Direct*INJECT*: Dosing Systems for Concentrated Liquid Biocides

John Vance[1]
KBRwyle, NASA Ames Research Center, Moffett Field, CA 94035

and

Lance Delzeit[2]
NASA Ames Research Center, Moffett Field, CA 94035

Reliable and mass-efficient techniques for biocide dosing are necessary to enable residual microbial control in spacecraft potable water systems. Direct*INJECT* is an approach to provide ultra-low flow rate injection of stable aqueous biocide concentrate solution (e.g., highly soluble silver salt). This method has the benefit of low consumable mass and is insensitive to the chemistry of the target water. With a 40 g Ag^+/liter solution, required dosing rates would be ~1 µl/minute during water processing (for a system similar to the ISS WPA), requiring only approximately 20 ml/crew-year of concentrate. The performance of three dosing systems were identified and characterized: pressure-driven flow through a robust micro-capillary tube with a solenoid valve shut-off, a miniature peristaltic pump, and a multi-piston pump with integrated valving. Several potential system reliability concerns are addressed including prevention or segregation of gas bubbles in the concentrate reservoirs as well as long-term materials compatibility and mechanical life.

Nomenclature

°C	=	degree Celsius
”	=	inch
Ag	=	silver
Ag^+	=	silver(I) ion
AgF	=	silver(I) fluoride
$AgNO_3$	=	silver(I) nitrate
COTS	=	commercial off-the-shelf
g	=	gram
g/l	=	grams per liter
Hz	=	hertz (cycles per second)
ISS	=	International Space Station
kPa	=	kilopascal
l	=	liter
ml	=	milliliter
mm	=	millimeter
N_2	=	nitrogen (gas)
nl	=	nanoliter
PAEK	=	polyaryletherketone
PEEK	=	polyetheretherketone
psi	=	pounds per square inch (gauge)
psid	=	pounds per square inch differential
psig	=	pounds per square inch gauge
PTFE	=	polytetrafluoroethylene

[1] Research Engineer, Bioengineering Branch, NASA ARC N239-15, Moffett Field, CA 94035.
[2] Physical Scientist, Bioengineering Branch, NASA ARC N239-15, Moffett Field, CA 94035.

μg	=	microgram
μl	=	microliter
μm	=	micrometer
ppb	=	parts per billion (mass)
ppm	=	parts per million (mass)
WPA	=	Water Processor Assembly

I. Introduction

THE reliable dosing of stable and effective chemical biocides is desired to enable residual microbial control in spacecraft potable water systems and prevent fouling by biofilms or proliferation of pathogenic species. The use of concentrated liquid biocides for such purposes has a long history in the NASA space program, with dosing traditionally done prior to launch or by intermittent manual injection.[1] Onboard the Apollo Command Module, astronauts were required to periodically inject sodium hypochlorite solution into the potable water system through an external port.[1] On Skylab, concentrated iodine solution was regularly metered into storage tanks with a calibrated manual pump that refilled semi-automatically from a pressurized reservoir.[1,2] Some development of automated liquid dosing systems was done at that time as well, but these do not appear to have been used operationally.[3] In later water systems, such as the Space Shuttle and the US Segment of the ISS, iodine was introduced to potable water with chemical resin beds.[4] After it was determined that long-term consumption of iodine at biocidal levels poses unacceptable human health risks, removal immediately prior to dispensing was required.

The ability to have biocidal efficacy at consumable levels and the potential for standardization of biocides across various platforms motivated NASA to investigate the move to ionic silver biocide (Ag^+) at approximately 400 ppb concentration, following decades of use on Soviet (and later Russian) spacecraft.[5] During the Shuttle era, NASA regularly treated US water by de-iodizing it and manually injecting concentrated AgF solution for compatibility with the water systems on *Mir* and the Russian segment of the ISS.[6] In the Russian segment of the ISS, their resupply water from earth contains electrolytic silver, and their recycled water contains Ag^+ introduced along with other minerals using proprietary "conditioning beds."[7]

In order to enable the move to Ag^+ biocide in exploration-class missions, reliable and mass-efficient systems for dosing Ag^+ must be developed. During the Apollo era, extensive work on electrolytic in-line dosing was conducted, however the technology was never flown.[8] More recently, there have been several projects working to extend the operational life of electrolytic systems.[9,10] Passive techniques based on ion-exchange resin,[11] a foam bearing a low solubility silver salt,[12] and dialysis across a semi-permeable membrane,[11,13] have also been subjects of research. Although long known as a possible option, little practical work has been done with dosing systems for automated injection of concentrated Ag^+ solution. This approach has several attractive attributes, including insensitivity to target water quality, minimal mass and volume costs, configuration flexibility, and process simplicity. However, engineering effort is required to ensure long-term system reliability, particularly due to a small number of required moving parts and necessity of long-term storage of potentially reactive biocide solutions.

