

Analysis of Chemical and Microbial Components Adsorbed on the Ion Exchange Bed in the Oxygen Generation System Recirculation Loop

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Since 2007, the Oxygen Generation System (OGS) on board the International Space Station (ISS) has produced oxygen via water electrolysis for crew respiration. As water is consumed in the OGS recirculating water loop, make-up water is furnished by the ISS potable water bus. In May 2011, ISS crew installed a mixed resin deionizing bed (ACTEX-311) in the recirculation loop to remove acidic byproducts from degradation of the cell stack membrane. The ACTEX-311 maintains neutral pH to minimize metallic corrosion and membrane degradation. The ion exchange resin in the ACTEX-311 is also known to reversibly adsorb dimethylsilanediol (DMSD). Three units were returned to ground for sampling and analysis of the water and resin to better understand the transport of acidic byproducts, DMSD, and any other species adsorbed by the ACTEX-311. Based on analysis results, the installed life has been limited to 675 days due to the presence of fluoride near the resin bed outlet. Fluoride is present near the outlet due to competitive binding of more strongly bound ions, including bicarbonate ion. The results of this cooperative effort are presented along with their implications for future ACTEX-311 installation.

Nomenclature

ACTEX = *Activated Carbon/Ion Exchange*
CDRA = *Carbon Dioxide Removal Assembly*
CFU/mL = *Colony Forming Units per milliliter*
CV = *Control Valve*

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DMSD = *dimethylsilanediol*
$DMSO_2$ = *dimethylsulfone*
ECLS = *Environmental Control and Life Support*
EDXRF = *Energy Dispersive X-Ray Fluorescene*
ESEM = *Environmental Scanning Electron Microscope*
FTIR = *Fourier Transform Infrared (spectroscopy)*
HF = *Hydrogen Fluoride*
Inlet DI Bed = *Inlet Deionizing Bed*
ITCS = *Internal Thermal Control System*
ISS = *International Space Station*
GC-MS = *Gas Chromatography-Mass Spectroscopy*
LOD = *Limit of Detection*
MCV = *Microbial Check Valve*
MEA = *Membrane Electrode Assembly*
mg/L = *milligrams per liter*
MMST = *monomethylsilanetriol*
µg/L = *micrograms per liter*
ppb = *parts per billion, equivalent to µg/L in dilute aqueous solutions*
ppm = *parts per million, equivalent to mg/L in dilute aqueous solutions*
OGA = *Oxygen Generation Assembly*
OGS = *Oxygen Generation System*
ORU = *Orbital Replaceable Unit*
R&R = *Remove and Replace*
RSA = *Rotary Separator Accumulator*
SA = *Sabatier Assembly*
Si = *Silicon*
SOV = *Shut Off Valve*
TOC = *Total Organic Carbon*
TIC = *Total Inorganic Carbon*
UPA = *Urine Processor Assembly*
V = *Volts*
WHC = *Waste and Hygiene Compartment*
WPA = *Water Processor Assembly*
WRS = *Water Recovery System*

I. Introduction

The Oxygen Generation Assembly (OGA) located within the Oxygen Generation System (OGS) rack electrolyzes recycled feedwater to form oxygen and hydrogen gases. The oxygen is vented directly to the ISS cabin atmosphere for crew respiration while the hydrogen is sent with carbon dioxide from the Carbon Dioxide Removal Assembly (CDRA) to the Sabatier Assembly (SA) where the hydrogen and carbon dioxide react to form water and improve the overall water balance on the vehicle. When the Sabatier is unavailable, hydrogen is discarded overboard through the external vent to space. In the confined and remote atmosphere of ISS, the premium energy cost of electrolysis as compared to the mass cost of delivering oxygen to station makes oxygen generation by water electrolysis an attractive option, even when hydrogen is vented overboard. The value of water electrolysis increased with the addition of the CDRA and SA which utilize the byproduct hydrogen to regenerate water.

First used to produce oxygen on ISS in July of 2007, the OGA was initially fed Shuttle fuel cell water from 10-liter bags through a pressurized accumulator bellows tank mounted on the OGS rack. In November of 2008, the Water Recovery System racks (WRS-1 and WRS-2) were installed to produce potable water for crew consumption, for operation of the Waste & Hygiene Compartment (WHC), and for oxygen generation in the OGA. Potable water destined for the OGA passes through an Inlet Deionizing Bed (Inlet DI Bed) to remove iodine/iodide and coalesce entrained gas. Any gas bubbles are detected by a gas sensor downstream, causing the feed water to shunt to the waste water bus or causing a system shutdown. This prevents oxygen entrained in the feedwater from mixing with the generated hydrogen in the recirculation loop water, thereby preventing a potentially combustible mixture. In the OGA, water is electrolyzed to yield oxygen and hydrogen gases in the Hydrogen Dome ORU, which contains the electrolysis cell stack, sensors, valves and a Rotary Separator Accumulator (RSA). The RSA separates the cathode (water) side

product hydrogen gas from the water. Water is recirculated by the positive displacement Pump ORU through filters, an ion exchange bed, delta-pressure sensors, and a heat exchanger that sends waste heat to an ISS Internal Thermal Control System (ITCS) loop. The hydrogen dome provides multiple barriers in the event of a failure. Figure 1 shows a simplified OGA diagram. As water is consumed, additional WPA product water is added to the recirculation loop. As of April 2, 2017, 12,093 pounds of oxygen (and 1512 pounds of hydrogen) have been produced for crew on ISS.

