

12-2021

Preliminary Development of The Dialysis-Membrane-based Passive Biocide Delivery System for Spacecraft Water Recovery Units

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Preliminary Development of The Dialysis-Membrane-based Passive Biocide Delivery System
for Spacecraft Water Recovery Units

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Chemical Engineering

by

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University of Arkansas
Bachelor of Science in Chemical Engineering, 2019

December 2021
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This thesis is approved for recommendation to the Graduate Council.

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Abstract

The purpose of this investigation is to explore the capabilities of a dialysis-membrane-based system for the in-line dosing of silver ions to treated water in spacecraft water recovery units. The spacecraft environmental control and life support system community (ECLSS) are interested in adopting silver ions as a biocide in future spacecraft water recovery processes since silver ions are effective biocide at concentrations that humans can safely consume. The system has been designed following the configuration of the Water Processor Assembly (WPA) aboard the International Space Station. In this configuration, silver ions have to be added at the last step in the WPA to inhibit the growth of microorganisms in the product water. The dialysis-membrane-based system has to supply silver ions into the potable water at concentrations ranging from 200 to 400 parts per billion during the entire water processing time. The silver ion delivery system has been prototyped by repurposing dialysis membranes used for the separation/purification of low molecular weight solutes. Consequently, the low molecular weight cutoff of the dialysis membrane controls the silver ion release from a concentrated silver ion reservoir and does not require any power. Both computational and experimental studies were conducted to examine the performance of the silver ion delivery and the feasibility of integrating this technology in future spacecraft water recovery units. The preliminary results from this investigation show that the dialysis-membrane-based passive biocide delivery system can supply sufficient silver ions to a stream of deionized water. Nevertheless, the outflow might require dilution, and the membrane may need to undergo preconditioning for optimal performance, especially for reuse.

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Acknowledgments

This thesis would not have been possible without the inspiration and support of many outstanding individuals I had the privilege to meet at the University of Arkansas.

First and foremost, I am incredibly grateful to my supervisor, Prof. Robert (Bob) Beitle Jr., Ph.D., for his invaluable advice, continuous support, and faith in my graduate research project. His extensive expertise has encouraged me in my academic research and life. His kind help and support have made my study and life in the United States a wonderful time. I would also like to thank Dr. Wickramasinghe and Dr. Roe for their technical support and willingness to be on my graduate committee. Additionally, I would like to express my gratitude to Dr. Dean Muirhead for his kindness, indispensable knowledge, and friendship. Without his tremendous understanding of spacecraft water recovery systems, it would be impossible to complete my study.

Finally, I want to extend my gratitude to Dr. Bryan Hill from the College of Engineering for offering my first graduate assistantship as a mentor for undergraduate engineering students and Dr. Karl Schubert for hiring me as a teacher assistant for the newly created Data Science Program at the University of Arkansas.

Dedication

This thesis is dedicated to my family in Santiago, Panama, and Baxter Springs, Kansas. I am immensely grateful to my sister Madelline for all the support she offered me throughout these past years. Without her help, love, and comprehension, my journey in the United States would have been an odyssey — I appreciate all the continuous text messaging and long calls with you. I also want to dedicate this thesis to my grandmother Crescencia “Chencha” Núñez Jordan de García for believing in me since I was a kid. Also, I could not have written this dedication without including my father, Rogelio García Núñez, and my mother, Norma Fernández González — I love you both so much!

I want to extend this dedication to my friends Jonathan Locke, Edgar Soriano Somarriba, Juan Marin Jr., and Jose Santos Batista for their supportive friendship. Most importantly, I want to dedicate my thesis to my parents-in-law, John & Tina Gaines, for letting me stay with them for the Fall 2021 semester — I wrote this thesis in their house.

Last but not least, I dedicate the entirety of this work to my wonderful wife, Jennifer Gaines. I am so grateful to her for reminding me to love myself and take care of my mental health. I am so lucky to have her in my life, and finishing this thesis would not have been possible without her unconditional love.

I also dedicate this thesis to my cats, Ollie and Daisy, for snuggling me every time I got home after a long day in the laboratory.

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1. Introduction

Since its start in 1957 with the launch of the Sputnik satellite by the Union of Soviet Socialist Republics (U.S.S.R.), space exploration has uniquely challenged engineers and scientists to develop technologies that require a high level of sophistication, efficiency, and robustness. Specifically, human space exploration has faced a vast number of technical challenges primarily due to the environmental hostility encountered in extraterrestrial destinations. Dangers such as microgravity, high radiation levels, vacuum, extreme pressures and temperatures, toxic atmosphere, and scarcity of energy and potable water have directly impacted valuable field research. Even though remotely-controlled and autonomous space missions have allowed safe space exploration, one can argue that onboard and on-the-ground scientists performing meticulous exploration tasks would be beneficial. Consequently, engineering a reliable Environmental Control Life-Support System (ECLSS) for crewed missions can increase human activity in space since this type of technology ensures a protected environment.

The most outstanding ECLSS, operating for more than 20 years, is aboard the International Space Station (ISS). This ECLSS comprises subsystems that concentrate on environmental monitoring, atmosphere and water management, and tertiary specialized equipment groups called assemblies.^{1,2} For instance, the Water Processor Assembly (WPA) and the Urine Processor Assembly (UPA) are assemblies from the Water Recovery System (WRS) subsystem, which in turn belong to the broader Water Management System (WMS) aboard the ISS. The WPA and the UPA generate potable water from non-potable sources such as urine, flushing water, humidity condensate, and Sabatier water product in the ISS.³ The WRS has a crucial task in the ISS since it is a regenerative system that allows water recycling. Generating potable water in space is a massive accomplishment since the ISS has to maintain a minimum of 697 liters of potable water

for crew reserve, and the cost of supplying 1 kg of cargo to Low Earth Orbit (LEO) has ranged from \$34,500 to \$1500 (U.S dollar cost estimates in the fiscal year 2021) in the last decade.^{4,5} Consequently, the WRS is a critical ECLSS component aboard the ISS, having a substantial impact on human space exploration by allowing launch cost reduction. Nevertheless, the WRS technology requires several improvements, especially if adopted for future extended crewed space missions.

Regenerative WRSs are indispensable for prolonged space flights. Any crewed mission longer than two weeks would reach an inflection point where the cost of integrating a regenerative ECLSS is lower than launching enough consumables.⁶ Hence, optimizing the physicochemical processes involved in a WRS becomes a vital task. If the same processes are adopted for future spacecraft missions (for Mars or extraterrestrial moons), each process might require adjustments and optimizations to account for a long life cycle and operability. For instance, the water-treatment units that the ISS WRS utilizes are distillation, filtration, catalytic oxidation, gas/liquid separation, heating/cooling, ion exchange (IX), and sterilization.⁴ Since these units are tuned for ISS microgravity operations, their integration in subsequent systems might require several modifications worth studying. This thesis investigates a new WRS technology for suppressing the growth of microorganisms in regenerated potable water, which could provide better capabilities for future WRS frameworks.

The suppression of microorganisms from potable water is a major effort in WRS operations since pathogens in product water can affect astronauts' health, a circumstance that could compromise an entire mission. Although systems like the WPA can reduce microorganisms to insignificant levels (levels compared to the initial intake), there would always be a sufficient amount of organic carbon in the product water that can activate the growth of heterotrophic

microbes after the water recovery process. On the ISS, this carbon is measured as Total Organic Carbon (TOC), and this parameter shall not exceed 30 milligrams per liter (mg/L) in regenerated water for the safety of the crew.^{7,8} Therefore, an appropriate response would be the addition of a biocide to the product water to prevent any microbial growth. Nevertheless, the biocide must be effective against a broad spectrum of pathogens at concentrations that do not impose a risk to the astronauts; otherwise, the biocide must be filtered out from the drinking water before consumption. To avoid the technical obstacle of removing a harmful biocide before the crew drinks the recovered water, the National Aeronautics and Space Administration (NASA) is considering silver-based biocides for future spacecraft WRS since silver ions (Ag^+), the active biocidal agent, inhibit microbial growth at concentrations that also allow for safe consumption of silver-containing water.⁹ Hence, devising a silver-based dosing system that can be integrated into an assembly analogous to the WPA would significantly contribute to the water recovery and management endeavor in future crewed spacecraft missions.

By exploring the capabilities of dialysis membranes for the controlled release of solutes, a biocide delivery technology has been formulated to continuously deliver Ag^+ into a stream of deionized (DI) water. Since a diffusion gradient virtually governs the entire dosing mechanism, the Ag^+ delivery does not require additional power; therefore, the biocide dosing system is referred to as passive. This investigation seeks to 1) determine the initial amount of biocide required for the controlled release, 2) estimate dialysis-membrane-based permeability parameters, 3) predict the required Membrane Molecular Weight Cutoff (MWCO), 4) perform multiple Ag^+ release tests, and 5) deduce which adjustments could tune the membrane system.

2. Background

2.1. Silver-based Biocide

The desired biocide for this spacecraft-WRS application provides for a preventive response against microbial growth in the product water. The biocide would not be involved in the primary action to sterilize reclaimed water from pathogens. Granted that there potentially would always be unavoidable TOC levels in the product water that could trigger the growth of heterotrophic microorganisms, adding a chemical that can inhibit reproduction is a simple solution. However, this biocide must not have adverse effects on astronauts when they consume the regenerated drinking water.

Historically, iodine and silver-based biocides have been utilized in spacecraft WRSs. While Russian teams have consistently used silver species as a biocide, the American counterpart has primarily implemented iodine. Although a silver biocide system was contemplated for the Apollo Missions, NASA selected hypochlorite and iodine-based biocides for the Apollo Missions and subsequently only iodine-based biocides for the SkyLab mission, the Shuttle program, and the ISS.¹⁰⁻¹⁴ Nonetheless, NASA has reexamined the implementation of silver-based biocides for long-duration space missions since iodine-containing water can cause thyroidal conditions, and removing iodine from the product water requires additional hardware.¹⁵⁻²⁰ On the other hand, NASA presumably did not continue using hypochlorite-based biocides due to their tendency to promote corrosion in the potable water system.¹¹ Silver-based biocides might allow better operating capabilities in a spacecraft WRS.

