Silver Foam as Long-Term Passive Biocide for Potable Water Systems

Tesia D. Irwin¹, Wenyan Li², Jerry Buhrow³, Angie Diaz⁴, and Luz M. Calle⁵
NASA, Kennedy Space Center, FL, 32899

and

Michael R. Callahan⁶
NASA Johnson Space Center, Houston, TX, 77058

A spacecraft water disinfection system, suitable for extended length space exploration missions, 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, the effluent should be chemically compatible with all materials in contact with the water, be safe for human consumption, and suitable to be shared across international spacecraft platforms and mission architectures. Silver ions are a proven broad spectrum biocide. Silver is also the potable water biocide of choice for future exploration missions. Currently, the proposed method for implementing silver biocide in spacecraft systems relies on silver electrode technology to produce a controlled amount of silver ions. Unfortunately, electrolytic-based silver dosing presents multiple inherent challenges that affect performance and increase maintenance requirements over time. To decrease the risk of failure, an alternative silver biocide delivery method is needed. Control-release technology is an attractive option for developing a passive high-reliability silver dosing device. The concept of a nanoparticle/polyurethane (PU) composite foam for the controlled release of silver was prompted by the controlled release technology developed by NASA for the delivery of corrosion inhibitors and indicators. This paper presents the technical background and results from the synthesis and properties testing of the silver nanoparticles (AgNPs)/PU composite foam that is being developed for use in spacecraft potable water systems.

Nomenclature

\( A \quad = \quad \text{surface area of the solute particles} \)
\( Ag^+ \quad = \quad \text{silver ion} \)
\( AgCl \quad = \quad \text{silver chloride} \)
\( AgClNPs \quad = \quad \text{silver chloride nanoparticles} \)
\( AgNPs \quad = \quad \text{silver nanoparticles} \)
\( Cb \quad = \quad \text{concentration in the bulk solvent/solution} \)
\( Cs \quad = \quad \text{particle surface concentration} \)
\( D \quad = \quad \text{diffusion coefficient of the solute in the solvent} \)
\( d \quad = \quad \text{thickness of the concentration gradient} \)
\( DI \quad = \quad \text{deionized} \)

¹ Research Scientist, The Bionetics Corporation, Mail Code: LASSO-001, Kennedy Space Center, FL, 32899.
⁵ NASA, Senior Research Scientist, Science and Technology Programs Division, Mail Code: UB-R3, Kennedy Space Center, FL, 32899.
I. Introduction

Silver is a proven broad spectrum biocide. The National Aeronautics and Space Administration (NASA) is interested in adopting silver biocide as a replacement for iodine for long duration exploration missions. Although iodine has been successfully used on the International Space Station (ISS), it can have adverse effects on the thyroid and must be removed before being consumed by astronauts. Currently, iodine removal is achieved through the use of additional hardware, which increases the overall complexity and mass of the disinfection system. Silver ion (Ag⁺) is an effective biocide, at concentrations that can be directly consumed by the crew, and is the biocide of choice used by the Russian Space Agency. If silver can be an acceptable biocide for future missions, this will allow for water to be standardized and shared across international spacecraft platforms and mission architectures. In general, an ideal biocide should have no adverse effect on humans, inhibit microbial growth and biofilm formation, and reduce microbial-induced corrosion in the water storage and distribution systems. Electrolytic-based silver dosing systems are the current lead technology for controlled dosing of silver ions in a spacecraft potable water system. However, long-term use of electrolytic systems has revealed multiple inherent problems, namely increased maintenance requirements and decreased stability as a result of electrode fouling and changes in surface area. In response to the need for an alternative approach for silver biocide delivery, that avoids these problems, the concept of a silver nanoparticle (AgNP) and polyurethane (PU) composite foam was conceived. This paper presents the background and results from the synthesis and properties testing of the AgNP/PU composite foam (referred to throughout as the AgNP foam) that is being developed for use in spacecraft potable water systems.

