

# Silver Foam: A Novel Approach for Long-Term Passive Dosing of Biocide in Spacecraft Potable Water Systems – Update 2021

Tesia D. Irwin<sup>1</sup>, Wenyan Li<sup>2</sup>, Angie Diaz<sup>2</sup>, and Luz M. Calle<sup>3</sup>  
*NASA, Kennedy Space Center, FL, 32899*

*and*

Michael R. Callahan<sup>4</sup>  
*NASA Johnson Space Center, Houston, TX, 77058*

**A spacecraft water disinfection system, suitable for extended length space exploration, should prevent or control the growth of microbes, prevent or limit biofilm formation, and prevent microbiologically influenced corrosion. In addition, the system should have minimal maintenance requirements, be chemically compatible with all materials in contact with the water, be safe for human consumption, and be suitable to be shared across international spacecraft platforms and mission architectures. Silver ions are a proven broad-spectrum potable water biocide under investigation for future exploration missions. The competing technology for dosing silver ions in future water systems is based on actively dosing the ions via electrolytic production. Several challenges with this approach have prompted additional investigations into alternative dosing techniques. Control-release technology is an attractive option for developing a high-reliability passive silver dosing device. This paper describes the development of a nanoparticle/polyurethane (NP/PU) composite foam for the controlled release of silver ions, and is intended to build upon the 2020 International Conference on Environmental Systems (ICES) paper number 128. This paper provides the technical background and performance results from the updated silver chloride (AgCl) NP/PU. The ultimate goal of the project is to develop a stable and reliable passive dosing silver ion release device for use in future spacecraft potable water systems.**

## Nomenclature

*Ag*<sup>+</sup> = silver ion

*AgCl* = silver chloride

*COTS* = commercial off-the-shelf

*ICES* = International Conference on Environmental Systems

*ICP-OES* = inductively coupled plasma optical emission spectrometry

*ISA* = ionic strength adjuster

*ISE* = ion selective electrode

*ISS* = International Space Station

*JSC* = Johnson Space Center

*NASA* = National Aeronautics and Space Administration

---

<sup>1</sup> R&D Engineer, The Bionetics Corporation, Mail Code: LASSO-008, Kennedy Space Center, FL, 32899.

<sup>2</sup> Research Scientist, Amentum, Mail Code: LASSO-001, Kennedy Space Center, FL, 32899.

<sup>3</sup> NASA, Senior Research Scientist, Exploration Systems and Development Office, Mail Code: UB-E, Kennedy Space Center, FL, 32899.

<sup>4</sup> NASA, Water Technology Lead, Crew and Thermal Systems Division, 2101 NASA Parkway/EC3, Houston, Texas, 77058.

*nm* = nanometer  
*NP* = nanoparticle  
*ppb* = parts per billion  
*ppm* = parts per million  
*psi* = pounds per square inch  
*PU* = polyurethane  
*PVA* = polyvinyl alcohol  
*SOA* = state-of-the-art  
*SWEG* = Spacecraft Water Exposure Guidelines  
*WHO* = World Health Organization  
*WPA* = Water Processor Assembly

## I. Introduction

Silver biocide is being investigated as the replacement for the current iodine exchange resin used within the International Space Station (ISS) Water Processor Assembly (WPA), and for future mission architectures. Several key benefits make silver ion ( $\text{Ag}^+$ ), the biocidal component in silver biocide, an attractive choice.  $\text{Ag}^+$  is an effective biocide at levels that are safe for human consumption, which means that there would be no need for a system to remove it before the potable water dispenser (PWD), unlike iodine that currently requires removal.  $\text{Ag}^+$  also has the potential to be used broadly across all spacecraft platforms, which would mean that water can safely be exchanged between different spacecraft leading to lower risk and higher mission flexibility. The current approach for dosing effective levels of  $\text{Ag}^+$  into water relies on the active release of  $\text{Ag}^+$  using electrolysis. To provide for an alternative passive dosing solution, the concept of a silver chloride nanocomposite polyurethane foam (referred to as Silver Foam or AgFoam) was developed. This paper follows two previous ICES papers of the same name, which further detail the concept creation and material synthesis decisions as well as some of the early benchtop properties testing.<sup>1,2</sup> In this paper the expedited long-term flow-through testing will be discussed, as well as further full-scale properties tests that were conducted in 2020 as a means to enhance the predictability of the  $\text{Ag}^+$  dosage amounts.

## II. Background

Passive dosing  $\text{Ag}^+$  technology is of particular interest for use in spacecraft potable water systems. Major advantages of passive dosing technologies are their inherent high reliability and suitability for quick adaptation within the current state of the art water recovery systems. To develop such technology, a number of requirements, standards, and guidelines are being considered. Primarily, for any  $\text{Ag}^+$  dosing technology, the system must dose  $\text{Ag}^+$  at a steady concentration that is both effective against microbial growth and safe for human consumption. The upper limit of the concentration range is set with consideration of the Spacecraft Water Exposure Guidelines (SWEG) for 1000-day missions, which is 360 ppb.<sup>3</sup> The tendency for  $\text{Ag}^+$  to be depleted via reduction to silver metal must also be taken into account, especially in the current WPA and water distribution system where metal alloys, such as stainless steel 316L and titanium 6AL-4V, are frequently used and known to cause silver deposition.<sup>4,5</sup> While an official concentration for biocidal effectiveness of silver has not been clearly defined, for our purposes this limit for silver is based on a literature review conducted by the World Health Organization (WHO) that compiled numerous silver biocide studies, as well as a more recent study conducted at Johnson Space Center (JSC) that was performed using the “Fab 5” bacteria that are most prominently present on the ISS.<sup>6</sup> The effective  $\text{Ag}^+$  concentration varies greatly from 20 to 200 ppb based on a number of different testing variables including treatment time, water turbidity, bacteria type, silver source, and particle size.<sup>7,8,9</sup> To hedge against the risk of under-dosing and potentially allowing bacteria the opportunity to build resistance to silver, we targeted the high end (200 ppb) of the effective kill range. Contact time requirements, determined by system flowrates, must also be considered because of their direct effect on the  $\text{Ag}^+$  release rate. The current WPA system on the ISS has flowrates of 0.10 – 0.15 L/min which is the range that will be targeted. The target life span of the AgFoam is a minimum of one year without replacement. This means that the system has to maintain dosing capabilities within the accepted range over the one-year period. In addition, the foam material must retain enough structural integrity to eliminate the risk of breaking apart and causing any issues to either the dosing system or downstream water system components. This would include any potential changes in  $\text{Ag}^+$  release rates, system clogging or significant pressure

drop issues, and release of unwanted chemicals into the downstream water supply – especially any materials that could be considered to affect the quality of the water for consumption.

$$\frac{dm}{dt} = A \frac{D}{d} (C_s - C_b) \quad (\text{Eq.1})$$

Where

$\frac{dm}{dt}$  is solute dissolution rate ( $\text{kg} \cdot \text{s}^{-1}$ )