The main characteristics that must be reviewed to evaluate the employment of a biocide are its solubility in water, biocidal efficacy, material compatibility, and safety for human consumption. Silver is a biocide in its ionic form. Therefore, highly-soluble silver sources are

preferred. The more soluble a silver substance is in water, the more Ag⁺ are generated in the solution. Table 1 lists some water-soluble silver salts that could be utilized for the application in question and shows that silver nitrate and fluoride are the most outstanding options. When selecting a silver salt, the effects of the counter ion should also be considered. A scenario could be the formation of a precipitate when the counterion combines with the silver cation in the product water, and this generation of insoluble particles eventually could foul the system and reduce the activity of the silver-based biocide. Undesirable counter ions can also be toxic and corrosive. For example, drinking water containing nitrate and fluoride ions can be safely consumed as long as the concentrations of 3 mg/L and 0.7 mg/L, respectively.²¹⁻²³ Regarding the safety of consuming silver-containing water, the human body can excreting 90% of Ag⁺ when ingested at low concentrations (i.e., 500 parts per billion).²⁴ Even at high Ag⁺ concentrations, the most significant condition that has been documented is argyria, the blue or gray-black staining of the skin by the exposure to or ingestion of silver.²⁵

Table 1: Aqueous Solubility of Silver Salts.²⁶⁻²⁹

<i>Silver Salt</i>	<i>Solubility in Water at 25°C (mg/ml)</i>
silver chloride	0.00195
silver carbonate	0.032
silver bromate	1.60
silver nitrate	4.20
silver sulfate	8.30
silver lactate	77.00*
silver fluoride	>1000.00
silver nitrate	2570.00

* Solubility at 20°C.

Moreover, the biocidal nature of Ag⁺ relies on its ability to disturb membrane respiratory electron transport, DNA replication, enzymes, proteins and promote the production of reactive oxygen species in most microorganisms.³⁰⁻³² However, the most immediate effect is cell lysis

due to the interaction between Ag^+ and the negatively charged lipids of the microorganisms.³³

The U.S Environmental Protection Agency and the World Health Organization have documented the broad antimicrobial properties of silver against bacteria, fungi, and viruses and reported effective concentrations starting at 100 parts per billion (ppb).^{34,35}

On material compatibility, the main challenge that silver-based biocides face is the Ag^+ uptake on wetted surfaces. Ag^+ can be depleted from solution to metal substrates via adsorption, oxidation, and precipitation processes. It has been shown that legacy spacecraft potable water systems piping materials such as titanium grade 2, titanium grade 5, Inconel 718, and 216L stainless steel can entirely absorb Ag^+ from static solutions in one week.³⁶ For metal surfaces, it has been correlated that high surface area to volume ratios corresponded to high Ag^+ loss by adsorption.³⁷ For instance, metallic domains such as small-diameter pipes would adsorb more Ag^+ than regions corresponding to a water tank. This relation imposes a considerable challenge since small surface-to-volume ratios have always been an attractive option when designing a spacecraft WRS. A practical approach to target this issue has been presented by Colón-Colón et al. (2020) and consists of coating the metal surfaces with polymeric materials having minimal Ag^+ uptake. Some of the fully silver-compatible polymeric materials this team studied are Perfluoro-elastomer, Ethylene Tetrafluoro-ethylene, and Polymethyl-methacrylate.

2.2. Biocide Dosing Systems

Future crewed space missions would rely on recycling and re-utilizing consumables due to the mass limitation imposed by launch costs, spacecraft volume, and the long travel duration associated with upcoming target locations (Mars, Jovian moons, etc.). Moreover, water is the primary reserve for these missions not only for being a hydration source but also a raw material for generating breathable oxygen and molecular hydrogen via electrolysis.³⁸ Therefore, designing

regenerative setups for spacecraft WMS is of utmost importance. As previously described, the ISS WRS collects water from non-potable sources to generate drinking water.

It is presumed that the design of future spacecraft WRS will follow the configuration of the WPA due to its success in generating quality potable water from non-potable sources. This consideration is substantial when devising an Ag⁺ dosing system since the WPA is a continuous-flow physiochemical process. Hence, the Biocide Delivery System (BDS) must be an in-line device capable of continuously delivering Ag⁺ at a steady rate and the appropriate levels for as long as the water recovery process takes. Conversely, if the WRS operated in a batch fashion, the most practical BDS would be an injector. Additionally, a batch WRS can require the treatment steps to be manually performed or closely monitored by the crew, which would prevent the astronauts from focusing on other tasks. For instance, in the first 6.5 years after installation, the ISS WRS has required a maintenance rate of 14.3 crew hours per 1000 kilograms (kg) of recycled water.³⁹

Furthermore, the continuous flow operability would depend on the volume of wastewater the spacecraft WMS can store. Large wastewater volumes could allow high flow rates and shorter water recovery times, but the performance requirements (local flow rates and pressure drops) of each water treatment unit in the WRS would ultimately impose this parameter. Since there would be a limit on how much wastewater can be stored and effectively collected from different generation points, the WRS will encounter downtime or a dormancy period, which would make the system function more like a semi-continuous flow process. For instance, the WPA has a 68-liters wastewater tank and runs at a volumetric flow rate of 100 milliliters per minute (mL/min), making the water recovery process approximately 11.33 hours long if wastewater is not constantly supplied.⁴⁰ The implication of WRS inactivity or a semi-continuous flow mode for

designing a BDS is that downtime should not have significant performance effects on the BDS; primarily, the BDS should be capable of dosing stable biocide levels upon start-up and require little maintenance. Long dormancy periods are also expected when the spacecraft does not have any crew and is left in orbit.

Long-term space exploration missions will require WRSs to treat relatively large volumes of wastewater. An orbital mission to Mars and its moons is estimated to last almost 1000 days.⁴¹ At the same time, crew members consume a minimum of two liters of water per mission day (L/day) only for drinking (water is also needed for food rehydration, personal hygiene, and medical use).⁴² For a crew of six people, these stipulations result in 12,000 liters (or 12,000 kilograms) of drinking water. However, this water can be reclaimed from humidity condensate, handwash, full-body wash, oral hygiene, urine, and other condensate sources aboard the spacecraft. For example, the human body can excrete 2.7 L/day of water; thus, recycling this water results in an integral approach.⁶ The WPA receives approximately 22 L/day of wastewater from sources like the ones mentioned and the Sabatier System, which captures carbon dioxide from the cabin atmosphere and generates water as a byproduct.^{40,43} As a result of processing this projected quantity of wastewater, the BDS would need to maintain enough biocide for the entirety of the space mission. If a WRS for a Mars mission can accept the same amount of wastewater as the WPA and follow a 500 ppb Ag⁺ concentration limit, the BDS would need to hold only 11 grams (g) of Ag⁺ (~17.3 g of silver nitrate). Hence, it must be evaluated in the BDS design whether the device can be saturated with the Ag⁺ source or would demand periodic Ag⁺ recharges. This precondition would depend on the nature of the Ag⁺ delivery mechanism that the BDS employs.

In-line BDS technologies can be classified as passive or active. In this discussion, a Passive Biocide Delivery System (PBDS) is an apparatus coupled with the WRS that does not require power to dose biocide. However, some PBDS can indirectly demand additional power for the WRS pump by contributing to the total pressure drop. On the other hand, an Active Biocide Delivery System (ABDS) primarily utilizes power to dose biocide. Although a PBDS does not use power for dosing biocide and can generally be lighter and less costly than active technologies, an ABDS can offer a high degree of automation and close-tolerance concentration control. Moreover, most PBDS designs rely on diffusion and desorption processes, whereas ABDS equipment has used electrochemical techniques and volumetric infusion of biocidal solutions. Some of these technologies are summarized in Table 2.

Table 2: Studied Biocide Delivery Systems.

<i>Technology</i>	<i>Biocide</i>	<i>Advantage</i>	<i>Disadvantage</i>	<i>Dosing Mechanism</i>
injector	hypochlorite, iodine, silver	<ul style="list-style-type: none"> • simple design • no complex physiochemical mechanism involved 	<ul style="list-style-type: none"> • requires power or manipulation • requires volume to store biocide solution 	infusion
electrolytic generator	silver	<ul style="list-style-type: none"> • direct release control • little pressure drop • no periodic recharge 	<ul style="list-style-type: none"> • electroplating • operating challenges in low conductivity water • requires power 	electrolysis
packed resin bed	iodine	<ul style="list-style-type: none"> • simple design • no power requirement 	<ul style="list-style-type: none"> • pressure drop • periodic recharge • release depends on upstream conditions 	ion exchange
foam cartridge	silver	<ul style="list-style-type: none"> • lightweight • no power requirement 	<ul style="list-style-type: none"> • Ag⁺ loading compromises foam structure 	dissolution

Table 2 also compares the BDS technologies reviewed for this work by compiling their biocide source, the dosing mechanism, and apparent operating advantages and disadvantages. Although an injector BDS is described in this analysis as a device that steadily inserts a biocide solution into the product water stream at a proper volumetric ratio, such technology has not been implemented in a WRS. The basis to avoid using a continuous injector might reside in the requirement for additional pumping hardware and storage for the biocide reservoir. It can be deduced from Eq. 1 that the volumetric flow rate of this injection system can be minimized by ensuring high concentrations in the biocide reservoir. Nevertheless, if the biocide line volumetric flow rate is minimized, a pump with remarkably accurate flow rates would be necessary, increasing hardware costs and integration. Contrarily, if the biocide concentration is set to low values, the volume of the biocide reservoir increases, creating an additional water requirement since the biocide solution is assumed to be aqueous. Consequently, a continuous injector BDS might not be an attractive technology for WRS frameworks.

$$Q_b = \frac{Q_{up}C_p}{C_b - C_p} \quad \text{Eq.1}$$

- Q_b: biocide line volumetric flow rate
- Q_{up}: upstream volumetric flow rate (~100 mL/min)
- C_p: product water biocide concentration (~200-400 ppb)
- C_b: biocide reservoir concentration

Despite the implications of adopting a continuous injector as a BDS, direct-load injectors were used in early spacecraft WMSs to achieve water sterility. In the Apollo 11 mission (1969), a sodium hypochlorite solution was periodically and manually injected into the water supply using 20 mL ampoules.⁴⁴ Similarly, the WMS aboard the Skylab station (1973-1974) included an iodine injector that could hold up to 75 mL of a 30,000 mg/L iodine solution and be controlled with a manual shutoff valve to provide a 100 mg/L iodine concentration to the potable water.¹⁰ The Mir space station (1986-2001) also used a manually-control injector consisting of a 20 mL

disposable polyethylene syringe.⁴⁵ Although the implementation of these injectors was successful for these missions, direct-load injectors are only suitable for batch water recovery processes.

