

An Evaluation of Technology to Remove Problematic Organic Compounds from the International Space Station Potable Water

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Since activation of the Water Processor Assembly (WPA) on the International Space Station (ISS) in November of 2008, there have been three events in which the TOC (Total Organic Carbon) in the product water has increased to approximately 3 mg/L and has subsequently recovered. Analysis of the product water in 2010 identified the primary component of the TOC as dimethylsilanediol (DMSD). An investigation into the fate of DMSD in the WPA ultimately determined that replacement of both Multifiltration (MF) Beds is the solution to recovering product water quality. The MF Beds were designed to ensure that ionic breakthrough occurs before organic breakthrough. However, DMSD saturated both MF Beds in the series, requiring removal and replacement of both MF Beds with significant life remaining. Analysis of the MF Beds determined that the adsorbent was not effectively removing DMSD, trimethylsilanol, various polydimethylsiloxanes, or

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dimethylsulfone. Coupled with the fact that the current adsorbent is now obsolete, the authors evaluated various media to identify a replacement adsorbent as well as media with greater capacity for these problematic organic contaminants. This paper provides the results and recommendations of this collaborative study.

Nomenclature

<i>WPA</i>	=	Water Processor Assembly
<i>ISS</i>	=	International Space Station
<i>TOC</i>	=	total organic carbon
<i>DMSD</i>	=	dimethylsilanediol
<i>ECLSS</i>	=	environmental control and life support systems
<i>OGA</i>	=	Oxygen Generation Assembly
<i>ORU</i>	=	Orbital Replacement Unit
<i>MF</i>	=	Multifiltration
<i>PDMS</i>	=	polydimethylsiloxanes
<i>TMS</i>	=	trimethylsilanol
<i>DMSO₂</i>	=	dimethylsulfone
<i>R&R</i>	=	removal and replacement
<i>IX</i>	=	ion exchange
<i>IATCS</i>	=	Internal Active Thermal Control System
<i>PW</i>	=	product water
<i>meq/L</i>	=	milliequivalents per liter
<i>EBCT</i>	=	empty bed contact time
<i>CCAA</i>	=	Common Cabin Air Assembly

I. Introduction

The on-orbit TOC (Total Organic Carbon) levels in the ISS (International Space Station) WPA (Water Processor Assembly) product water have risen significantly and approached water quality limits on three occasions including July 2010, February 2012, and August 2103 as shown in Figure 1. Elevated product water TOC can have an adverse effect on crew health as well as Regenerative ECLSS (Environmental Control and Life Support Systems) including the Oxygen Generation Assembly (OGA) Hydrogen Orbital Replacement Unit (ORU) cell stack. The response to the elevated TOC levels included replacement of ORUs such as WPA Multifiltration (MF) Beds that otherwise may have had significant life remaining.

The constituents that were responsible for the elevated TOC were identified after the fact by ground analyses as primarily DMSD and to a lesser extent polydimethylsiloxanes (PDMS), trimethylsilanol (TMS) and dimethylsulfone (DMSO₂)¹. It was recognized that an enhancement to the WPA, specifically a change to the quantities and/or types of sorbents in the MF Bed to more effectively remove those contaminants, would reduce the risk of elevated TOC. Such a reduction of risk would minimize the premature change-out of MF Bed ORUs and would reduce the risk of adverse impacts on the life of the OGA Hydrogen ORU.

It was further recognized that a potential change to the make-up of the WPA MF Bed would be an opportunity to identify a replacement for the obsolete activated carbon used in the WPA MF bed: Barnebey Cheney 580-26.

Boeing led a cooperative project with NASA, United Technologies Aerospace (UTAS), Umpqua, and Wyle Laboratory to evaluate a redesign of the ISS WPA MF bed. The focus of the multi-company team redesign evaluation was two-fold:

- Identify effective sorbents to remove DMSD, PDMS, TMS and DMSO₂ from WPA process water
- Identify a replacement for the obsolete Barnebey Cheney 580-26 coconut shell activated carbon

The results are detailed in this report including literature review findings, updated ersatz formulation, sorbent test results, and recommendations for further action.

II. Literature Review

The primary objective was to investigate the removal of DMSD, PDMS, TMS and DMSO₂ from the WPA water. Of these compounds, DMSD has proven to be the primary compound detected in the WPA product water aboard ISS. In the past three years, distinct rises in total organic carbon (TOC) of the WPA product water have been linked to elevated DMSD levels. These resultant increases in TOC from the breakthrough of DMSD led to the removal and replacement (R&R) of both MF and the ion exchange (IX) beds within the WPA. Removal of DMSD would mitigate the observed TOC spikes, increase bed life in the WPA, and reduce the chances of DMSD masking other potential organic breakthroughs.

In order to adequately understand DMSD and siloxane behavior in an aqueous environment, a literature review of the current understanding with respect to degradation and removal was conducted. This review investigated both peer-reviewed technical papers as well as industry related data and reports.

A. PDMS Degradation

Significant literature exists pertaining to the degradation of PDMS in the environment. PDMS comes from a variety of sources such as household cleaners, paints and coatings, and personal care products^{2,3,4}. These products are ultimately discharged to wastewater systems, either through normal use or when discarded as refuse. Commonly, PDMS will make its way to the soil either from landfill leachate or land applied sewage sludge. Once PDMS enters the soil, it can readily undergo hydrolysis to smaller water soluble siloxanes, including DMSD, TMS and trimethylsilane. This hydrolysis is catalyzed by the presence of clays such as kaolinite, beidellite and nontronite. Degradation in environmental systems is also influenced by metal contents of the soil and relative humidity⁵. The resultant smaller siloxanes (including DMSD and TMS) have considerably higher solubilities than their parent compounds and are more typically found in the aqueous phase where they will further degrade to H₂O, CO₂ and SiO₂ in the environment^{4,6,7}.

B. Siloxane Removal

Much of the literature pertaining to siloxane removal focuses on remediation of air streams. Due to PDMS volatility, it has a propensity to partition into the atmosphere. This can be problematic for facilities that treat biogas derived from digestion of organic matter and for sewage treatment plants in general. In addition to methane, biogas contains a variety of volatile compounds, including PDMS⁸, which is problematic due to the formation of SiO₂ during the combustion process for energy recovery. The SiO₂ has a propensity to adhere to metallic or catalyst surfaces, which decreases the efficiency of the biogas combustion process³. Many techniques have been employed to remove PDMS from the biogas streams. The most successful methods have been the use of porous media such as activated carbon, silica gel, zeolites and carbon cloth to remove influent siloxanes from biogas streams prior to combustion. These removal techniques work well in these applications and are becoming common at many biogas facilities.