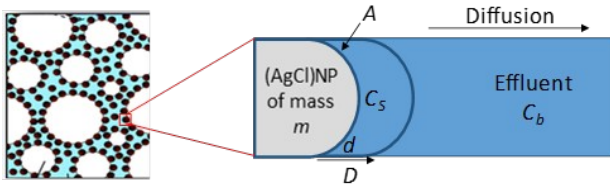
$m$  = mass of dissolved material (kg)

$t$  = time (s)

$A$  = surface area of the solute particles ( $\text{m}^2$ )

$D$  = diffusion coefficient ( $\text{m}^2 \cdot \text{s}^{-1}$ )

$C_s$  = concentration of the solute in the solvent



**Figure 1.** Illustration of the Noyes-Whitney equation in relation to AgFoam. A cross section of the AgFoam is represented to the left, which shows the PU foam (blue), the foam pores (white), and the (AgCl)NPs (black). To the right is an enlarged depiction of a single (AgCl)NP (grey).

solubility to its dissolution rate. The second is the mass loading and distribution of silver particles within the foam structure. These constraints determine the total available surface area, consumable mass, sizing and ultimate lifetime of the biocide delivery system. By controlling these parameters as a function of flowrate, it is possible to control the dosing rate for the system.<sup>10</sup>

For the silver compound nanoparticle, AgCl was selected. The selection was based on the saturation limit of AgCl which is 2000 ppb. This limit is relatively close to the target dosing range of 200 – 500 ppb when compared to the solubility of other potential silver compounds.<sup>11</sup> The lower solubility of AgCl helps ensure a slower and more consistent Ag<sup>+</sup> release rate, while also helping to prevent the possibility of overshooting the desired silver concentration range. The foam matrix selected was polyurethane. The advantages of polyurethane foam are that it is highly porous, provides a high surface area, and has well-documented biocompatibility.<sup>12,13</sup>

### III. Methods and Materials

#### A. AgFoam Synthesis

AgFoam composites were made using AgCl nanopowder (99.9% purity) procured from Nanoshel (P/N), and a commercial two-part polyurethane foaming system, FlexFoam-iT!<sup>TM</sup> III (Smooth-On. P/N). To generate the AgFoam, the appropriate amount of Part B, or the polyol phase of the two-component foam system, was weighed directly into a polypropylene beaker. Next, the (AgCl)NPs were weighed, pulverized using a pestle and mortar to eliminate any clumps, and added into the beaker of Part B. The (AgCl)NP laden polyol phase was then mixed until the particles were well incorporated into the polyol. The appropriate amount of the FlexFoam-iT! Part A component, or isocyanate, was then added and the resulting slurry was mixed vigorously for 30 seconds. The AgFoam was then cured for 24 hours at room temperature in the same polypropylene beaker it was mixed in. Once cured, the foam was de-molded and cut into AgFoam samples. Foams were generated at (AgCl)NP loading ratios of 10 and 20%. All synthesis and sample storage was performed in low-light conditions to reduce the potential for photo-reduction of the AgCl.<sup>14</sup> To achieve low-light, all work is performed in a lab with no windows with only the overhead safety lights on. Whenever possible samples are also placed in a secondary dark box or wrapped in foil to further reduce light exposure.

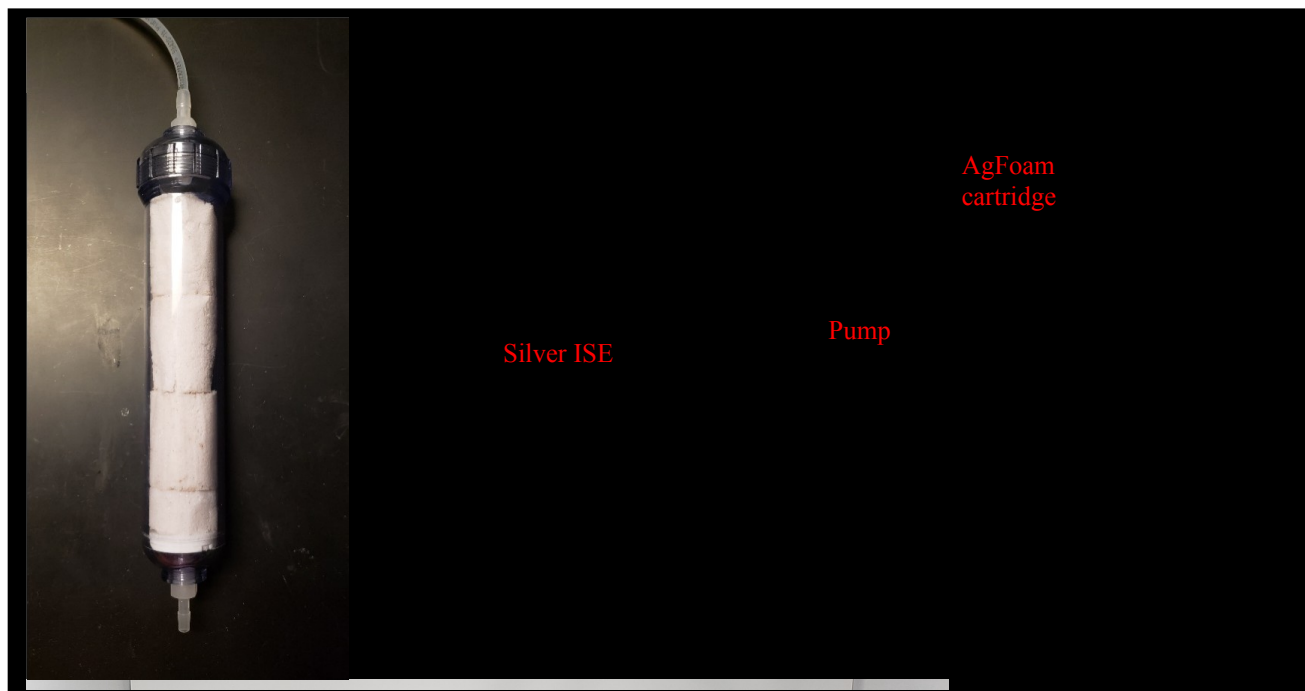
AgFoam was conceptualized and designed to meet the above requirements of an Ag<sup>+</sup> passive dosing device. The AgFoam composite is comprised of two key components. The first component is a silver compound in a nanoparticle form. The nanoparticle provides the source material for the active biocide in a high surface area form. The second component is the foam material. The micro-porous structure of the foam is used to provide a stable, high surface area material within which the silver compound nanoparticles can be embedded and immobilized. By providing a lattice structure and holding the particles in place, the foam maintains a consistent surface area for the nanoparticle/water interface while also preventing particle agglomeration and loss to the downstream flow. The AgFoam composite structure is depicted in Figure 1. As water flows through the foam structure, Ag<sup>+</sup> is released to the bulk solution via dissolution of the silver compound nanoparticles. To ensure a near constant release of Ag<sup>+</sup>, several design parameters are considered. The first is governed by the Noyes-Whitney Equation (Eq.1), which relates the compound particle size and

