Silver Foam: A Novel Approach for Long-Term Passive Dosing of Biocide in Spacecraft Potable Water Systems – Update 2023

Tesia D. Irwin[1], Angie Diaz[2], Jennifer Gooden[2], Mary Hummerick[2], Wenyan Li[2], Nilab Azim[3], and Deborah Essumang[3]
NASA, Kennedy Space Center, FL, 32899

and

Michael R. Callahan[4]
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 continued development of a nanoparticle/polyurethane (NP/PU) composite foam for the controlled release of silver ions and is intended to build upon the 2022 International Conference on Environmental Systems (ICES) paper number 97. This paper provides the technical background and performance test results (ongoing long-term silver ion release testing and product variability testing) from the silver chloride (AgCl) NP/PU composite foams. 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^+ = silver ion
AgCl = silver chloride
ARC = Ames Research Center
ICES = International Conference on Environmental Systems
ISE = ion selective electrode
ISS = International Space Station
JSC = Johnson Space Center
NASA = National Aeronautics and Space Administration
nm = nanometer
NP = nanoparticle

[1] R&D Engineer, The Bionetics Corporation, Mail Code: LASSO-008, Kennedy Space Center, FL, 32899.
[2] Research Scientist, Amentum, Mail Code: LASSO-001, Kennedy Space Center, FL, 32899.
[3] NASA, Research Scientist, Exploration Systems and Development Office, Mail Code: UB-E, Kennedy Space Center, FL, 32899.
[4] NASA, Water Technology Lead, Crew and Thermal Systems Division, 2101 NASA Parkway/EC3, Houston, Texas, 77058.

ppb = parts per billion
PU = polyurethane
PWD = potable water disperser
SWEG = Spacecraft Water Exposure Guidelines
WHO = World Health Organization
WPA = Water Processor Assembly

I. Introduction

SILVER biocide is being investigated by NASA as the replacement for the current iodine water disinfectant used within the International Space Station (ISS) Water Processor Assembly (WPA), and for future mission architectures. Several key benefits make silver ion (Ag^+), the biocidal component in silver biocide, an attractive choice.[1] Ag^+ is an effective disinfectant at levels that are safe for human consumption; unlike iodine, there is no need to remove silver ion biocide at the potable water disperser (PWD). Ag^+ can also lower the life support risk and improve long term mission flexibility since it has the potential to be used across international spacecraft platforms.

Currently, both active and passive silver ion dosing systems are being developed. Current active dosing approaches focus on the active release of Ag^+ using electrolysis which is being investigated at Johnson Space Center (JSC) as well as the direct injection from a concentrate solution being studied at Ames Research Center (ARC). The passive dosing approach, as a compatible alternative to these active methods, relies on the concept of a silver compound nanocomposite polyurethane foam (referred to as Silver Foam or AgFoam). This paper follows four previous ICES papers, which further detail the concept creation, material synthesis decisions, the Ag^+ release properties testing results, the mathematical model that predicts the dosing behavior of the AgFoam, the risk mitigation plan for technical development, and the method to reduce total organic carbon (TOC) release from AgFoam (one of the higher identified risks).[2,3,4 5]

Since last year, the focus of the AgFoam project was to perform tasks that will further lower the development risk of AgFoam as an Ag^+ dosing technology, while also investigating its alternative function as microbial barrier or microbial check valve (MCV) which will be reported on in a future paper once testing is complete.

This paper provides the performance test results of AgFoam as a passive dosing device of silver ion (ongoing long-term silver ion release testing), and the progress made in risk mitigation efforts (product variability).

II. AgFoam Long-Term Dosing Test Results

Silver Foam was developed as a disinfectant passive dosing device and a potential replacement for the iodine ion exchange resin bed, currently used in ISS WPA system. A simplified schematic of the WPA is shown in **Figure 1**, with the current iodine ion exchange resin bed circled in red. Wastewater delivered to the WPA is temporarily stored in the Wastewater Tank, which includes a bellows that maintains a pressure to push water and gas into the Mostly Liquid Separator (MLS). The MLS separates gas from wastewater and removes odor-causing contaminants before venting the gas phase to cabin air. Next, the water is pumped through the Particulate Filter and Multifiltration (MF) Beds to remove particular and dissolved inorganic and non-volatile organic contaminants. The process water stream then enters the Catalytic Reactor, where low molecular weight organics are oxidized in the presence of oxygen, elevated temperature, and a catalyst. Finally, the Ion Exchange (IX) Bed removes dissolved products of oxidation and adds iodine for residual microbial control. The product water is subsequently stored in the Water Storage Tank prior to delivery to the ISS potable water bus.

