Silver Ion Biocide Delivery System for Water Disinfection

Benjamin M. Slote[1], Edward Salley[2], Daniel Carr[3], Michael C. Kimble[4]
Reactive Innovations, LLC, Westford, MA 01886

and

Niklas Adam[5]
NASA Johnson Space Center, Houston, TX 77058

U.S. space exploration missions have long considered returning to the Moon and exploration of Mars that challenge life support systems. For these long duration missions, there is interest in replacing the iodine water treatment system with ionic silver, a proven biocide. For long duration exploration missions, it is imperative that an effective biocide be used that prevents microbial growth, biofilm formation, and microbially induced corrosion in the water storage and distribution systems while minimizing logistical supply requirements associated with the biocide delivery system. Two biocide delivery systems have been developed that electrochemically produce silver ions for disinfecting water throughout the water storage and distribution system. One system uses a newly developed hybrid micro-filtration and ion-exchange membrane to produce an abundance of silver ions at the 1000 ppb level upstream in the water distribution system to prevent biofilm growth. This is followed by a downstream collection module that electrochemically removes these silver ions before the water is discharged. Another approach uses a membraneless reactor to produce a 1000 ppb silver ion concentration level that also has a mechanically driven electrode cleaning mechanism that removes oxide films ensuring long life operation. By maintaining a sufficiently high level of silver ions throughout the water storage and distribution system, biofilm formation is suppressed. This approach addresses present concerns where spurious silver deposition occurs on the container and flow line surfaces thus lowering the silver ion concentration to unsatisfactory disinfection levels.

Nomenclature

A	=	Amps
Ag	=	Silver
DMSO	=	Dimethyl Sulfoxide
e^-	=	Electron
F	=	Fluorine
H^+	=	Proton
H_2	=	Hydrogen
H_2O	=	Water
ISS	=	International Space Station
K^+	=	Potassium Ion
KOH	=	Potassium Hydroxide
mA	=	milli-amp
Na	=	Sodium
OH^-	=	Hydroxide Ion
ppb	=	Part per Billion (mass base)
S	=	Siemen (ohm^{-1})
SIAM	=	Silver Ion Addition Module
SIRM	=	Silver Ion Removal Module

[1] Research Engineer, bslote@reactive-innovations.com, 2 Park Drive, Unit 4.
[2] Senior Research Scientist, esalley@reactive-innovations.com, 2 Park Drive, Unit 4.
[3] Research Engineer, dcarr@reactive-innovations.com, 2 Park Drive, Unit 4.
[4] President, mkimble@reactive-innovations.com, 2 Park Drive, Unit 4.
[5] Niklas.m.adam@nasa.gov, 2101 NASA Parkway.

I. Introduction

U.S. space exploration missions have long considered returning to the Moon, exploration of Mars, and even excursions to dock with asteroid. These long-term missions offer significant challenges to life support systems. An article by Jones and Kliss highlights these life support challenges for various destinations, transport duration time, habitat type, and habitat duration with a goal of replacing the iodine water treatment system with ionic silver.[1] Iodine treated water has been used successfully with the International Space Station; however iodine reportedly imparts a bad taste to the water, and its use requires that the iodine be removed before being consumed by astronauts due to its adverse effects on the thyroid.[2] It is imperative that an effective biocide is used to prevent microbial growth, biofilm formation, and microbially-induced corrosion in the water storage and distribution systems; moreover, the system must rectify the present issue by posing no potential for adverse health effects.

Biofilms are formed when free-swimming microbes attach themselves to substrates. The individual microbes send out chemical signals that attract others to the colony. A polysaccharide coating, which is resistant to the permeation of molecules such as antibiotics, is secreted over the colony. While some biofilms are composed of benign and even beneficial organisms, many pathogens are film-formers. Biofilms of pathogens are particularly troublesome, as individual cells will be sloughed off at intervals, continuing the contamination of the water stream. The waste products excreted by biofilms of bacteria, molds and yeast can attack the substrate on which they are attached, causing "microbiologically induced corrosion." Once formed, biofilms are difficult to remove by chemical means, thus the goal is often to prevent their formation in the first place.

Disinfection and prevention of biofilm formation in potable water supplies has long been accomplished by humans even without a scientific understanding of the process. The beneficial effect of copper and silver metal on potable water supplies has been known since ancient times. With the rise of bacteriological and environmental science, the advantageous effect produced in aqueous environments was understood to be due to the biocidal action of the ionic forms of these metals. Industrial and commercial applications of ionic copper-silver disinfection methods were in development by the 1950s. In conjunction with the Garrett Corporation, NASA developed a miniature silver ionization water purifier for the Apollo program.[3,4] This technology electrochemically oxidized silver into the water treatment process. Unused silver ions were contained in the exit water and consumed by astronauts in this process. NASA has verified and accepted 400 ppb silver ion biocide treated water for potable water standards per the ISS Medical Operations Requirement Document.[5]

Silver is relatively harmless to the body at bacterial effective levels. The Environmental Protection Agency dictates that drinking water should have no more than 100 ppb silver, a level that is non-toxic.[6] Unlike other heavy metals such as mercury and lead that chemically bond and accumulate in the body, approximately 99% of silver is excreted.[7] It is for this reason that conventional antimicrobial silver systems have not bothered to collect unused silver ions. However, cases of extreme exposure have caused upper respiratory or mild eye irritation, and prolonged exposure can cause argyria.[8]

Recent work by NASA has examined using stock solutions of silver biocide that are metered into water storage systems. These solutions are based on U.S. procedures used for water transfer operations on the ISS which presumably will be used for delivering biocide in longer duration missions.[9] Consequently, much recent focus has been applied to the material compatibility issues of the biocide and the wetted areas of the containment metal.[10,11] These studies have examined the stability of silver biocide when in contact with various metals including 316L stainless steel, inconel 718, and nitronic 40. In all of these studies, the silver ion concentration decreased over time to unacceptable levels needed for prevention of biofilm growth. Sporadic silver deposits were noted on the metallic surfaces that could be caused by galvanic reaction or by the presence of other biocide components (Na and F) to precipitate out the silver. Agitation of the vessels was also noted to dislodge deposited silver freeing up new nucleation sites for continued silver deposition from other silver ions in the solution. Importantly, because the silver ion concentrations are much lower than the recommended 100 ppb level in these investigations, there is a high probability that biofilms will form; and once they are formed, they are very difficult to remove as previously discussed.

From these prior studies, the use of a silver biocide solution that is metered in could be problematic for long duration water disinfection needs mainly due to the unknown silver ion concentration that can vary over time and location. One issue is that effective water disinfection requires the presence of a residual disinfectant wherever the

water resides including the storage tanks and the distribution lines. To overcome this, an electrochemical antimicrobial silver reactor was developed to produce an effective biocide for treating potable water for long duration missions.

II. Technical Approach

Rather than meter in a silver ion biocide solution into the water storage and distribution system, silver ions can be generated *in situ* electrochemically via oxidizing silver electrodes. This can be accomplished using a membraneless approach similar to the earlier Apollo system where the electrodes are separated by a gap with a flowing water stream. In this approach, the low ionic conductivity of the water requires a higher electrochemical potential to overcome ohmic losses. Another reactor approach is to place an ion-exchange membrane between the electrodes where the membrane serves as the electrolyte source lowering the ohmic drop. Both of these reactor approaches have been produced and evaluated as discussed below.