II. Background

The design and development of a AgNP foam for long-term use in spacecraft potable water systems requires an understanding of all potential obstacles and clear guidelines for success. A literature review was performed to gain knowledge of known limitations in current silver biocide technologies to guide the design of the AgNP foam. A brief overview of those limitations is given here to provide background reasoning for future assumptions and design choices. The most important requirement of the AgNP foam is that it needs to deliver a controlled concentration of Ag⁺ in its effluent. This target concentration needs to be based on requirements for safe consumption while also meeting the requirements for an effective biocide. The Spacecraft Water Exposure Guidelines (SWEGs) were created to compile previous silver ion exposure limits into a set of safety guidelines, based on continuous exposure over time. The SWEGs have been established for exposures of 1, 10, 100, and 1000 day class missions as the allowable concentration of silver in the drinking water may change slightly depending on mission duration. For 1000-day class exploration missions, the maximum allowable silver concentration is set at 0.360 parts per million (ppm). Silver has been used as a biocide for many years and in many applications. The World Health Organization (WHO) conducted a literature review of silver biocide studies from numerous researchers. The determined effective range, based on their review across different strains of bacteria and varying conditions, is anywhere from 20 ppb to 100 ppb. Solubility is one of the most important properties for compounds that are being considered as possible sources of Ag⁺ ions. Table 1 shows the solubility constants of these compounds.
Table 1. Solubility product constants for various silver compounds.$^{5,6}$

<table>
<thead>
<tr>
<th>Silver compound</th>
<th>Formula</th>
<th>Solubility product constant (Ksp) at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>Ag</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Silver sulfide (α-form)</td>
<td>Ag₂S</td>
<td>6.69 x 10⁻⁵⁰</td>
</tr>
<tr>
<td>Silver sulfide (β-form)</td>
<td>Ag₂S</td>
<td>1.09 x 10⁻⁴⁹</td>
</tr>
<tr>
<td>Silver arsenate</td>
<td>Ag₃AsO₄</td>
<td>1.03 x 10⁻²²</td>
</tr>
<tr>
<td>Silver iodide</td>
<td>AgI</td>
<td>8.51 x 10⁻¹²</td>
</tr>
<tr>
<td>Silver phosphate</td>
<td>Ag₃PO₄</td>
<td>8.89 x 10⁻¹⁷</td>
</tr>
<tr>
<td>Silver bromide</td>
<td>AgBr</td>
<td>5.35 x 10⁻¹³</td>
</tr>
<tr>
<td>Silver chromate</td>
<td>Ag₂CrO₄</td>
<td>1.12 x 10⁻¹²</td>
</tr>
<tr>
<td>Silver oxalate</td>
<td>Ag₃C₂O₄</td>
<td>5.40 x 10⁻¹²</td>
</tr>
<tr>
<td>Silver carbonate</td>
<td>Ag₂CO₃</td>
<td>8.46 x 10⁻¹²</td>
</tr>
<tr>
<td>Silver chloride</td>
<td>AgCl</td>
<td>1.77 x 10⁻¹⁰</td>
</tr>
<tr>
<td>Silver sulfate</td>
<td>Ag₂SO₄</td>
<td>1.20 x 10⁻⁹</td>
</tr>
<tr>
<td>Silver bromate</td>
<td>AgBrO₃</td>
<td>5.34 x 10⁻⁵</td>
</tr>
<tr>
<td>Silver nitrate</td>
<td>AgNO₃</td>
<td>Highly soluble</td>
</tr>
<tr>
<td>Silver fluoride</td>
<td>AgF</td>
<td>Highly soluble</td>
</tr>
</tbody>
</table>

For the purposes of developing a AgNP foam with a dissolution rate of Ag⁺ that meets the above safety and biocide dosing requirements, we decided to choose a compound with a solubility limit that is close to the target Ag⁺ dosing range of 50 to 300 parts per billion (ppb). It is also important to consider the safety of the other ions that will be formed during dissociation since they will likely also end up in the effluent drinking water. For these reasons, we chose to move forward with silver chloride (AgCl). The relatively low solubility limits of AgCl in comparison with other silver compounds should result in a AgNP foam with a low and more consistent dissolution rate of Ag⁺. This is because the release rate of Ag⁺ into the effluent is a primary function of the surface area of the particles being dissociated and the silver compound’s solubility limit.$^7$ This relationship is shown in the Noyes-Whitney Equation (Eq.1) and demonstrated a visual representation in (Fig.1).$^8$

\[
\frac{dm}{dt} = A \frac{D}{d} (C_s - C_b)
\]  
(Eq.1)