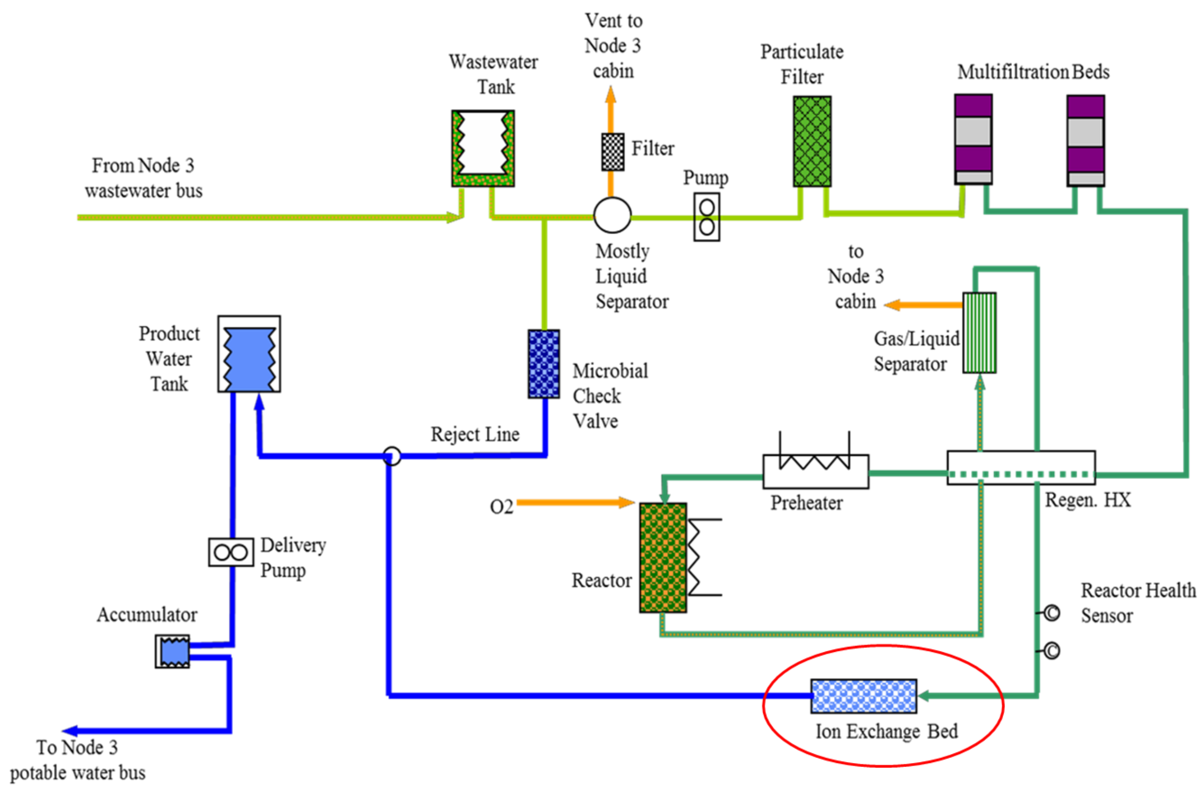

Figure 1. Illustration of ISS WPA Process, where iodine ion exchange resin beds are used as a disinfectant dosing device (labelled Ion Exchange Bed) and Microbial Check Valve. [6]

The key performance parameter of the AgFoam is its ability to achieve long term passive dosing of silver ion at a target range (200 to 500 ppb), which is based on potable limits in the Spacecraft Water Exposure Guidelines (SWEG) as well as the World Health Organization (WHO), and target flow rate of 0.1L/min. To achieve this requirement, in the simplest terms, AgFoam using direct and targeted diffusion from the particle surface area. The low solubility limit of AgCl, the Ag^+ source, coupled with the high particle surface area and overall AgFoam volume is what ensures that this diffusion takes place at the appropriate rate while the open-cell structure of the PU foam component holds the nanoparticles in place and alleviates flow restrictions. The concept design and flow-through math model can be found in more detail in our previous paper, ICES-2022-097.[5] **Figure 2** is a depiction of the dosing mechanism of the AgFoam, showing an SEM image of the AgFoam on the left with a zoomed in graphical representation of the Noyes Whitney equation for diffusion on the right as it relates to Ag^+ dissolution from the AgFoam.

The accelerated 1-Year Flow-Through test performed last year provided the successful proof-of-concept testing to show that a reasonably sized cartridge of AgFoam can achieve Ag^+ release rates within the target range at the target flowrate of 0.1 L/min for the amount of water that is required for 1 crew member for 1 year.[4] This demonstrated the technical feasibility of AgFoam as a viable approach for passive silver ion dosing.

A long-term realistic flow-through test was initiated in July of 2022. This test mimics the intermittent flow conditions of the ISS WPA system and will provide more reliable data to predict the dosing performance during operation for 4 crew members over a target duration of 1 year. It is also planned to test to fail, which will allow for a better understanding of the true failure mode of the AgFoam.