## B. Silver Measurement

To facilitate  $\text{Ag}^+$  release rate testing, both  $\text{Ag}^+$  and total silver measurements were taken. For  $\text{Ag}^+$  measurement, a ThermoFisher Scientific silver/sulfide ion selective electrode (ISE) was used. Calibration of the ISE was performed before each use using the “low-level” or “high-level” calibration recommendations given by the manufacturer. A 20% ionic strength adjuster (ISA) is added to all ISE samples per the manufacturer’s recommendations. The 1000 ppm  $\text{AgNO}_3$  standard, used to calibrate the ISE, was also crosschecked periodically using inductively coupled plasma optical emission spectrometry (ICP-OES). Measurements of total silver were performed using an iCAP 7600 ICP-OES Analyzer (Thermo Fisher Scientific) with sample introduction via Teledyne CETAC Technologies ASX-560 Autosampler. For these measurements, all sample preparation was done under dark conditions (similar to those described in Section III.A) to ensure that there was no loss of silver due to exposure to light or precipitation. To stabilize the samples, 5% nitric acid was prepared from 67-70% nitric acid (Trace Metal Grade A509-P212, Fisher Chemical) using ultrapure water (18 M $\Omega$ ). The 5% nitric acid was added to 10 mL of the original water sample at predetermined dilutions. The samples were wrapped in aluminum foil and allowed to sit overnight prior to making the measurements. An internal standard of 10  $\mu\text{g}/\text{mL}$  Yttrium (4400-1000671, CPI International) was used for all samples, blanks, and standards. A two-point curve (10 ppb, 20 ppm) was made using 100  $\mu\text{g}/\text{mL}$  Instrument Calibration Standard 2 (CL-CAL-2, SPEX CertiPrep) and 100  $\mu\text{g}/\text{mL}$  Quality Control Standard 27 (QCS-27, HPS) check standards. After every 10 samples, a reanalysis of check standards (1 ppm) and blanks helped verify the standard procedure adapted from EPA method 200.7xiii. For the ICP-OES analysis, pump speed was set to 50 rpm and the nebulizer and auxiliary gas flow were 0.5 L/min. Coolant gas flow was 12 L/min, and RF power was 1250 W. Exposure to UV and visible light was 30 and 5 seconds, respectively. The wavelength for silver was 328.068 nm on axial mode.

## C. AgFoam Property Testing

In contrast to last year’s AgFoam properties testing, full-scale 20% AgFoams were used in all flow-through tests this year. This was done to demonstrate feasibility at a reasonable and realistic scale so that true dosage amounts did not need to be approximated using a scaling factor. Full-scale samples were hand cut from single batches of AgFoam, and care was taken to ensure that each sample was cut to fit the flow-through cartridge closely to minimize the potential for channeling. Samples were also taken from central portions of the AgFoam only to minimize variation in pore quality that can occur near the “skin” of the foam. All testing was completed using the test setup depicted in .



**Figure 2. Full-scale Flow-through Test Setup.** Close-up of flow-through cartridge packed with a full-scale sample of 20% AgFoam (left). Sample cartridge hooked up to peristaltic pump for flow-through testing (right). The silver ISE is also shown next to the pump; everything is housed within a dark box to prevent photoreduction of  $\text{Ag}^+$ .

Empty polystyrene filter cartridges (part number EC-2010C) purchased from Hydronix Water Technology were used to package the AgFoam. The AgFoam cartridge is then connected to a peristaltic pump by silicone tubing that pumps water through the cartridge from bottom to top at a set rate. Bulk drums of DI water were used for our influent water supply, and samples were collected from the outlet tubing at the top of the cartridge. During any periods with no water flow, the tubing at both ends of the cartridge was pinched closed so that the filter remained submerged in water rather than being allowed to drain and reintroduce air. All testing was completed using the same sample cartridge packed with 27.76 g of 20% AgFoam. The sample was intentionally not pretreated and therefore testing began with a dry sample of foam to determine if further pretreatment would be necessary. Three different experiments were completed using this same test set-up: the Accelerated 1-Year Test, the Variable Flowrate Test, and the Start/Stop Behavior Test. Each experiment was completed independently, in that order.

The purpose of the Accelerated 1-Year Test was to determine if a full-scale cartridge of AgFoam could achieve and maintain the required range of 200 – 500 ppb of  $\text{Ag}^+$  released for an amount of water equivalent to the demands of 1 crewmember for 1 year. The total amount of water requiring treatment was determined using the assumed value of 2.5 L/crewmember/day. Assuming a full 365 days, the total amount of water to be treated was determined to be 912.5 L. At the target flowrate of 0.1 L/min, a total of 152 hours of run time is necessary to treat the full amount of water. For ease of scheduling, this run time was rounded up to 160 hours total. Using a flowrate of 0.1 L/min, DI water was pumped through the foam for 16 hours before turning the system off and allowing the foam to soak for 8 hours. This cycle was repeated for five days, with the system remaining off for two full days during the weekend, before repeating the cycle for five more days. To determine the impact of longer periods of system soaking, an additional weekend of soaking was run at the end of the test, followed by 6 hours of flowing. Samples were taken at 10-minute increments for the first hour after each start-up, then at 30-minute increments for the following 7 hours, and at every hour for the last 8 hours. All  $\text{Ag}^+$  measurements were taken immediately after sampling to eliminate the possibility for variation due to silver deposition. Effluent samples were also taken twice daily and reserved for iCAP testing to confirm ISE results.

The Variable Flowrate Test was designed to demonstrate the effects of changes in system flowrate on the amount of  $\text{Ag}^+$  released, since flowrate changes directly affect the contact time. A range of flowrates was tested, from 0.4 L/min down to 0.005 L/min. Prior to testing, all flowrates were calibrated using a stopwatch and graduated cylinder to ensure accuracy. Testing was initiated by allowing the system to reach equilibrium at the typical run flowrate of 0.1 L/min for 30 minutes. Once at equilibrium, the flowrates were each individually tested by resetting the pump rate and pumping at each flowrate for 30 minutes before setting the pump to the next flowrate. Samples were collected at various times throughout each flowrate test.

The Start/Stop Behavior Test was designed to determine the impact of various soak times on the  $\text{Ag}^+$  concentration of the water that remains in the AgFoam cartridge during periods where the system is not in operation. System soak times ranging from 30 minutes up to 8 hours were tested using the following technique. All flow was conducted at a constant flowrate of 0.1 L/min. At the start of each test, the system was flushed by running water through for 1 hour to allow the system to reach equilibrium. The pump would then be shut off and the system was left off for the appropriate amount of soak time. Once the system had been off for the appropriate amount of time, the pump was turned on again and was allowed to run for 1 hour with samples collected throughout the full hour. Samples were collected continuously for the first 10 minutes, then at 10-minute increments for the rest of the hour.