While means to remove siloxanes from air streams are abundant in the literature, methods for removal from water are comparatively scarce. This lack of information can be attributed to the nature of PDMS. PDMS typically have very low solubility in water but relatively higher vapor pressures, which leads to siloxanes partitioning into the atmosphere. Hydrolysis results in smaller siloxanes (i.e. DMSD, TMS, etc.) that are considerably more water soluble and have been observed to bond weakly to organic and humic material⁶. One reference identified a synthetic adsorbent that in laboratory testing removed DMSD from the aqueous phase⁹. To further validate this removal technique, Wyle Laboratory conducted a feasibility study using the identified adsorbent. In this study, ENV+ resin, a

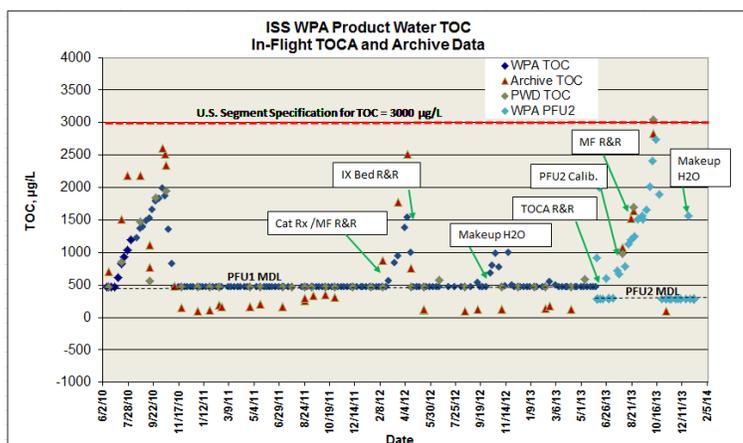


Figure 1. ISS WPA product water TOC from in-flight TOC analyzer (TOCA) and archive data.

hydroxylated polystyrene-divinylbenzene copolymer, was evaluated for DMSD removal. It was found that the ENV+ had an approximate capacity of 0.3 mg-DMSD/g-Resin¹⁰. While this is relatively low, the ENV+ did perform much better than other adsorbents tested during the evaluation. The structure of the ENV+ is a highly hydroxylated polymer chain, which was considered a desirable property when choosing which adsorbents to include in the isotherm evaluations.

C. Microbial Degradation of Siloxanes

A few studies have been performed to determine the biodegradability of PDMS. Pure and mixed cultures of *Pseudomonas fluorescens* and *Pseudomonas putida* were found to biodegrade silicone oils under aerobic conditions¹¹. The microbial degradation of octamethylcyclotetrasiloxane to DMSD occurred under anaerobic conditions in composted sewage sludge as compared to no DMSD formation in sterilized control samples¹². Approximately 3% of the octamethylcyclotetrasiloxane was converted to DMSD anaerobically in 100 days of incubation¹².

Dimethylsilanediol can biodegrade in soils to CO₂ and inorganic silicate¹³. In all tested soils, [¹⁴C] labeled dimethylsilanediol was biodegraded to ¹⁴CO₂¹³. A method was developed for studying biodegradation of DMSD in the presence of another substrate such as 2-propanol in liquid culture. A combination of a fungus, *Fusarium oxysporum* Schlechtendahl, and a bacterium, an *Arthrobacter* species, were able to produce ¹⁴CO₂ from [¹⁴C] DMSD¹³. The *Arthrobacter* sp. was also able to grow on dimethylsulfone as its primary carbon source¹³.

D. Vendor Inquiries

The literature review did not yield significant results in identifying adsorbents that would successfully remove siloxane compounds from the aqueous phase. The most promising adsorbent was the Biotage Isolute ENV+, which was discussed above. Contact was initiated with Biotage to determine if adsorbent material larger than the commercially available 90 μm could be produced for further testing. The nominal size of 90 μm is unacceptable for use in a packed bed configuration. Initially, Biotage was interested in producing larger media. However, after multiple attempts to secure larger media sizes, Biotage indicated inability to provide the larger media size. Additional inquiries were made to Sigma-Aldrich and Norit Carbon, both of whom had little to no advice or expertise in removing siloxanes from water. Norit Carbon did offer support in the area of siloxane removal from air streams.

III. Siloxane Removal Evaluation

A. Methodology

To determine the removal efficiency of DMSD, PDMS and TMS, a series of adsorption isotherms and sub-scale column testing was proposed. The adsorption isotherm testing would encompass a single point isotherm to screen candidate adsorbents, followed by a multiple point adsorption isotherm to evaluate the capacity of down selected adsorbents. Once adsorbents with sufficient capacity were identified, sub-scale column testing would be conducted to determine breakthrough, pressure drop and fine generation associated with the new material. While the plan to evaluate the removal of the respective constituents was concise, no adsorbents with sufficient capacity were identified during the isotherm phase of the testing. Due to the lack of promising adsorbents, only multiple point isotherms were conducted during this evaluation.

B. DMSD Removal

The first phase of the evaluation to find an adsorbent to remove DMSD was to characterize the existing MF Bed constituents for their respective DMSD removal efficiency. The MF Bed consists of four different media types: (1) 580-26 activated carbon; (2) IRN-150 Mixed Bed Ion Exchange Resin; (3) IRA-67 Anion Exchange Resin; and (4) IRN-77 Cation Exchange Resin (in addition to IRN-78 Anion Exchange resin – the two make up IRN-150). The nature of DMSD elution from the MF beds on-orbit gave some indication that it was weakly bound to the bed materials. The isotherm testing consisted of a DMSD challenge of 40 mg/L stock solution that was placed in 45 mL centrifuge vials with varying aliquots of adsorbent material. The isotherm samples were then mixed for 24 hours to come to equilibrium and then sampled for DMSD. The data from these tests indicated that the IRN-150 mixed bed ion exchange resin in the MF bed was the only material to have appreciable affinity for the DMSD. The 580-26 activated carbon and the IRA-67 anion resin showed little to no affinity for DMSD removal (Figure 2). To better understand which portion of the IRN-150 resin was removing the DMSD, each individual component was evaluated with additional isotherms. The results showed that IRN-78, the anion portion of the mixed bed, was responsible for all of the DMSD removal. This observation is further validated by the behavior of the DI bed in the WPA, which is

comprised primarily of IRA-78. The DI bed also removed DMSD on orbit and exhibited a similar TOC trend that was observed prior to the R&R of MF Bed S/N 0003. In addition to determining the adsorption affinity for each MF bed material, the data also gives a reference point to help in determining what levels of DMSD removal other adsorbents need to achieve.

The first step in identifying what types of materials would remove DMSD from solution was to conduct single point isotherms for a variety of adsorbents. This screening process is advantageous as it allows for a quick assessment of capacity and the identification of adsorbent properties that lend themselves to successful DMSD removal. The materials tested in this evaluation included: Norit RO 0.8 (extruded activated carbon); Optipore SD-2 (polymeric); Optipore L-493 (polymeric); Dianon Sepabead SP207 (polymeric material with bromide groups); Amberlite XAD (porous phenolic); activated aluminum and calcium cation exchange resin); SP850 (porous methacrylate); XAD 7HP (porous acrylic); HP2MG (methacrylate); silica gel; molecular sieves (aluminosilicates); Ambersorb 572 (synthetic carbon); Schunk 4652 (graphite based); Carboxen 1016, 569, 1021, 1000, 1018, and 1012 (various pore sizes); Carbosieve S-III; Carbosieve G; PoroPak P (polymer based); and PoroPak PS (polymer based).