Where

\[
\begin{align*}
\frac{dm}{dt} &= \text{solute dissolution rate (kg} \cdot \text{s}^{-1}) \\
m &= \text{mass of dissolved material (kg)} \\
t &= \text{time (s)} \\
A &= \text{surface area of the solute particles (m}^2) \\
D &= \text{diffusion coefficient (m} \cdot \text{s}^{-1}) \text{ of the solute in the solvent} \\
d &= \text{thickness of the concentration gradient (m)} \\
C_s &= \text{particle surface (saturation) concentration (kg or moles/L)} \\
C_b &= \text{concentration in the bulk solvent/solution (kg or moles/L)}
\end{align*}
\]

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

In order to develop a Ag⁺ ion dosing system that is robust, passive, and requires minimal maintenance, we explored all of the currently known delivery systems. Based on this review and our expertise in controlled release technology,
the concept of a particle composite foam for the controlled release of silver was conceived. The particle composite foam consists of AgNPs embedded in a PU foam. The PU foam was chosen because it has desirable properties, detailed below, that should lend well to being durable for long-term missions and providing a stable release. PU foam has a high and stable surface area which is a key factor in reaching our target Ag⁺ ion concentration of 500 ppb. It is also a flexible material and has been used widely as packing material, making it potentially useful, even when stored for long periods of time on spacecraft, and is also a safe material to pass potable water through. PU foam synthesis is also well documented and well tested, making it easier to replicate.

Silver ion’s high reactivity, while being one of the main factors in silver’s ability to be a biocide, also creates challenges in finding materials that are compatible with it. The ion’s high reactivity means that keeping it in solution for extended periods of time can be difficult because of the interaction between the ions and the material it is in contact with. Many different material compatibility studies have been conducted with silver biocide and have recently been compiled by Li et al. (Table 2). Light exposure also causes the photoreduction of the Ag⁺ ion in silver biocide over time. These factors will be important to keep in mind for future prototype designs that incorporate the use of a passive silver biocide delivery system. Separate materials compatibility testing is being performed for silver biocide. However, for the design of the AgNP foam we will assume that deposition of silver metal will still be a factor moving forward.