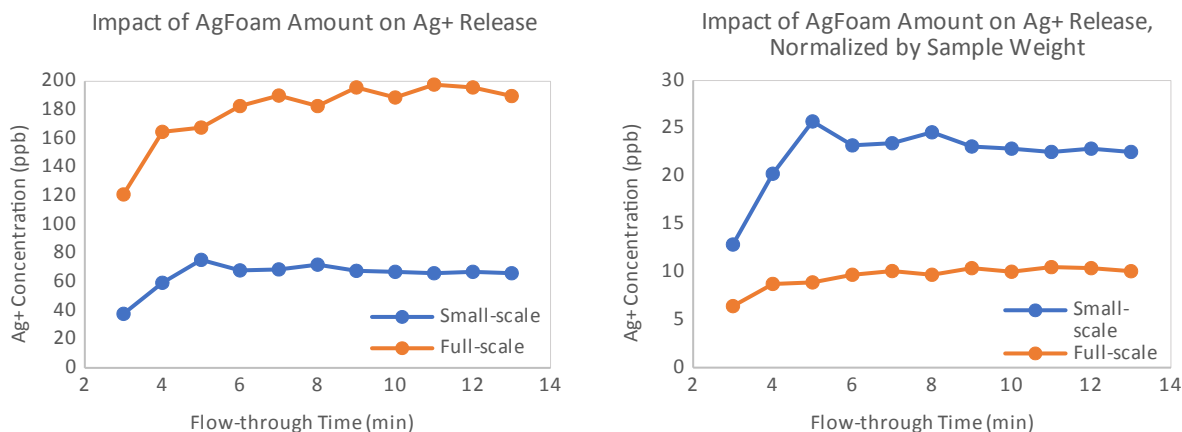
## IV. Results and Discussion

All properties testing completed this year was intended to advance the project in two key areas: feasibility and predictability. Due to improvements in AgFoam synthesis, primarily through enhanced mixing and better particle distribution, 20% AgCl loaded AgFoams were produced with comparable mechanical qualities to that of the 10% foams. Therefore, in order to maximize the amount of  $\text{Ag}^+$  released while optimizing for overall weight and volume, 20% AgFoams were used for the majority of the properties testing.

### A. Scalability

To determine how  $\text{Ag}^+$  release rates would increase with increases in the amount of AgFoam used, a full-scale sample of 10% AgFoam was prepared and loaded into the COTS cartridge used for all full-scale testing. The results of the flow-through testing, for both the small-scale (2.93 g) and full-scale (18.84 g) samples, are shown in Figure 3, normalized for weight. Both samples were taken from the same batch of 10% AgFoam to minimize the influence of batch variation. As expected, the amount of  $\text{Ag}^+$  released does not scale linearly as the amount of AgFoam used is increased. In the small-scale sample weighing 2.93 g, the  $\text{Ag}^+$  dosage plateaued at an average of 68 ppb. For the full-

scale sample, weighing 18.84 g, the dosage plateaued at 190 ppb. While the amount of foam used was increased by 6.4 times, the amount of Ag<sup>+</sup> released only increased by a factor of 2.8. Therefore, the full-scale foam released 56.3% less Ag<sup>+</sup> than was expected assuming a close-to-linear scalability. This diminishment in return as scale is increased could be due to the increased difficulty that influent water may have in fully saturating the larger foam sample given the same amount of flow-through time. At the time of this experiment, pretreatment of the AgFoam to allow for more complete saturation had not yet been thought of. This idea will be discussed more in the following section, and repeated scalability testing on pretreated AgFoams may be performed to determine the extent of the effect that a lack in initial saturation may be causing.

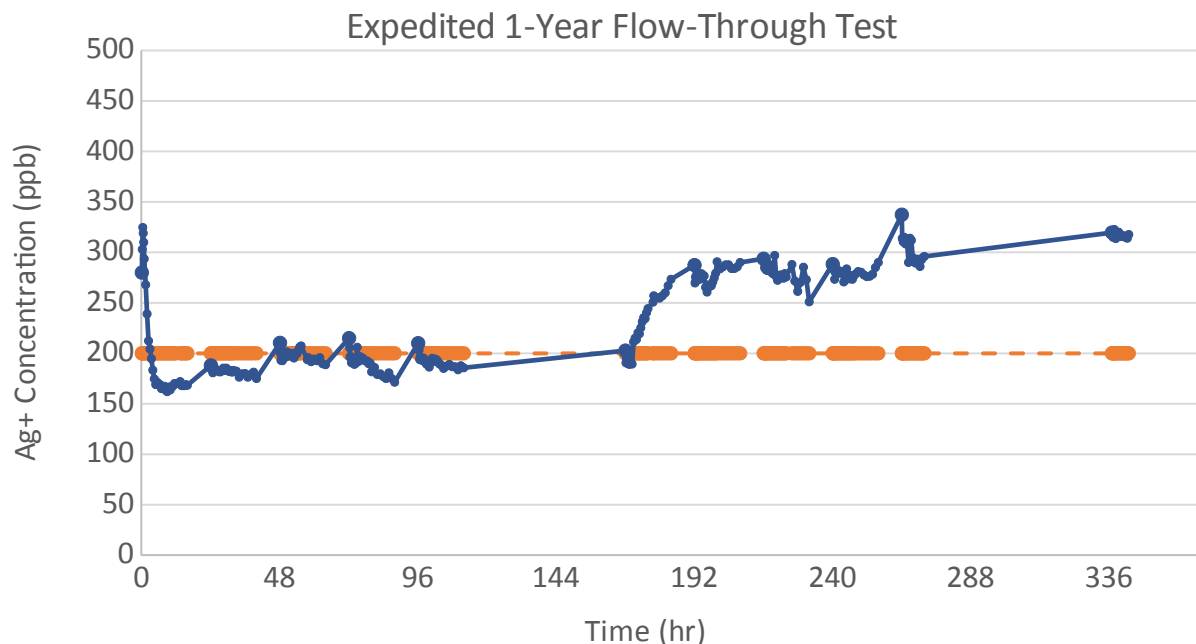


**Figure 3. Scalability Test Results.** Full-scale and small-scale samples from the same batch of 10% AgFoam were subjected to flow-through testing to determine the impact on Ag<sup>+</sup> release caused by AgFoam amount. (left) Raw data from both tests; small-scale sample weight of 2.93 g and full-scale sample weight of 18.84 g. (right) Test data normalized by sample weight.

Based on these results and improvements in the AgFoam synthesis technique, it was decided that 20% silver compound loaded foams would be used in all future full-scale testing to hedge against the diminishment of return that was seen in this brief scaling experiment. Further testing of a wider range of AgFoam sample sizes is needed to predict the impact of changes in AgFoam cartridge size.