III. Hybrid Membrane Silver Ion Reactor

One approach under consideration for long duration space missions is a silver ion reactor that electrochemically introduces an abundance of silver ions upstream in the water treatment process to prevent biofilm growth. This is followed by a downstream collection module that electrochemically attracts unused and spent silver ions. Low levels of silver are said to be compatible for human ingestion. However, with Reactive's approach most of the silver ions are collected at the point of discharge to allow the entire water system to have an abundance of residual silver ions to impart disinfection control. This addresses present concerns where the ionic silver content is depleted due to contact with metallic surfaces in the container and flow line.[2]

Figure 1 shows a schematic of a Silver Ion Addition Module (SIAM) that uses a hybrid ion-exchange & microfiltration membrane placed between electrodes. In this design approach, the anode and cathode are separated by a thin 2-5 mil thick membrane that serves as the electrolyte source. Water flows normal to the membrane due to the micro-filtration design that also has ionically conductive pathways due to the ion-exchange faction of the hybrid membrane. In this manner, the electrodes remain separated without silver ions re-plating on the upstream cathode as can happen in un-separated cell approaches.
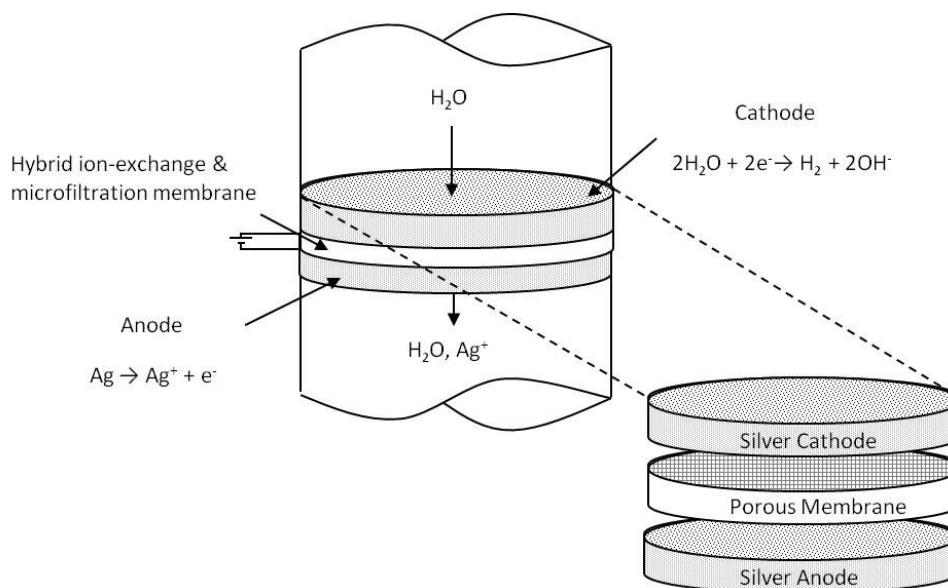

Figure 1. Hybrid membrane for the Silver Ion Addition Module (SIAM)

With a hybrid membrane silver ion reactor, silver ions are produced on the anode located in the downstream position from the cathode. Thus, the silver ions are swept away with the water that permeates the cell as shown in Figure 1. This is an important aspect of this design approach to overcome a major deficiency with membraneless

reactors where silver ions can re-deposit on the cathode. Since the silver ions are produced on the downstream side of the cell, there is a uniform silver ion distribution in the radial and angular dimensions in the water volume unit leaving the reactor. This minimizes concentration gradients that can give rise to tertiary current distributions leading to spurious silver deposition in the flow lines.

One approach would be to package this Silver Ion Addition Module (SIAM) upstream in the water treatment process so that silver ions are spread throughout the system preventing biofilm growth. Downstream in the water treatment process before the water is extracted for potable usage, a similar hybrid membrane is placed to collect unused and spent silver ions. This downstream unit is the Silver Ion Removal Module (SIRM) and operates on the reverse principle of the SIAM. Figure 2 shows a schematic of the silver ion removal unit where metal ions are preferentially electrochemically reduced on the upstream side of the membrane. Oxidation of the hydroxide ions introduced upstream in the SIAM will occur on the downstream side of the SIRM balancing the water pH.
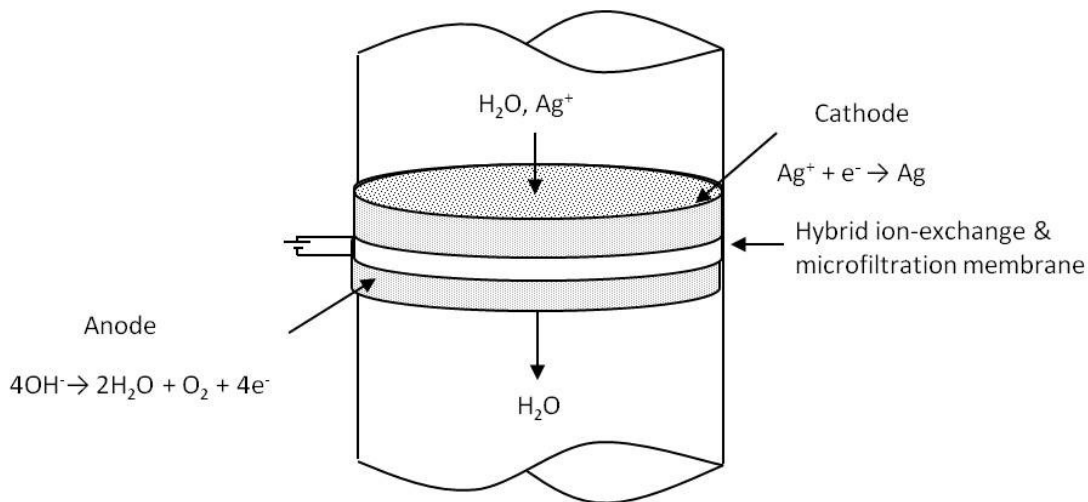

Figure 2. Schematic of the Silver Ion Removal Module (SIRM)

Two operational scenarios are anticipated with the hybrid membrane approach. In one scenario, the SIAM is used to add an abundance of silver ions (*e.g.*, 1000 ppb Ag^+) to the upstream water system and collect the remaining silver ions downstream in the process with the SIRM. This approach ensures a sufficient quantity of silver ions exists throughout the wetted water regions preventing biofilm growth. The other operational scenario would be to use just a SIAM module itself to add a smaller quantity of silver ions on the order of 100 ppb without using a downstream collection device.

A. Modified Nafion Membrane-Based Reactor

An electrochemical cell was formulated that used a perforated Nafion 115 membrane to permeate water while separating a platinum mesh cathode and a silver mesh anode. Nafion is a water compatible ion-exchange material that enables cations to conduct through it when hydrated. Perforations consisting of 5 to 20 holes each with a 10-mil diameter were uniformly placed over a 0.5" diameter Nafion membrane. While water flowed through the cell at 100 ml/min, a constant current density was applied while monitoring the cell potential over time. After 60 seconds of operation, an aliquot of the downstream water was taken where the silver ion concentration was measured using a Hach colorimetric chemical analysis method (Method #8120). Figure 3 shows the data for this initial run at 0.15 A/cm^2 and at a higher 1.48 A/cm^2 current density. At the low current density, the cell voltage is one volt and no silver ions were produced in the downstream flow. However, at a higher 1.48 A/cm^2 level, two different tests gave disparate results. In one test, the voltage rose to slightly less than 2 volts, however, it started to decay before the 60 second collection period eventually going to zero with no silver ions being produced in the downstream aliquot. The presence of the silver mesh contacting the relatively acidic ion-exchange membrane coupled with the oxidation process enabled silver ions to migrate upwards to the cathode depositing silver throughout the ion-exchange membrane. This caused the membrane to eventually short-out as shown by dendritic silver deposits on the membrane in Figure 4 and as evidenced by the voltage dropping to zero. A subsequent test was assembled and operated at 1.48 A/cm^2 giving a voltage slightly higher than 2 volts and a 40 ppb silver ion concentration in the