During the operation of OGA on ISS, the recirculation loop water chemistry has experienced changes, upsets, and recoveries. A previous reduction in pH and recovery to neutral pH has been described elsewhere[1,2]. Since July 2007 activation, concentrating acidic byproducts from the degradation of the cell stack membranes drove the dead-ended recirculation loop pH well below neutral. Near neutral pH was recovered via ISS crew installation of a mixed resin deionizing bed (ACTEX-311) in the recirculation loop in May 2011. The ACTEX-311 removes acidic byproducts of cell stack membrane degradation to keep the loop water pH near neutral. Removal of byproducts also helps minimize metallic corrosion and membrane degradation, both of which may degrade water transport across the membranes. Three expended recirculation loop ACTEX-311 units were returned to ground for sampling and analysis of the water and resin to better understand the adsorption and transport of acidic byproducts, bicarbonate, silicon compounds, dimethylsulfone ($DMSO_2$), and other contaminants adsorbed by the ACTEX-311 ion exchange mixed anion / cation resin. $DMSO_2$ is consistently present at low levels in the feed water and builds up in the dead-ended recirculation loop.[2] Silicon containing compounds, including silica (SiO_2), dimethylsilanediol (DMSD), and monomethylsilanetriol (MMST), are present as organosilicon breakdown products.[2,5,6] The results of this cooperative analysis effort are presented along with their implications for future ACTEX-311 installations.

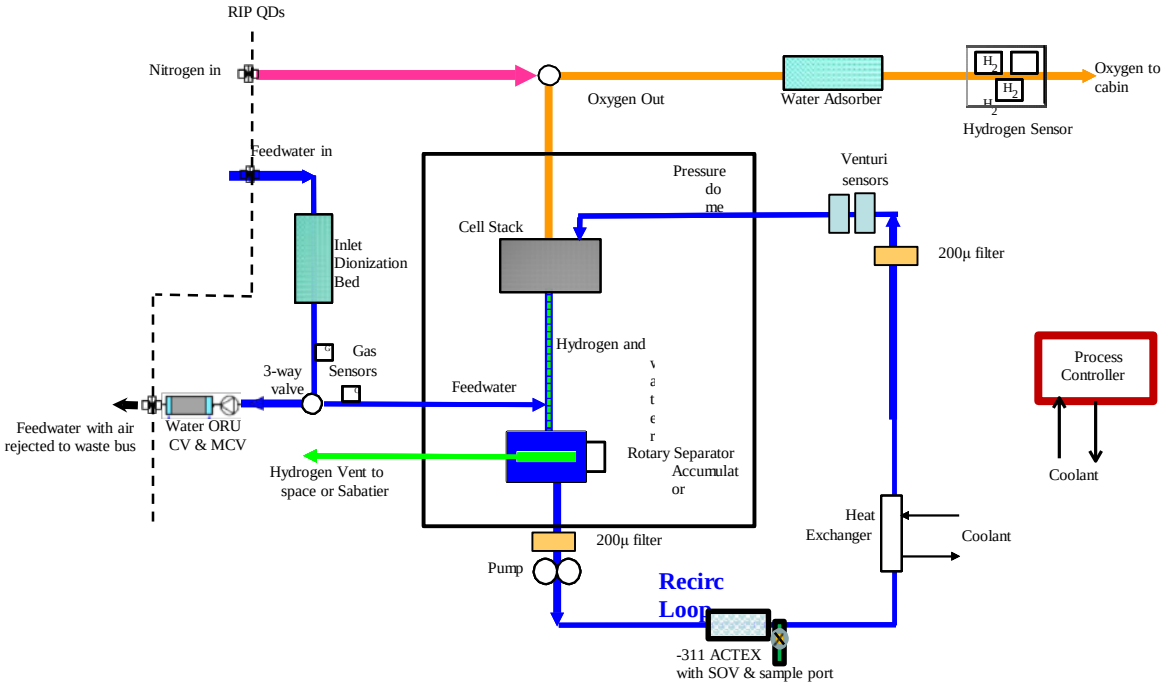


Figure 1. Simplified Oxygen Generation Assembly (OGA) diagram.

II. Methods

Three ACTEX-311 units were returned to ground for analysis. The first ACTEX-311 S/N 2002 was removed from the OGA recirculation loop on 3 October 2012 after 496 days of installation. It was returned to JSC where the resin was tested for remaining capacity in a manner similar to methods used for ACTEX-310 resins. Results were inconclusive. Realizing that the fluoride removal from the OGA recirculation loop was an unexpected use and environment for this hardware, the OGA community decided that different test methods would be needed. For the

follow-on ACTEX-311 analyses, Boeing Huntsville Central Laboratory employed methods that were developed to analyze Multifiltration Beds from the Water Processor Assembly.[3,4]

The second installed ACTEX -311 S/N 1012 was removed from the OGA recirculation loop on ISS on 8/8/2014 after 675 days installed. S/N 1012 was returned on SpX-4, kept in refrigerated storage and then sampled by the Johnson Space Center (JSC) Advanced Water Technology Team 19 February 2015. Samples were received by Boeing Huntsville Central Laboratories 25 February 2015. ACTEX-311 S/N 2006 was installed 8 August 2014 and removed 14 June 2016 from the OGA recirculation loop after 676 days installed. S/N 2006 was returned on SpX-9, kept in refrigerated storage and then sampled at JSC 8 September 2016. Samples were received at Boeing Huntsville Central Laboratories 14 September 2016.