### B. Accelerated 1-year Test

Based on the results from scalability testing, as well as the short-term flow-through testing performed the previous year on small-scale foams, we decided to perform the expedited 1-year flow-through test on a 20% loaded AgFoam. The sample weight required to fill the cartridge was 27.76 g, slightly heavier than an equivalent volume of 10% AgFoam due to the higher (AgCl)NP loading. Testing was performed using a dry sample of AgFoam to determine if dry sample cartridges would be feasible or if pretreatment is necessary. Figure 4 shows the full results over the 15-day test period. Green markers represent the first sample taken for each new day, and the large gaps in data indicate weekends where the system remained off while still full of water.



**Figure 4. Expedited 1-Year Flow-Through Test Results.** Ag<sup>+</sup> concentrations of 100 mL effluent water samples taken over a total flow time of 152 hours, during which 912.5 L of water were treated (approximately the amount of water required for 1 crew/1 year). Test extended 6 hours to repeat weekend soak conditions. New days are marked in green; lower acceptable Ag<sup>+</sup> limit shown as dashed orange line.

On the first day of testing, Ag<sup>+</sup> concentrations started at 280 ppb before peaking at 325 ppb and falling off steeply over the first 4 hours before plateauing at approximately 170 ppb. This initial drop in concentration was expected to occur since this sample had not undergone any washing or pretreatment prior to testing. The peak is likely caused by exposed or potentially loose (AgCl)NPs that cause an increase in Ag<sup>+</sup> release as they are washed away. Over the next four days, the Ag<sup>+</sup> release remained stable with an average of 190 ppb. This release rate is just below the targeted lower limit for release of 200 ppb; however it was not low enough to lead to a termination of the test.

An interesting phenomenon was observed after the first weekend of soaking time, where the flow-through cell remained off but still full of water. Over the course of the 16 hours of flow-through time after the weekend of soaking, the Ag<sup>+</sup> release increased significantly from 200 ppb to 287 ppb. The release concentration then remained steady over the next four days, at an average of 284 ppb. It is hypothesized that the increase in the average amount of Ag<sup>+</sup> being dosed from 190 ppb the first week to 284 ppb the second week is due to the extended period of soaking over the weekend. This extended soaking period may have allowed water to fully penetrate the actual struts of the polyurethane and replace air pockets that may have remained trapped within the pores of the foam, especially those pores that are not fully open-cell. The purging of air and more complete exposure of the AgFoam to water would cause an increase in the overall surface area of (AgCl)NPs that are in direct contact with water, which would in turn increase the amount of Ag<sup>+</sup> that is dissolved into solution. Air bubbles were also observed and noted throughout the test to be decreasing in size and frequency. To further test this theory and determine if there would be another significant increase in the amount of Ag<sup>+</sup> released, the system was turned off and soaked for an additional weekend before being turned back on for 6 hours. During those 6 hours, the average Ag<sup>+</sup> release was 317 ppb, a 33 ppb increase over the average of the previous 4 days of run time. While this may indicate a slight increase in concentration, the jump was not as significant as the first increase of 97 ppb after the first weekend of soaking. This observation of increases in Ag<sup>+</sup> dose following longer periods of soaking has prompted further questions on how best to precondition the AgFoam to maintain a steady release from day one. Future testing using AgFoams that have undergone various pretreatments to remove all air prior to flow-through testing are necessary to fully understand the system.

The average amount of Ag<sup>+</sup> released over the entire testing period, with the exception of the spike on the first day that is likely due to the removal of loose and exposed (AgCl)NPs, was 234 ppb. This test was considered a success

in dosing the targeted amounts of  $\text{Ag}^+$  into the effluent water. It also raised further questions and led to insight on the need for pretreatment of the AgFoam prior to packaging which will guide future experiments aimed to improve performance and consistency. With proper pretreatment, the  $\text{Ag}^+$  release is expected to be more consistent and well above the 200 ppb lower limit.

### C. Dosage Response to Changes in Flowrate

Flow-through testing, over a range of flowrates that far exceeds the WPA flowrate range, was performed in order to gain a broader understanding of the impact that changes in flowrate have on the amount of  $\text{Ag}^+$  released. Figure 5 shows the  $\text{Ag}^+$  dosage at different flowrates, reported as average values once the system had reached a steady dosage for each flowrate. At a zero flowrate when the cartridge is left to soak, the water within the cartridge reaches an  $\text{Ag}^+$  concentration of 1470 ppb, close to the theoretical concentration of  $\text{Ag}^+$  when  $\text{AgCl}$  is at saturation, which is 1505 ppb of  $\text{Ag}^+$ . As the system flowrate is adjusted from 0.006 L/min up to 0.4 L/min, the  $\text{Ag}^+$  dosage concentration decreases as expected due to the fact that the flowrate is inversely proportional to contact time, decreasing from 1150 ppb to 102 ppb. At higher flowrates (0.1 – 0.4 L/min) the change in  $\text{Ag}^+$  dosage with respect to flowrate is slow and nearly linear, with an average decrease in  $\text{Ag}^+$  dosage of 65.44 ppb per every 0.1 L/min increase in flowrate. At flowrates below 0.1 L/min, the change in  $\text{Ag}^+$  dosage is far more rapid and follows an exponential trend.