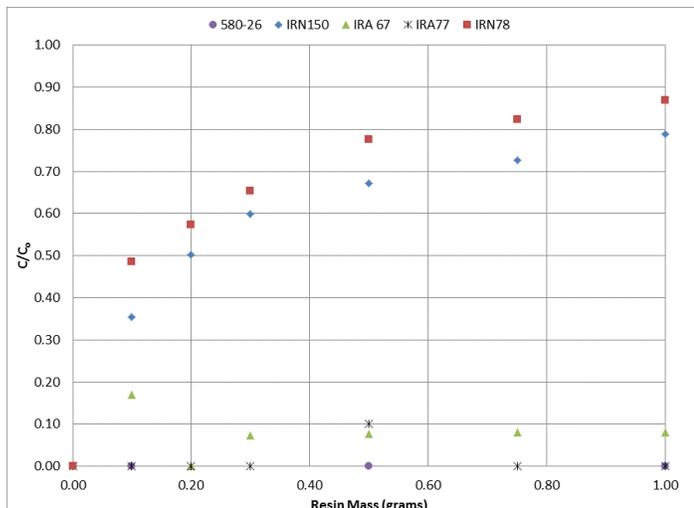


Figure 2. Comparative adsorption isotherms of the existing WPA adsorbent media.

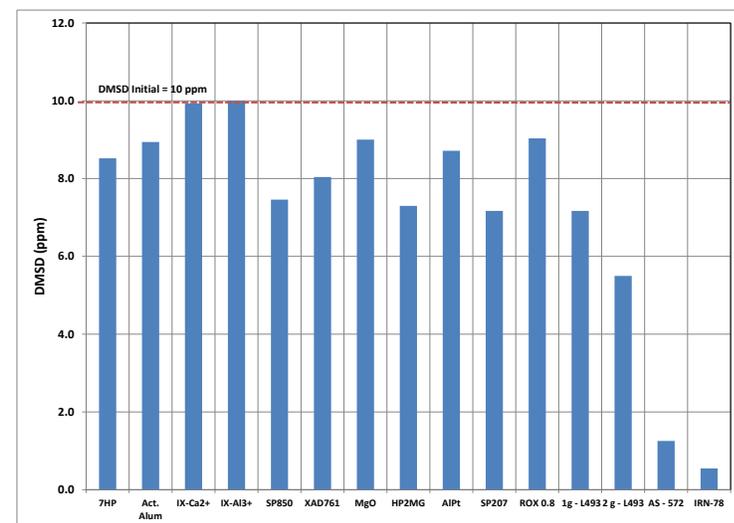


Figure 3. Initial adsorbent screening using single point isotherm to evaluate DMSD removal.

adsorbents turned to identifying those that had similar properties to the Ambersorb media. A direct replacement for Ambersorb marketed by the chemical company Sigma-Aldrich is the Carboxen line of synthetic adsorbents. The Carbonex adsorbents are carbon based synthetic adsorbents used in chromatography and solid phase extraction techniques. A variety of adsorbents exist in the Carboxen line, some of which had similar properties to the Ambersorb 572. To fully evaluate these adsorbents, eight were selected that possessed similar or near similar pore size distribution. Another adsorbent that was discovered by the team was Schunk FU 4652. Schunk FU 4652 is graphite based activated carbon and was initially proposed to Boeing for removal of contaminants from air. The Schunk FU 4652 media has porosity characteristics similar to that of Ambersorb 572 and also has a grain size of 600 μm , which is advantageous with regards to pressure drop across an MF bed. In addition to the Carboxen and Schunk

A majority of the materials had been tested in previous programs for trace contaminants removal in aqueous environments and had shown varying degrees of success depending on the challenge compound. The results from this study showed that a majority of the adsorbents have very low affinity for DMSD (Figure 3). Low level removal is observed in some instances, but in most cases a removal efficiency of less than 20% was observed. The only candidate that showed any promising removal potential (other than ion exchange resins) was Ambersorb 572 (AS-572). The Ambersorb material is a synthetic activated carbon that has a unique pore size distribution and high surface area. This material is also used to remove the active biocide and related breakdown products from the Internal Active Thermal Control System (IATCS) aboard ISS. Unfortunately, the Ambersorb was discontinued as a Rohm and Hass product in 2010.

With the success of the Ambersorb 572 in removing DMSD, the search for

FU 4652 adsorbents, two silica gels and two silica based polymer adsorbents (PoroPak) were also tested. The selected adsorbents were first evaluated with the single point isotherm evaluation using a DMSD feed concentration of 22 mg/L (Figure 4). The Wyle DMSD analysis is direct determination of DMSD, while UTAS analyses measured the concentration of Si to determine DMSD concentration.

From the single point adsorption isotherms it is observed that most of the selected adsorbents had very low affinities for DMSD. Two candidates showed moderate affinity for DMSD, Carboxen (C1000) and Schunk FU 4652. One issue surrounding the Carboxen 1000 is that it only comes in a limited size range, and the largest off the shelf grain size is 180 μm . This grain size would present significant problems with respect to pressure drop in the MF beds. Due to this and the Schunk FU 4652 higher capacity for DMSD, Carboxen 1000 was not evaluated further.

To further investigate the Schunk FU 4652 media's ability to remove DMSD, comparative multi point isotherms were conducted for Schunk FU 4652 and IRA78 (DI bed Anion Resin). In this study, IRA78 is seen as a baseline comparative media as it has the highest capacity of all MF bed adsorbents for DMSD. Additionally, any adsorbent would need to have a similar or higher capacity than IRA78 to be considered a viable candidate for use in the MF bed. The isotherm method was similar to the method used in the evaluation of the current MF bed adsorbents for DMSD capacity. The results from the isotherm demonstrated that Schunk FU 4652 had less affinity than IRA78 for DMSD (Figure 5). The isotherm data was then used to determine an approximate capacity for each adsorbent, with IRA78 = 3.0 mg-DMSD/g-R and Schunk FU 4652 = 0.76 mg-DMSD/g-R. These values indicate that the IRA78 has significantly more capacity for DMSD than the Schunk FU 4652 adsorbent. The IRA78 is an anion exchange resin, which gives it a negative charge and enhances its ability to remove the DMSD. The Schunk FU 4652 is not

chemically functionalized; therefore it has no very little polarity and relies on physical adsorption to remove the DMSD from solution.