Each ACTEX-311 was sampled using sterile sampling supplies and containers. Sampling was accomplished by JSC in a cleaned, disinfected Class II biosafety hood. Prior to opening the ACTEX-311, ports were wiped with 5-10% unstabilized hydrogen peroxide (H_2O_2) and lint free cloths and then left to dry. The inlet port was removed and the outlet port was opened to drain residual water (75-125 mL) into a sterile container. The resin was collected in rough layers with sterile scoops and placed into clean sterile 50 mL centrifuge tubes. All three screens were also collected and returned to Huntsville Central Labs. The canister hardware was retained by JSC for refurbishment. Samples were kept cool prior to and during shipping to Huntsville Central Laboratory.

Selected resin samples underwent chemical and microbial analyses to determine loadings of various constituents, with fluoride being of primary interest due to its corrosive effects if left in the recirculation loop water. Inlet, outlet, and a synthetic "composite" sample composed of similar amounts of all samples collected from a particular piece of hardware were analyzed. Residual water underwent microbial analysis and limited chemical analysis.

A schematic of the chemical analysis plan is shown in Figure 2. Separate aliquots of the inlet, outlet, and "composite" resin samples were desorbed in both 0.5 M NaOH (base) and 0.5 N HCl (acid). The desorbates were then analyzed. Additional resin samples were dried to determine a conversion factor from wet weight to dry weight. The concentrations in the desorbates of various constituents were then converted to a loading per dry mass of resin. Results are reported both in mg/g dry resin and in mmole/g dry resin.

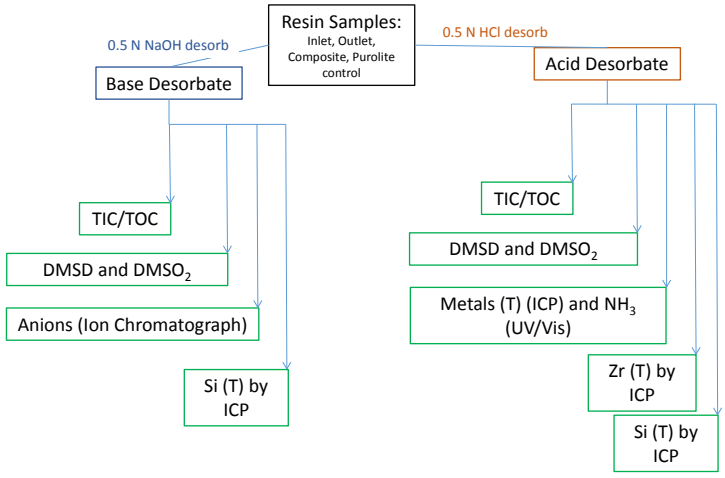


Figure 2. Resin analysis schematic

Microbiological analysis was performed on aliquots of the inlet resin, outlet resin, and residual water samples. Resin samples were weighed, and microorganisms were released from the resin into sterile phosphate buffered saline by standard vortexing and sonication techniques. The residual water sample was vortexed and sonicated in the same manner as the resin samples. Enumeration of microorganisms was performed in duplicate via membrane filtration method 9215 from Standard Methods for the Examination of Water and Wastewater, 17th ed., 1989. Membrane filters were placed onto R2A medium and mEmmon's medium. The R2A plates were incubated for 7 days at 28°C for bacterial enumeration. The mEmmon's plates were incubated for 5 days at 25ºC (77°F) for fungi enumeration. Colonies were counted after the incubation period.

Unique bacterial colony morphologies were isolated from the countable plates and identified using fatty acid methyl ester (FAME) analysis MIDI Sherlock® microbial identification software version 6.1 and Biolog® bacterial analysis using substrate utilization patterns. Organisms that could not be identified were compared with previously unidentified ISS ECLS organisms using MIDI dendrogram comparison analysis.

III. Results and Discussion

A. Chemical Analysis

Results of chemical analysis of the acid and base desorbates for the three resin sample types from both ACTEX-311s are reported in Table 1. Values are reported in both mg/g of dry resin and mmol/g of dry resin. Values for unused resin are included for comparison. The unused resin was not washed prior to analysis to remove organics; TOC values are therefore omitted.

The primary purpose of the ACTEX-311 is to remove fluoride from the recirculation loop water. Fluoride is a degradation product of the cell stack membrane, and will lower pH within the cathode side and contributes to corrosion of cell stack components as hydrogen fluoride (HF) if not removed. The resin loadings indicate that fluoride has migrated to the outlet end of the bed and is likely near breakthrough for both beds. In particular, the data for S/N 2006 indicate the highest fluoride loading on the outlet sample (the "composite" sample had the highest loading for S/N 1012). Immediately prior to R&R of S/N 2006, a recirculation loop water sample was collected. Analysis showed no detectable fluoride (<0.03 mg/L or <0.002 mmol/L). This data taken together indicate that S/N 2006 performed as intended for the installed life of 675 days, as did S/N 1012. Extension of installed life is not recommended as this would risk desorption of fluoride into the recirculation loop.

It is notable that the total fluoride sorbed on the ACTEX-311 resin is estimated to be 12-15 meq. In both cases, the total fluoride indicates that the membrane degradation is proceeding at a low background level and is not being accelerated by metal ions produced through corrosion or by excess fluoride.

Table 1. Acid and base desorbate analysis results for both S/N 1012 and 2006 for three sample types. Composite resin is a sample made up by combining similar amounts from all sample tubes (i.e. a synethisized composite).