Presumably, the first in-line BDS developed for a WMS application was the Electrolytic Silver-ion Generator (ESIG) intended for the Apollo missions (1961–1975). The in-line ESIG was an ABDS and consisted of a flow-through compartment enclosing a silver anode that discharged Ag⁺ to the water in accordance with electrolysis reactions when a voltage was applied. Although the technology was thoroughly tested, the ESIG was not adopted for the Apollo missions, presumably since fouling on the surfaces of the electrodes may have compromised its performance.^{12,46} The next in-line BDS technology was devised for the Space Shuttle (1981-2011) and comprised a flow-through packed bed containing tri-iodinated IX resins.⁴⁷ This PBDS was known as the Microbial Check Valve (MCV) and provided bacterial isolation by delivering iodine into the water lines in the Space Shuttle (the MCV can also serve as a mechanical check valve). The MCV killed most microorganisms in contact with the resin and provided downstream sterility via iodine leaching. Nevertheless, the iodine leakage often became an excessive stripping of iodine from the resin, which increased the iodine taste in the drinking water and shortened the life of the resin.¹³ Some of the approaches that were considered to enhance the Space Shuttle MCV were the chemical improvement of the iodine resin and applying in-line regeneration phases.^{48,49} These constraints did not impede the utilization of the iodinated resins in the WPA.

The ISS utilizes two iodinated packed beds in the WPA: the Ion-eXchange Bed (IXB) and the MCV. As Figure 1 shows¹⁴, the WPA has a recirculating configuration that allows out-of-spec product water to be redirected to consecutively flow throughout all the water-treatment

stages until the quality targets are met. In this operating arrangement, the wastewater does not reach the product water due to the direction of the flow, but microorganisms can propagate from the wastewater to the product water. Therefore, the purpose of the MCV is to provide sterility on the recirculating line against back-flow bacterial contamination from the wastewater. While the MCV maintains bacterial suppression with minimal iodine stripping, the IXB supplies residual iodine to the treated water (1-4 mg/L) and captures undesired ions from previous water-treatment steps.^{4,40} In the WPA, the IXB is the PBDS; therefore, it would be necessary to replace the IXB with a silver-based PBDS and MCV if future spacecraft or habitats adopt a configuration for their WRS similar to the WPA. However, a technology for removing undesired ions would still be required if a catalytic reactor is upstream and the silver-based PBDS does not have any ion-capture capability.

The implementation of the IXB in the WPA has been successful, but the iodine has to be removed from the product water upon consumption. As stated early, iodine can affect thyroids; consequently, removing it from the water requires additional hardware.⁵⁰ Although a silver-based BDS will not impose this condition since silver-containing water is harmless at the target levels, no outstanding silver-based IXB has been developed explicitly for WRS applications. This possible lack of technology may be attributed to the poor structural integrity, strict upstream concentrations for IX, and excessive Ag^+ release of some silver-based IX resins.¹⁷ Additionally, there is always a pressure drop associated with packed beds.

Once NASA reconsidered the use of a silver-based BDS, the ESIG technology was revised. New studies confirmed that a flow-through ESIG could provide a steady-state Ag^+ release; however, this system faces two significant operating challenges. Firstly, the very-low conductivity expected in the product water compromises the performance of the electrolytic-

based Ag^+ release and requires the size of the electrodes to be maximized.¹⁸ Secondly, the Ag^+ output is reduced by oxidative layers that foul the surface of the electrodes at high pH (> 6.0) and after long operating times (> 8.0 hr).^{18,20,46} Cleaning strategies can be applied periodically to remove fouling, but these actions demand the installation of moving parts or manual maintenance.

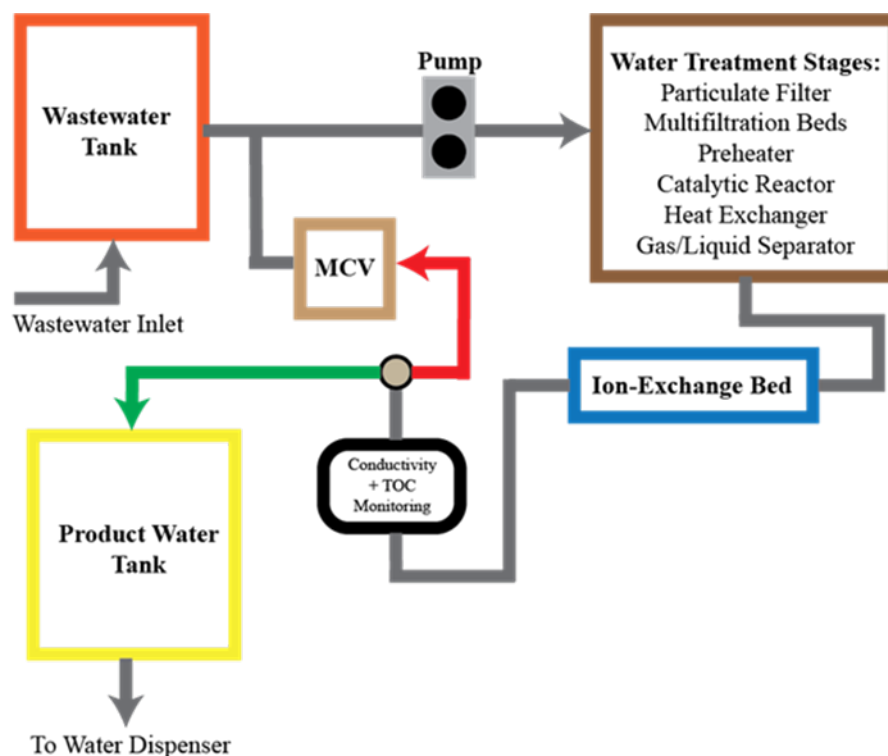


Figure 1: The International Space Station (ISS) Water Processor Assembly (WPA), simplification adapted from Parker et al.¹⁴

Furthermore, NASA has also contemplated a PBDS consisting of a foam matrix impregnated with silver nanoparticles (AgNP) and immobilized in a flow-through cell.⁵¹ This technology resembles a packed bed but weighs less and can lead to relatively lower pressure drops. The silver-loaded foam (AgFoam) is made of a polyurethane composite, providing a high-surface-area and stable structure that can hold the AgNP . Ag^+ is released into the water as it flows through the micro-porous foam material via dissolution. Nonetheless, the foam structure is

mechanically compromised when the AgNP loading exceeds 10% of the maximum the composite can hold.¹⁶ Because of this limitation, it may not be possible to load the foam to levels that can virtually offer an infinite source of Ag⁺. Consequently, the foam may need to be periodically recharged with AgNP. The team working on this project managed to increase the AgNP loading to 20% and showed that this system could deliver Ag⁺ at an average concentration of 234 ppb during an expedited 1-year flow-through test (912 L of water were processed at a rate of 100 mL/min).¹⁵ Therefore, this technology becomes a solid challenger to the PBDS developed for this work.

2.3. Silver Ion Delivery Systems Requirements

NASA has imposed the requirements that must be satisfied to develop a competitive and attractive silver-based BDS for spacecraft WRS.^{52,53} The system should steadily and continuously release Ag⁺ at a concentration ranging from 200 to 400 ppb, and the Ag⁺ release should be tuned for DI water conditions flowing at 0.1 to 0.15 L/min. Moreover, the Ag⁺ dosage should function at a pH range between 4.5 to 9.0. The hardware should be less than or equal to 5 kg and capable of operating at ambient temperature and system pressures up to 200 KPa. Equally important, the BDS should be robust, small, easily maintainable, and functional in microgravity environments. Furthermore, the BDS technology should be suited for automation and fully functional following long-term dormancy periods (up to 1 year).

2.4. Dialysis-Membrane-based Passive Biocide Delivery System

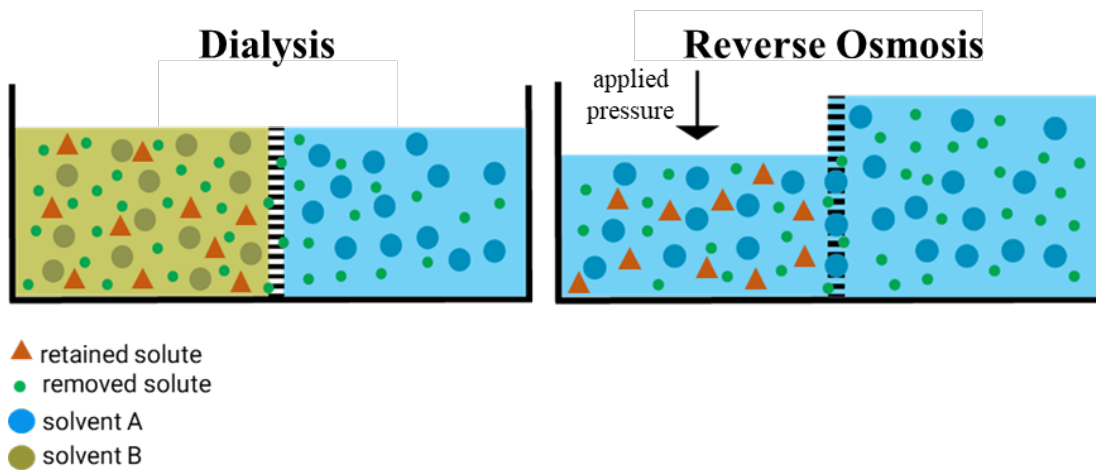


Figure 2: Dialysis vs. Reverse Osmosis.