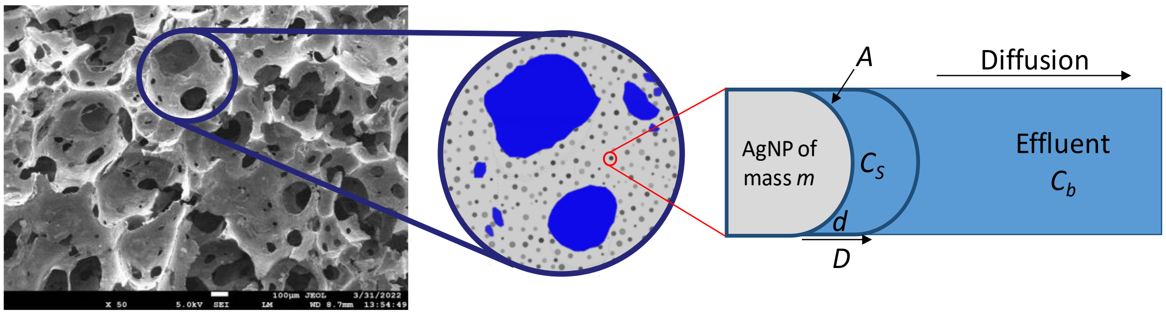

Figure 2: Illustration of the Noyes-Whitney equation in relation to the dosing function of the AgFoam. A cross section of the AgNP/PU composite foam is represented to the left, which shows the PU foam (light grey), the open foam pores (blue), and the AgNPs (black). To the right is an enlarged depiction of a single AgNP (grey).

A. Experimental Conditions

This test is designed to replicate the flow condition of ISS WPA, with an output target for four crew members that is based on the water consumption rate of 2.5L/crew/day, namely a water treatment target of 3650 L/year. To model the frequency and duration that the ISS WPA operates at we used the volume over time data from the Wastewater Tank. Since the Wastewater Tank is a bellows tank, it also controls the flow of water downstream (shown as a decrease in volume). Using this data, we can calculate the average process times as well as the down time between cycles which allows us to better mimic the realistic flow-through conditions and ranges in our own testing.

A typical WPA ISS operation cycle is shown below in **Figure 3**, which was adapted using a one-month snapshot of the WPA during standard operation provided to us by Layne Carter. To limit the buildup of biofilm on the Wastewater Tank bellows, the tank is cycled at least once every 48 hours. Based on the "nominal" one-month of online tank volume data that we received, the Wastewater Tank fluctuates between 2.5 and 40.5 liters in volume by expanding and contracting the bellows. The average operating time over this window was 7.5 hours (varying from 2.75 up to 18.5 hours), whereas the average down time was 31 hours (varying from 10.75 up to 48.75 hours).

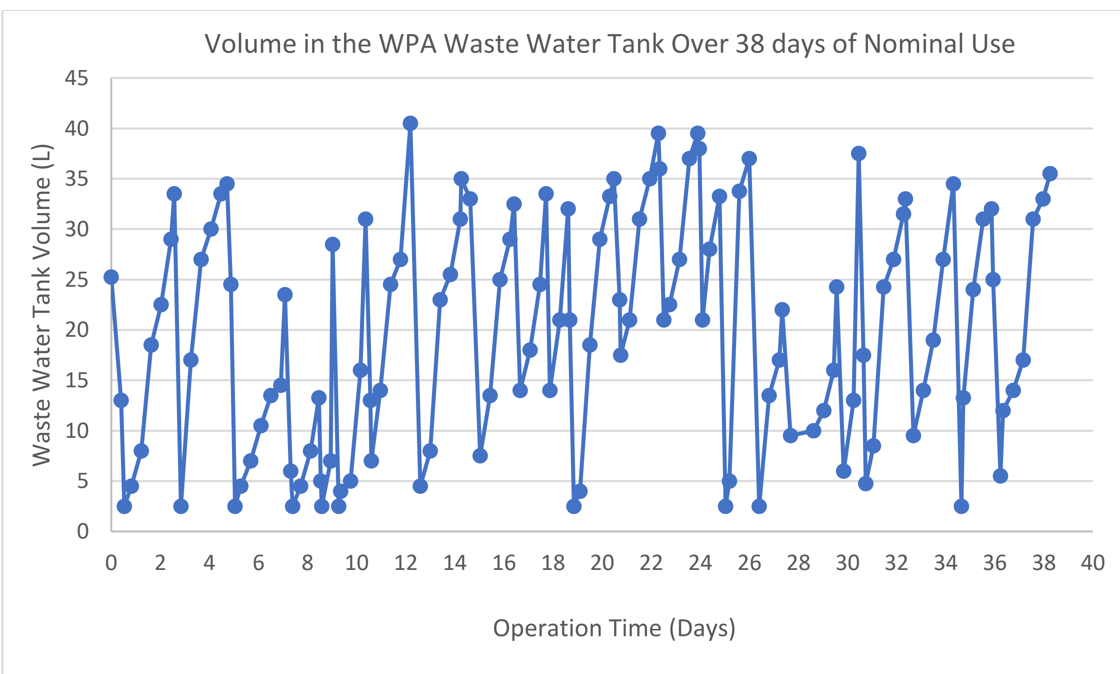

Figure 3. A representative water level trend in the WPA tank during nominal tank operation.