Loading on dry resin, mg/g or mmol/g ↓	**Composite Resin**		**Inlet resin**		**Outlet resin**		**Unused Resin***
ACTEX-311 S/N →	1012	2006	1012	2006	1012	2006	n/a
TIC, mg/g	6.59E-01	1.20E+00	3.00E+00	2.62E+00	1.24E-01	2.03E-01	4.74E-02
TIC, mmol/g	5.49E-02	1.69E-02	2.50E-01	2.18E-01	1.03E-02	1.69E-02	3.95E-03
TOC, mg/g	1.31E+00	4.41E-01	2.41E-01	<LOD	1.31E+00	7.40E-01	n/a*
TOC, mmol/g	1.09E-01	3.68E-02	2.01E-02	<LOD	1.09E-01	6.16E-02	n/a*
Total Silicon (Si), mg/g	3.20E+00	3.20E+00	5.79E-02	6.63E-02	3.39E+00	4.76E+00	5.09E-03
Total Silicon (Si), mmol/g	1.14E-01	1.14E-01	2.06E-03	2.36E-03	1.21E-01	1.70E-01	1.81E-04
Fluoride (F^-), mg/g	1.39E+00	1.02E+00	<LOD	1.26E-01	1.28E+00	1.57E+00	<LOD
Fluoride (F^-), mmol/g	7.33E-02	5.38E-02	<LOD	6.61E-03	6.74E-02	8.26E-02	<LOD
Chloride (Cl^-), mg/g	2.29E-02	1.02E-02	<LOD	<LOD	1.52E-02	1.12E-02	1.42E-02
Chloride (Cl^-), mmol/g	6.47E-04	2.87E-04	<LOD	<LOD	4.29E-04	3.17E-04	4.01E-04
Phosphate (PO_4^{3-}), mg/g	<LOD	<LOD	1.22E-01	3.67E-02	<LOD	<LOD	<LOD
Phosphate (PO_4^{3-}), mmol/g	<LOD	<LOD	1.29E-03	3.84E-04	<LOD	<LOD	<LOD
Sulfate (SO_4^{2-}), mg/g	5.16E-02	1.49E-01	4.32E-01	4.99E-01	<LOD	1.19E-02	<LOD
Sulfate (SO_4^{2-}), mmol/g	5.37E-04	1.55E-03	4.50E-03	5.20E-03	<LOD	1.24E-04	<LOD
SiO_2, reactive, mg/g	2.32E+00	3.26E+00	9.79E-03	2.59E-02	2.37E+00	5.37E+00	<LOD
SiO_2, reactive, mmol/g	3.87E-02	5.43E-02	1.63E-04	4.32E-04	3.94E-02	8.93E-02	<LOD
Dimethylsulfone, mg/g	1.83E-02	1.59E-02	1.24E-02	1.53E-02	2.82E-02	1.76E-02	<LOD
Dimethylsulfone, mmol/g	1.95E-04	1.69E-04	1.31E-04	1.63E-04	3.00E-04	1.87E-04	<LOD
Silver (Ag), mg/g	1.45E-03	1.35E-03	4.03E-03	2.00E-03	6.74E-04	<LOD	<LOD
Silver (Ag), mmol/g	1.34E-05	1.25E-05	3.73E-05	1.85E-05	6.24E-06	<LOD	<LOD