### Table 2. Summary of the Silver Compatibility Studies

<table>
<thead>
<tr>
<th>Study</th>
<th>Composition</th>
<th>Geometry</th>
<th>Surface Treatments</th>
<th>Silver Solution</th>
<th>S/V (cm³)</th>
<th>Silver Loss Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Callahan et al., 2007</td>
<td>SS 21-6-9</td>
<td>Tube</td>
<td>passivated</td>
<td>0.5 ppm (AgF) 4.59</td>
<td>10.20%/day</td>
<td>high</td>
</tr>
<tr>
<td>Inconel 718</td>
<td>washer</td>
<td>passivated</td>
<td>0.5 ppm (AgF) 0.14</td>
<td>1.5%/day</td>
<td>med</td>
<td></td>
</tr>
<tr>
<td>Roberts et al., 2007</td>
<td>SS 21-6-9</td>
<td>Coupon 10x10x1.5 mm</td>
<td>passivated</td>
<td>0.5 ppm (AgF) 0.14</td>
<td>3%/ 1st day; 30% after 21 days</td>
<td>high</td>
</tr>
<tr>
<td>Inconel 718</td>
<td>same</td>
<td>passivated</td>
<td>0.5 ppm (AgF) 0.14</td>
<td>&gt;10%/first day; 88% after 21 days</td>
<td>high</td>
<td></td>
</tr>
<tr>
<td>SS 316L</td>
<td>same</td>
<td>passivated</td>
<td>0.5 ppm (AgF) 0.14</td>
<td>&gt;10%/1st day; 70% after 21 days</td>
<td>high</td>
<td></td>
</tr>
<tr>
<td>Adam 2009</td>
<td>SS 316L</td>
<td>washer</td>
<td>passivated</td>
<td>0.5 ppm (AgF) 0.2, 0.5, 1.0, 5.0, 8.2</td>
<td>90%/loss: 411, 190, 180, 63 hours for S/V 0.2, 0.5, 1.0, 5.0</td>
<td>high</td>
</tr>
<tr>
<td>Inconel 718</td>
<td>washer</td>
<td>passivated</td>
<td>0.5 ppm (AgF) 0.2, 1, 8.2</td>
<td>90%/loss (days): 32.1 (0.2), 1.4 (1.0)</td>
<td>high</td>
<td></td>
</tr>
<tr>
<td>Inconel 718</td>
<td>washer</td>
<td>electropolished</td>
<td>0.5 ppm (AgF) 0.2, 1, 8.2</td>
<td>90%/loss (days): 108.3 (0.2), 17.7 (1.0), 0.5 (8.2)</td>
<td>high &amp; med</td>
<td></td>
</tr>
<tr>
<td>Beringer et al., 2014</td>
<td>Inconel 718</td>
<td>Test panels</td>
<td>thermal oxidized &amp; Ag plated</td>
<td>0.35 ppm (AgF) 0.14</td>
<td>maintain about 1 year</td>
<td>low</td>
</tr>
<tr>
<td>SS (E-Brite)</td>
<td>Test panels</td>
<td>thermal oxidized &amp; Ag plated</td>
<td>0.39 ppm (AgF) 0.14</td>
<td>maintain about 1 year</td>
<td>low</td>
<td></td>
</tr>
<tr>
<td>Petala et al., 2014</td>
<td>SS 316L</td>
<td>Test Panels 76x12.7x1.6 mm</td>
<td>120 grit sanded passivated (P) passivated &amp; electropolished (P&amp;E)</td>
<td>Electrolytic Ag 0.5 ppm 5.0</td>
<td>near 100% loss for all samples after 7 days</td>
<td>high</td>
</tr>
<tr>
<td>SS 15-5</td>
<td>same</td>
<td>thermal oxidized</td>
<td>0.5 ppm 5.0</td>
<td>100%/loss after 7 days</td>
<td>high</td>
<td></td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>same</td>
<td>0.5 ppm 5.0</td>
<td>100%/loss after 7 days</td>
<td>high</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FEP &amp; PTFE</td>
<td>same</td>
<td>0.5 ppm 5.0</td>
<td>&gt;60%/loss after 7 days</td>
<td>high</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPR</td>
<td>same</td>
<td>0.5 ppm 5.0</td>
<td>Near 100%/loss after 7 days</td>
<td>high</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS 316L</td>
<td>Test Panels 76x12.7x1.6 mm</td>
<td>120 grit sanded passivated (P) passivated &amp; electropolished (P&amp;E)</td>
<td>Electrolytic Ag 0.5 ppm 5.0</td>
<td>Ag loss after 7 days: 316L P&amp;E (21%) vs 316L P (94.75%)</td>
<td>high</td>
<td></td>
</tr>
<tr>
<td>SS 15-5</td>
<td>same</td>
<td>thermal oxidized</td>
<td>10 ppm 5.0</td>
<td>loss after 7 days: 78%</td>
<td>high</td>
<td></td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>same</td>
<td>10 ppm 5.0</td>
<td>loss after 7 days: 100%</td>
<td>high</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FEP &amp; PTFE</td>
<td>same</td>
<td>10 ppm 5.0</td>
<td>loss after 7 days: FEP 15%, PTFE 5%</td>
<td>med</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPR</td>
<td>same</td>
<td>10 ppm 5.0</td>
<td>loss after 7 days: 60%</td>
<td>high</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wallace et al., 2016, 2017</td>
<td>SS 316L</td>
<td>Washer</td>
<td>passivated</td>
<td>0.4 ppm (AgF) After 100 ppm for 24 hours</td>
<td>residual Ag at 28 days (ppb): 0.25 (control 350)</td>
<td>high</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>Panel 0.7x0.5x0.12 in</td>
<td>passivated by 20% HNO₃</td>
<td>Same as above</td>
<td>0.15</td>
<td>residual Ag at 28 days (ppb): 0.24 (control 350)</td>
<td>med</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>Panel 0.7x0.5x0.12 in</td>
<td>Ag plated at 500 ppm</td>
<td>Same as above</td>
<td>0.15</td>
<td>residual Ag at 28 days (ppb): 0.35 (control 350)</td>
<td>low</td>
</tr>
</tbody>
</table>
III. Methods and Materials