A PBDS could be devised by selecting a dialysis membrane that sufficiently restricts the biocide diffusion from a saturated solution. Since the PBDS has to be an in-line device, a dialyzer can demonstrate this concept. A dialyzer is a flow-through apparatus in which a semi-

permeable membrane separates two fluids with different solute concentrations. As the two streams of fluids are in contact with the membrane, the solute migrates from one medium to the other, following the dialysis principle. Indeed, the dialysis device that follows this arrangement is referred to as a steady-state dialyzer since both fluids are supplied at a constant volumetric flow rate and entering concentration. Unfortunately, a steady-state dialyzer would be challenging to integrate into a system like the WPA (Figure 1) since adding a biocide solution stream would require additional hardware. Unlike a steady-state dialyzer, a dynamic dialyzer only has one convective region. Figure 3 illustrates the solute transport occurring in both types of dialyzers.

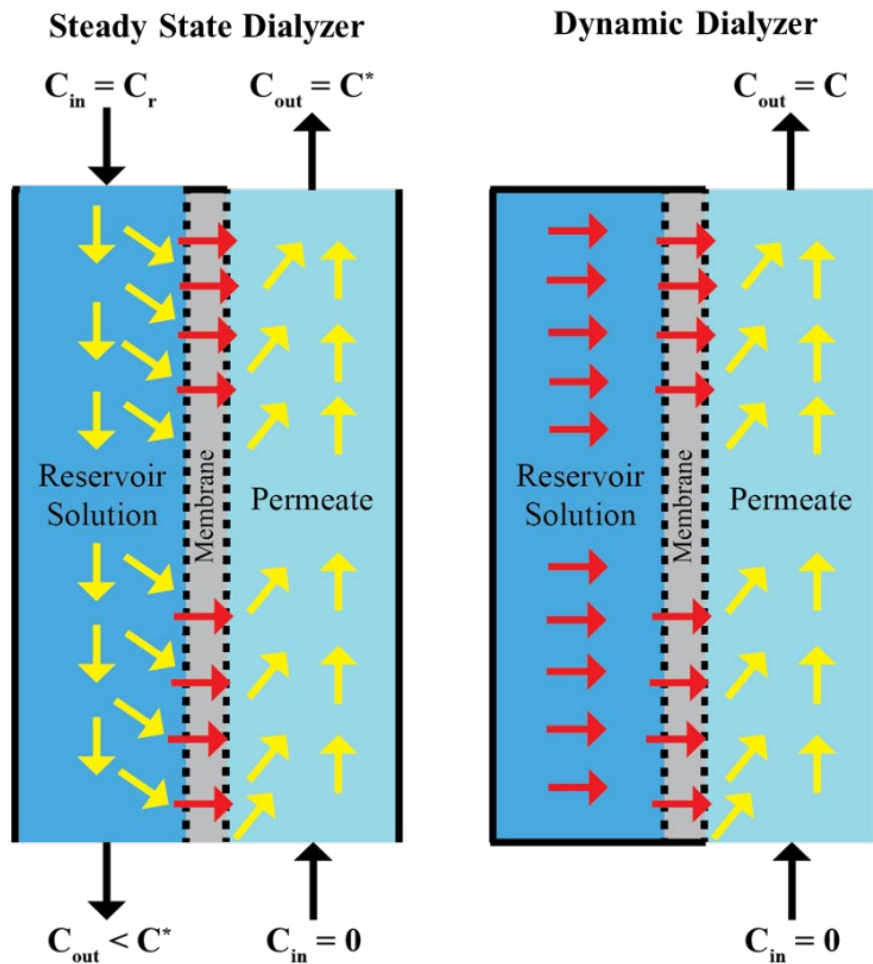


Figure 3: Steady-state Dialyzer vs. Dynamic Dialyzer.

In Figure 3, the red arrows indicate diffusive transport, and the yellow arrows show diffusive and convective transport. The black arrows point out the flow direction of each stream. The solute can diffuse through the membrane since the membrane is partially filled with solvent. In both dialysis setups, a minimal amount of solvent penetrates the membrane. However, the normal pressure applied by the reservoir and the permeate side to the surface of the membrane equalizes to a level that impedes any significant solvent flux. Hence, the free volume of the membrane is filled with solvent creating a diffusive bridge for the solute. In a non-porous membrane, the solute diffuses through a liquid phase in an interconnected tortuous path inside the solvent-swollen membrane.

Since the reservoir solution is not constantly resupplied in a dynamic dialyzer, the solute delivery to the permeate side becomes a transient process. The solute diffuses from the reservoir solution to the membrane and then reaches the convective permeate region. As the solute crosses the membrane, the perpendicular flow of the receiving fluid removes the solute from the system. The solute release ceases when the concentration difference across the membrane is insufficient to drive diffusion. Nevertheless, a dynamic dialyzer can still provide a quasi-steady-state release for prolonged periods if the proper membrane size is selected. This objective can be achieved if the MWCO of the membrane is optimized.

The MWCO of a membrane is quantified in Daltons (Da), a quantity equal to the atomic mass unit, and specifies the smallest average molar mass of a solute that will not completely diffuse across the membrane.⁵⁸ Since Ag⁺ is 107.8682 Da, a membrane with an MWCO of 107.8682 Da is appropriate to obtain minimal fluxes resulting in a stable biocide release in the dialysis system. Therefore, this work explores the performance of non-porous polymeric membranes since this type of dialysis membrane poses a very-small pore size distribution.⁵⁹

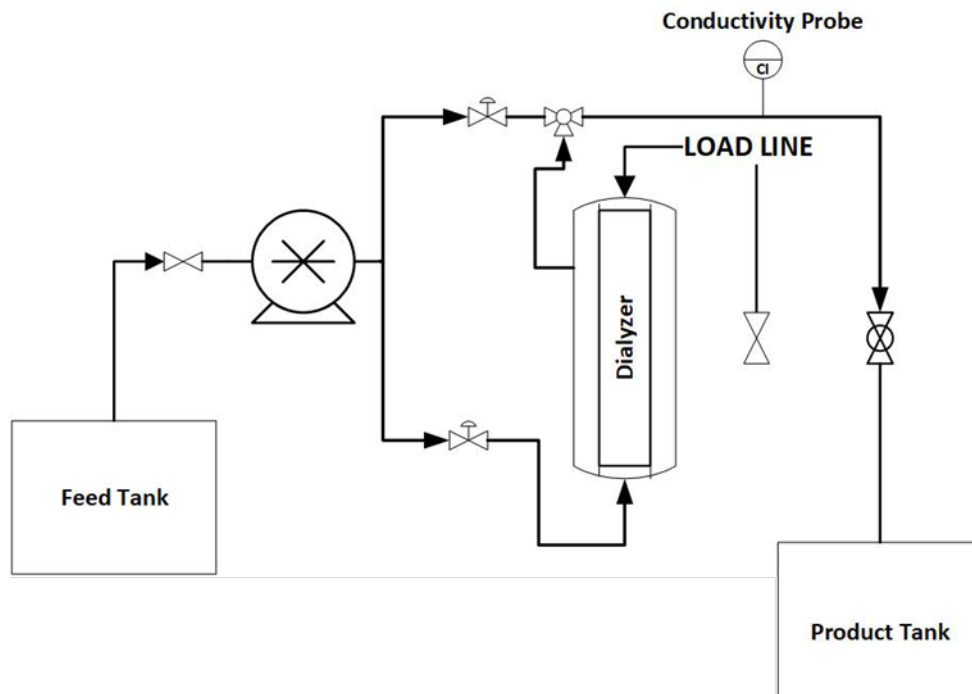


Figure 4: Ag⁺ Dosing System by Beitle et al.⁶⁰

This work continues exploring the approach exhibited in Figure 4, but it focuses on the performance of the dialyzer only. A computational model is employed to understand the Ag⁺ release in this dialysis-membrane-based system with the purpose of estimating permeability parameters that can be later used to determine a proper MWCO. In addition, the proposed simulation models the Ag⁺ release for a processing time of up to eight hours since this is the time it takes to pump 50 L of DI water through the dialyzer at a volumetric flow rate of 100

mL/min. This volume is considered to be sufficiently similar to the 68-L wastewater tank found in the WPA.⁴⁰ Moreover, dialyzers containing membranes with smaller MWCO than the size used by Beitle et al. are also experimentally tested for 8 hours. Figure 5 provides a detailed two-dimensional (2D) schematic of the dialyzer showing the direction of the flow and the main components of the device.

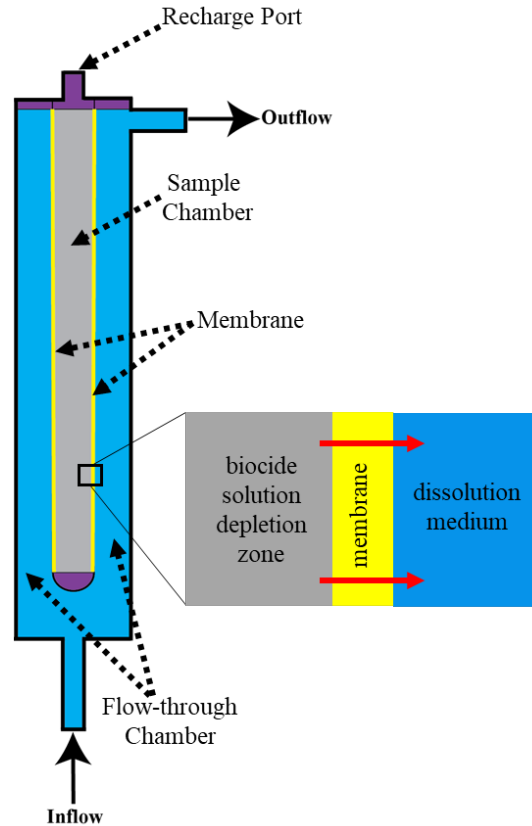


Figure 5: Two-dimensional View of a Flow-through Dynamic Dialyzer.

As a silver-based PBDS, the dialyzer system offers the following preliminary characteristics: 1) the dialyzer has a dry weight of less than 300 g, 2) the flow through the device does not generate any pressure drop, 3) the material of the dialysis membrane tolerate 2.0-9.0 pH conditions, 4) microgravity does not affect the diffusion process, 5) no power is required for the biocide release, and 6) the dialyzer has an acceptable size (2.2 cm x 45.0 cm).