Loading on dry resin, mg/g or mmol/g ↓	Composite Resin		Inlet resin		Outlet resin		Unused Resin*
ACTEX-311 S/N →	1012	2006	1012	2006	1012	2006	n/a
Aluminum (Al), mg/g	3.21E-03	3.12E-03	<LOD	1.07E-03	3.67E-03	2.84E-03	<LOD
Aluminum (Al), mmol/g	1.19E-04	1.16E-04	<LOD	3.96E-05	1.36E-04	1.05E-04	<LOD
Barium (Ba), mg/g	<LOD	1.26E-04	9.24E-05	1.95E-04	8.69E-05	6.82E-05	<LOD
Barium (Ba), mmol/g	<LOD	9.16E-07	6.73E-07	1.42E-06	6.33E-07	4.97E-07	<LOD
Calcium (Ca), mg/g	<LOD	<LOD	1.92E-03	<LOD	1.80E-03	5.15E-04	<LOD
Calcium (Ca), mmol/g	<LOD	<LOD	4.79E-05	<LOD	4.50E-05	1.29E-05	<LOD
Cobalt (Co), mg/g	1.00E-02	1.37E-02	2.16E-02	1.71E-02	8.21E-03	5.21E-03	<LOD
Cobalt (Co), mmol/g	1.70E-04	2.33E-04	3.67E-04	2.89E-04	1.39E-04	8.84E-05	<LOD
Chromium (Cr), mg/g	1.06E-02	1.08E-02	3.03E-02	2.91E-02	1.74E-03	1.51E-03	<LOD
Chromium (Cr), mmol/g	2.04E-04	2.08E-04	5.83E-04	5.60E-04	3.34E-05	2.90E-05	<LOD
Copper (Cu), mg/g	<LOD	<LOD	3.88E-04	<LOD	<LOD	<LOD	<LOD
Copper (Cu), mmol/g	<LOD	<LOD	6.11E-06	<LOD	<LOD	<LOD	<LOD
Iron (Fe), mg/g	1.76E-03	1.45E-03	1.92E-03	1.46E-03	3.19E-03	7.84E-04	<LOD
Iron (Fe), mmol/g	3.15E-05	2.78E-05	3.44E-05	2.81E-05	5.72E-05	1.51E-05	<LOD
Magnesium (Mg), mg/g	7.71E-04	9.04E-04	1.61E-03	1.11E-03	6.95E-04	3.89E-04	<LOD
Magnesium (Mg), mmol/g	3.17E-05	3.72E-05	6.61E-05	4.58E-05	2.86E-05	1.60E-05	<LOD
Manganese (Mn), mg/g	8.02E-04	8.79E-04	1.68E-03	1.06E-03	7.61E-04	3.72E-04	<LOD
Manganese (Mn), mmol/g	1.46E-05	1.60E-05	3.06E-05	1.93E-05	1.38E-05	6.77E-06	<LOD
Molybdenum (Mo), mg/g	7.55E-04	<LOD	3.16E-03	2.31E-03	<LOD	<LOD	<LOD
Molybdenum (Mo), mmol/g	7.87E-06	<LOD	3.29E-05	2.40E-05	<LOD	<LOD	<LOD
Nickel (Ni), mg/g	1.68E-01	1.31E-01	3.57E-01	1.65E-01	1.36E-01	4.78E-02	<LOD
Nickel (Ni), mmol/g	2.87E-03	2.23E-03	6.08E-03	2.81E-03	2.31E-03	8.14E-04	<LOD
Lead (Pb), mg/g	2.34E-03	3.41E-03	<LOD	<LOD	2.67E-03	3.13E-03	<LOD
Lead (Pb), mmol/g	1.13E-05	1.64E-05	<LOD	<LOD	1.29E-05	1.51E-05	<LOD
Zinc (Zn), mg/g	8.33E-04	6.71E-04	1.77E-03	7.72E-04	8.04E-04	3.52E-04	<LOD
Zinc (Zn), mmol/g	1.27E-05	1.03E-05	2.71E-05	1.18E-05	1.23E-05	5.38E-06	<LOD
Zirconium (Zr), mg/g	3.93E-02	2.06E-02	8.80E-03	1.43E-02	2.37E-02	1.22E-02	5.75E-05
Zirconium (Zr), mmol/g	4.31E-04	2.26E-04	9.64E-05	1.57E-04	2.60E-04	1.34E-04	6.30E-07
Total Silicon (Si), mg/g	3.08E+00	2.12E+00	8.02E-02	1.03E-01	4.00E+00	1.63E+00	1.06E-03
Total Silicon (Si), mmol/g	1.10E-01	7.56E-02	2.86E-03	3.66E-03	1.42E-01	5.80E-02	3.77E-05
Ammonium (NH_4^+), mg/g	1.86E-03	8.78E-03	2.09E-03	8.02E-03	2.13E-03	6.39E-03	<LOD
Ammonium (NH_4^+), mmol/g	3.15E-02	4.88E-04	3.55E-02	4.45E-04	3.62E-02	3.55E-04	<LOD

*Unused resin was not rinsed to remove TOC prior to analysis

Cation loadings in general are very low, and the total measured cation loading on S/N 2006 is lower than that observed on S/N 1012. The primary differences in cations appears to be reduced nickel, reduced zirconium, and increased ammonium for the recently analyzed S/N 2006 as compared to S/N 1012. This agrees with typically low to non-detectable measurements of cations in the recirculation loop return-to-ground water samples. The lack of cations on the resin (zirconium in particular) indicates that little to no corrosion is taking place within the OGA.

Selected data are graphed in Figure 3. The graphs show similar behavior in both resin beds. The weakly sorbed fluoride is displaced and pushed towards the bed outlet by bicarbonate (measured as TIC) and sulfate. Both the presence of bicarbonate and the displacement of fluoride help to explain why the remaining capacity analysis results

from the first returned ACTEX-311 (S/N 2002) were inconclusive. Both bicarbonate and fluoride would have been displaced by chloride ion used in the test, leading to falsely high estimates of remaining capacity.