downstream solution. The potential shows a continuing decay as shown in Figure 3 that would eventually short-out as the prior run did.
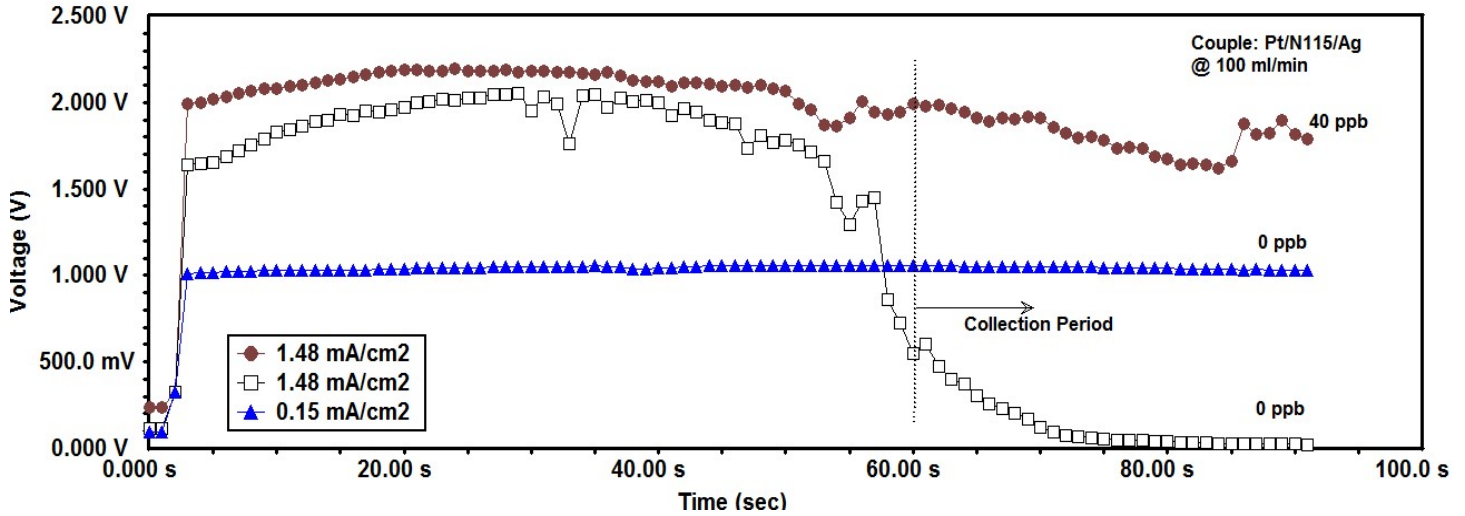

Figure 3. Silver oxidation performance in a Pt/Nafion 115/Ag couple at 100 ml/min
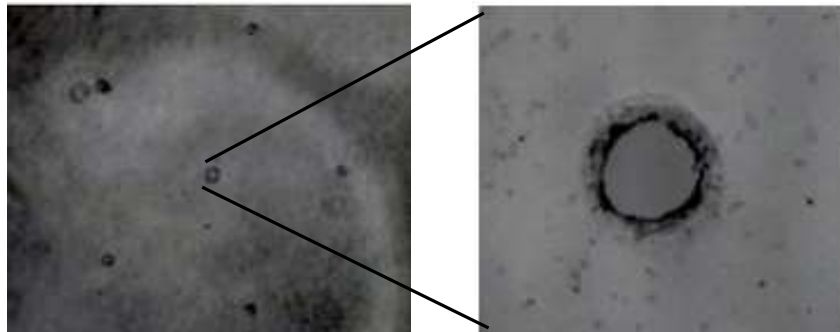

Figure 4. Silver dendritic growth in a Nafion membrane separator causing electrical shorts between the electrodes, left) six perforations spanning a 0.5" diameter membrane, right) silver dendrite growth shown by the dark region about the perforation

    From this testing, it is apparent that placing a silver anode directly on the membrane is deleterious to a long life operating system since silver ions will readily migrate through the ion-exchange membrane depositing on the upstream cathode and shorting the cell. Accordingly, a new cell design was produced that introduced a platinum mesh inner-layer between the hybrid membrane and the silver anode. This design offsets the silver mesh anode from the membrane while the platinum inner-layer mesh enables surface diffusivity of protons to complete the electrical circuit. Figure 5 shows a schematic of this inner-layer anode mesh design for the SIAM.
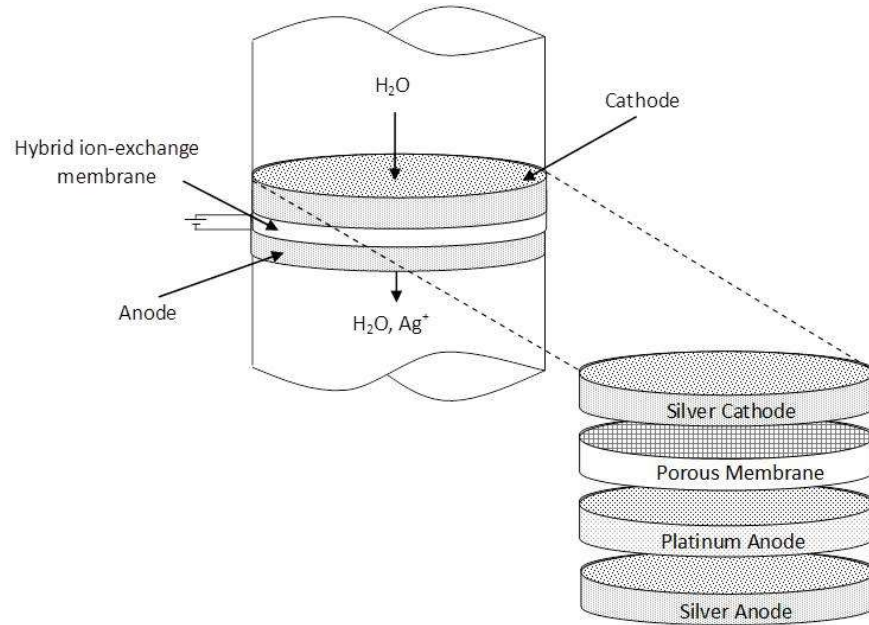
Figure 5. SIAM unit with a platinum mesh inner-layer electrode to offset the silver electrode from the membrane

An assessment of the SIAM reactor using the platinum inner-layer mesh on the anode side was conducted at varying flow rates of 50, 100, and 200 ml/min at applied current densities of 0.15, 0.74, and 1.48 A/cm^2 as shown in Figure 6. Reactor effluent aliquots were taken after running the cell for 60 seconds using Hach colorimetric methods to measure the silver ion concentration. Some general trends are apparent in that higher current densities and lower flow rate operation increases the silver ions produced. Of particular interest as well is that the voltage is more stable over time as a result of the platinum mesh inner-layer on the anode mitigating or slowing down the rate of silver dendritic growth through the reactor.
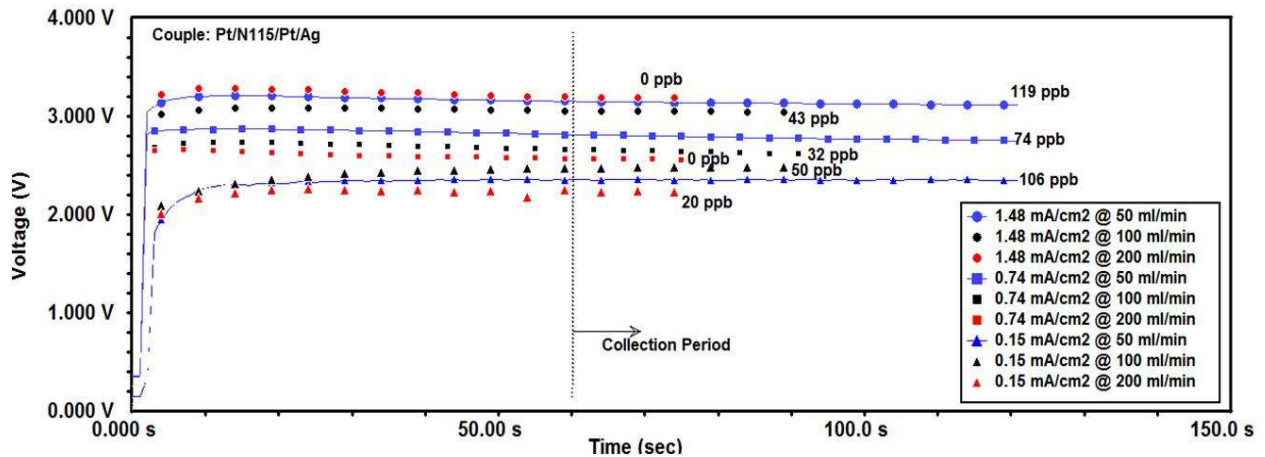