B. Test Results (As of May 2023)

The following figures show the test results of the long-term flow-through test.

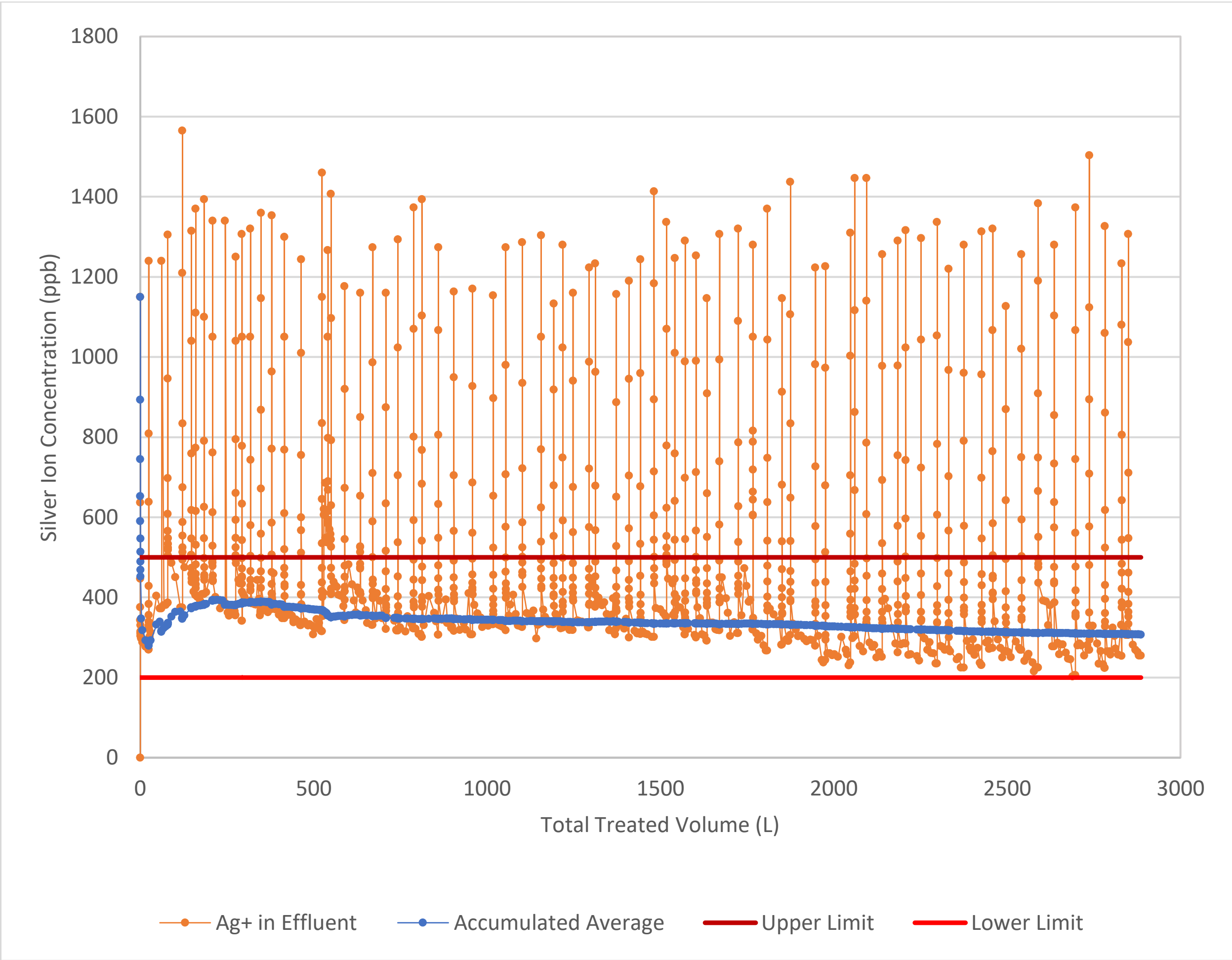

Figure 4. The long-term realistic AgFoam flow-through test results plotted versus total treated volume.

To date, the long-term flow-through test is still producing effluent water with an Ag^+ concentration that is within the target range of 200-400 ppb. The spikes in the effluent trend of the plot represent the initial 10 minutes of sampling after startup of the system and are taken so that the effects of downtime between system operation on the startup trend can be seen. Since the product water would never be taken directly out of the effluent of the AgFoam cartridge and instead feeds into the product water tank (which is approximately 20L), an accumulated average concentration line is plotted in red. This accumulated average trend accounts for the inherent buffering capacity that a product water tank has on minimizing these brief spikes in dosed Ag^+.

Figure 4 shows the long-term flow-through data plotted versus the total treated volume whereas **Figure 5** shows the same data but plotted over time so that the variation in down-time can be visualized.