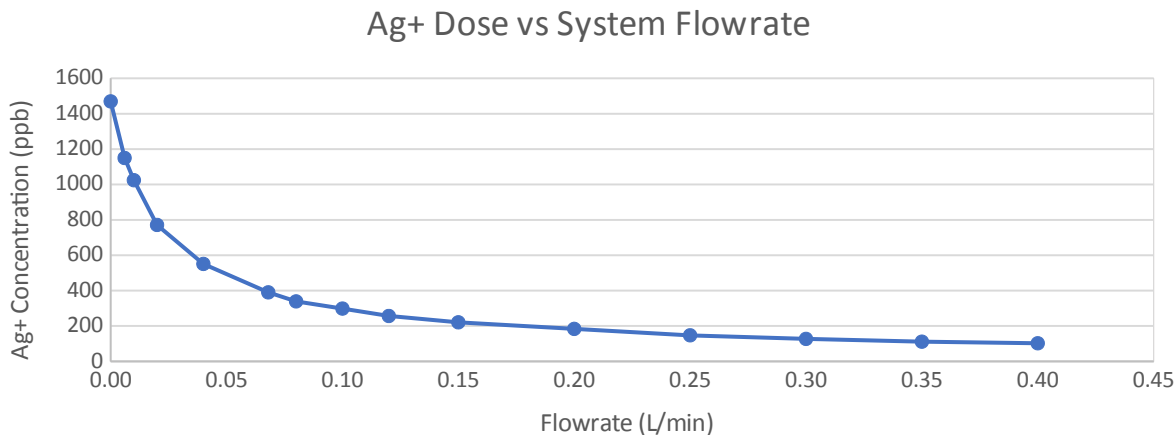
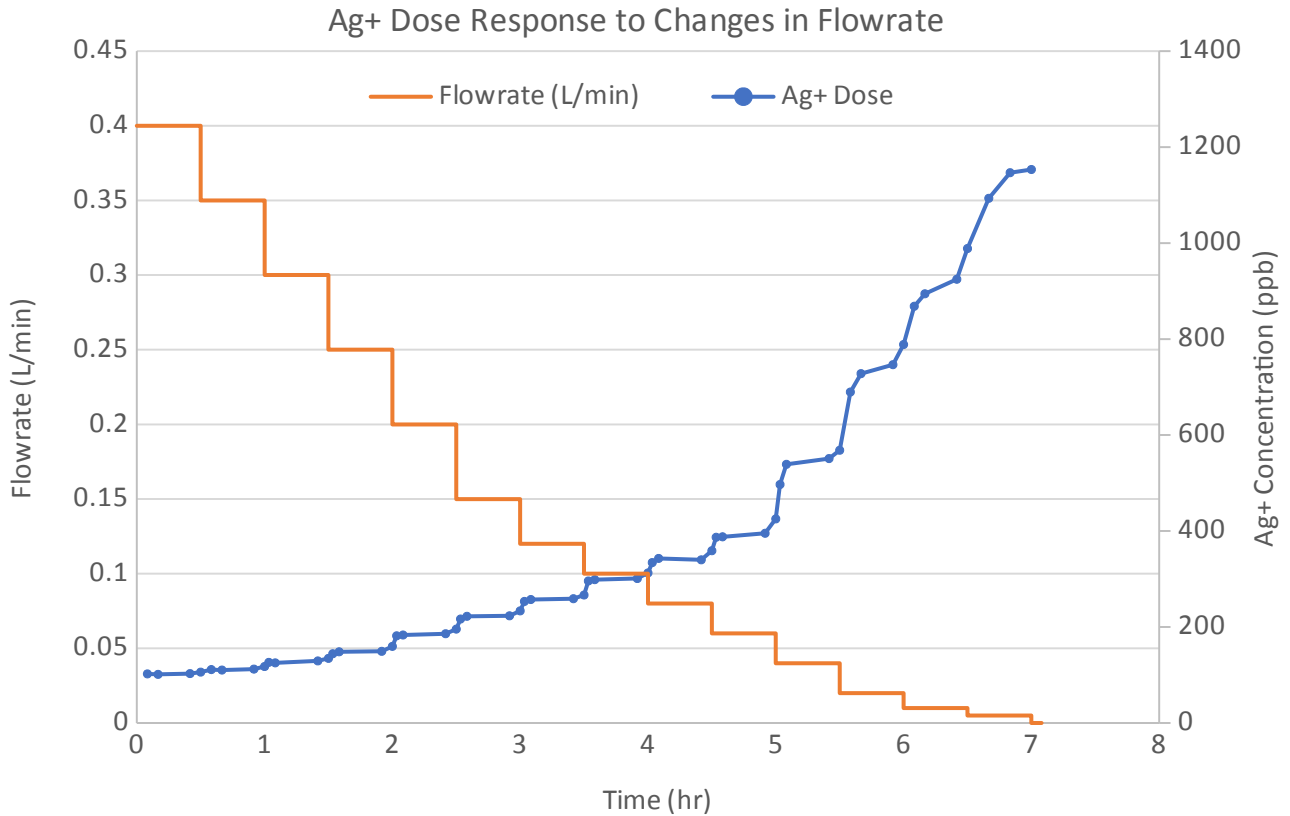


Figure 5.  $\text{Ag}^+$  Dose vs System Flowrate Test Results. Data shown represents the  $\text{Ag}^+$  concentration for each flowrate adjustment, shown as the average value once the system reached equilibrium and began dosing at a constant rate.

Figure 6 shows the same data as the figure above. However, here the data is shown in full and is plotted over time so that the transitional periods between each flowrate change can be seen. The respective flowrate change over time is also plotted against a separate axis. By plotting the data in this way, we can visualize the amount of time required for the system to reach equilibrium after each change in flowrate. The higher the system flowrate, the faster the new equilibrium is reached. At flowrates down to 0.08 L/min, the adjustment to equilibrium happens within the 2 minutes between the first and second samples taken after each adjustment in flowrate. As the flowrate decreases further, the time to hit equilibrium increases all the way up to approximately 30 mins for the lowest flowrate of 0.006 L/min.

The relationship between the time needed to hit equilibrium and the flowrate can be explained by the amount of time required to fully turn over the volume of water that's held in the cartridge, which has a total volume of 290 mL. At higher flowrates, this turnover rate is also higher than at lower flowrates since the system is being flushed with more water for the same amount of time. This turnover rate can not be accurately determined without further experimentation that would require a different sampling strategy. It does however give us valuable insight into the predictability of this system, particularly over the target flowrate range of 0.1 – 0.15 L/min. Knowing that adjustments in flowrate within this range cause a nearly instant change in  $\text{Ag}^+$  dosage and reach equilibrium rapidly will result in a simpler system that is easier to model and make dosage predictions for with respect to environment changes. The smooth and gradual change in  $\text{Ag}^+$  dosage as flowrates change also indicates that this process has a high potential for being accurately predicted using a mathematical model.



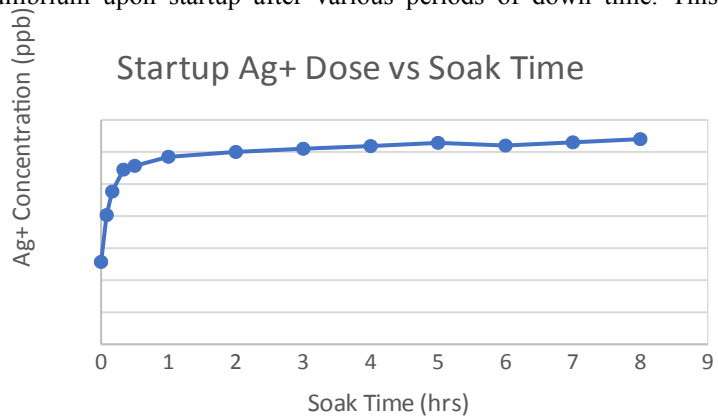


**Figure 6. Ag<sup>+</sup> Dose Reponse to Changes in Flowrate.** Changes in Ag<sup>+</sup> release over time are shown in blue and plotted against the right axis; corresponding system flowrate is shown in orange and plotted against the left axis. Effluent samples are taken immediately before and after a flowrate change, and periodically between these changes to track how quickly the system adjusts to changes in flowrate.