Figure 6. Electrochemical silver ion production using a platinum inner-layer mesh to offset the silver electrode from the membrane separator

B. Hybrid Membrane Development

The SIAM reactors that used a commercial off-the-shelf Nafion membrane perforated with a number of 10 mil diameter holes still exhibited cell short-circuiting over a few minutes of operation. This is due to stagnant flow regions on the downstream side of the membrane where produced silver ions could migrate upstream toward the cathode driven by diffusive and electromigration forces that are still greater than the convective forces. High flow

International Conference on Environmental Systems

rates (high convective forces) can overwhelm the opposing diffusive and electromigration forces, however, the silver ion production rate is significantly reduced as shown above in Figure 6. Simply using a perforated Nafion membrane can enable water to readily flow through it while providing ionic conductivity, however, this approach results in a very non-uniform flux of water through the membrane enabling downstream stagnant regions that facilitate silver dendritic growth through the membrane.

To overcome this membrane deficiency, Reactive Innovations, LLC developed a new hybrid membrane that had both micro-filtration capabilities and ion-exchange properties. This membrane was based on casting the Nafion® unhydrolyzed resin at 300 °C where the resin was mixed with dissolvable filler materials. After hydrolyzing the membrane and dissolving these fillers, the resulting membrane had micro-filtration capability along with ionic conductivity, the exact properties needed for the SIAM and SIRM to enable water to flow normal to the membrane surface.

Membranes were casted with thicknesses ranging from 2 to 10 mils and with dimensions upwards of 6" x 6". These membranes undergo a hydrolysis step to give the films the proper ion exchange properties to be used as an ion exchange membrane. The unhydrolyzed Nafion pellets begin in the sulfonyl fluoride ($-SO_2F$) form, thus they do not have ion exchange properties. The chemical treatment steps begin with a hydrolysis step to hydrolyze the resin into the K^+ form. The hydrolysis process takes place in a solution of 15% KOH / 35% DMSO / 50% DI water at a temperature of 80°C for 30 minutes to a few hours, depending on the thickness of the film. The film is then thoroughly washed with DI water two to three times by soaking for 30 minutes in fresh room temperature water. The washing step removes all un-reacted KOH from the film. After washing, the Nafion resin is in the K^+ form and the acid conversion step can begin. The acid conversion step converts the K^+ ions for H^+ ions leaving the membrane in the acid form. This is done using a 10 to 15% nitric acid solution. The acid conversion step is an equilibrium exchange process and is repeated two to three times with fresh solution. The membrane is then rinsed in room temperature water. After the two chemical treatment steps, the film can be used as an ion exchange membrane. During this hydrolysis process, dissolvable fillers are removed whose initial size and loading impart micro-filtration properties.

With this method, the hybrid membranes had an ionic conductivity of 0.013 ± 0.0014 S/cm (maximum level with commercial Nafion is 0.09 S/cm), a micro-filtration flow capability that supported 100 ml/min of water flow at less than 0.5 psid, and a mechanical strength that supported handling and assembly into the cell. Figure 7 shows hybrid membranes made with an average 5.4 mil diameter dissolvable filler particle loaded at weight ratios of 6:1, 10:1, and 16:1 (Nafion:filler). As shown, the higher the particle loading, the more that permeable sites are present along with an improved dispersion of the permeable sites across the lateral dimension of the membrane.

Figure 7. 5.4 mil filler particles at ratios of 6:1, 10:1 and 16:1 (Nafion:filler)

C. SIAM Reactor

Using the hybrid membrane, a SIAM reactor was assembled using a platinum inner-layer mesh on the anode side. Figure 8 shows photographs of the SIAM reactor along with the varying components inside the reactor.
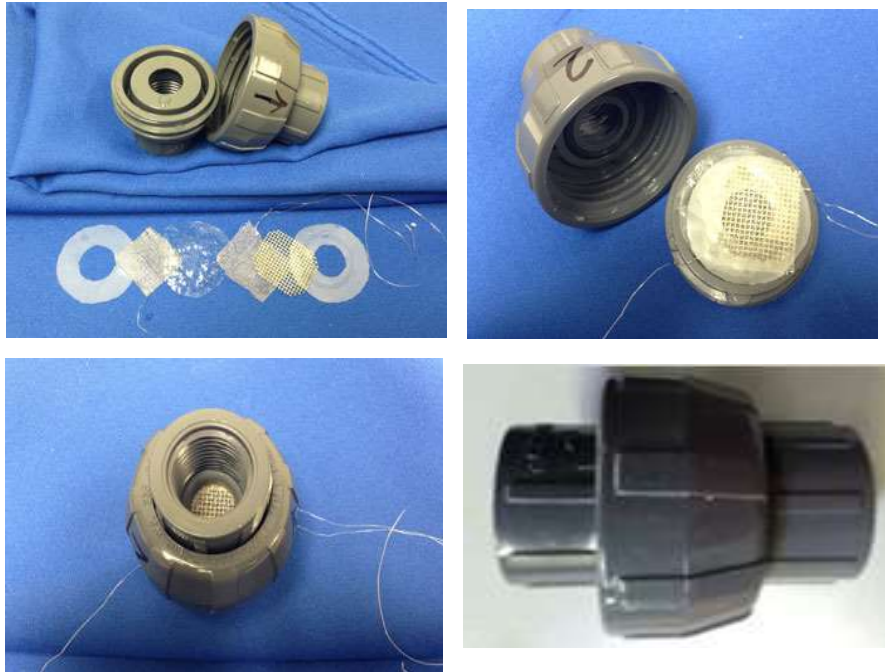
Figure 8. Photographs of the Silver Ion Addition Module (SIAM) components

This SIAM reactor was operated at 50 ml/min with an applied voltage of 1.8 volts while monitoring the current over time. An aliquot of the reactor effluent was measured after running the cell for approximately 600 seconds giving a silver ion concentration of 108 ppb as shown in Figure 9. For comparisons, a Nafion 115 membrane separator with multiple 5 mil diameter perforations was assessed in the SIAM reactor giving a silver ion concentration of 55 ppb. As shown in Figure 9, the hybrid membrane shows good stable performance upwards to 1200 seconds while the Nafion membrane shows a continuing decline in the electrochemical performance.
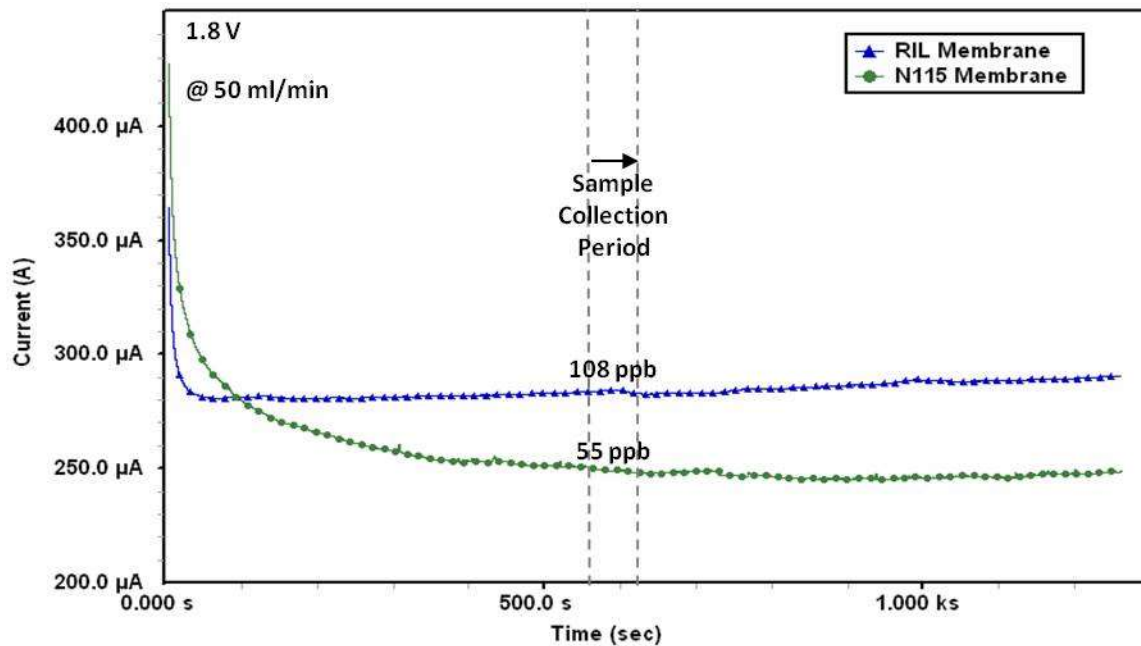