Figure 5. The long-term realistic AgFoam flow-through test results plotted over time.

III. Risk Management Progress: Product Variability

As mentioned earlier, One-Year Flow-Through test performed in 2021, demonstrated the technical feasibility of AgFoam as a viable approach for passive silver ion dosing. Afterwards, a risk management plan was developed to provide an overview document to identify knowledge gaps, to evaluate technical risks and to monitor progresses. It will also help us to evaluate the risk level associated with each knowledge gap and prioritize the tasks to mitigate the more severe risk when possible.

After the initial assessment, many knowledge gaps were identified and each was ranked based its severity and likelihood. These technical risks can be roughly organized into four main categories: Material Characteristics, Service Environment, Product Variability, and Performance Predictability (Math Model), as shown in the following table.

Table 1: AgFoam Initial Risk Assessment (updated 07/2021)

CATEGORY	KNOWLEDGE GAP	SEVERITY	LIKELIHOOD	RISK LEVEL
MATERIAL CHARACTERISTICS	TOC Leaching Affecting Potability	HIGH	HIGH	– 9 –
	Insufficient Lifespan (for dosing)	HIGH	LOW	– 6 –
	Pressure Drop (caused by PU foam)	MEDIUM	LOW	– 3 –
	Chloride Release at Corrosive Levels	LOW	LOW	– 1 –
SERVICE ENVIRONMENT	Channeling of Water through AgFoam	MEDIUM	LOW	– 3 –
	pH Effects on Performance	LOW	LOW	– 1 –
	Temperature Effects on Performance	LOW	LOW	– 1 –
	Material Incompatibility with Ag+	MEDIUM	ELIMINATED	– 0 –
	Photoreduction of AgCl	MEDIUM	ELIMINATED	– 0 –
	Water Impurity Effects on Ag+	MEDIUM	ELIMINATED	– 0 –
MATH MODEL &PREDICTABILITY	Cartridge Geometry (L/D)	MEDIUM	MEDIUM	– 5 –
	Dosage Swing, Start and Stop Flowrates	MEDIUM	ELIMINATED	– 0 –
	Flowrate Effects on Ag+ Dose	MEDIUM	ELIMINATED	– 0 –
	Unstable Dosage, Constant Flowrate	LOW	ELIMINATED	– 0 –
	AgFoam Scalability	LOW	ELIMINATED	– 0 –
PRODUCT VARIABILITY	Complete Saturation of AgFoam (no trapped air)	MEDIUM	HIGH	– 7 –
	AgFoam Batch Variability	MEDIUM	MEDIUM	– 5 –
	Variation in Nanoparticle Surface Area	MEDIUM	MEDIUM	– 5 –
	Non-homogeneous AgCl Distribution	LOW	HIGH	– 4 –

A. Risk Mitigation Progress Made before July 2022

Table 1 shows the risk assessment performed in July 2021. Note that three risks in the Service Environment category have been eliminated: material incompatibility with Ag^{+} (by choosing flight grade plastic material to hold AgFoam), Photoreduction of AgCl (by protecting AgFoam from light via packaging), and Water impurity effect on Ag^{+} (tested using a water with similar purity of WPA product water or ISS potable water). There are also four eliminated risks in the Math Model and Predictability category: Dosage swing (test completed with the Start/Stop flow test [4]), Flowrate effect (testing completed at various flow rates[4]), Unstable dosing at constant flowrate (test completed with the 1 year accelerated test[4]), and AgFoam Scalability (test done using full scale foam[4]).

Recently, more progress was made to address the Cartridge geometry knowledge Gap (Math Model & Predictability) by establishing a realistic math model using cartridge geometry factors as variables to predict AgFoam dosing concentration.

As shown in the Risk Assessment, the highest-ranking risk identified was the potential for TOC leaching into the potable water from the polyurethane at a rate high enough to impact the potability of the water. The next highest-ranking risks primarily had to do with product variability as well as lifespan. Due to the high risk level, elimination of the "TOC Leaching" knowledge gap became our new focus. The AgFoam washing process, which involves flushing DI water continuously through the AgFoam, also aimed to eliminate any trapped air in the foams therefore addressing the "Complete Saturation" knowledge gap.

B. Risk Mitigation Progress Made after July 2022

One of the objectives of the current long term realistic test is to understand failure mode and address the lifespan risk under the Material Characteristics category. The other current risk mitigation focus is Product Variability, specifically the size and quality variability of the AgCl nanoparticles which causes variability in AgFoam batches, nanoparticle surface area, and AgCl distribution within the AgFoams.

Three AgFoam samples were washed to reduce TOC release to below 50ppb, details of the washing process can be seen in ICES-2022-097.[5] They were then tested for their dosing behavior as a part of the initial product variability test. Unfortunately, their dosing concentrations were all lower than expected, ranging from 20 to 120 ppb of Ag^{+} at flow rate 0.1 L/min, compared to the AgFoam used for 1 year accelerated test (range 220 to 350 ppb).