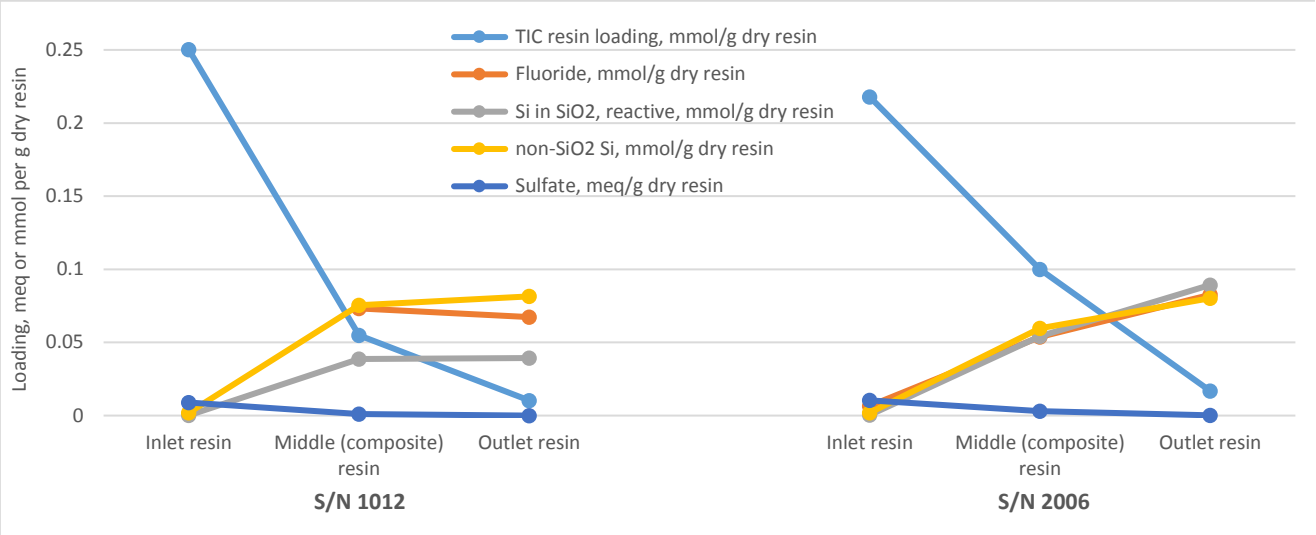


Figure 3. Selected anion (and silica) loadings desorbed from resin in ACTEX-311 S/N 1012 (left) and S/N 2006 (right), in mmol (or meq for sulfate) per dry gram of resin. Middle (composite) resin sample is a synthetic composite made by mixing similar amounts of resin from each sample collected.

When comparing S/N 1012 and S/N 2006 in Figure 3, note that the outlet sample from S/N 2006 is more highly loaded with fluoride than the outlet sample from S/N 1012. This may be due to decreased resolution in sampling (6 total resin samples for S/N 2006 as compared to 7 total resin samples for S/N 1012). Variation in the "composite" sample may be an effect of both sampling resolution and recombination of separate resin samples to form a synthetic composite. Bicarbonate is thought to be primarily present as a result of CO_2 diffusion through Teflon® flexible tubing within ISS making up the recirculation loop. There may also be some contribution of bicarbonate from degradation of the cell stack membrane. Silicon species, including silica, DMSD, and MMST, are also displaced. Both DMSD and MMST are likely present as breakdown products of organosilanes in the ISS atmosphere and condensate[3,5,6], and silica is likely present as a product of the digestion of these compounds in the WPA Catalytic Reactor, which oxidizes low molecular weight organics.

Although the relatively higher loading on the outlet sample of S/N 2006 makes it appear that fluoride was breaking through, no detectable fluoride (<0.03 mg/L or <0.002 mmol/L) was present in the recirculation loop water sample taken immediately before ACTEX R&R. Both ACTEX-311s analyzed indicate that fluoride is near breakthrough at the outlet of the resin bed. The installed life of 675 days is sufficient to prevent fluoride buildup in the loop, and extension of installed life is not recommended as the remaining capacity resin ion-exchange capacity margin for fluoride is not precisely known. Additionally, any change in the amount of bicarbonate, the amount of fluoride, and possibly temperature (which affects resin degradation rate) will likely affect this practical capacity.

Silicon, in the form of SiO2, DMSD, and MMST, appears to be displaced towards the outlet of the resin bed. This is consistent with the polar, non-ionic nature of these molecules and with the previous S/N 1012 analysis. Figure 4 compares actual TOC measured with calculated TOC assuming that non-silica Si is either DMSD or MMST. The organic carbon on S/N 1012 appears to be a mix of DMSD and MMST, with the actual TOC falling between the TOC calculated assuming either all DMSD or all MMST. The TOC on S/N 2006, in contrast, appears to be primarily MMST. The calculated TOC loading assuming all MMST (no DMSD) agrees with the measured TOC loading. The recirculation loop water in the sample taken immediately prior to S/N 2006 R&R had 1.97 ppm DMSD and 8.5 ppm MMST, per analysis provided by the JSC Environmental Chemistry Laboratory, confirming the greater amount of MMST.

TOC loadings in general were lower on S/N 2006 than on S/N 1012, likely due to an increased amount of monomethylsilanetriol (MMST, one carbon per molecule) and a decreased amount of dimethylsilanediol (DMSD, two carbons per molecule). $DMSO_2$ (dimethylsulfone) loadings are negligible as expected. Although the major component of TOC in the recirculation loop water is $DMSO_2$, it is not retained on the ACTEX-311 resin[2].

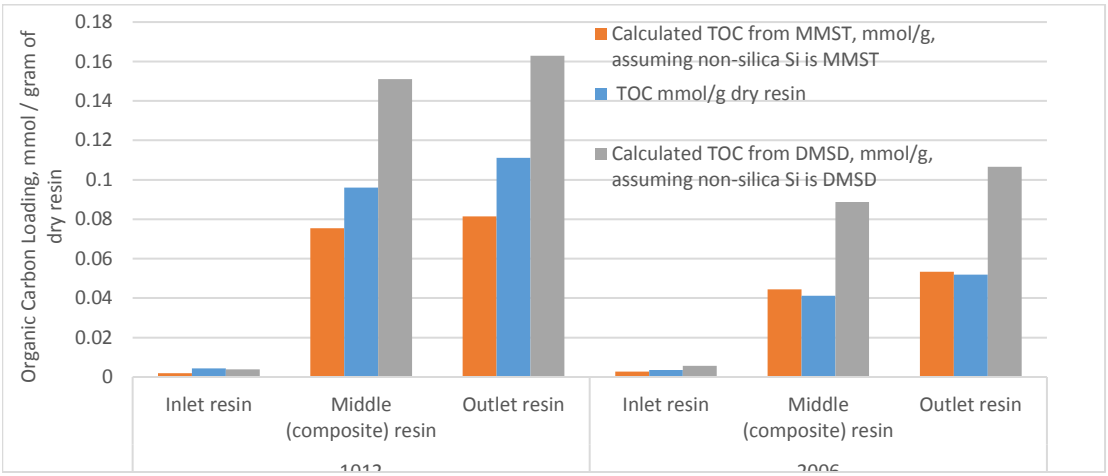
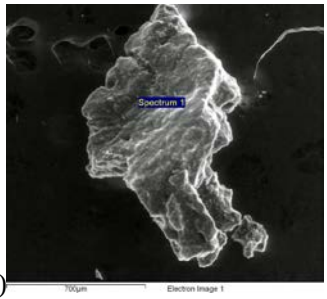