A. Silver Nano Particle Synthesis

For the initial foam design and synthesis, AgCl has been chosen as the silver ion source due to its solubility limit of 2 ppm in water, which is close to the target dosage concentration of 500 ppb that is calculated below in section III-B. A previously conducted literature review resulted in a multitude of options for AgCl nanoparticle (AgClNP) production. For simplicity, we have chosen the following simple method of AgClNP synthesis which was obtained from an article by M. R. H. Siddiqui, et al. and later modified.\(^1\)\(^,\)\(^2\) 0.5 M hydrochloric acid (HCl) is added to 200 mL of 0.1 M silver nitrate (AgNO\(_3\)) solution until the precipitation of AgCl has stopped. The greyish-white precipitate is then filtered, washed with deionized water (DI), and dried at 60°C. We later modified this process by adding in polyvinyl alcohol (PVA) to the silver nitrate solution as a stabilizing agent.\(^3\) Figure 2 shows the resulting AgClNPs from this synthesis through scanning electron microscope (SEM) imaging.

B. Silver Nanoparticle Composite Foam Design

For the target dosing capability of the foam design to be successful, the following requirements and conditions need to be taken into consideration. The concentration of the Ag\(^+\) ion needs to be high enough to be an effective biocide while also being low enough to be safe for astronaut consumption for extended duration missions. The high reactivity of the Ag\(^+\) ion also needs to be accounted for in the dosing requirements as its instability in solution will cause the effective concentration to decrease with time, assuming that the system materials are not completely inert. This results in loss due to Ag\(^+\) ion deposition. Testing of materials in contact with the Ag\(^+\) ion will need to be conducted to determine the actual deposition loss. However, for the initial silver foam design and synthesis, we will assume a deposition loss of 80%. Given the above requirements and assumptions, the initial target silver disinfectant concentration was chosen to be 500 ppb. This target provides a theoretical Ag\(^+\) ion concentration of 100 ppb after the assumed deposition loss, which is both within the range of previously studied silver biocides and below the allowable limit of 0.360 ppm per day that is required by the SWEGs.

Since we are using a PU foam as the matrix for our AgClNPs, we will assume a stable surface area and surface concentration. The foam will provide a stable surface area, whereas the particle surface area changes over time. The surface concentration should also remain stable, due to the fact that Ag\(^+\) ion diffusion is faster inside the foam where there is a large surface area of AgCl nanoparticles and short diffusion distances from particles to the pore surface. The surface concentration is expected to be close to saturation. These assumptions are based on the Noyes-Whitney Equation\(^3\) (Eq.1) which characterizes the relationships between particle surface area, surface concentration and bulk solution concentration with time.

With these assumptions, a calculation (Eq.2-Eq.6) was performed to determine the amount of PU foam that would be necessary to treat 2.5 L of water per crew per day for a full year. All synthesis will take place terrestrially.

Assuming 2.5 L water per crew per day:

\[
Water \ consumption \ per \ crew \ per \ year = \frac{2.5 \ L \ water}{day} \times \frac{365 \ days}{year} = 912.5 \ L \ water/yr \quad (Eq.2)
\]

Assuming an 80% deposition loss and target silver disinfectant concentration of 100 ppb:

\[
Total \ silver \ concentration \ needed = \frac{100 \ ppb}{(1 - 0.80)} = 500 \ ppb
\]

\[
Silver \ ion \ needed \ per \ crew \ per \ year = 500 \ ppb \times \frac{0.001 \ mg}{1 \ L} \times \frac{1 \ g}{1000 \ mg} \times \frac{912.5 \ L}{yr} = 0.456 \ g \ Ag \ ion/yr
\]

![Figure 2: SEM of synthesized AgCl nanoparticles using the method described by M. R. H. Siddiqui, et al. \(^1\). Magnification of x500. (10 μm scale)](image)
Given that the molecular weights (MW) of AgCl and Ag\(^+\) are 143.32 and 107.87 g/mol, respectively, and that AgCl is 1-to-1 silver and chlorine ions:

\[
\text{Amount of AgCl needed per crew per year} = 0.456 \frac{g \text{ Ag ion}}{\text{yr}} \times \frac{143.32 \text{ g AgCl}}{107.87 \text{ g Ag ion}} = 0.606 \frac{g \text{ AgCl}}{\text{yr}}
\]  