After some initial diagnostic tests that examined the foam making process, the foam filter packing configuration, and AgCl nanoparticle size and distribution in the AgFoam, it became clear that the cause of the product variability is the batch variability of the AgCl nanoparticles.

The size of the old particles is small and more homogenous, while the new particles are larger and tend to form hard clusters, as shown in the SEM images in **Figure 6**. Consequently, the dispersion of the new particles is less stable, which can result in their poor distribution in the AgFoam. This can be easily seen by direct observation of silver foam samples after light exposure, as shown in **Figure 7**, due to a unique photoreduction reaction that causes AgCl to change color from white to black/grey after light exposure. Both the size and the consequential dispersion property can result in lower release rate and lower effluent Ag^{+} concentration.

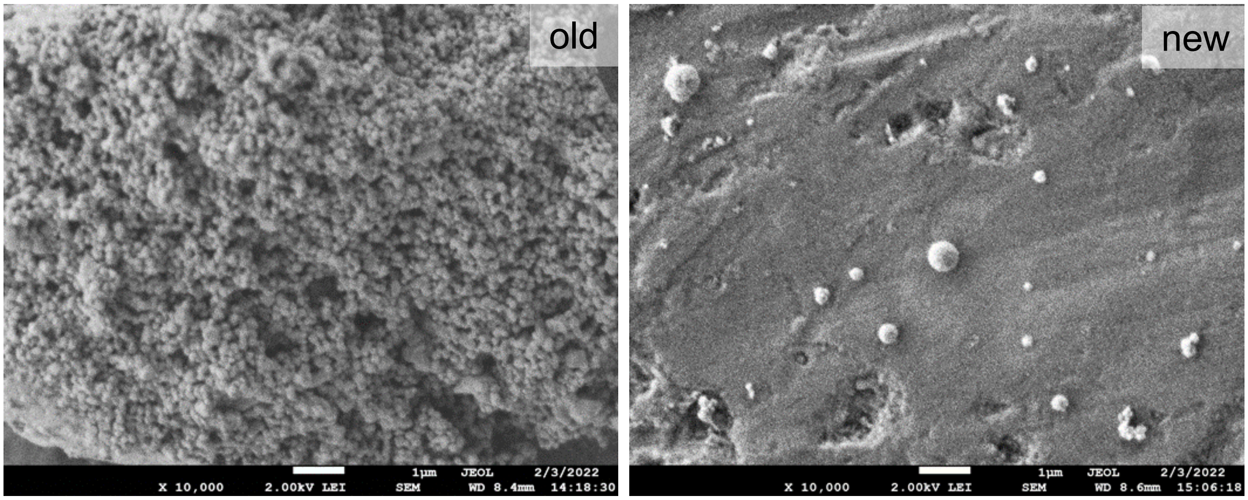

Figure 6. SEM images of the old (left) and the new (right) AgCl particles

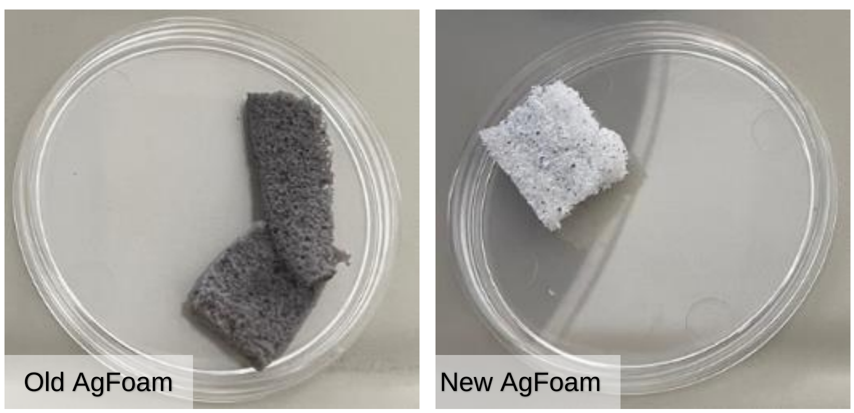

Figure 7. Images of both old and new AgFoam samples made using different batches (old and new) of AgCl Nanoparticles. AgFoams were exposed to light to photoreduce any AgCl present thus turning it grey.

In addition, the size effect of the particles on the dissolution rate of Ag^{+} release can be demonstrated by directly testing the dissolution rate of the AgCl nanoparticles. Test results for four separate batches of AgCl nanoparticles are shown in **Figure 8**. The particles labeled “Old AgCl” refer to the first batch of nanoparticles received which are the same ones used in the AgFoam that is currently being used in the long-term flow-through testing. The batches labeled “Batch 1” and “Batch 2” are the 2 subsequent batches that have been manufactured since the original batch in response to our concerns over changes in product characteristics. The particles labeled “Freeze Dried” are the latest batch which we received from the vendor semi-dry and performed additional processing and freeze drying on which resulted in similar release rate to the original “Old AgCl” particles. Each test is preformed twice to show repeatability, labeled #1 and #2 for each particle batch. For each dissolution test, 27 mg of particles was added quickly into 100 mL DI water after the particles were ground using a pestle and mortar. The Ag^{+} concentration was measured over time using ISE for a total of 30 minutes.