Figure 9. SIAM reactor showing stable performance using Reactive's hybrid micro-filtration and ion-exchange membrane

D. SIRM Reactor

One of the strategies for this silver ion biocide delivery system previously discussed is to operate the SIAM unit in the reverse mode to collect excessive silver ions before water is discharged. This scenario would place a SIAM unit upstream in the water storage and distribution system to place an abundance of silver ions in the water stream while a second unit is placed downstream, the Silver Ion Removal Module (SIRM), to remove excess silver ions. To demonstrate this, a SIRM unit was assembled using the hybrid membrane in a test facility shown schematically in Figure 10.
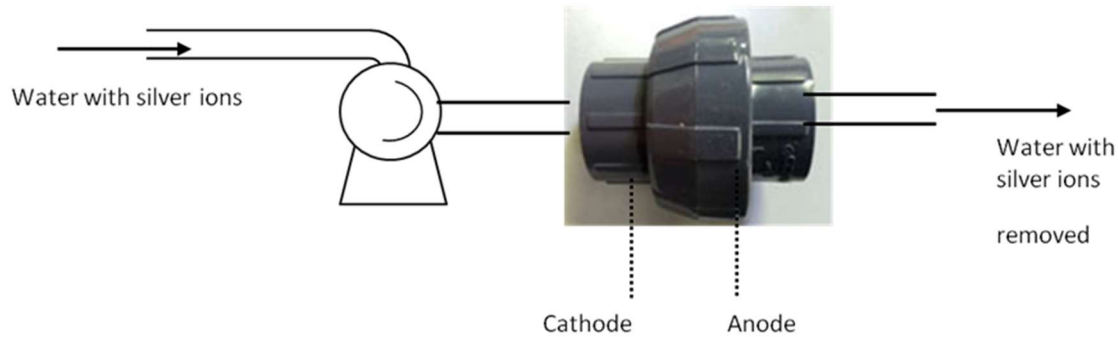

Figure 10. Schematic for assessing the SIRM unit for removing silver ions from a water stream

An inlet water stream with a 61 ppb silver ion concentration was introduced to the SIRM at 50 ml/min. With no applied current to the reactor, the downstream silver ion concentration was 61 ppb as shown in Figure 11. A current of 5 mA was then applied to start reducing silver ions in the influent stream onto the upstream cathode. This removed silver ions partially culminating in a 36 ppb downstream concentration from an inlet concentration of 61 ppb. A higher current was then applied at 10 mA where the downstream silver ion concentration went to zero indicating that all silver ions were removed using the SIRM. Thus, the SIRM can be used to remove excess silver ions from the water stream avoiding their ingestion by the flight crew during long duration missions. This approach can also be used to minimize the initial silver quantity exchanging SIAM and SIRM units over time.
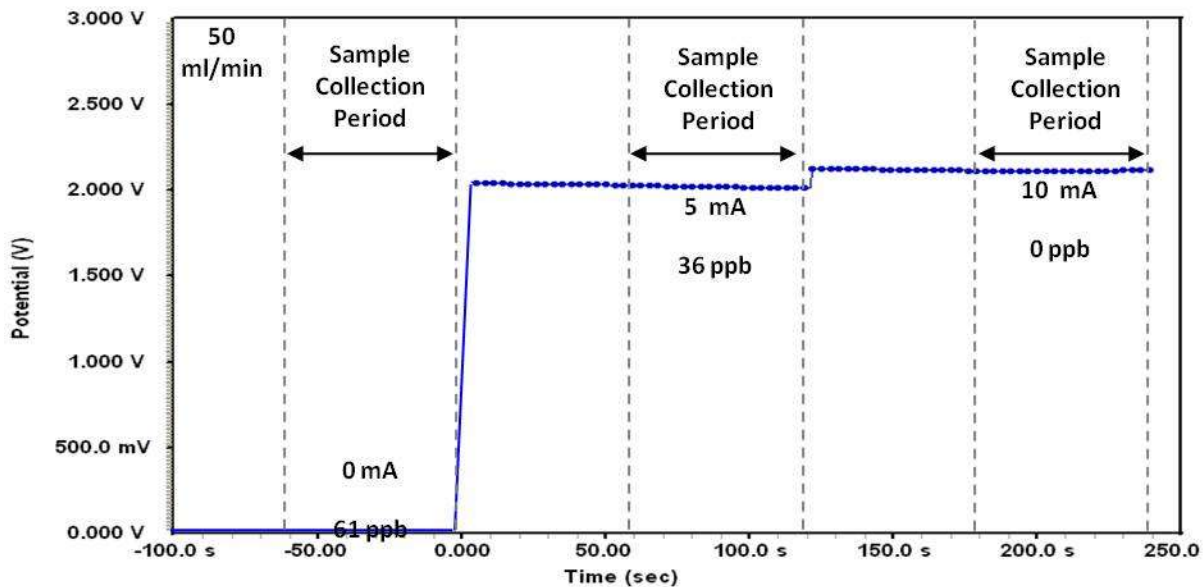

Figure 11. Effective removal of silver ions in the SIRM reactor with an influent concentration of 61 ppb silver at 50 ml/min

IV. Membraneless Silver Biocide Cell

For long duration space missions, the use of an ion-exchange membrane separator in the silver ion reactor poses a risk in that spurious silver deposits in the membrane will lead to the reactor shorting out. Chemical treatment methods can be used to strip the deposited silver from the membrane such as using acids, however, this is logistically problematic for space missions. Furthermore, the silver ion concentration produced in the hybrid membrane approach tended to maximize in the 100 ppb level at flow rates in the 50-100 ml/min range for an approximate 0.2 in^2 (0.5" diameter) SIAM unit. Higher current density operation tends to react water over silver oxidation, thus, the only method to increase the silver ion concentration is to increase the membrane area. Increasing the membrane area reduces the water permeation flux enabling silver ions to readily diffuse and electromigrate upstream to the cathode and deposit out. Keeping the voltage and current density low minimizes water oxidation such that any gas generated is readily dissolved in the water. Multiple SIAM units could be used in a parallel flow stream, however, this increases the part count and reduces the system reliability. Accordingly, we developed a membraneless silver ion biocide cell to examine its merits for a long duration space mission.

A. Silver Electrode Fouling

Immersing two silver electrodes in the process water enables silver ions to be produced electrochemically operating one of the electrodes as an anode. To minimize ohmic losses, the electrodes are placed close together where flowing water between the electrodes sweeps silver ions away from the electrodes. This is the type of silver ion cell originally developed for the Apollo program. However, with this approach, silver ions are readily able to re-deposit on the cathode that can grow toward the anode shorting the cell. Thus, it is imperative that the reactor design avoids stagnation zones where silver ions can readily deposit on the cathode shorting the cell.