Figure 4. Calculated TOC assuming all non-silica Si is MMST (orange, first column) compared measured TOC to (blue, second column) and to calculated TOC assuming all non-silica Si is DMSD (gray, third column). While S/N 1012 carbon loading appeared to be a mix of DMSD and MMST, S/N 2006 carbon loading appears to be primarily MMST

Retaining screens were inspected during disassembly of both units. The screens and internal surface of S/N 1012 had visible black residue (suspected to be carbon), prompting analysis of the residue on the screens as well as collection of swabs of the internal surface for microbial analysis.

ESEM/EDXRF and FTIR were used to characterize the resin beads and black particles observed on retaining screens during sampling. Analysis revealed the presence of resin beads, carbon particles, and presence of a fluoropolymer material consistent with Braycote™ on those particles. Figure 5 shows an image of one of the black particles and an associated EDXRF spectrum confirming that it is, indeed, carbon as suspected during sampling. Carbon is likely present from previous use of the same hardware as an ACTEX-310, which does contain a carbon adsorbent in addition to an ion exchange resin.

(a) 

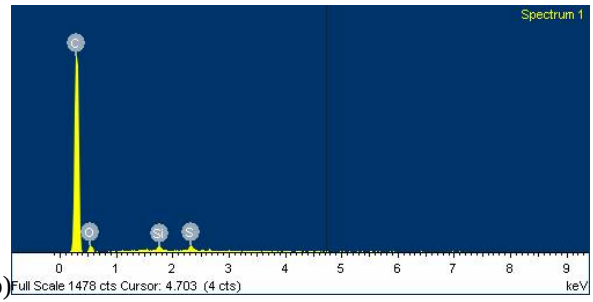
(b) 

Figure 5. ESEM image (a) and EDXRF spectrum (b) of black particle from midbed screen. The black particle is indeed carbon.

Figure 6 shows an ESEM image of a sphere (resin bead) on the outlet screen and EDXRF spectra taken at several points. Along with carbon and oxygen (expected), note the presence of sulfur (S) on bead surface, likely due to sulfonic acid cation exchange sites in the resin as very little $DMSO_2$ or other sulfur containing compounds were detected in the resin desorbates. Also note the presence of fluorine (F) in some of the particles adhered to the sphere, likely due to the presence of a fluorocarbon grease such as Braycote.

In summary, all materials on the screens and supports were appropriate given their previous use. The screens from S/N 2006 appeared clean with ony resin beads visible on the surface. Based on data from S/N 1012 screens, the screens from S/N 2006 were not analyzed.