The results from the comparative isotherm study showed that the leading adsorbent, Schunk FU 4652, did have capacity for DMSD, but it was significantly less than that exhibited by the current ion exchange resin IRA 78. One advantage of the Schunk FU 4652 media is that the adsorption of DMSD is essentially irreversible, while the ion exchange resin will elute DMSD in the presence of more strongly bound anions.

In order to understand the system impacts associated with implementing an adsorbent to remove DMSD from the WPA product water, an analysis was conducted evaluating capacity and adsorbent volume.

Each tube in the MF bed

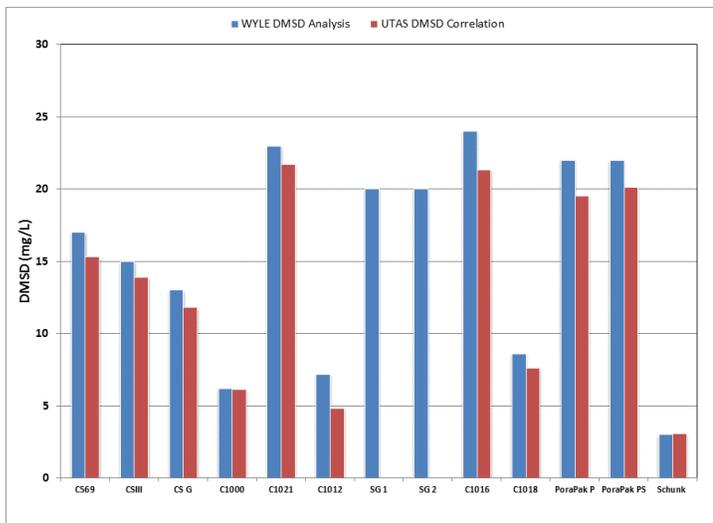


Figure 4. Single point isotherm data for various adsorbents tested for DMSD removal.

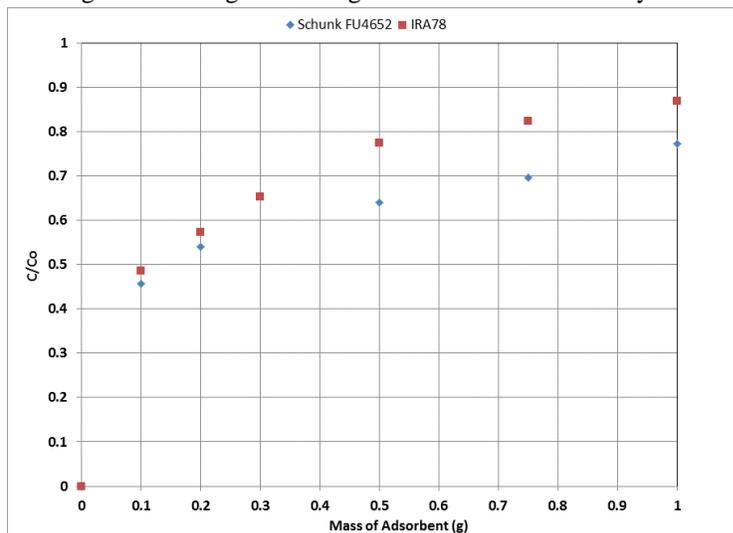


Figure 5. Comparative adsorption isotherm of Schunk FU4652 and IRA78 ion exchange resin.

contains approximately 4.0 L of adsorbent volume, which gives an overall volume of 40.0 L. Considering a worst case scenario, where the Schunk FU 4652 volume would occupy all 40.0 L of the MF bed, it is observed that the resultant volume of product water throughput would be approximately 1500 lbs. However, by using one entire MF bed for removal of DMSD using Schunk FU 4652, approximately 5000 lbs. less product water could be produced. This is based on the capacity that has been observed for DMSD by the current adsorbents in the MF bed. In order to make a significant impact to additional MF bed throughput, the selected adsorbent would need to possess at least an order of magnitude greater capacity than Schunk FU 4652 currently exhibits.

C. PDMS Removal

An evaluation was also conducted to characterize the removal efficiency of the cyclic siloxane octamethylcyclotetrasiloxane. This siloxane was selected from the four siloxanes present in the ersatz due to its perceived higher solubility in water. Single point isotherms were conducted using a variety of adsorbent media.

Samples were then sent to Wyle Laboratories for analysis. The results showed that no detectable octamethylcyclotetrasiloxane was present in any of the samples, including the stock challenge solution. Additionally, the silicon analysis from each sample varied widely. It had been suspected that the analysis of these samples would be problematic due to the limited solubility of the siloxane (~300 µg/L) and the inability to directly analyze for the parent compound. Further attempts to characterize the PDMS removal were abandoned due to the difficulty in accurately monitoring the siloxane in solution.

D. TMS Removal

TMS is another subsequent breakdown product from PDMS degradation. To determine TMS removal affinity, the leading adsorbents from the DMSD isotherm testing were used in a single point isotherm test (Figure 7). The results show that TMS can be removed effectively by the Schunk FU 4652 media, as well as other selected adsorbents.

IV. DMSO₂ Removal

DMSO₂ is a ubiquitous component of the water sent into the WPA that is not well removed by either the MF Beds or the Catalytic Reactor in the WPA. It is primarily a component of the urine distillate produced by the Urine Processor Assembly¹⁴. Although DMSO₂ itself is not generally a hazardous material, it is present at low concentration (median concentration is 120 µg/L) in the product water (PW) and contributes to the overall TOC level. DMSO₂ is problematic in that it concentrates in the OGA recirculation loop where it has been measured at concentrations as high as 49 mg/L, which is over 400 times the median concentration measured in the WPA product water. The effect of this compound on the OGA is unknown, but concerns have been raised about the possibility of electrochemical or microbial breakdown to produce sulfur compounds that might harm the cell stack. Identification of a sorbent to remove DMSO₂ is necessary whether that sorbent is used in the WPA or in the OGA itself.

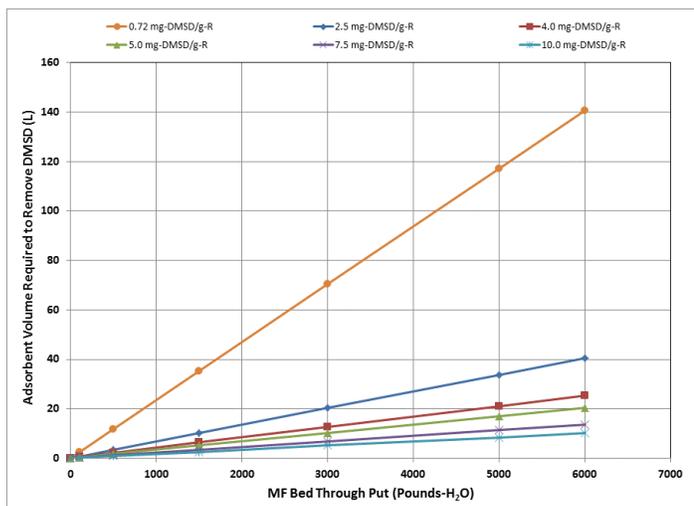


Figure 6. System evaluation to determine additional MF Bed throughput corresponding to Schunk FU4652 DMSD capacity and theoretical adsorbent capacities.