The Direct*INJECT* Project was started to develop and characterize the performance of practical dosing systems for stable concentrated liquid biocide solutions in microgravity at very low, well-controlled, flow rates. The most attractive candidate biocides for injection are the highly soluble silver salts, $AgNO_3$ and AgF, although other compounds such as silver lactate and silver acetate (with much lower solubilities) may be of interest due to their benign counter-ions. Stable halide compounds, as well as other biocidal compound, may also be of interest if they have a high enough solubility in water. The expected performance of various silver salts in relevant dosing configurations and applications has been investigated in a previous study,[14] as has that of active chemical dosing of silver salt vs. passive and electrolytic dosing of Ag^+, iodine (by resin bed, current state of the art), and selected bromine compounds (by methods to be developed).[15] Dosing of concentrated liquid biocides can be in-line (e.g., immediately post-wastewater processing, at the Water Processor Assembly (WPA) outlet/Potable Water Bus (PWB) inlet) or directly into storage vessels (e.g., alleviating biocide depletion over time). In order to minimize hardware and consumables mass, we focused our efforts on enabling reliable dosing at the lowest practicable flow rates. This method also offers reduced complexity vs. staged-dilution dosing systems, which have been considered previously. Additionally, by limiting the silver salt concentration in the biocide solution by more than an order of magnitude below the saturation limit, the risks of precipitation and chemical attack by the relatively aggressive AgF or $AgNO_3$ solution are reduced. In this work, we consider a nominal 40 g/l Ag^+ concentrate and an assumed 100 ml/minute (ISS WPA) production rate, resulting in a dosing rate of 1.0 μl/minute to produce 400 ppb Ag^+ effluent. Assuming 2,000 L

water consumption per crew-year (5.5 L/crew-day), biocide solution consumption will be only 20 ml of biocide solution/crew-year (for a dilution ratio of 1:100,000). Consumables and hardware masses are very small, allowing for a low mass and volume system. While constant rate dosing would be appropriate for water processing systems that have constant production rates during operation, future systems may have variable production rates, calling for variable rate dosing systems. Also, it may be desirable to be able to adjust dosing system rate to account for water processing systems with different production rates, which may support different crew sizes, while maintaining the same Ag^+ concentration in the biocide concentrate. The practicality of variable rate dosing and of dosing below and above the nominal 1.0 µl/minute rate assumed here is addressed later in the paper.

Three dosing systems for initial conceptual and experimental development work were identified: 1) pressure-driven flow through a robust polymer-jacketed micro-capillary tube with a solenoid shut-off valve, 2) a miniature peristaltic pump and 3) a multi-piston pump with integrated valving. Other pump technologies of interest were found, including: miniaturized syringe pumps and piston pumps with separate valving modules, diaphragm (piezoelectric, shape-memory alloy, and electrostatic) pumps, and magnetic shape memory alloy peristaltic pumps, but these are not included in the present work. In preliminary experiments, we confirmed that all three systems could dose deionized water at the desired ~1.0 µl/minute flow rate into ambient pressure, and confirmed that the peristaltic and multi-piston pump systems could pump into 3 psi (20 kPa) backpressure. . Their flow profiles were also characterized. We began extended-duration operation of the three systems, beginning with a 7-day experiment, to investigate long-term reliability and materials compatibility, and confirmed that Ag^+ loss during continuous flow-through is minimal. We also examined the literature for reservoir systems appropriate to the different dosing techniques. Finally, we began investigating potential failure modes and associated work to understand and mitigate these.

II. Dosing Systems – Construction and Principles of Operation

A. Pressure-Driven Flow through a Capillary Tube with Shut-Off Valve

The first system is based on pressure-driven flow through a micro-capillary tube with a solenoid valve shut-off, with biocide concentrate supplied from a pressurized reservoir. Laminar, incompressible flow through a cylindrical tube is governed by the Hagen-Poiseuille law, where volumetric flow rate $Q = \Delta P \pi R^4 / 8 \eta L$, where ΔP is the pressure difference across the tube, R is internal radius, η is dynamic viscosity, and L is tube length. Keeping the tube dimensions constant, flow rate changes with variation in the difference between inlet and outlet pressures and the changing viscosity of the aqueous biocide concentrate with temperature. The variation of differential pressure can thus be limited by proper choice of pressure regulator and design of the PWB to limit the pressure change that occurs as the receiving vessel is filled. Increasing the reservoir pressure will limit the effect of PWB inlet pressure variation on dosing rate, at the cost of greater pressure ratings for system components and higher pressure gas supply. Care must be taken to ensure that the dosing system is adequately ventilated and that heat from the solenoid valve coil is removed, particularly in the absence of natural convection due to microgravity. Assuming the typical crew habitability standard of 18-27 °C for cabin temperature,[16] flow rate variation due to changes in viscosity would be on the order of +/−10% of nominal (at 22.5 °C). With these conditions taken into account, the injection rate can be limited to an acceptable range. A variable flow rate could be produced using an electronically controlled pressure regulator or by varying the duty cycle of the solenoid valve. In a flight system, pressurant gas could be supplied from compressed N_2 supplies, which are used to pressurize water storage vessels and as a diluent to maintain cabin atmosphere pressure and composition.