Another important design aspect of the silver ion reactor especially for long duration space missions pertains to the electrode surfaces. As the silver anode undergoes oxidation to produce silver ions, resistive oxide layers form on the electrode surface decreasing silver ion production. To enable long duration operation, the electrode surface must be periodically cleaned removing the oxide layer to ensure a pristine silver surface. This is shown in Figure 12 showing a silver anode with a resistive oxide layer that formed over 8 hours of operation in a silver ion biocide reactor in comparison to a silver anode that was cleaned for three minutes removing the oxide layer. Reversing the polarity of the electrodes during operation helps to reduce the oxide formation, however, over time significant oxide layers can grow on each electrode deleterious affecting the silver ion production.

Figure 12. Silver electrodes that have been in the biocide generator operating for 8 hours; the top electrode is untreated, while the bottom electrode has undergone three minutes of abrasion cleaning

In a biocide generation test where the electrodes went untreated, electrical performance maintained relatively steady for about 18 hours before beginning a precipitous increase in resistance as shown in Figure 13. In the test where the electrodes were removed and polished with a square steel rod coated with 10-20 micron diamond powder

every one to five hours, the cell performance remained stable for the entirety of the 27 hours of operation also shown in Figure 13.
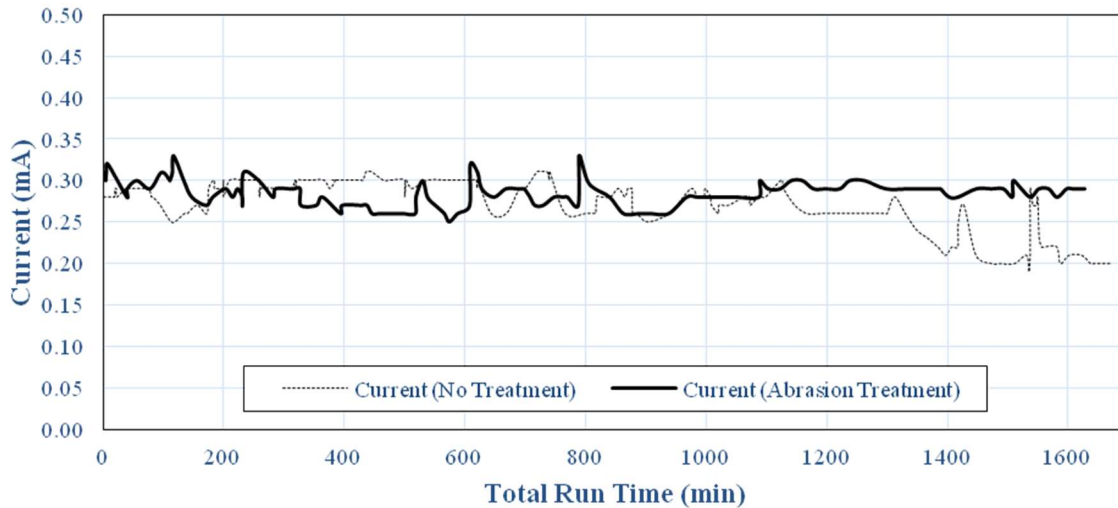

Figure 13. Long duration silver ion biocide cell testing showing the effect of electrode treatment vs. no treatment

B. Tubular Membraneless Silver Ion Biocide Reactor

Given the needs to minimize stagnant flow regions in the silver ion reactor, along with the importance of periodically removing the oxide layer as well as reversing the polarity, a concentric tubular silver ion reactor was developed that has a mechanical electrode treatment mechanism to sustain the electrochemical performance over long durations.

This tubular reactor is shown in Figure 14 designed to process water at 100 ml/min. The reactor has an internal silver rod electrode with a ¼" diameter and a length of 7.5 inches for a surface area of 5.9 in^2 (38 cm^2). The outer electrode is a rigid 20-mil-thick, 0.46"-ID silver tube that can double as the cell housing or placed within a plastic housing. This cell has a gap distance of 0.11" enabling water to flow between the electrodes at 100 ml/min with negligible pressure drop.

Figure 14. Membraneless tubular silver ion biocide cell

Fundamental testing of the membraneless cell showed that switching the cell polarity at roughly 4-minute intervals could optimize cell stability. Since the electrodes are of two different sizes with the tubular design, we altered the polarity-switch timings to reflect this difference, while maintaining 8-minute periods. Since the exterior electrode makes up 64% of the total electrode area, this electrode is operated cathodically for 64% of the 8-minute cycle, or 5.1 minutes and when the polarity is reversed the internal electrode is operated cathodically for 2.9 minutes.

To determine the functional effects of recirculating water containing silver ions, the tubular silver ion cell from Figure 14 was used to quantify the performance. This cell was operated with polarity switching, but with no abrasion. A vessel containing 12 L of distilled water was used as both the inlet source and the outlet basin for the system and the biocide cell was operated in this manner to perform three tests for a total of 18 hours of runtime. The generator was operated using three different voltage settings (2.0 V, 2.5 V and 3.0 V) to mimic scenarios where a

silver ion solution would be recirculated through the cell. Silver ion concentrations were measured using an ion-selective electrode (Van London-pHoenix Co.) which is quicker and more accurate than the colorimetry method, as the electrode is calibrated daily. As shown in Figure 15, the concentration of silver ions quickly reached 400 ppb in all of the tests and then continued to rise above this level as the device continued operating. This shows that in the absence of a control system the continuous running of the system will result in increasing levels of silver ions in solution. It also shows that the presence of silver ions at a concentration of 400 ppb in the inlet feed stream does not have any foreseen adverse effects on the performance of the system.
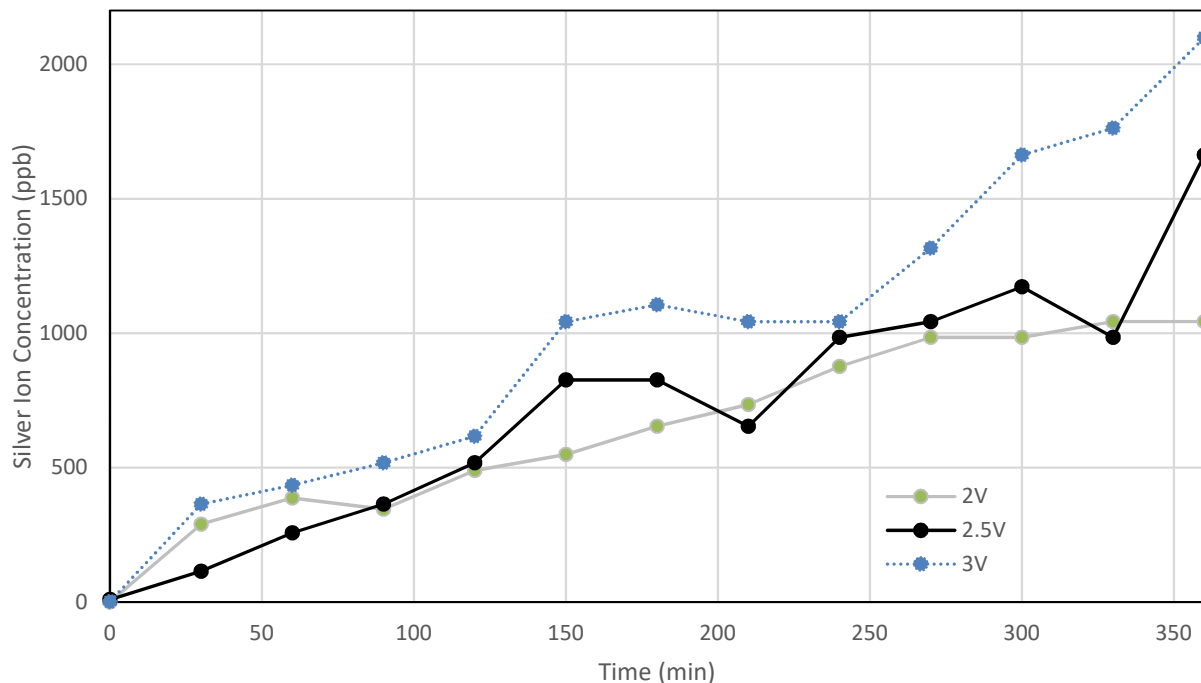

Figure 15. Silver ion concentration vs. time for six-hour recirculation tests with applied potentials of 2.0, 2.5, and 3.0 V

Since the system will process recirculated water containing silver ions after initial startup generation, the biocide generator will only be tasked with providing make-up silver ions to reach the concentration control target of 400 ppb. Water usage (consumption) may result in fresh water being introduced to the system, requiring an addition of silver ions. Of course, silver loss via deposition on the tank and piping (consumption) will reduce the silver ion concentration, requiring generation of more silver ions. Essentially, the human consumption rate plus the silver deposition consumption rate will likely be used to determine the necessary silver ion generation rate.