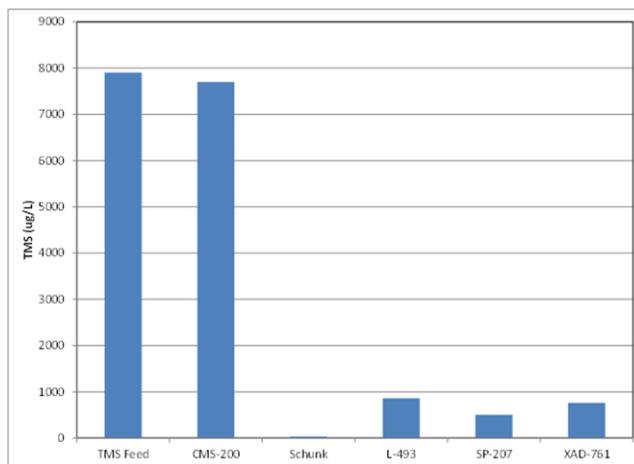


Figure 7. TMS removal efficiency with select adsorbents.

A. DMSO₂ Screening Experimental Methods

The same group of sorbents and resins that were tested with DMSD were tested with DMSO₂. Initial tests used a 12 mg/L solution of DMSO₂ in water, although the median PW concentration is only 120 µg/L. The use of 12 mg/L DMSO₂ allowed the use of a TOC analyzer, which reduced analysis time. For the initial screening tests, each sorbent or resin was first washed with water several times until the TOC measured in the wash water was less than 1 mg/L. Dry masses of 0, 1, and 2 grams of each sorbent were exposed to 40 mL of an aqueous solution of 12 mg/LDMSO₂ on a rotary shaker overnight. After 22 hours, the TOC in each solution was measured.

B. DMSO₂ Screening Results

Data are shown in Figure 8. It is clear from the initial screening that the most effective sorbent is the Schunk FU 4652. Norit Darco, Norit RO, Optipore L493, and Optipore SD-2 also performed well. Based on these results, these five sorbents were selected for low level testing.

C. DMSO₂ Low Level Experimental Methods

Dry masses of 0, 0.5, and 1 g of each of the five chosen adsorbents including Schunk FU 4652, Norit Darco, Norit RO, Optipore L493, and Optipore SD-2 were exposed to 40 mL of a 1.2 mg/L (1200 µg/L) solution of DMSO₂ on a rotary shaker overnight. After 22 hours, the remaining DMSO₂ concentration in each solution was measured.

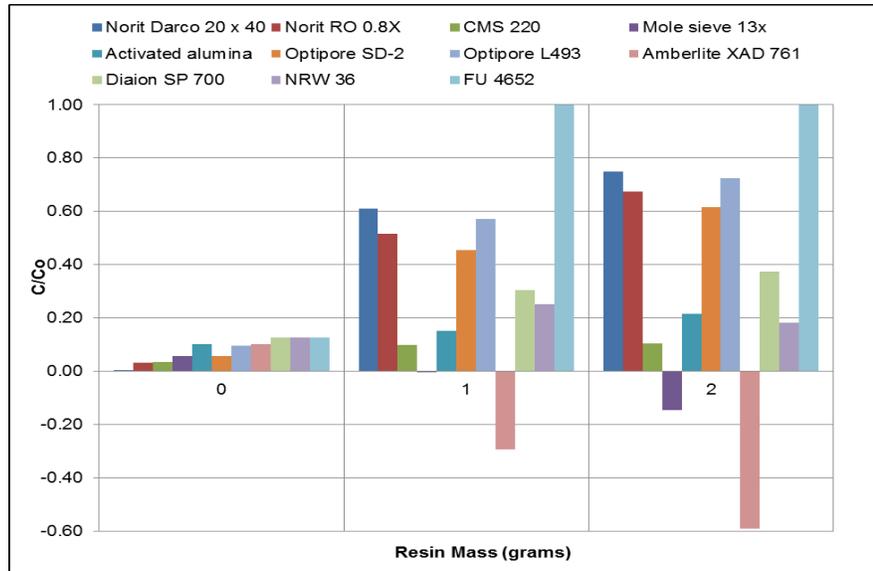


Figure 8. Removal efficiency for initial screening tests of sorbents (by dry mass) with 40 mL of 12 mg/L DMSO₂.

D. DMSO₂ Low Level Results

The results are provided in Figure 9. It is clear from the low concentration tests that the most effective sorbent for DMSO₂ removal is Schunk FU 4652.

E. DMSO₂ High Concentration Testing

Tests described above were aimed at low concentrations of DMSO₂ similar to those measured in Product Water on the ISS. However, concentrations in the OGA recirculation loop are much higher because the DMSO₂ is concentrated as the water is used for oxygen generation. One final set of tests was run to measure the removal efficiency at higher concentrations to support estimates for the amount of resin that would be needed in the OGA recirculation loop. Removal efficiency at concentrations as high as 600 mg/L DMSO₂ is over 80%. Data and results are shown in Table 1.

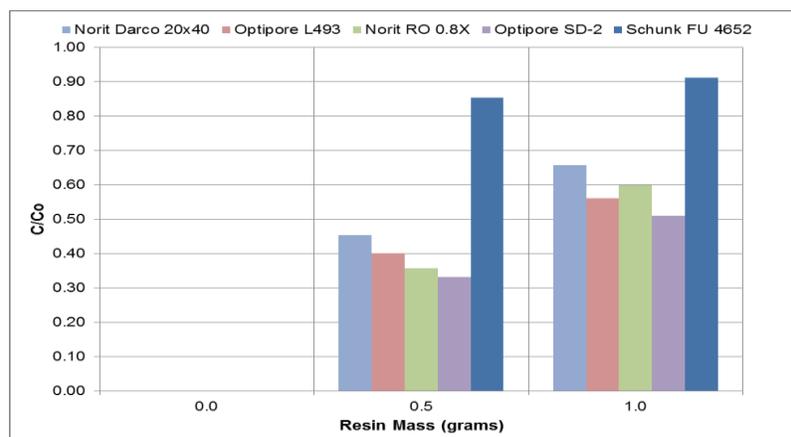


Figure 9. Removal efficiency of resins at low concentration (1200 µg/L of DMSO₂).

DMSO ₂ Concentration in Test Solution (mg/L)	Resin Mass (g)	Removal Efficiency	Measurement Method
120	1	0.81	TOC
600	1	0.89	TOC
12	1	1.00	TOC
12	2	1.00	TOC
1.2	0.5	0.85	Extraction
1.2	1	0.91	Extraction

Table 1. High Concentration DMSO₂ Test Results for Schunk FU 4652.