3. Research Methods

The research methodology outlined by the author on the conference proceeding *ICES-2021-383* presented at the *50th International Conference of Environmental Systems* is the same as the one described in this thesis.⁶¹ Firstly, the transient Ag⁺ release by the dialyzer is computationally modeled in COMSOL Multiphysics®. Secondly, commercially-available dynamic dialyzers are experimentally tested to obtain Ag⁺ release data. These results are used to evaluate the feasibility of adopting the dialysis-membrane-based system as a PBDS for WRS applications.

3.1. Computational Model

Two main phenomena occur in a dialysis system: Laminar Fluid Flow (LFF) and Transport of Diluted Species (TDS). Thus, modeling a dialyzer becomes a mathematical multiphysics problem. In other words, the Partial Differential Equations (PDE) that describes the physics involved in the system can only be solved entirely if both mathematical expressions are combined. In the dialyzer system, while the PDE that characterizes the LFF can be solved independently, the PDE for TDS requires the fluid velocity fields from the LFF solution as inputs to properly model convective mass transport. Consequently, the computational modeling of the dialyzer is carried on COMSOL Multiphysics® (version 5.5) since this software offers a convenient workflow for solving PDE systems using the Finite Element Method (FEM).⁶²

There are five steps on COMSOL Multiphysics® that must be followed to model a system: 1) geometry design, 2) material property selection, 3) physics selection, 4) mesh generation, and 5) study type selection. For this computational model, only the domains where LFF and TDS occur are relevant in the geometry of the system. Thus, the interior and exterior housing components of the dialyzer do not have to be included in the geometry since their effects can be incorporated with boundary conditions. Although a three-dimensional (3D) geometry can be

drawn for the computational model, computational cost can be reduced if the system allows a 2D representation. Fortunately, the dialyzer has a symmetry that permits the proposed reduction of dimensionality. Figure 6 shows how the dialyzer can be represented by a 2D symmetric plane.

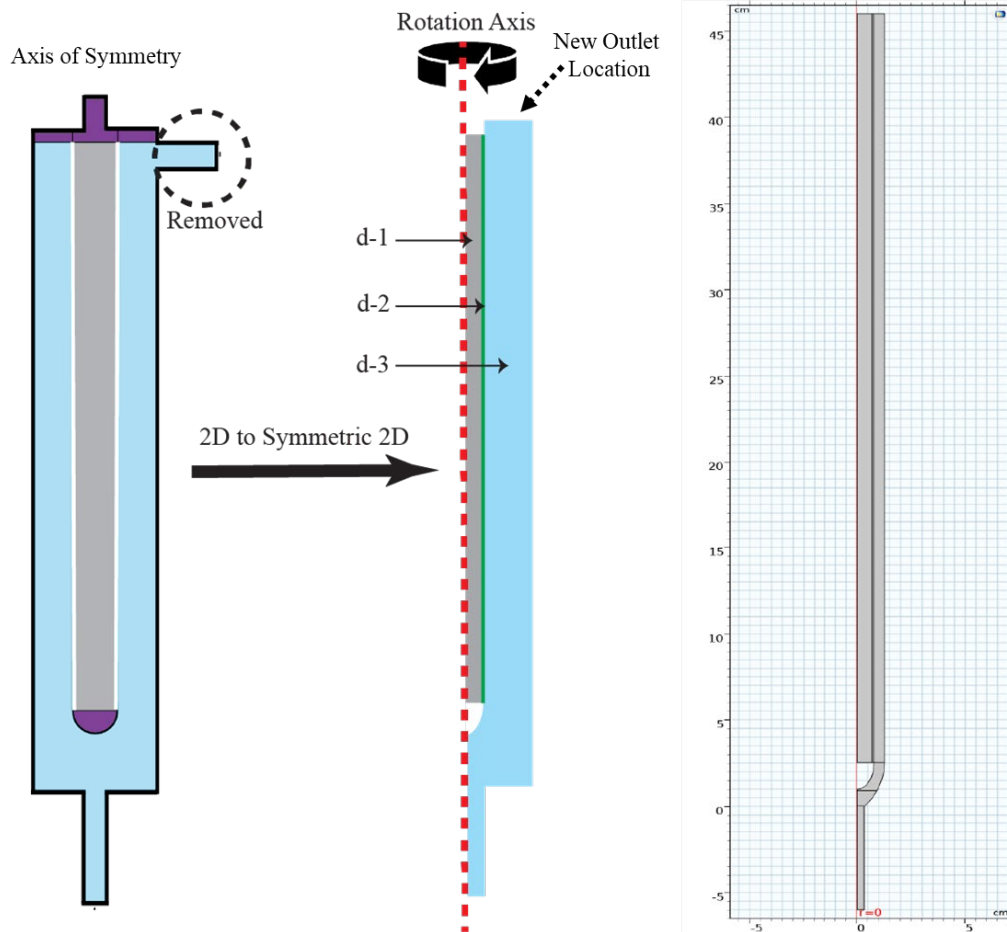


Figure 6: Two-dimensional Symmetric Representation for the Dialyzer System.

For the material property selection, the only material relevant to this study is room-temperature water. Liquid water was also selected for the membrane domain (d-2) despite the membrane material being inherently polymeric. Instead of drawing the random tortuous network through which solutes diffuse inside the membrane, a diffusive resistivity condition is set for d-2. All physical properties of water at room-temperature significant to the model are incorporated from the COMSOL Multiphysics® material library.

For the physics selection, the LFF and TDS modules were imported into the model. Eq. 2 and Eq. 3 are PDEs for the LFF and TDS, respectively. Eq. 2 derives from the Navier-Stokes equations for single-phase incompressible fluids with stationary conditions, while Eq. 3 arises from the mass conservation for time-dependent systems.^{63,64} In the LFF module, the following boundary conditions and parameters were added: volumetric flow rate at the inlet (100 mL/min), pressure at the outlet (1 atm), slip condition at the walls corresponding to the interface between the fluid and the dialyzer housing, and a global zero gravity condition. The LFF module was only defined in the domain corresponding to the flow-through chamber (d-3) since this is the only location in the system where fluid flow exists. In the same fashion, the following boundary conditions and parameters were specified in the TDS module: no inflow Ag⁺ concentration at the inlet, flux continuity at the outlet, no-flux conditions at walls, and zero initial Ag⁺ concentrations and constant diffusion coefficients (corresponding to the aqueous Ag⁺ diffusion coefficient at infinite dilution, $1.648 \times 10^{-9} \text{ m}^2/\text{s}$, $D_{\text{Ag}^+, \text{w}}$ ⁶⁵) at both the d-2 and sample chamber domain (d-1).

$$\rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot [-p\mathbf{I} + \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T)] + \mathbf{F} + \rho \mathbf{g} \quad \text{Eq.2}$$

u: velocity vector (m/s)

ρ: density (kg/m³)

p: pressure (atm)

μ: viscosity (Ns/m²)

I: identity tensor

F: volume force vector (N/m³)

g: gravity vector (m/s²)

$$\nabla \cdot (-D \nabla C_{\text{Ag}^+} + C_{\text{Ag}^+} \mathbf{u}) = \frac{dC_{\text{Ag}^+}}{dt} \quad \text{Eq.3}$$

D: diffusion coefficient (m²/s)

C_{Ag⁺}: Ag⁺ concentration (mol/m³)

t: time (s)

As prescribed on *ICES-2021-383*, the Ag⁺ permeability (the Ag⁺ diffusion coefficient in d-2, P_{Ag⁺,m}) was assumed to be a constant parameter due to expected isothermal conditions and invariable membrane thickness and fluid viscosity.⁶¹ Thus, P_{Ag⁺,m} was expressed in the TDS module as the product between the aqueous Ag⁺ solubility inside the membrane (H) and the D_{Ag⁺,w}.^{66,67} Eq. 4 describes this mathematical relationship.

$$P_{Ag^+,m} = HD_{Ag^+,w} \quad \text{Eq.4}$$

D_{Ag⁺,w}: diffusion coefficient (m²/s)

H: aqueous Ag⁺ solubility inside the membrane

P_{Ag⁺,m}: diffusion coefficient (m²/s)

In this analysis, the parameter “H” becomes the primary unknown for modeling the dialysis system since there is no direct correlation between H and MWCO. Nevertheless, H can be estimated using the parameterization functionality that COMSOL Multiphysics® offers since the target Ag⁺ concentrations are known. That is to say; the computational model is solved for several values of H until the solutions provide an Ag⁺ release that resides between the 200-400 ppb for most of the 8.0 hr processing time. The subsequent unknown that must be determined is the initial concentration of Ag⁺ in the sample chamber (reservoir solution). As a result, various permutations of initial Ag⁺ loads and H values are carried out in the parameterization study. Additionally, due to the exploratory nature of this study, the counter ion from the silver source was not included in this simulation.

For the mesh generation, the geometry of the system was meshed using the physics-controlled functionality that COMSOL Multiphysics® provides. This meshing capability closely follows the underlying principles of the selected PDEs and only requires a size input from the user. The mesh size selection is summarized in the result section. Figure 7 shows the final mesh size for each physics module.

As figure 7 reveals, the meshing for each physics module is different. The LFF and TDS required distinct meshes since LFF occurs only in the flow-through chamber, while the TDS takes place in all the domains. Furthermore, a stationary solver was chosen to solve the LFF module since the PDE describes a steady-state fluid flow. Conversely, a time-dependent solver was selected to solve the TDS module due to the transient behavior of the diffusion process. After the stationary solver provides a convergent solution, these results are exported from the LFF module to the TDS model and specified in the time-dependent solver.