(Eq.3)

Assuming AgCl loading is 5\% in the foam, and 50\% of the silver is released during its useful service life:

\[
\text{Foam mass} = \frac{0.606 \text{ g AgCl}}{0.05 \times 0.5} = 24.2 \text{ g}
\]

(Eq.4)

Assuming the density of the PU foam is 6 lbs per cubic foot:

\[
\text{Volume of foam per crew per year} = 24.2 \text{ g} \times 6 \frac{\text{lbs}}{ft^3} \times \frac{453.592 \text{ g}}{\text{lb}} \times \frac{ft^3}{28316.8 \text{ ml}} = 252.3 \text{ ml}
\]

(Eq.5)

These calculations (Eq.2-Eq.6) show that the estimated amount of silver foam needed per crew member per year is approximately 24 g or 250 ml. This estimation shows that an AgNP PU foam is a viable option for spacecraft systems due to its low weight requirements. However, the volume of the system will potentially need to be optimized by increasing silver loading or increasing foam density.

C. Foam Preparation and Properties Testing

The AgNP/PU composite foam was synthesized using the traditional 2-step polyurethane foam synthesis process and modifying it to incorporate the AgNPs, illustrated in Figure 3.\textsuperscript{11} An isocyanate premix is prepared by adding 42\% of the desired alcohols to the entire amount of diisocyanate, with a ratio of NCO:OH of approximately 2:1. This premix is cured at 50\°C for 36 hours. The alcohol premix is then synthesized, consisting of the remaining alcohols, surfactants and catalysts. The premix is then homogenously mixed, and then added to the isocyanate premix, along with AgCl nanoparticles, using a high speed shear mixer, followed by the addition of a physical blowing agent. The foam is cured at 90\°C for 20 minutes, following by cold curing over night at ambient laboratory conditions.

Figure 3: Illustration of the 2-step synthesis process used to create polyurethane foam with incorporated AgCl nanoparticles. For larger images of the synthesized AgNPs and AgNP composite foam see Fig.5-7.

Three different loading percentages of AgNPs were used to synthesize 5\%, 10\%, and 20\% AgNP containing PU foams. By varying the amount of AgNPs that were incorporated into the foam, the foam quality can be tested at each percentage to determine what effects the AgNPs have on the overall durability of the foam matrix. The foam synthesis process can then be modified to improve the foam structure if necessary. Varying the amount also allows us to determine what effect the increasing amounts of AgNP have on the Ag\(^+\) ion release rate so that we can tailor the foam to reach the target Ag\(^+\) ion concentration for the given flowrate range.

Release property testing of the synthesized foams will be performed to determine both short-term and long-term dissolution rates. For short-term dissolution testing, silver foam samples will be allowed to soak in DI water. Soaking will be done in glass beakers that are sealed and covered with aluminum foil to prevent evaporation and light exposure. The Ag\(^+\) ion concentration will be determined using an Ion Selective Electrode (ISE) probe to measure the dissolution of Ag\(^+\) ion over short periods of time. This will allow us to more quickly optimize the silver foam by giving us an understanding of how long it takes for a known amount of foam to release Ag\(^+\) ion to the point of saturation (2 ppm).
Once the Ag\(^+\) ion release rate of the silver foam has been optimized, testing of the long-term dissolution rate will be conducted in a flow cell similar to the one depicted on Figure 4. This flow cell will simulate the release rate for a continuous system, which is closer to the requirements of a spacecraft system. The ISE will again be used to determine the Ag\(^+\) concentration of the effluent water. Actual foam densities for all foams that are synthesized will also be measured using simple displacement, both saturated and unsaturated. Water quality testing of the effluent will also be measured using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) to determine if the PU is leaching into the water. This will be used to test the safety of the effluent for consumption as well as to provide data to prove or disprove the durability of the PU as a foam structure.

