chemistry of Petroleum and Emerging Technologies, Petroleum Preprints Volume 56 #1, p95. ACS National Meeting, Anaheim, Ca, 2011.

Monje O., Nolek, S.D., and R.M. Wheeler. 2011. Ammonia Offgassing from SA9T. Paper AIAA-2011-5101.

Monje O., B. Brosnan, A. Flanagan, and R.M. Wheeler. 2010a. Characterizing the adsorptive capacity of SA9T using simulated spacecraft gas streams. Paper AIAA-2010-6063.

Monje O, B. Brosnan, A. Flanagan, and R.M. Wheeler. 2010b. Characterizing the dynamic performance of SA9T. Paper AIAA-2010-6269.

Monje O., P.R. Kenny, N.A. Sexson, B. Brosnan, and R.M. Wheeler. 2009. Subscale testbed for characterizing dynamic performance of regenerable adsorbents for filtering trace contaminants from cabin atmospheres. SAE Paper 2009-01-2526.

Monje O., J.C. Stutte, A. Flanagan, D.C. Lewis, and R.M. Wheeler. 2008. Characterizing the influence of temperature and vacuum quality on the desorption kinetics of commercial adsorbents. SAE Paper 2008-01-2096.

Monje O., J. Catechis, and J. Sager. 2007a. Effects of relative humidity on the adsorption of dichloromethane by Carbosieve SIII. SAE Paper 2007-01-3249.

Monje O., I. Eraso, C. O'Keeffe, and R.M. Wheeler. 2007b. Testbed for determining the filtering capacities of COTS adsorbents. SAE Paper 2007-01-3137.

Nirmalakhandan, N.N., Speece, R.E. 1993. Prediction of activated carbon adsorption capacities for organic vapors using quantitative structure-activity relationship methods. Environ. Sci. Technol. 27:1512–1516

Brown, R.C. 1995. Review: Activated Carbon Filters in Respiratory Protective Equipment, International Journal of Occupational Safety and Ergonomics, 1:330-373.

Perry, J.L., Sargusingh, M.J., and Toomarian, N. 2016a. Functional interface considerations within and Exploration Life Support System architecture. ICES-2016-90.

Perry, J.L., Sargusingh, M.J., and Toomarian, N. 2016b. Guiding requirements for designing life support system architectures for crewed exploration missions beyond low-Earth orbit. AAIA 2016-5641.

Perry, J.L., and M.J. Kayatin. 2015. Trace Contaminant Control Design Considerations for Enabling Exploration Missions. ICES 2015-108.

Perry, J.L. 2009. A Design Basis for Spacecraft Cabin Trace Contaminant Control, SAE 2009-01-2592.

Perry, J.L. 1998. Elements of Spacecraft Cabin Air Quality Control Design. NASA/TP-1998-207978, NASA Marshall Space Flight Center, Huntsville, Alabama, 1998, pp. 51-56, 140-144.

Perry, J.L. 1994. Trace Contaminant Control Simulation Computer Program—Version 8.1, NASA TM-108457, NASA Marshall Space Flight Center, Huntsville, Alabama, 1994, pp. 2, 19-24.

Richards, J., Koss, L., and Monje, O. An Automated Test Bed for Rapid Characterization of Sorbent Materials for Siloxane Removal in Contaminated Airstreams. ICES-2015-298.

Robell, A.J., Arnold, C.R., Wheeler, A., Kersels, G.J., and Merrill, R.P. 1970. Trace Contaminant Adsorption and Sorbent Regeneration, NASA CR-1582, pp. 32-45.

Schaefer, M. Measurement of Adsorption-Isotherms by Means of Gas Chromatography. Thesis M.S. Chemical Engineering, University of Wisconsin-Madison, 1991.

Tyn, M.T., and W. F. Calus, 1975. Estimating Liquid Molal Volume, Processing, 21:16-17.

Vohra, M. Treatment of Gaseous Ammonia Emissions Using Date Palm Pits Based Granular Activated Carbon. Int. J. Environ. Res. Public Health V17, 1519, 2020; doi:10.3390/ijerph17051519.

Vohra, M., Al-Suwaiyan, M., and Hussaini, M. Gas Phase Toluene Adsorption Using Date Palm-Tree Branches Based Activated Carbon. Int. J. Environ. Res. Public Health V17, 9287, 2020; doi:10.3390/ijerph17249287.