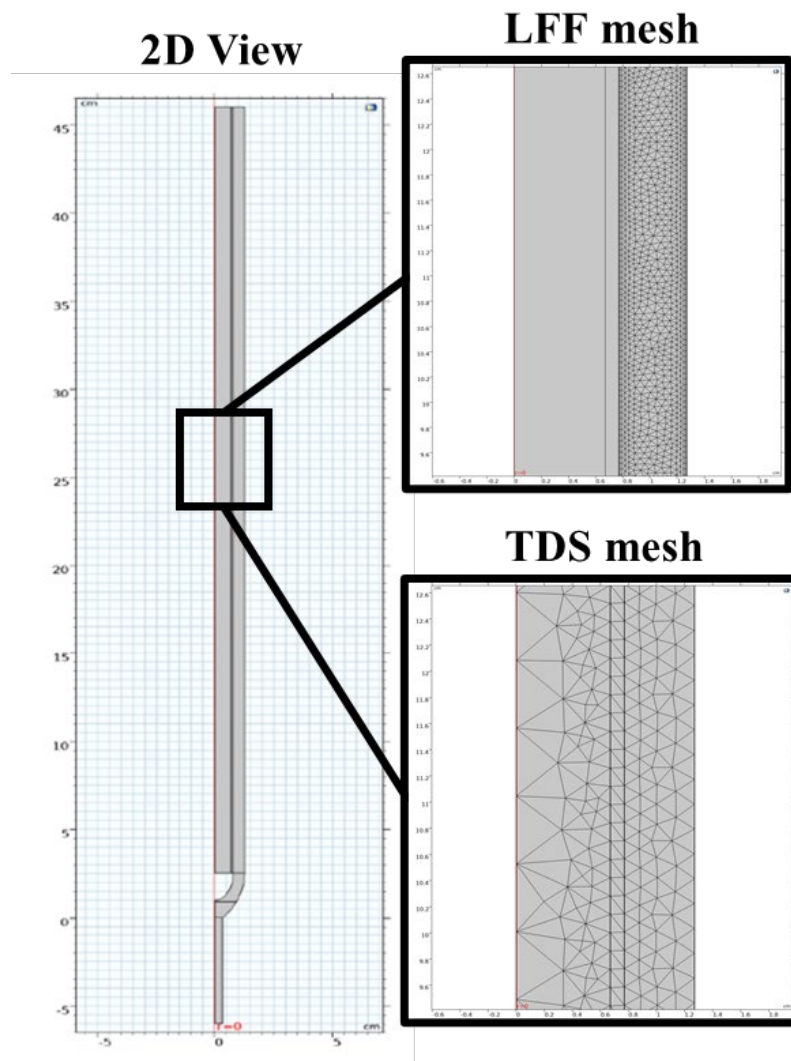


Figure 7: Meshing for LFF and TDS Modules.

3.2. Experimental Testing

The experimental testing consisted of flowing DI water through a dialyzer at a 100 mL/min volumetric flow rate and measuring the outflow Ag⁺ concentration for 8.0 hr. The initial Ag⁺ load was based on the best performing results from the computer simulation. Although Table 1 suggests that the most advantageous silver salt is silver nitrate, silver lactate was used for the experimental tests due to its availability and safer handling. As stated on ICES-2021-383, it is understood that silver lactate would never be a potential Ag⁺ source since the TOC levels can increase in a WRS due to lactate ions.⁶¹ It is believed that utilizing this silver salt would provide results insignificantly divergent from silver nitrate-based tests. Figure 8 shows the experimental setup.

The dynamic dialyzer utilized in this experiment was the Tube-A-Lyzer® (25-30 mL) from Repligen© (Rancho Dominguez, California). This dialysis device contained a dry Biotech Grade Cellulose Ester (CE) membrane tubing with an MWCO distribution between 100-500 Da. This MWCO was the smallest size the manufacturer distributed. Moreover, an EVOQUA Deionization System (Pittsburgh, Pennsylvania) was used to obtain ~50 L of DI for each experiment.

Three experimental tests were run for a dialyzer, and each test had the same initial Ag⁺ load. Once the test was finished, the remaining silver solution inside the sample chamber was withdrawn, and the flow-through and sample chambers were flushed with DI water. The dialyzer was stored filled with DI water between experiments. Furthermore, an electrical conductivity (EC) meter with a 0.1 cell constant by Atlas Scientific© (Long Island City, NY) was employed to take continuous in-line measurements. A correlation curve was constructed using the Hanna Instruments© HI96737 Silver Portable Photometer (Smithfield, Rhode Island) to translate the EC

data to concentrations in ppb. The dialyzer was covered with aluminum foil to minimize the precipitation of silver lactate due to light exposure; most silver salts are sensitive to light.⁶⁸ An static mixer was also implemented to enhance mixing in the outflow.

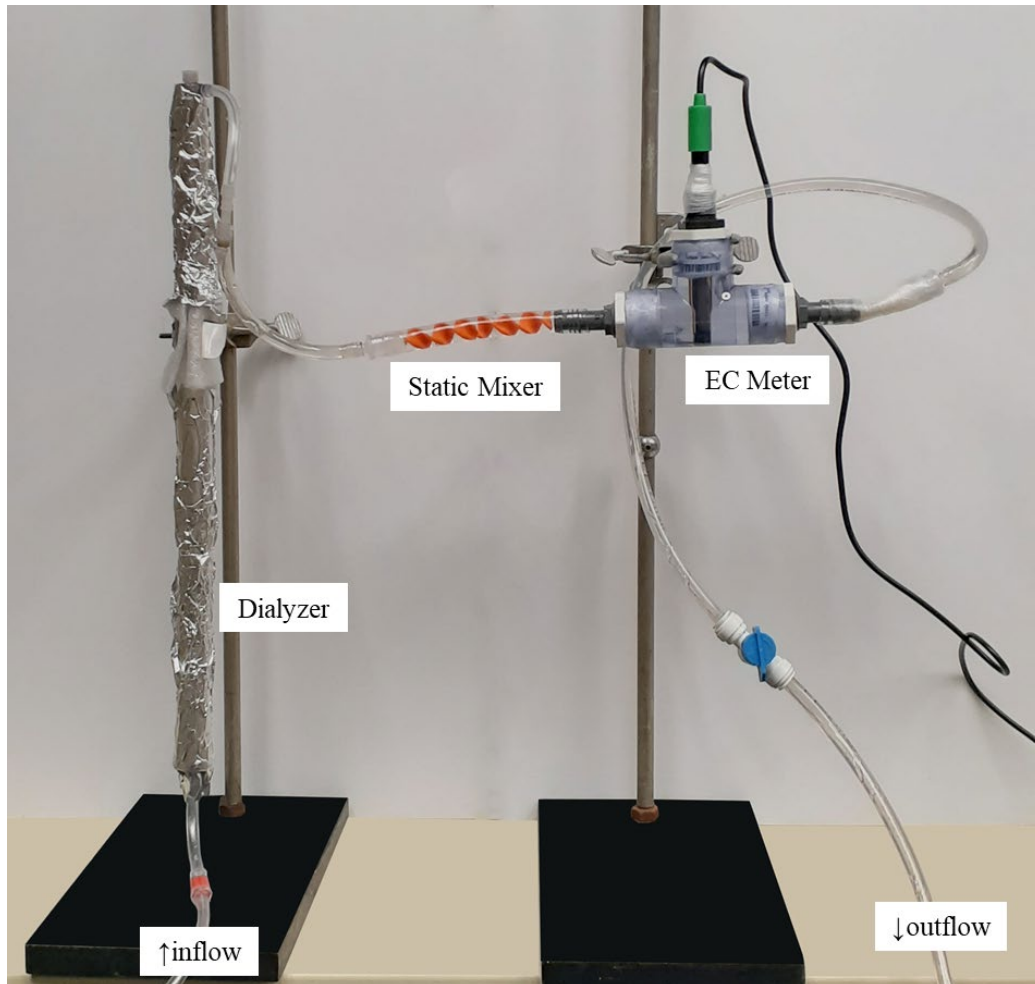


Figure 8: Dialysis-Membrane-based Passive Biocide Delivery System – Experimental

Setup

4.1. Computational Results

The numerical solvers that computed the solutions for the LFF and TDS modules on COMSOL Multiphysics® generated absolute convergence errors below 10^{-2} . These

convergences were verified by confirming that mole/mass conservation was held in the system. For the LFF module, the solution was verified by checking that the amount of fluid that entered the dialyzer (kg/s) was equal to the one leaving the system. Similarly, the TDS solution was verified by validating that the number of Ag⁺ moles that crossed the membrane corresponded to the total moles at the outflow for the 8.0 hr study. While the solver provided correct solutions for the LFF study using a “normal” mesh size, several mesh sizes had to be generated to obtain an optimal solution for the TDS study. Table 3 compiles the meshing performance for each physics module. Each local mesh size is equivalent to a reference proportionality set by the global dimensions of the corresponding domains. Therefore, the local LFF and TDS mesh sizes should not be compared since they are generated separately within their module.

As Table 3 shows, the “finer” mesh size gave the lowest absolute error of 6 % for the TDS module. Other mesh combinations and options did not converge, were too coarse, or generated domain meshes with a much thinner region than the specified minimum element size. Although mesh refinement generates even smaller errors, the solutions were not realistic. Consequently, the 6% error was considered sufficient to carry out the parameterization analysis.

In the parametrization analysis, H was allowed to take values from 0.0001 to 0.1. These values for H were permuted with four initial Ag⁺ concentrations: 50 mol/m³, 100 mol/m³, 500 mol/m³, and 1000 mol/m³. The most outstanding results were obtained with an initial Ag⁺ load of 100 mol/m³; thus, the dialyzer was loaded with this concentration for the experiments.

Table 3: Mesh Size and Convergence.