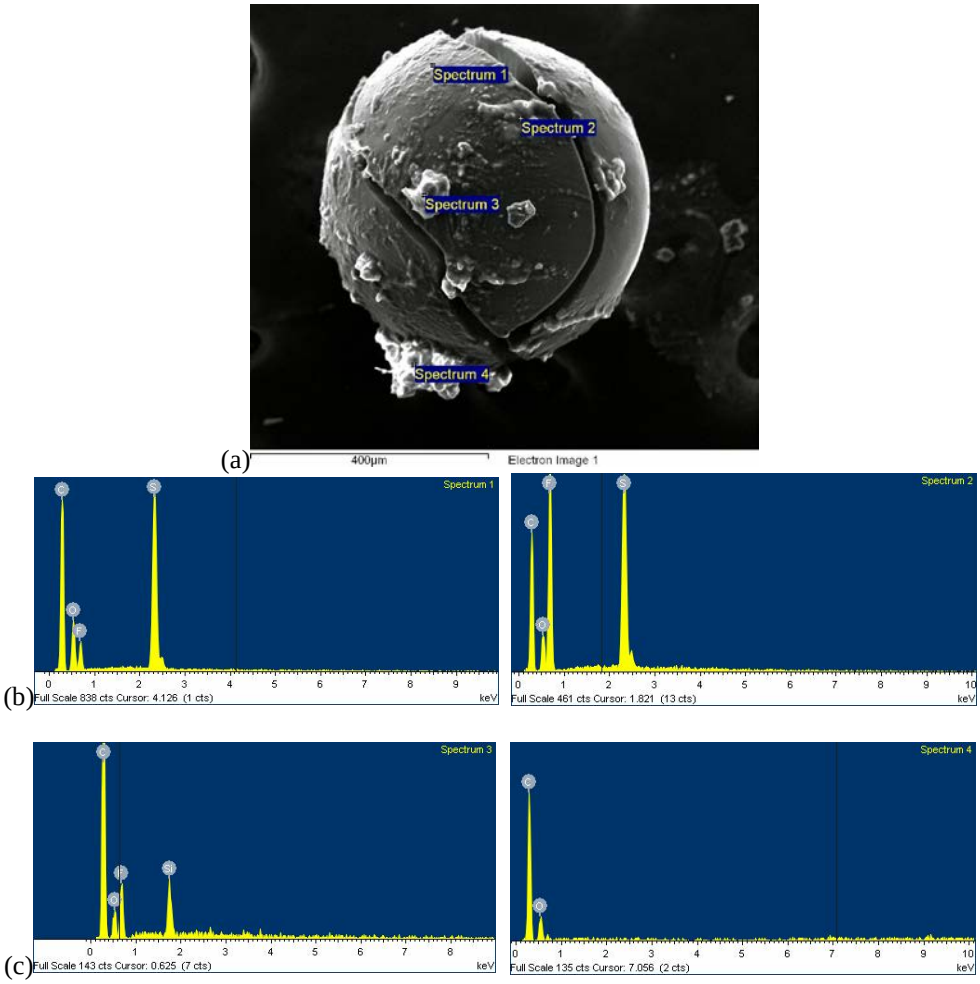


Figure 6. Sphere (resin bead) from outlet bed screen. ESEM image (a) and EDXRF spectra from two points (b) and (c). Along with carbon and oxygen as expected, note the presence of sulfur (S) on bead surface and fluoride (F) in some of the particles adhered to the sphere.

B. Microbial Analysis

Microbial analysis results are summarized in Table 2. The amount and type of microorganisms identified are within expectations when compared to return-to-ground sample analysis history for the recirculation loop water and for other ISS ECLS water samples. Some differences in abundance were observed relative to recirculation loop water, where *Ralstonia pickettii* is typically the predominant organism. This difference may be due to a variety of factors, including the different chemical and physical environments in the water and the resin bed, possibly in conjunction with typically longer times between removal and analysis for the resin bed as compared to the water. All organisms have been previously isolated from ECLS samples, although *Micrococcus luteus* may be a contaminant.

Table 2. Microbial analysis results for water and resin samples from S/N 2012 and S/N 2006 ACTEX-311

Sample Name	Enumeration	Units	Organisms Identified
Water, S/N 1012	1.60E+04	CFU/mL	1) *Variovorax paradoxus* 1.00E+04 CFU/mL 2) *Sphingomonas echinoides* 6.00E+03 CFU/mL 3) *Ralstonia pickettii* <5.0E+02 CFU/mL (isolated from TNTC plate)
Water, S/N 2006	6.40E+02	CFU/mL	1) *Variovorax paradoxus* 2.60E+02 CFU/mL 2) *Brevundimonas diminuta* 1.70E+02 CFU/mL 3) *Sphingomonas echinoides* 90 CFU/mL 4) Unidentified non-fermenting gram-negative rod most closely related to *Flavabacterium** 40 CFU/mL 5) *Ralstonia pickettii* 20 CFU/mL
Inlet Resin, S/N 1012	5	CFU/g	*Micrococcus luteus***
Inlet Resin, S/N 2006	1	CFU/g	Unidentified non-fermenting gram-negative rod (most closely related to Phyllobacterium)
Resin Sample #5, S/N 1012	<5	CFU/g	n/a
Resin Sample #7 (Outlet), S/N 1012	<5	CFU/g	n/a
Outlet Resin, S/N 2006	<1	CFU/g	n/a
Microbial swab of the case inlet, S/N 1012	3.80E+02	CFU/cm^2	1) Unidentified non-fermenting gram-negative rod (most closely related to *Zoogloea*) 3.80E+02 CFU/cm^2 2) *Phyllobacterium myrsinacearum* <20 CFU/cm^2 (isolated from TNTC plate) 3) *Ralstonia pickettii* <2 CFU/cm^2 (isolated from TNTC plate)
Microbial swab of the inlet side of cylinder, S/N 1012	60	CFU/cm^2	1) Unidentified non-fermenting gram-negative rod (most closely related to *Zoogloea*) 58 CFU/cm^2 2) *Phyllobacterium myrsinacearum* 2 CFU/cm^2
Microbial swab of the case outlet, S/N 1012	3	CFU/cm^2	1) *Burkholderia glumae* 2 CFU/cm^2 2) *Sphingomonas sanguinis* 1 CFU/cm^2

**This organism may be a contaminant introduced during samping and/or handling or hardware or samples.

IV. Conclusion

Since 2007, the Oxygen Generation System (OGS) on board the International Space Station (ISS) has produced oxygen via water electrolysis for crew respiration. From initial activation until early 2011, concentrating acidic byproducts from degradation of the cell stack membranes drove the dead-ended recirculation loop pH well below neutral. Near neutral pH was recovered via ISS crew installation of a mixed resin deionizing bed (ACTEX-311) in the recirculation loop in May 2011. The ACTEX-311 removes acidic byproducts of cell stack membrane degradation to keep the loop water pH near neutral.

Three units were returned to ground to evaluate remaining installed life and to better understand retention and transport of acidic byproducts, organosilicons, $DMSO_2$, bicarbonate, silica, and other contaminant species adsorbed by the ACTEX-311 ion exchange mixed anion / cation resin. Analysis of resin and water confirmed that measurable fluoride is retained on the ion exchange resin. However, fluoride is present near the outlet as a result of being displaced

by more strongly bound ions, including bicarbonate ion and sulfate ion. These strongly adsorbed ions also displace DMSD, MMST, and silica (SiO_2). Analysis confirmed that $DMSO_2$, which is the major contributor to recirculation loop water TOC, is not retained on the ion exchange resin. These observations led to limiting the ACTEX-311 installed life in the OGS to 675 days to ensure that low to non-detectable fluoride levels and near neutral pH is maintained in the recirculation loop water.

Future work includes improving fluoride detection limits and development of models to predict the effects of shelf life and varying water chemistry on ACTEX-311 installed life. In addition, a redesigned ACTEX with greater resin capacity is planned for an advanced OGA to be demonstrated on ISS for future NASA exploration missions.

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