V. ISS Wastewater Ersatz

An ersatz solution was developed in anticipation of sorbent challenge testing with candidate adsorbents for DMSD, and to a lesser extent PDMS, TMS and DMSO₂ removal. Furthermore, it was anticipated that an ersatz solution would be needed for later phase testing of replacement candidates for the Barnebey Cheney 580-26. A total of 11 ISS wastewater samples from 11/17/2009 – 11/09/2011 were used as a basis for the ersatz.

A. Ersatz Constituent Ground Rules

Ersatz constituents included specific organic compounds from ISS wastewater with mean concentrations greater than 100 µg/L. The volatile organic compounds included methanol, ethanol, 1-propanol, 2-propanol, and acetone. The ersatz also contained other specific organic compounds such as urea and caprolactam. Organics were grouped structurally and included one compound per group. Alcohols were subdivided into aliphatic, aromatic and branched aliphatic forms. The ersatz targeted the mean concentration of TOC in the 11 wastewater samples. The difference between the mean TOC and the sum of the characterized organic means were made up by a ratio increase applied to each characterized organic (excluding all volatile organics and siloxanes). All volatile organics and siloxanes were added at their observed mean concentrations (unless restricted by solubility).

The inorganic ersatz favored the selection of the higher concentration compounds including specific inorganic constituents that had concentration greater than 100 µg/L mean concentration. The ersatz mixture included an inorganic from each of the ion exchange resin affinity groups. The inorganic ersatz also included carbonates and bicarbonates. In order to balance pH and counter ion concentrations and mean conductivity, excess concentrations of specific inorganics were utilized. The inorganic concentrations were converted to meq/L for an ionic balance check and the pH was adjusted with bicarbonate and organic acids as needed.

B. Ersatz Constituents

A number of solution iterations were necessary based on solubility, trade-offs with target concentrations, chemical availability, and stability to develop a verified stable ersatz. Six separate solutions are made up as stock solutions for ersatz make-up:

- 1) Inorganic Concentrate (4 compounds) – a 100X concentrate
- 2) Freely Soluble Organic Concentrate (14 compounds) – a 100X concentrate
- 3) Acetate Concentrate (2 compounds) – a 100X concentrate
- 4) Less Soluble Organics (6 compounds) – target concentration
- 5) Dimethylsilanediol (1 compound) – 200 mg/L start solution
- 6) Siloxanes (4 compounds) – 1 mg (solid) or 1 uL (liquid) of each

The final resultant ersatz solution is shown in Table 2.

Chemical	Target Conc. (mg/L)	Chemical	Target Conc. (mg/L)
Benzyl alcohol	14.3	Ethanol	13.3
Propylene glycol	17.6	2-propanol	0.2
Dimethylsilanediol	21.6	Methanol	4.4
Diethylphthalate	2.9	1-propanol	0.2
N,N-Dimethylformamide	1.4	Decamethylcyclopentane- siloxane	to solubility
Benzoic acid	3.0	Dodecamethylcyclohexa- siloxane	to solubility
Acetate (as acetic acid)	13.5	Octamethylcyclotetra- siloxane	to solubility
Urea	0.6	Hexamethylcyclotri- Siloxane	to solubility
Methyl sulfone	0.2	Potassium (as potassium iodide)	0.4
Trimethylsilanol	0.2	Sodium (as sodium fluoride)	0.1
Caprolactam	1.1	Ammonium (as ammonium bicarbonate)	7.0
4-ethylmorpholine	0.2	Calcium (as calcium sulfate)	1.3
2-ethoxyethanol	1.2	Nickel (as nickel acetate tetrahydrate)	1.4
Benzothiazole	0.2	Zinc (as zinc acetate)	7.5
2-ethyl-1-hexanol	0.4	Fluoride (as sodium fluoride)	0.4
1-methyl-2-pyrrolidinone	0.8	Chloride (as potassium chloride)	0.2
2-(2- butoxyethoxy)ethanol	2.2	Bicarbonate (as ammonium bicarbonate)	22.4
Acetone	2.7	Iodide (as potassium iodide)	0.2

Table 2. Final ersatz for activated carbon replacement testing.

VI. Activated Carbon Replacement

Single contaminant equilibrium testing with phenol was used as a quick screening method for activated carbon selection. Umpqua Research Co. performed equilibrium tests on every batch of prepared sorbent used in the MF bed prior to loading to verify that the sorbent met historic loading capacity for phenol. In an effort to quickly eliminate poor performing candidate carbon replacements, carbons including Calgon Olc, Calgon Olc AW, Carbon Resources, GC 8x30, GC 8x30S, GC 12x40SAW, and Iodocarb IGS 1213-064 were all challenged with phenol solution and compared to 580-26 loading. After the initial screening with phenol solutions, the top performing candidates were challenged with organic selected compounds found in the ISS wastewater including caprolactam, 4-ethylmorpholine, benzyl alcohol, and diethylphthalate.

A. Phenol Equilibrium Test Procedure

One gram (wet) of each of the selected sorbents was placed in contact with 100 ml of contaminant solution. The sorbent / solution mix was agitated for at least 12 hours, and the solution was analyzed for TOC along with control solutions with no sorbent. The difference between the control (no sorbent) TOC and the final TOC of the solution with sorbent is the amount of contaminant TOC loaded on the sorbent. The carbon ratio of the contaminant is used to calculate the actual contaminant loading in mg/g of wet sorbent.

B. Phenol Equilibrium Test Results

Equilibrium test results with a 570 mg/L phenol test solution indicated that there was only a small difference between the candidate coconut shell activated carbons and the discontinued 580-26 activated carbon. All candidate carbons outperformed 580-26 by a slight margin. Based on this data, Carbon Resources and General Carbon 8x30S were selected for equilibrium testing with organic compounds found in ISS wastewater including caprolactam, 4-ethylmorpholine, benzyl alcohol, and diethylphthalate. Schunk FU 4652 was also selected for small column testing for 580-26 replacement due to its tested capacity for removal of DMSO, TMS, and DMSO₂.

C. Small Column, Single Contaminant Test Procedure

Small column, single contaminant loading was required to ensure that the candidates do not require excessive Empty Bed Contact Time (EBCT) to come to equilibrium with the contaminant of concern. Small column loading data gives more confidence in the actual loading capacity when the candidate sorbent is in service.

Four milliliters each of the three candidate carbons and the 580-26 “control” were placed in 0.8 cm diameter glass tubes (small columns) and contained with glass wool. The small columns were fed contaminant solutions at a rate of 2 mL / min for a face velocity of 4 cm / min and an EBCT of 2 minutes. This was a much higher relative flow rate than occurs with the on-orbit Multifiltration Beds but was necessary to allow testing to complete in a reasonable time frame. Single contaminant dilutions of benzyl alcohol, caprolactam, 4-ethylmorpholine, and diethylphthalate were used as challenge solutions for carbons including Carbon Resources, General Carbon 8x30S, and Schunk FU 4652. The 580-26 activated carbon was used as a control. Influent and effluent TOC levels along with the carbon ratio of each contaminant was used to monitor contaminant concentrations.