C. Membraneless Silver Ion Removal Module

One of the strategies previously discussed for this silver ion biocide delivery system is to operate a silver removal module to collect silver ions before water is discharged. This reduction module may be comprised of a silver cathode – where silver ions from the water stream will be deposited – placed opposite a dimensionally stable anode. The anode material may be platinum, titanium, palladium, or another metal that will not release ions into the stream via oxidation.

A test was conducted to determine the capability of such a silver ion removal module. A diagram of the test setup can be seen in Figure 16. A potential was applied to the silver ion generator module from Figure 14 for one hour, during which the measured silver ion concentration in the 100-ml/min, recirculating water stream rose from 0 ppb to 672 ppb to 976 ppb. After one hour, the power to the generator was turned off, and a potential was applied to a small silver ion removal module. Data from this test, displayed in Figure 17, show that the measured silver ion concentration dropped to 171 ppb after five minutes and to 134 ppb after 40 minutes. The data indicates that a larger

silver ion removal module with an optimized electrode gap distance would be able to efficiently remove most, if not all, of the silver ions before the water is consumed by the crew.
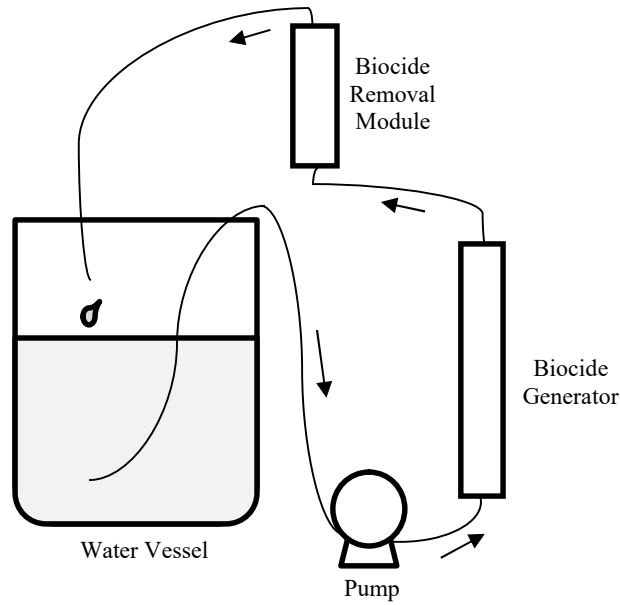

Figure 16. Process flow schematic of silver ion generation and removal test setup
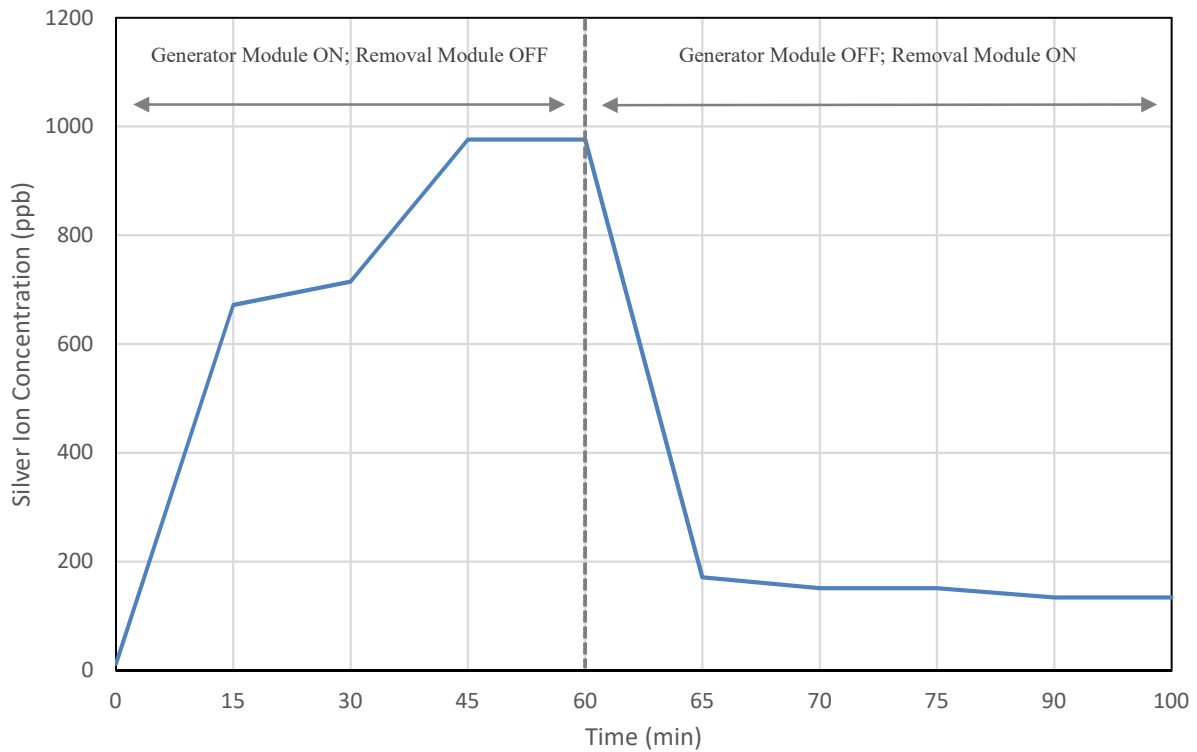

Figure 17. Test performed on a recirculating water stream shows production of silver ions by a biocide generator followed by removal of these ions by a reduction module

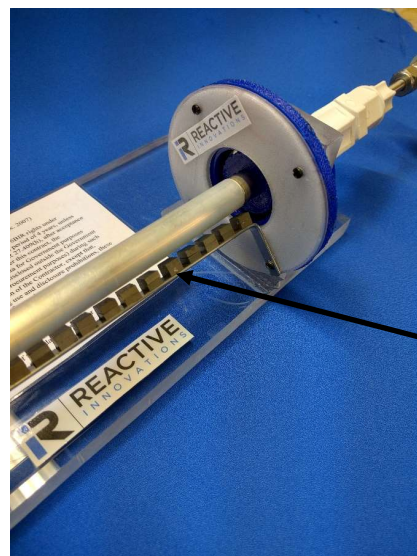**D. Magnetically-Driven Electrode Polisher**

For long duration missions, a mechanism is necessary to periodically polish the electrode surfaces. A motorized system was designed and developed that rotates a magnet around the outside of the tubular reactor that can magnetically drag an interior abrasive rod located in the concentric gap region of the electrodes. This abrasive rod contains an iron-based interior rod that is coated with a diamond dust layer. This magnetically-controlled abrasion system eliminates the need for special seals since abrasion rod is entirely located within the reactor able to freely move about driven by the externally applied magnetic field. Figure 18 shows photographs of the prototype featuring the magnetically-driven electrode cleaner.

The prototype is mounted on a polycarbonate platform, where we have installed a DC drive motor. The motor and gear assembly work to rotate a bar attached to the larger gear which has a collection of magnets that protrude in the axial direction of the reactor. When power is applied to the motor, this series of magnets rotate around the reactor, facilitated by ball bearings in the large gear and the opposing flange at the other end, to force a textured iron bar at the reactor's interior to scrape against the electrodes cleaning off oxidation and silver "whiskers".