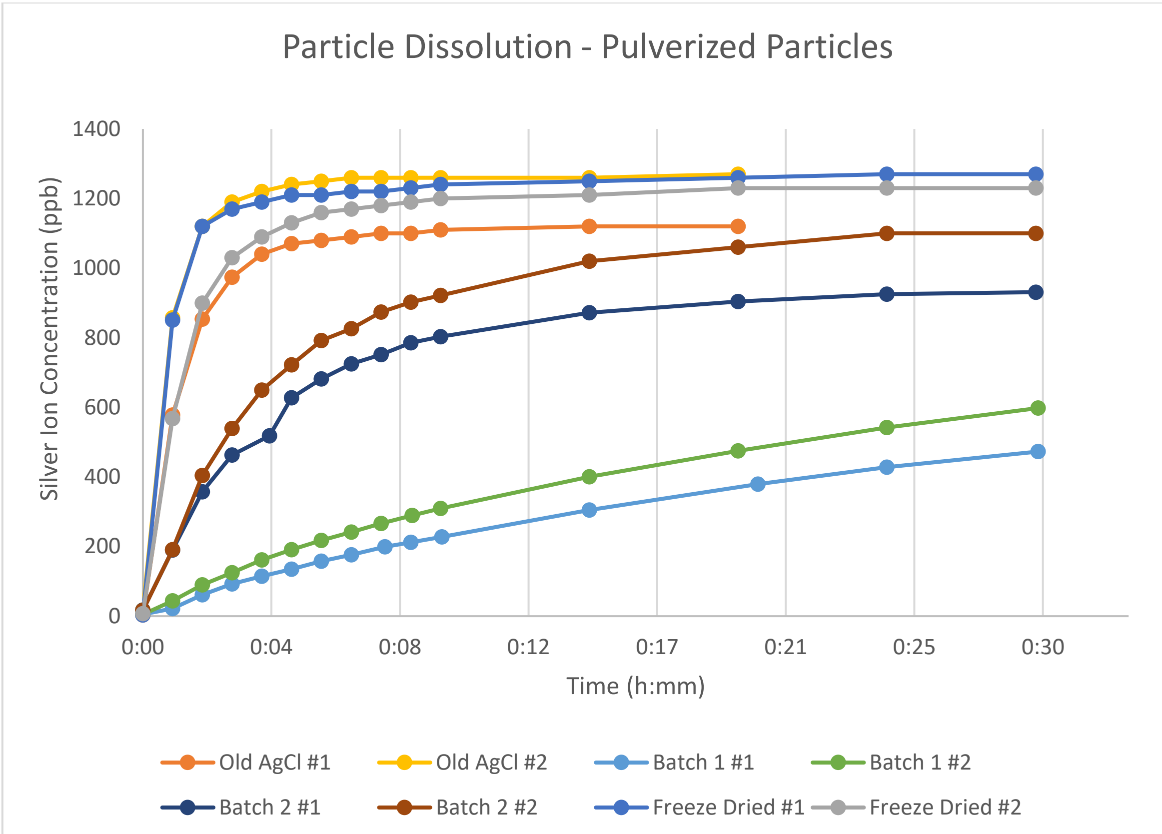

Figure 8. Dissolution rate test results for various batches of AgCl nanoparticles.

Quality of the AgCl nanoparticles is the critical core component of the AgFoam, but this risk is considered medium as we have developed a method for AgCl nanoparticle synthesis at Kennedy Space Center (KSC). However, since scaling up of the nanoparticle synthesis process is not the focus of this project, we seeked out and were able to identify a commercial product that has shown to be successful in past foams. The recent product variability issues from the commercial product have led us to re-consider the decision, and we have decided to work with the vendor to address these issues. To address the particle product variability issue, several simple quality control tests were developed that verify particle size, dispersion stability, and surface chemistry, before the particles are used for AgFoam synthesis.

During the initial trouble shooting with the vendor, it appeared that changes in the drying process might have contributed to the large particle cluster formation. To test this, it was suggested that the vendor provide samples at various stages before complete drying. Two batches of AgCl nanoparticles were received from vendor, and SEM/EDS was performed. Based on SEM observation, as shown in **Figure 9,** there are still some clusters larger than 30 um, as shown in Figure 9B, with some small particles (about 100 nm) and some larger crystalline cubic particles around 1µm on the surface (Figure 9C). There are also a significant number of individual nanoparticles and individual particles around 1 µm, as shown in Figure 9D.

Based on these observations, a potential simple solution for the variability issue would be separation of the small particles from the big clusters. This was achieved using the following steps (1) disperse particles in water, allowing large particles to settle briefly, then (2) transfer of the suspension to a centrifuge tube and centrifuging the dispersion containing small particles to rid most of the water, and (3) freeze drying the small particles to get a free flow powder, which is then ready for AgFoam synthesis.