Model: Transport of Diluted Species (TDS)				
<i>Local Mesh Size</i>		<i>Mole Balance</i>		<i>Absolute Error %</i>
<i>Membrane</i>	<i>The Rest of the Domains</i>	<i>IN (mol)</i>	<i>OUT (mol)</i>	
Extremely Fine	Extremely Fine	2.92786x10 ⁻⁴	2.097389x10 ⁻⁴	28.36%
Extra Fine	Extra Fine	2.21746x10 ⁻⁴	1.321123x10 ⁻⁴	40.42%
Finer	Finer	1.50974x10 ⁻⁴	1.600357x10 ⁻⁴	6.00%
Finer	Fine	1.85852x10 ⁻⁴	3.942799x10 ⁻⁵	78.79%
Extra Fine	Fine	1.85852x10 ⁻⁴	3.942799x10 ⁻⁵	78.79%
Extremely Fine	Fine	1.85857x10 ⁻⁴	2.883193x10 ⁻⁵	84.49%
Extra Fine	Finer	1.84133x10 ⁻⁴	1.019482x10 ⁻⁴	44.63%
Extremely Fine	Finer	1.84137x10 ⁻⁴	1.019489x10 ⁻⁴	44.63%
Extremely Fine	Extra Fine	1.83548x10 ⁻⁴	1.348904 x10 ⁻⁴	26.51%
Normal	Fine	1.87619x10 ⁻⁴	3.967029x10 ⁻⁴	78.86%
<i>Convective Domain</i>	<i>Membrane + Reservoir</i>			
Extra Fine	Extremely Fine	1.93779x10 ⁻⁴	2.150164x10 ⁻⁴	10.96%
Fine	Finer	1.29001x10 ⁻⁴	4.657828x10 ⁻⁵	63.89%
Fine	Extra Fine	1.60434x10 ⁻⁴	6.740748x10 ⁻⁵	57.98%
Fine	Extremely Fine	1.79179x10 ⁻⁴	8.440938x10 ⁻⁵	52.89%
Model: Laminar Fluid Flow (LFF)				
<i>Local Mesh Size</i>		<i>Mass Balance</i>		<i>Absolute Error %</i>
<i>Convective Domain</i>		<i>IN (Kg/s)</i>	<i>OUT (Kg/s)</i>	
Normal		0.0016637	0.0016637	0.00%

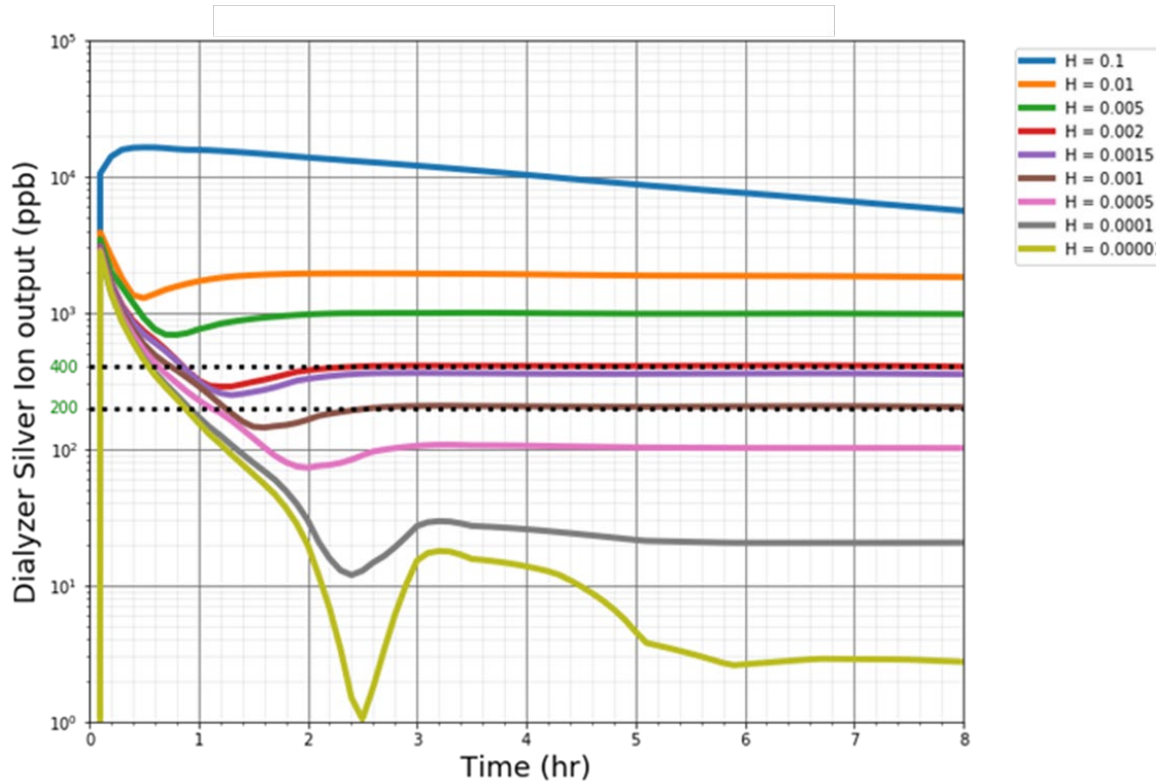


Figure 9: Dialyzer Ag⁺ Output vs. Time for Varying H and Initial Ag⁺ Load of 100 mol/m³.

The Ag⁺ release data shown in Figure 9 (Ag⁺ concentration at the dialyzer outlet) suggested that a 0.0015 value for H provided a stable Ag⁺ release between the 200-400 ppb target and maintained a concentration at about 300 ppb during the pseudo-steady state. The other values provided a release that was outside the desired concentration range. The best-performing H corresponded to a $P_{Ag^+,m}$ of 2.472×10^{-12} m²/s. This permeability value indicated that the diffusivity of Ag⁺ inside the membrane was two-order of magnitude smaller than the free aqueous diffusivity. Moreover, Figure 9 also shows a significant concentration spike at start-up that did not equilibrate to desired levels after almost an hour. For the H = 0.0015 curve, this concentration spike reached levels up to 3000 ppb. Although this outcome was anticipated since this system has a transient nature, the maximum magnitude of this instance was unknown.

Hence, this rise in concentration could be regulated using the dilution strategy suggested by Beitle et al.⁶⁰ The results also revealed that the Ag⁺ release reached the desired pseudo-steady state after approaching a minimum level. The dialysis system must be tuned to provide the lowest concentration spike possible and a minimum release level above 200 ppb. For the $H = 0.0015$ curve, this process took approximately 40 minutes. These results must be compared with the experimental data.

4.2. Computational Results

Figure 10 compiles Ag⁺ release data from three experimental tests. Additionally, the best result from the computer simulation ($H = 0.0015$) is also included in this plot. In the experimental runs, some features of the release behavior predicted by the computer model were observed. For instance, a highly transient concentration output was also seen at the beginning of the testing. However, this concentration spike decreased faster over the first 12 minutes in all tests than the release predicted by the model. In addition, the experimental data showed that the Ag⁺ release also followed a concentration increase after stretching to a minimum. Nevertheless, the concentration increase did not evolve as anticipated by the model; instead, it progressed to higher concentrations at a more prolonged pace. Consequently, the pseudo-steady-state release was never observed in the experimental runs.

Experimental Test #1 generated an unstable Ag⁺ release that experienced more than one concentration drop over the first four hours. After the final steep decline in concentration, the outflow Ag⁺ level progressively grew to concentrations that never reached the lower target limit. In contrast, Experimental Test #2 yielded an Ag⁺ dosage that resided between the required concentration bounds for almost five hours after the initial jump in concentration. After approximately 5.4 hours, the Ag⁺ release produced concentrations above the upper 400 ppb limit

and continued rising for the remainder of the test. The results from this second run were considered the best result throughout all tests. Lastly, the Ag⁺ delivery concentrations from Experimental Test #3 were substantially higher than the previous runs. The concentration drop in this test reached a minimum value of 366.53 ppb before rising to levels above 1000 ppb. After six hours, the Ag⁺ concentration was observed to flatten around 1250 ppb. In the same test order, the following Ag⁺ delivery rates were estimated for the concentration-rising phase: 17.50 ppb/hr (4.0 hr – 8 hr), 76.25 ppb/hr (4.0 hr – 7.6 hr), and 200.00 ppb/hr (2.0 hr – 5.6 hr).

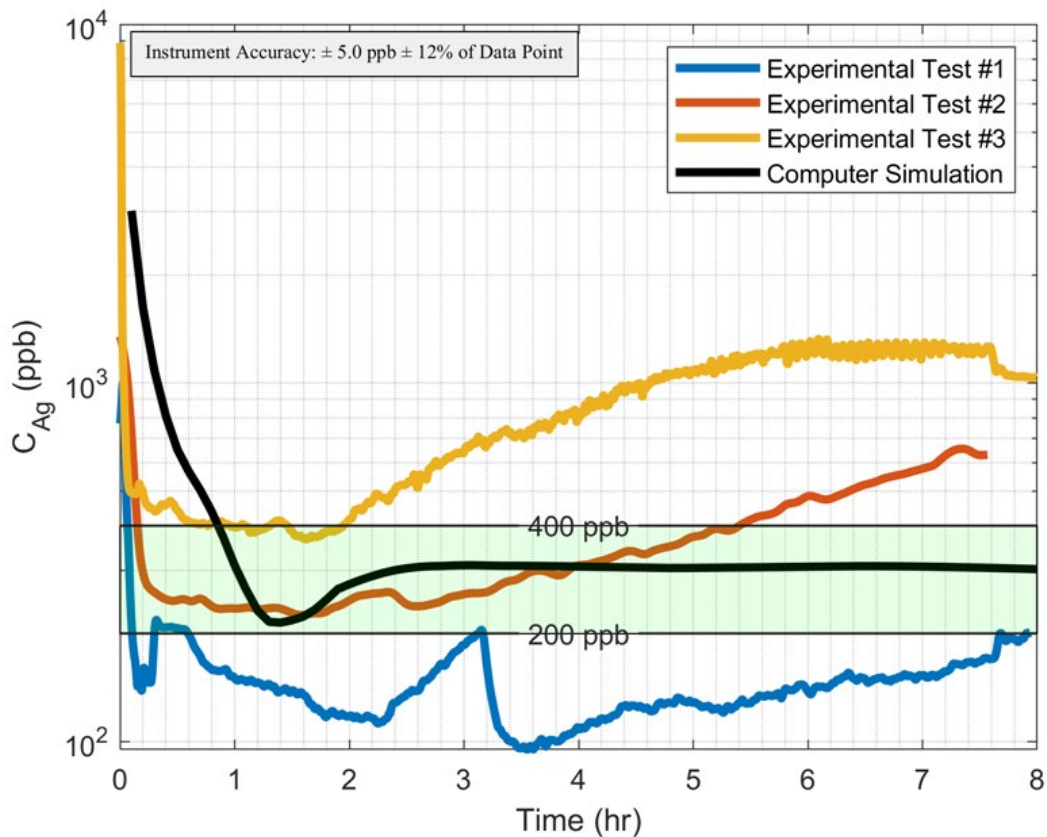


Figure 10: Silver Ion Release by Dialysis-membrane-based Passive Biocide Delivery System.