**D. Realistic Start/Stop Behavior**

Start/Stop Behavior testing was completed to gain a better understanding of how the AgFoam would perform after varying periods of system down time. Through this testing, we aimed to determine how long it would take for the water soaking in the cartridge to hit a plateau at or near the equilibrium of AgCl. We also intended to learn how long it would take the system to return to equilibrium upon startup after various periods of down time. This information will give us the ability to better understand and predict the changes in Ag<sup>+</sup> during a true long-term test that emulates the flow patterns of the WPA.

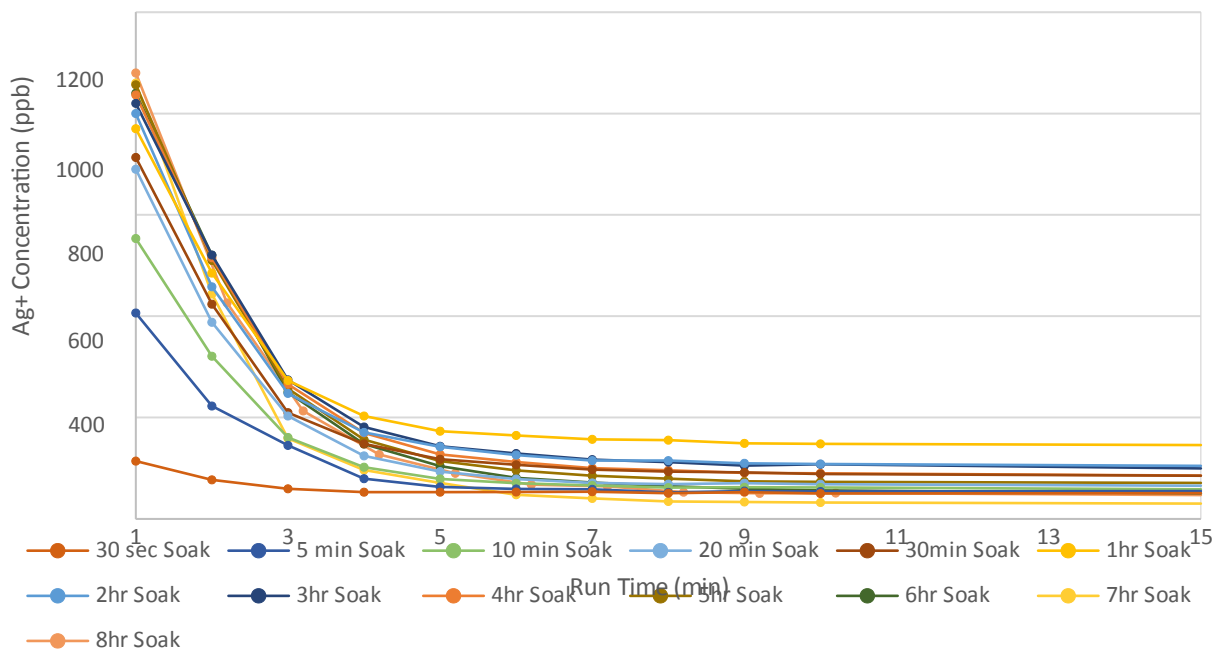
Figure 7 shows the Ag<sup>+</sup> concentration for samples taken immediately upon startup, with respect to the amount of soak time or system down time. Soak times of 30 seconds up to 8 hours were tested. The concentration at startup increases from 510 ppb at 30 seconds of soaking, up to 1280 ppb at 8 hours of soaking. The majority of the climb in concentration occurs in the first hour of soaking, which reached a Ag<sup>+</sup> concentration of 1170 ppb or 78% of saturation. After an additional 7 hours of soaking the Ag<sup>+</sup> concentration at startup only increases by 0.11 ppm, putting



**Figure 7. Startup Ag<sup>+</sup> Dose vs Soak Time.** Each point plotted represents the sample taken immediately upon startup of the system after the corresponding amount of soak time.

it at 85% of the theoretical saturation value of 1505 ppb for  $\text{Ag}^+$  from  $\text{AgCl}$ . To understand the repeatability and time necessary for the system to begin dosing at a steady rate after startup, additional sampling was performed and is shown in Figure 8. The concentration changes as the system continues to run at 0.1 L/min are shown for each of the 13 soak tests that were performed. In each case, at approximately 5 minutes of run time the  $\text{Ag}^+$  concentrations had dropped from their respective peaks at startup and leveled out at approximately 450 ppb. Overall, the startup tests have shown that the amount of  $\text{Ag}^+$  that is built up in the cartridge volume during downtime is predictable and has a short-lived affect on the  $\text{Ag}^+$  release after startup.

Ag+ Dosage Trends at Startup Following Various Soak Times



**Figure 8.  $\text{Ag}^+$  Dosage Trends at Startup Following Various Soak Times.** 13 separate soak tests of different soak times ranging from 30 sec to 8 hr are shown. Each test was run for a minimum of 30 min to confirm that the system had reach steady state, the first 15 min are shown as a closeup view so that the initial changes in concentration can be seen more clearly.

### E. ICP-OES Verification of ISE Results

As an added validation step to ensure the accuracy of the  $\text{Ag}^+$  results from the Expedited 1-Year test, samples were taken twice daily during the entirety of the test and held for ICP-OES analysis. Apart from serving as a way to cross-check the ISE  $\text{Ag}^+$  results, ICP-OES testing also provides insight into whether or not solid particle shedding is occurring. This is because ICP-OES measured total silver and samples go through a digestion step before analysis. Therefore, if solid particles of  $\text{AgCl}$  or other silver containing compounds ended up in any of these samples they would cause a spike in concentration in the ICP-OES results. This type of periodic check is important so that we can assure that the only silver being added into the effluent water is in the ionic and biocidal form, and that we are not unknowingly overdosing the water with solid silver or silver compounds. The data from this testing is shown in Table 1. Each ICP-OES sample is compared to the ISE taken immediately before it to provide the most accurate comparison between the two techniques.

Throughout the entire test period, all of the ICP-OES values for silver remained close in value to the  $\text{Ag}^+$  values measured using the ISE. The average standard deviation between the two test methods was extremely low, at 0.004. This data validates the results of the Expedited 1-Year test. It also shows that there is no reason, currently, to believe that any ( $\text{AgCl}$ )NPs or other silver solids are being shed from the system. This cross-validation method will continue to be used in future long-term flow-through studies to maintain a high confidence in all  $\text{Ag}^+$  results.

**Table 1. Comparison of Silver in Samples Between ICP-OES and ISE Measurements.** Water samples are taken from the effluent of the AgFoam cartridge and analysed using both ICP-OES and ISE. Samples for ISE analysis are taken immediately before those for ICP-OES analysis. Separate samples are used to avoid contamination in ICP-OES samples that could be caused by the use of ISA for ISE measurement.