**Figure 4:** Proposed foam cell design for testing release rates of silver foams.

**IV. Results and Discussion**

Initial synthesis of AgClNPs using the method described in section III-A resulted in particles that were 1 \(\mu\)m in size (Figure 5). This first batch of particles also showed evidence of the formation of silver metal in some areas, leading us to believe that some of the particles were experiencing reduction reactions. This is to be expected due to the characteristic photosensitivity of AgCl. The first batch of particles were also tightly clustered together, which made it challenging to incorporate them homogenously into the PU foam during its synthesis.

**Figure 5:** SEM images of AgClNPs (1 \(\mu\)m scale) synthesized using the method described above and viewed at 10k magnification (left). Same AgClNPs viewed at 25k magnification (1 \(\mu\)m scale) to show sites of reduction reactions (right).

To help alleviate the agglomeration problem of AgClNPs, further experimentation, using polyvinyl alcohol (PVA) as a surfactant stabilizer, was conducted. The resulting AgClNPs from this modified process were much smaller and very few were clustered together compared to our previous results without the PVA. Using SEM imaging, the particles were determined to be approximately 30 nm in size (Figure 6). The PVA further optimized the synthesis process by
increasing the formation rate, and allowing for easier separation of the nanoparticles from the reaction solution. As anticipated, this modified process also leads to particles that were easier to incorporate into the foam.

**Figure 6:** AgClNPs obtained after modifying the process with PVA as a surfactant under SEM beam at 10k (1 μm scale) (left) and 50k (right) magnification (100 nm scale). Resulting AgClNPs were determined to be 30 nm in size.

These nanoparticles were then added into the PU foam using the method described in section III-C at different concentrations to determine the impact that various percentages of silver ion addition has on the structural properties of the foam. SEM imaging (Figure 7) was used to closely inspect the changes in the foam surface.

**Figure 7:** SEM images of silver foam at same magnification (100 μm scale): 5% AgCNP loading (left), 10% AgCNP loading (right)

At 5% AgCNP loading, there were no noticeable changes in the structural integrity or porosity of the foam. However, at 10% AgCNP loading, the resulting foam falls apart more easily and does not have the structural memory that the foam with the 5% loading retained. Under SEM (Figure 8), the 10% foam appears to have a lower degree of crosslinking, fewer pores, and less surface area than the 5% foam, which explains the noted decrease in porosity. An EDS scan was also conducted on the 10% foam to verify the presence of both Ag⁺ ions and Cl⁻ anions in the AgCNP foam composite.
While we have been able to successfully incorporate AgClNPs into a PU foam, short-term and long-term release property testing will need to be completed to determine if the 5% loading is sufficient for spacecraft water system treatment. From there, we must further optimize the foam synthesis to determine the upper limit of AgCl loading that is possible, while still maintaining the foam’s structural properties. It may be necessary to explore different types of foam, such as PU foam with a silicone surfactant coating or even a pure AgCl metal foam.\textsuperscript{14}

V. Conclusion

Silver disinfectant has great potential as the biocide of choice in future exploration missions. This has prompted the development of a silver delivery system that is reliable and easily maintained. A silver nanoparticle composite foam is an attractive option for such delivery system because it would inherently be a passive dosing technology with minimal maintenance requirements. Preliminary calculations show that the system should also be very lightweight (approximately 24 grams per crew per year) and relatively small (approximately 250 ml per crew per year). It would also serve as a microbial check valve, and would possibly double as a packing material during periods of inactivity. Initial synthesis and testing have shown that the AgClNP foam retains the polyurethane foam’s structural integrity at levels of AgClNP loading below 5%. However, at 10% loading, the foam’s structure was compromised. Further foam optimization is needed to determine the upper loading limit. Extended release property testing also needs to be conducted in order to optimize the foam for a 100 ppb release of silver ion that is sustainable over extended periods of time. In the event that the silver foam cannot be modified to passively release the appropriate amount of silver ion, other foam modifications, such as surface coatings and different types of foam, can be pursued to determine their effectiveness. Overall, these preliminary results show that a silver nanoparticle composite foam is a promising passive delivery mechanism for future spacecraft drinking water systems.

Acknowledgments

The authors would like to acknowledge funding from the Advanced Exploration Systems (AES) Life Support Systems (LSS).

References