A second round of tests was conducted to document the effects of a new storage approach for the dialyzer. As previously mentioned, the first dialyzer was stored filled with DI water after each experiment. It is essential to point out that the interior components of the dialyzer were not

soaked with DI water before the first experimental run. Therefore, it was considered that DI water could have promoted membrane swelling during storage, which in turn caused an increase in the Ag⁺ release after each run. Following storage recommendations for regenerated CE dialysis membranes, it was decided to store the second dialyzer filled with an aqueous solution of 1% hydrogen peroxide (H₂O₂) instead of DI water.⁶⁹ Figure 11 shows the Ag⁺ release data from this second testing stage in which a new dialyzer with the same membrane MWCO was used.

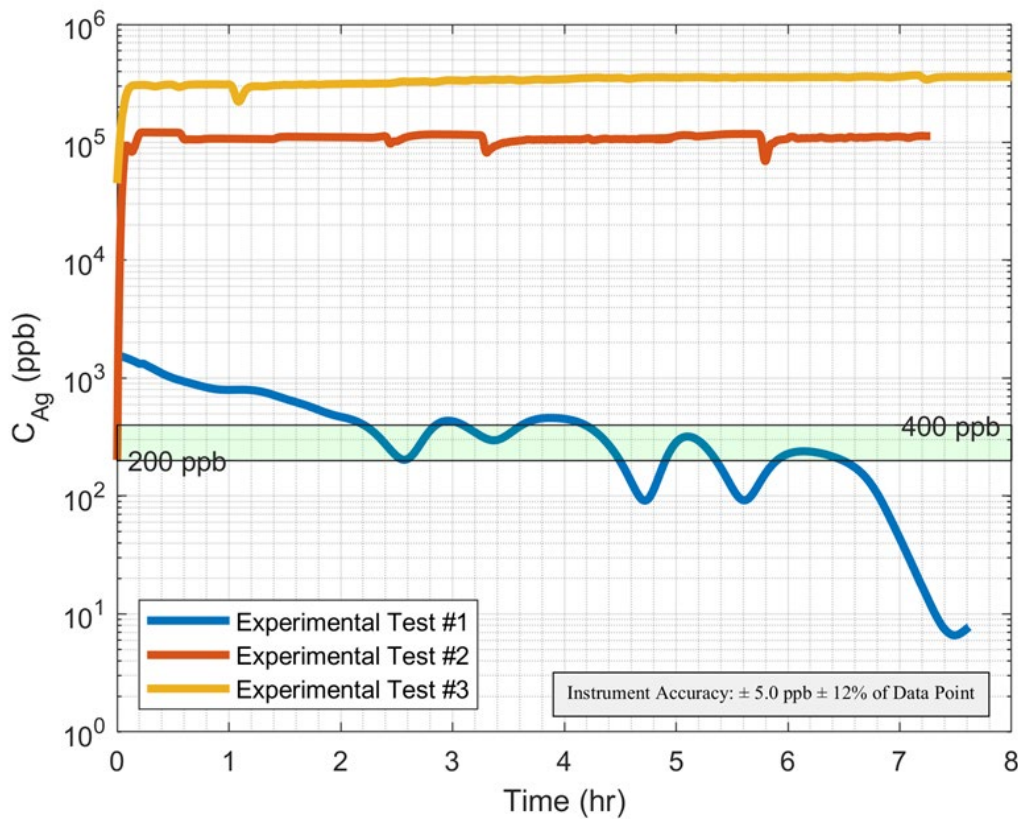


Figure 11: Silver Ion Release by Dialysis-membrane-based Passive Biocide Delivery System – 1% H₂O₂ Storage Solution.

The Ag⁺ release data presented in Figure 11 diverges from the computational model and first experimental tests. In this consecutive testing, Experimental Test #1 generated an Ag⁺ release that kept substantially decreasing throughout the run. This release started with a maximum value above 1000 ppb and did not reach target levels after 2.20 hours had passed. This result was

inconsistent with the performance obtained in the first data set from Figure 10 and experienced several concentration drops. Although the new Experimental Tests #2 and #3 provided a stable Ag⁺ release, the overall output concentration was three orders of magnitude higher than the desired concentration range ($> 10^5$ ppb). Additionally, the Ag⁺ delivery by these last two tests also evolved differently from the first run and the data from Figure 10. Instead of generating an initial concentration spike that decreased until reaching a minimum level, the release rapidly raised to a value at start-up and maintained a relatively steady concentration from that point. The immediate effect that may be attributed to the H₂O₂ storage treatment was the extreme enlargement of the free-permeable volume inside the membrane. Other chemical treatments must be examined not only for post-usage storage but also as a preconditioning action.

5. Conclusion

This work carried out the preliminary development of the dialysis-membrane-based PBDS for spacecraft water recovery units. The dialysis-membrane-based PBDS consisted of an in-line dynamic dialyzer in which a saturated solution of silver ion was loaded. This silver load was held in an interior compartment comprised of a dialysis membrane bag. Once water flowed in contact with the membrane, Ag⁺ were released via diffusion. This system offers a passive release (no additional power requirement), insignificant pressure drop, low weight, and optimizable size, making this technology attractive for WRS operations in long-term crewed space missions. This study sought to determine if this system could be tuned to deliver an Ag⁺ output between 200 and 400 ppb continuously to a stream of DI water. Two approaches were employed to study the performance of the proposed system: equation-based computational modeling and experimental testing. The computational model was built using COMSOL Multiphysics®, and the testing was

performed on a commercial dynamic dialyzer. The Ag⁺ release from both methods was compared.

The computer simulation generated data showing how the proposed system could reach a pseudo-steady-state Ag⁺ release at the target concentrations lasting seven hours following an initial transient phase. This transient phase consisted of a spike in concentration that rose above the upper limit at start-up and then approached a minimum level over the first 50 minutes. This computational model revealed that the Ag⁺ permeability should be three orders of magnitude smaller than ionic diffusivity in water for the best-performing release. This result corresponded to an Ag⁺ solubility coefficient of 0.0015 inside the membrane and an initial Ag⁺ load of 100 mol/m³. The parameterization study concluded that any initial load starting at 100 mol/m³ was sufficient for an eight-hour release.

Some of the modeled trends in Ag⁺ release were observed in the data collected from the experimental runs. In the first round of tests, the Ag⁺ release also generated a rapid concentration spike at start-up. However, this initial concentration spike decreased faster than the results obtained from the computational model. After the outflow concentration approached a minimum value, the Ag⁺ concentration progressively increased instead of reaching a plateaued level like the modeled system. The initial Experimental Test #2 provided an Ag⁺ release that stayed the longest in the desired 200-400 ppb range. Contrarily, the data from the initial Experimental Test #3 generated Ag⁺ concentrations above the 400 ppb limit for most of the experimental time. However, this Ag⁺ release behaved the most similar to the computational model. It is presumed that all three initial tests could have reached the desired pseudo-steady-state Ag⁺ release if the tests were kept running for a more extended period (> 8.0 hours). Moreover, it was observed that the total Ag⁺ output increased as the dialyzer was re-utilized.

This outcome may indicate that the membrane swells after each use. However, this outcome was contemplated since the commercial membrane employed in the experiments was inherently a single-use disposable material intended for other applications. Furthermore, it was decided to run an additional round of tests to document the effects of a new post-run storage method. By storing the dialyzer filled with a solution of H_2O_2 , it was concluded that this procedure might enhance the expansion of the non-porous free space inside the membrane. This chemical treatment did not succeed as intended. Nonetheless, stable Ag^+ releases with out-of-spec concentration were generated in the last experimental runs.

More experimentation is required to thoroughly test the performance of the dialysis system as a PBDS. Although the permeability parameter obtained from the computational model is compelling, there is no direct correlation or conversion between permeability and MWCO size. Consequently, the computational result cannot be directly used to obtain a better membrane based on an MWCO size. Nevertheless, the model developed by Yasuda et al. may be employed to estimate an MWCO based on the degree of hydration.⁶⁷ This approach will require additional experiments to determine the hydration of several membrane materials. Moreover, in the case the initial concentration spike cannot be avoided or tuned to reside in the target concentration range, the Ag^+ release could be adjusted using the strategy developed by Beitle et al.⁶⁰ The following tasks must be completed to fully assess the performance of the dialysis-membrane-based PBDS into a spacecraft WRS: extend the Ag^+ release experiment for more than eight hours, test other highly soluble silver salts, acquire and employ membranes with lower MWCO sizes (< 100-500 KDa), document the effects on the membrane by chemical preconditioning, integrate and deploy a strategy for diluting the outflow concentration when this exceeds the limit, and develop a more robust computational model that includes the effects of the counter ion in the Ag^+ release.

6. List of Abbreviations

2D	Two-dimensional
3D	Three-dimensional
ABDS	Active Biocide Delivery System
Ag ⁺	Silver Ions
AgFoam	Silver-loaded Foam
AgNP	Silver Nanoparticles
BDS	Biocide Delivery System
CE	Cellulose Ester
d-1	sample chamber domain
d-2	membrane domain
d-3 f	low-through chamber domain
DAg ⁺ ,w	aqueous Ag ⁺ diffusion coefficient at infinite dilution
DI	Deionized
EC	electrical conductivity
ECLSS	Environmental Control Life-Support Systems
ESIG	Electrolytic Silver-ion Generator
FEM	Finite Element Method
H	aqueous Ag ⁺ solubility coefficient inside the membrane
H ₂ O ₂	Hydrogen Peroxide
ISS	International Space Station
IX	Ion Exchange
IXB	Ion-eXchange Bed

LEO	Low Earth Orbit
LFF	Laminar Fluid Flow
MCV	Microbial Check Valve
MWCO	Membrane Molecular Weight Cutoff
NASA	National Aeronautics and Space Administration
PA _{g+,m}	Ag ⁺ permeability inside the membrane
PBDS	Passive Biocide Delivery System
PDE	Partial Differential Equation
ppb	parts per billion
TDS	Transport of Diluted Species
TOC	Total Organic Carbon
UPA	Urine Processor Assembly
WMS	Water Management System
WPA	Water Processor Assembly
WRS	Water Recovery System

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