Sample	ICP-OES SilverConcentration (ppm)	ISE SilverConcentration (ppm)	Standard Deviation
9/21 9:45 am	0.216	0.212	0.002
9/22 8:00 am	0.186	0.185	0.001
9/22 11:00 am	0.188	0.183	0.003
9/23 8:00 am	0.188	0.193	0.003
9/23 12:00 pm	0.198	0.195	0.002
9/24 9:20 am	0.188	0.190	0.001
9/24 2:00 pm	0.19	0.190	0.000
9/25 9:00 am	0.184	0.195	0.006
9/25 2:00 pm	0.182	0.192	0.005
9/28 10:00 am	0.206	0.211	0.003
9/28 2:00 pm	0.244	0.234	0.005
9/29 8:00 am	0.279	0.277	0.001
9/29 2:00 pm	0.286	0.275	0.005
9/30 8:00 am	0.291	0.283	0.004
9/30 2:00 pm	0.286	0.274	0.006
10/1 9:00 am	0.280	0.280	0.000
10/1 2:00 pm	0.292	0.273	0.009
10/2 9:00 am	0.298	0.310	0.006
10/2 2:00 pm	0.308	0.293	0.008
10/5 12:30 pm	0.308	0.316	0.004
<b>Average Standard Deviation:</b>			<b>0.004</b>

## V. Conclusion

Passive dosing technology is an attractive and strong contender for the replacement of the current iodine biocide SOA systems used in spacecraft water treatment. With the right material design, an Ag<sup>+</sup> passive dosing system can be an option that is inherently reliable, long lasting, low maintenance, and compatible with the targeted service environment. In previous years, the components and synthesis process of the AgFoam have been continuously improved upon and optimized with the goal of downselecting to the most promising candidate. The focus of this year's testing was on proving the feasibility and predictability of a scaled up AgFoam using the information gained in the previous downselection of materials and synthesis techniques. In scalability testing, it was discovered that the 10% AgFoam released Ag<sup>+</sup> at levels 56.3% lower than expected based on the assumption of linear scalability. The decision was made to increase (AgCl)NP loading up to 20%. The Expedited 1-Year Flow-Through test, using a full-scale 20% foam resulted in an average Ag<sup>+</sup> release of 234 ppb, which is above the 200 ppb threshold required for effective biocidal activity. This test also revealed an interesting phenomenon of an increase in dosing after the first weekend down-time or soaking. It is hypothesized that this jump from 190 to 287 ppb, followed by steady release at the new level, is due to the effect that soaking the system over the weekend had on the overall purging of air from within the struts and closed cells of the foam. Pretreatment studies will be performed to determine if this hypothesis is correct and if so, how we can prevent this jump from occurring by fully saturating the AgFoam prior to use. To

enhance the full understanding of how the  $\text{Ag}^+$  release responds to changes in system conditions, testing was performed over a range of flowrates as well as soak times. In both cases, the data shows smooth trend lines that lead us to believe that the AgFoam dosing response has the potential to be accurately modeled mathematically. If this can be accomplished and validated through more realistic long-term flow-through trials, it will allow for accurate predictions of the amount of  $\text{Ag}^+$  being dosed and will make the overall system more robust. While there is still more work that can be done in optimizing and understanding different aspects of the AgFoam, the  $\text{Ag}^+$  release property testing that has been completed validates the feasibility of this approach to dose  $\text{Ag}^+$  at the effective range and in a manner that is reliable.

### **Acknowledgments**

The authors would like to acknowledge funding from NASA's Advanced Exploration Systems (AES) Life Support Systems (LSS) Project.

### **References**

- <sup>1</sup> Irwin, T., Li, W., Buhrow, J., Calle, L., and Callahan, M. "Silver Foam as Long-Term Passive Biocide for Potable Water Systems," *49th International Conference on Environmental Systems*, ICES-2019, 7-11 July 2019, Boston, Massachusetts.
- <sup>2</sup> Irwin, T., Li, W., Diaz, A., Calle, L., and Callahan, M. "Silver Foam: A Novel Approach for Long-Term Passive Dosing of Biocide in Spacecraft Potable Water Systems – Update 2020," *International Conference on Environmental Systems*, ICES-2020.
- <sup>3</sup> Spacecraft Water Exposure Guidelines for Selected Contaminants, Vol 1., National Academies Press, Washington DC, 2004.
- <sup>4</sup> Petala, M., Tsiridis, V., Darakas, E., Mintsouli, I., Sotiropoulos, S., Kostoglou, M., Karapantsios, T., and Rebeyre, P., "Silver Deposition on Wetted Materials Used in the Potable Water Systems of the International Space Station," *46th International Conference on Environmental Systems*, ICES-2016, 10-14 July 2016, Vienna, Austria.
- <sup>5</sup> Petala, M., Tsiridis, V., Mintsouli, I., Pliatsikas, N., Spanos, T., Rebeyre, P., Darakas, E., Patsalas, P., Vourliasc, G., Kostoglou, M., Sotiropoulos, S., Karapantsios, T., "Silver Deposition on Stainless Steel Container Surface in Contact with Disinfectant Silver Aqueous Solutions," *Applied Surface Science*, Vol 396, 2017, pp.1067-1075.
- <sup>6</sup> Ott, M., Almengor, A., and Harris, J., "FY19 Silver Disinfection," NASA Johnson Space Center., Test Report 09302019.
- <sup>7</sup> Alternative drinking-water disinfectants: bromine, iodine and silver. Geneva: World Health Organization; 2018. Licence: CC BY-NC-SA 3.0 IGO.
- <sup>8</sup> Adam, N., "Compatibility Study of Silver Biocide in Drinking Water with Candidate Metals for the Crew Exploration Vehicle Potable Water System," SAE Technical Paper 2009-01-2459, 2009.
- <sup>9</sup> Nawaza, M., Hanb, M.Y., Kimc, Tschung-il, Manzoora, U., Amina M.T. "Silver disinfection of Pseudomonas aeruginosa and E. coli in rooftop harvested rainwater for potable purposes", *Science of The Total Environment*, Volume 431, 1 August 2012, Pages 20–25.
- <sup>10</sup> Lu, J. X., and Murray, J., "Biochemistry, Dissolution and Solubility" *National Center for Biotechnology Information, U.S. National Library of Medicine* [online library], URL: <https://www.ncbi.nlm.nih.gov/books/NBK431100/> [cited 18 March 2019].
- <sup>11</sup> Li, W., Calle, L., Hanford, A., Stambaugh, I., and Callahan, M. "Investigation of Silver Biocide as a Disinfection Technology for Spacecraft – An Early Literature Review," *48th International Conference on Environmental Systems*, ICES-2018, 8-12 July 2018, Albuquerque, New Mexico.
- <sup>12</sup> Marois Y, Guidoin R. Biocompatibility of Polyurethanes. In: Madame Curie Bioscience Database [Internet]. Austin (TX): Landes Bioscience; 2000-2013. Available from: <https://www.ncbi.nlm.nih.gov/books/NBK6422/>
- <sup>13</sup> Lamba, N., Woodhouse, K., Cooper, S.L., *Polyurethanes in Biomedical Applications*, CRC Press, New York, 1998.