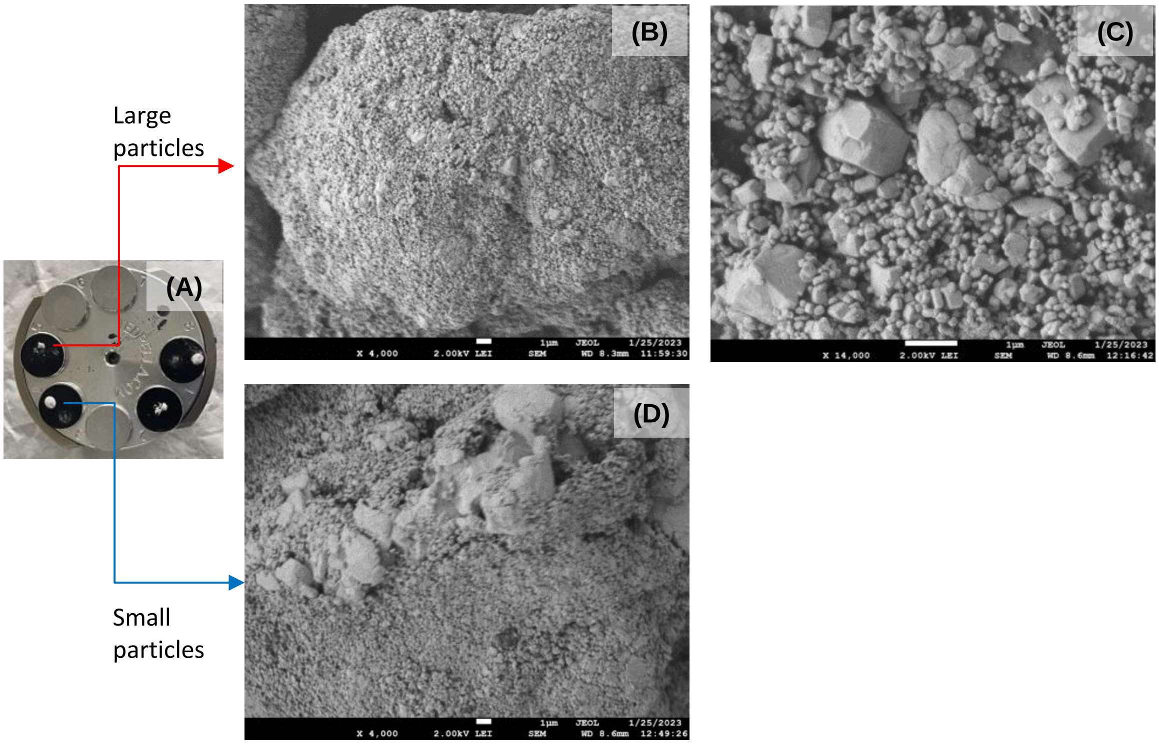

Figure 9. The SEM results of a new batch of AgCl particles.

IV. Summary

The top priority of the AgFoam project is demonstrate the technical feasibility of the AgFoam design. After this was accomplished by the accelerated One-Year Flow-Through test performed last year, a risk management plan was put together to guide the next phase of development. After the initial assessment, many knowledge gaps were identified, their risk level evaluated, and they were organized into four main categories: Material Characteristics, Service Environment, Product Variability, and Performance Predictability (Math Model). This paper presents the risk mitigation plan, and reports development efforts to further reduce the risk level and close the knowledge gaps in two categories: Material Characteristics (Lifespan) and Product Variability (AgFoam Batches, Nanoparticle Surface Area, and AgCl Distribution).

AgFoam Lifespan is currently being addressed with a realistic long-term flow-through test which aims to mimic the WPA processing schedule for a crew of four members for one year. As of May 2023, the AgFoam is still dosing withing the target Ag^+ concentration range. To address the Product Variability risk category, several product quality tests have been developed and used in conjunction with discussions with the vendor to determine the source of AgCl variability and a method to eliminate it. Slight modification to the most recent batch of AgCl nanoparticles has resulted in particles that match the dissolution rate of the old batch of good AgCl particles, indicating that these modified particles have a high chance of producing successful AgFoams. SEM imaging of the newest batch of particles also shows smaller and more homogeneous particle size (even before any modification) which should lead to better dispersion throughout the foam matrix and in turn reduce AgFoam Batch variability and variability caused by poor AgCl distribution.

To eliminate both risks, further work is still required. The long-term flow-through test will conclude in July 2023; however, the test may still be prolonged to determine how and when dosing failure will occur. To eliminate variability risks, more AgFoams still need to be synthesized and tested using the newly modified AgCl nanoparticles. Utilization of the AgFoam as an MCV is also currently being investigated and will be summarized in future papers.

Acknowledgments

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

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