D. Small column, Single contaminant Test Results

The Schunk FU 4652 outperformed the other candidate carbons with the lone exception of benzyl alcohol loading. The General Carbon 8x30S benzyl alcohol removal was 74.6 mg/cc and the Schunk removed 71.7 mg/cc. Schunk FU 4652 removed 268 mg/cc diethylphthalate, 28.1 mg/cc 4-ethylmorpholine, and 19.7 mg/cc caprolactam. The Schunk FU 4652 displayed a much sharper breakthrough curve compared to the other candidates. This is likely due to the differences in physical characteristics of Schunk FU 4652 as compared to activated

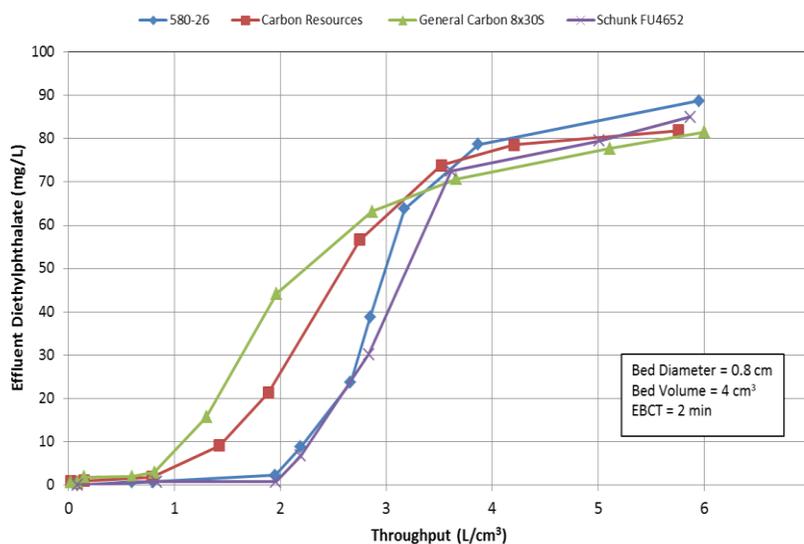


Figure 10. Small column testing with diethylphthalate.

carbons. Physically, the Schunk FU 4652 is comprised of relatively small (600 μm diameter) uniform spherical beads as compared to randomly shaped activated carbons. The small spheres present a small diffusion distance and uniform flow paths. All candidates outperformed 580-26 except when the challenge solution was diethylphthalate. The only candidate with higher capacity for diethylphthalate was the Schunk FU 4652, as shown in Figure 10.

E. Small Column Testing with ISS Wastewater Ersatz

Small column testing with a challenge solution containing the full spectrum of expected contaminants in ISS

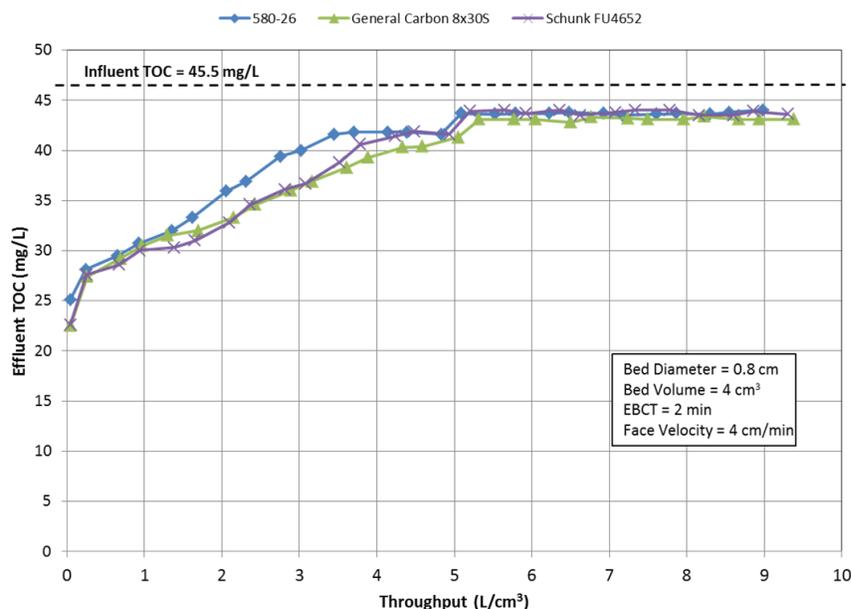


Figure 21. Small column TOC loading with ISS wastewater ersatz.

Influent and effluent TOC, conductivity, and pH were monitored over the course of the test. The TOC loading is provided in Figure 11 and both the Schunk FU 4652 and General Carbon 8x30S had greater capacity for ISS wastewater as compared to the 580-26.

wastewater was required to ensure that competition between various compounds does not adversely affect performance of the sorbent.

Schunk FU 4652 and General Carbon 8x30S were tested in small (4 cc) columns with an ersatz solution based on returned ISS wastewater analyses from 2009 – 2011 as defined in Section V. The face velocity during these tests was much higher than will be seen in actual operation, and EBCTs were much shorter. This was necessary to accelerate the test. The 580-26 activated carbon was carried through all testing as a control for comparison when using this accelerated testing technique.

VII. Schunk 4652 Leachate Characterizations

From the isotherm evaluations to remove siloxanes and the associated breakdown products, it was observed that the leading adsorbent candidate was Schunk FU 4652. To further evaluate the Schunk FU 4652, a three month leachate test was initiated on washed and unwashed aliquots. This leachate test is a standard procedure to determine the potential for inorganic, organic, and fines generation. The washing procedure followed a previously developed method in which the media was washed in separate MeOH and HNO₃ solutions which was then followed by a DI water rinse until the conductivity reached a value < 1.0 μS/cm. The unwashed sample was rinsed in DI water only prior to leachate testing. Samples were taken every two weeks and analyzed for TOC, anions, cations and metals.

The results from the leachate tests showed that the Schunk FU 4652 media is extremely clean and exhibits minimal generation of inorganic/organic constituents and particles (Table 3). The washed Schunk FU 4652 actually showed higher TOC values through the evaluation, which is likely due to residual MeOH from the washing procedure. Metals data (not shown) was also encouraging, as all metals except for silicon (~ 500 μg/L level) on the unwashed Schunk FU 4652 were below detection limit for the duration of the test. From this testing it can be concluded that Schunk FU 4652 does not pose a risk from a leachate standpoint.