The prototype has an internal silver rod electrode with a ¼" diameter and a length of 12 inches for a surface area of 9.4 in^2 (61 cm^2). The outer electrode is a rigid, 12" long, 20-mil-thick, 0.46"-ID silver tube (area = 17.3 in^2 or 112 cm^2) that can double as the cell housing or can be placed within a plastic housing. This cell has a gap distance of 0.11", enabling water to flow between the electrodes at 100 ml/min with a negligible pressure drop.
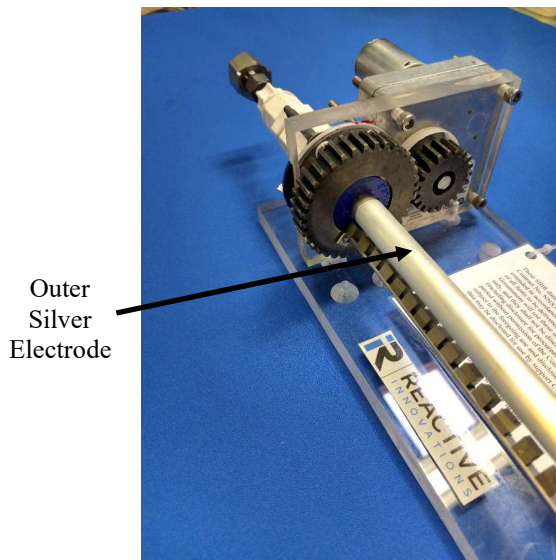
Figure 18. Photographs of a magnetically driven abrasion system for cleaning the silver ion biocide electrodes

For initial testing of the prototype with a 100-ml/min flow stream, the abrasion system was turned on, and the cell was operated (using polarity cycling) between 1 V and 2 V. This voltage range was sufficient to produce silver ion concentrations across our studied 100 ppb to 1,000 ppb range. As shown in Figure 19, the relationship between applied potential and silver ion output may be reasonably linear.
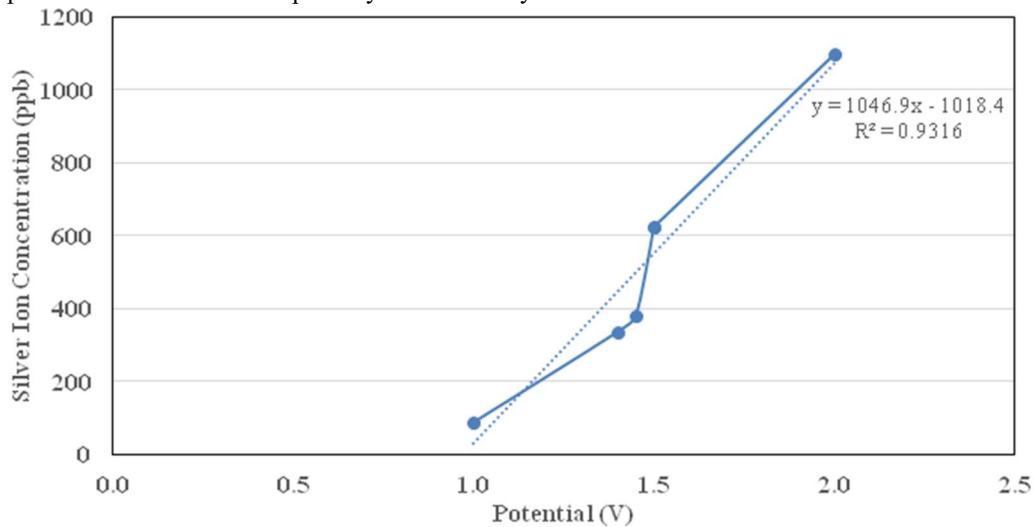

Figure 19. Effect of voltage setting on silver ion concentration at a water flow rate of 100 ml/min

This generator was then operated for a 90-minute test at 100 ml/min with polarity switching and abrasion systems on. Data for the first 80 minutes of this test is shown in Figure 20. As the generator ran, the operator took measurements of silver ion concentration and attempted to control the voltage to produce a silver ion concentration of 400 ppb. At a setting of 1.45 V, the silver ion content was about 360 ppb. Two more samples were measured at the same concentration over the next 15 minutes, showing production stability. The operator attempted a fine adjustment to bring the silver ion level closer to 400 ppb. At 1.50 V the silver ion concentration was measured at 406 ppb three times over 20 minutes. This testing indicates that an operator or an electronic system can be used to control the biocide generation device. The system can be controlled via an inline sensor or periodic testing of samples using an ion-selective electrode. The measurement feedback can be used to adjust the potential applied to the biocide cell or to turn the power to the cell off or on.
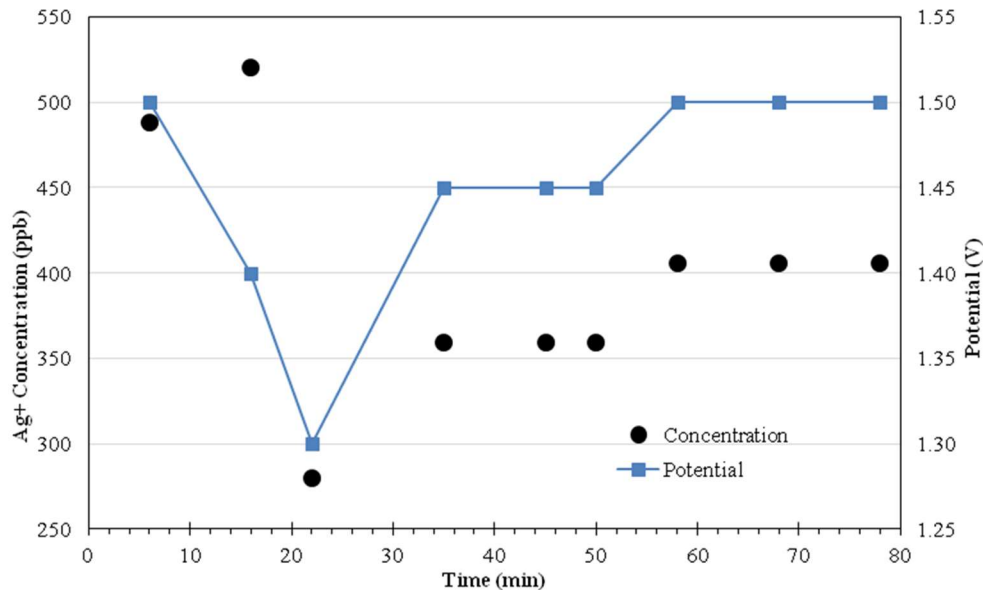

Figure 20. Prototype operation showing the effect of manual voltage control on silver ion generation at 100 ml/min water flow

V. Conclusions

Two silver ion biocide reactors have been developed for treating the water storage and distribution system for long duration space mission. One approach uses a hybrid membrane separator placed between two electrodes that enables water to permeate through the membrane while also allowing ion conduction. This culminated in compact Silver Ion Addition Modules (SIAM) and Silver Ion Removal Modules (SIRM) that could produce and remove approximate 100 ppb silver ion concentration from the water. Limited lifetime is expected with the membrane-based approach due to dendritic silver deposition within reactor hardware that can electrically short the cell. A membraneless silver ion reactor was also developed that used concentric silver electrodes to avoid stagnant flow regimes within the reactor. Reversing the polarity of the electrodes helps to maintain a stable silver ion production level and avoid dendritic silver growth that can short-circuit the cell. A mechanical cleaning mechanism has also been shown that can be used to magnetically drag an internal cleaning rod placed between the electrodes to periodically polish the electrodes removing oxide film formation. This enables the silver ion biocide cell to operate for longer periods of time overcoming resistive oxide layers that build up. With the membraneless silver ion reactor, silver ion concentrations well over 1000 ppb may be readily attained which can be scaled back by reducing the applied potential, or where a SIRM unit or comparable membraneless reactor may be used to extract these silver ions before discharging the water. The membraneless silver ion reactor offers an alternative to iodine systems, eliminating concerns of iodine ingestion and its health impact on the thyroid over long duration missions.

Acknowledgments

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