	Washed Schunk Day 14	Washed Schunk Day 28	Washed Schunk Day 50	Washed Schunk Day 80	Unwashed Schunk Day 14	Unwashed Schunk Day 28	Unwashed Schunk Day 50	Unwashed Schunk Day 80
Cations								
(mg/L)								
Li	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Na	<0.05	<0.05	0.12	<0.05	0.12	5.8	5.4	<0.05
NH ₄	<0.05	<0.05	0.47	<0.05	0.47	<0.05	<0.05	<0.05
K	<0.05	<0.05	0.64	<0.05	0.64	0.70	0.35	<0.05
Mg	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ca	<0.05	<0.05	0.28	<0.05	0.28	<0.05	0.23	<0.05
Anions								
(mg/L)								
F	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cl	<0.05	<0.05	5.6	<0.05	5.6	0.11	0.11	0.07
NO ₂	<0.05	0.12	<0.05	0.09	<0.05	0.46	0.75	1.1
SO ₄	<0.05	<0.05	0.35	<0.05	0.35	0.35	0.14	<0.05
NO ₃	<0.05	0.68	<0.05	0.84	<0.05	<0.05	<0.05	<0.05
PO ₄	<0.05	<0.05	0.16	<0.05	0.16	0.12	<0.05	<0.05
TOC								
(mg/L)	0.19	0.27	0.27	0.28	0.14	0.15	0.18	0.12

Table 3. Three month leachate data from washed and unwashed Schunk FU 4652.

VIII. Conclusions and Recommendations

A. Conclusions

Literature review, vendor inquiries, and beaker isotherm testing of approximately 25 different adsorbents for removal of dimethylsilanediol, polydimethylsiloxanes, trimethylsilanol, and dimethylsulfone failed to identify an adsorbent with enough capacity and affinity to ensure that ionic breakthrough occurs before organic breakthrough in the ISS Multifiltration Beds. Schunk FU 4652 had limited capacity for DMSD (0.76 mg/g-R) with irreversible binding not subject to elution due to strong anions., Schunk FU 4652 also had capacity for TMS (0.35 mg/g-R) and DMSO₂ (0.48 mg/g-R at low levels with linear removal of over 75% up to 600 ppm). A theoretical calculation indicated that greater than 200 L of Schunk FU 4652 would be required to remove all of the DMSD in a cumulative throughput of 10,000 lb. of ISS wastewater, an impractical amount due to required launch weight and space.

A new ISS wastewater ersatz solution was developed based on the mean concentrations of organic and inorganic chemicals measured in return to ground samples from 2009 – 2011. The stable ersatz solution contained target quantities of DMSD, TMS, DMSO₂, and PDMS and reproducible accuracy to target concentrations of organic and inorganic chemicals in ISS wastewater. The new ISS wastewater ersatz solution was used for the activated carbon replacement testing and is recommended for testing to qualify a replacement activated carbon and optimize MF Bed packing.

Based on an article found during the literature review phase of this work (published by Dow Corning in the Journal of Environmental Science and Technology (Ref. 5)), PDMS can be formed by a hydrolysis reaction catalyzed by metal silicates in clay soils. The hypothesis was developed that siloxanes from crew hygiene and medical products, lubricants, adhesives, etc. in the air on ISS collect on the hydrophilic coating of the common Cabin Air Assembly (CCAA) heat exchangers. The coating contains metal silicates similar to those found in clay soils. Testing showed DMSD formation from deposition of linear siloxanes on ground hydrophilic coating stored for 20 days with and without moisture. Hydrolysis of PDMS to DMSD on the hydrophilic coating of the CCAA heat exchangers may be the primary route of DMSD infiltration into humidity condensate. Removal of PDMS from the air prior to the CCAA heat exchangers may be the best way to lower DMSD in wastewater since removal of PDMS from air is very easy with porous adsorbents and commercial processes are available.

Activated carbon replacement testing for the Barnebey Cheney 580-26 in the MF Beds identified Schunk FU 4652 as the best candidate, and this sorbent should be considered for future MF Bed packing since it provides limited capacity for removal of DMSD, TMS, and DMSO₂ coupled with better capacity for wastewater chemical components as compared to 580-26. The Schunk FU 4652 will be re-named Ambersorb® 4652 and marketed by The Dow Chemical Company with the same material specifications. The General Carbon 8x30S also had better capacity for wastewater chemical components as compared to 580-26 and is an alternate replacement to protect from future obsolescence. Both materials are relatively clean and small levels of non-hazardous identified leachates and impacts on downstream sorbents would be minimal.

B. Recommendations

MF Bed Media Tests:

The following testing is recommended to qualify Schunk FU 4652 (Ambersorb® 4652) for replacement of the Barnebey Cheney 580-26 in the ISS Multifiltration Beds. That testing should include ersatz challenge testing at nominal on-orbit flow rates with ion exchange resin, gamma irradiation followed by leachate testing, and launch load testing using crush strength.

- a) Ersatz Challenge Testing – The goal is to ensure no major differences in capacity breakthrough profiles, constituents, or constituent migration patterns.
 - Two scaled tubes, one with Schunk Carbon (1/10th scale of the 30% total MF Bed sorbent volume), the second with the various ion exchange resins (1/10th scale of the 70% total MF Bed sorbent volume)
 - Sampling ports after the 1st tube and the 2nd tube
 - 1/10 scale flow-rate
 - Challenge with the full ersatz model with the tubes in series
 - Periodically sample after the 1st and 2nd tubes for TOC, conductivity, Si and a less frequent full analysis
 - Run test for 2 weeks after first signs of DMSD breakthrough from the 2nd tube
 - Dissect and section the two scaled tubes post-test. Evaluate capacity and the migration of organic and inorganic constituents (via solvent extraction for the carbon and acid/base elution for the ion exchange resins). Compare/contrast to the data acquired from MF beds returned from orbit
 - Calculate this to be a 32 day test to flow 1/10 the volume (1000 lbs.) through the tubes running 24 hours per day
- b) Gamma Irradiation / Leachate Testing – The goal is to ensure no adverse impact to material and the item that the material is packed in due to irradiation.
 - Pack two tubes with Schunk Carbon
 - Have one tube undergo irradiation – comparable to the irradiation dosage an MF bed undergoes
 - After irradiation, flow DI water through the two tubes separately at a representative scaled flow rate with post-tube filters in place
 - Evaluate comparative pressure drop and particle size/quantities captured on the filters
 - Remove carbon from the two beds and do comparative capacity tests
 - Place irradiated and non-irradiated materials into separate vessels with DI water and periodically analyze water (1-month, 6-months, 1-year, 2-years)
- c) Launch Load Test – The goal is to ensure that material is at least as resistant to launch vibration fine generation as the 580-26.
 - Conduct crush strength on 12 representative particles
 - Compare/contrast to prior 580-26 crush strength data and current MF Bed design spring load

CCAA Porous Adsorbent/Adsorbent Mixture Design and Test:

Testing and CCAA integration of a porous adsorbent or adsorbent mixture proven to remove PDMS from air prior to the CCAA heat exchangers to reduce the level of DMSD in humidity condensate and wastewater is also recommended.

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