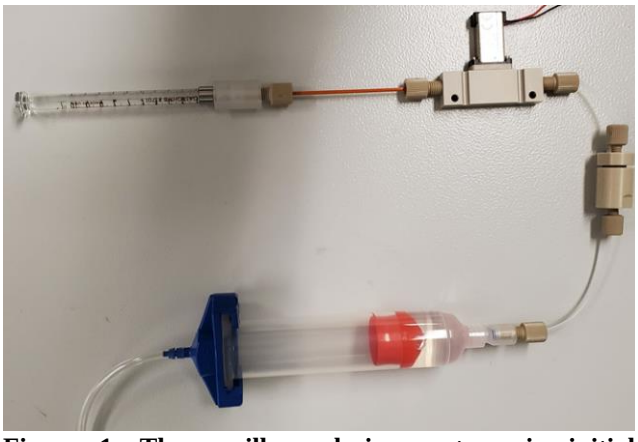

Figure 1. The capillary dosing system, in initial configuration. Counter-clockwise from bottom center: air-driven syringe reservoir with piston, PEEK frit and housing, solenoid valve and manifold, PEEKSil capillary tube, and microsyringe for flow rate measurement.

The capillary dosing system was constructed entirely from COTS parts, and is shown in Figure 1. The pressurized liquid reservoir was a 30 ml polypropylene pneumatic dispensing syringe (Nordson EFD, part # 7012134, 100 psi (700 kPa) service), with an "Tight Fit" high-density

polyethylene piston (Nordson EFD part # 7012186) and associated adapter assembly (Nordson EFD, part # 7012056). The adapter is plumbed to a regulated UHP nitrogen supply (0-30 psi (210 kPa)). The outlet of the syringe was connected to a 10 μm pore PEEK frit filter in a PEEK holder (IDEX, part #s A-720 and A-355) to protect the valve and capillary , followed by a normally-closed miniature solenoid valve (to allow flow shut-off) with connecting flange (PEEK body and FFKM diaphragm, 0.4 mm orifice (Bürkert, part #s 273206 and 694895). The solenoid valve was selected due to its construction with inert and chemically resistant materials, low internal volume, 100% duty cycle, and long cycle life rating by the manufacturer (3×10^7 cycles under laboratory conditions, medium not specified). Power consumption is only 0.9 W during dosing; the heat generated should easily be removed with appropriate heat sink and/or ventilation. A PEEK jacketed, fused silica micro-capillary tube (25 μm inner diameter, 1/16" (1.6 mm) outer diameter, 100 mm long (PEEKSil-type, IDEX part # 62510)) is connected to the solenoid valve outlet. The outlet of the capillary tube is then connected to a flow-measuring device. The use of a jacketed capillary tube allows for ease of connection, mechanical robustness, and a highly inert flow path with tight diametric tolerance. With 20 psid (140 kPa) across the above micro-capillary tube, expected water flow rate at room temperature was calculated to be approximately 1 μl/minute.

B. Miniature Peristaltic Pump

The second dosing system chosen was a miniature peristaltic pump which (in a flight system) could be fed by a flexible bladder reservoir at ambient pressure. Such pumps are designed to be more than an order of magnitude smaller and lighter than typical laboratory grade pumps. By decreasing effective rotor size, higher rotation speed is used for a given flow rate, and the frequency of the pump cycle is increased. This is important because peristaltic pumps have pulsatile flow patterns, causing variation in biocide concentration in the dosed effluent over the cycle. It also allows for smother rotation of the pump head by the driving system, in this case a stepper motor which removes the need for reduction drives and feedback control.

The miniature peristaltic pump was the most promising found on the market for this application and is manufactured by Aquatech Co. of Japan (part # RP-TXP5S-P04A-DC3VS) with a nominal flow rate: 0.03-40 μl/minute. The pump, shown in Figure 2, is driven by a micro-stepped motor and uses silicone tubing (0.5mm inner diameter, 1.5mm outer diameter). The stepper motor is powered by a controller with an associated speed readout (Aquatech, part #s RE-C100 and RE-F100), also shown in Figure 2. Liquid flow is driven by an eccentric rotor, which compresses the tubing against the inner diameter of the pump housing. Pump operation is further described at the manufacturer's website.[15] Pump maximum service pressure is given by the manufacturer as 4.4 psi (30 kPa), which should be sufficient for discharge into the PWB inlet. Pump service life at 25-30 μl/minute with pure water (discharge pressure assumed to be ambient) is rated by the manufacturer at ~1000 hours, with motor failure observed at >2000 hours; pump tubing failure was not observed, as the tests concluded after motor failure.[16] We expect that a more robust stepper motor could be integrated with the modular pump head, allowing for much longer service life at low rotational speeds. Given this modification, tubing life would limit pump service duration, and this would depend on

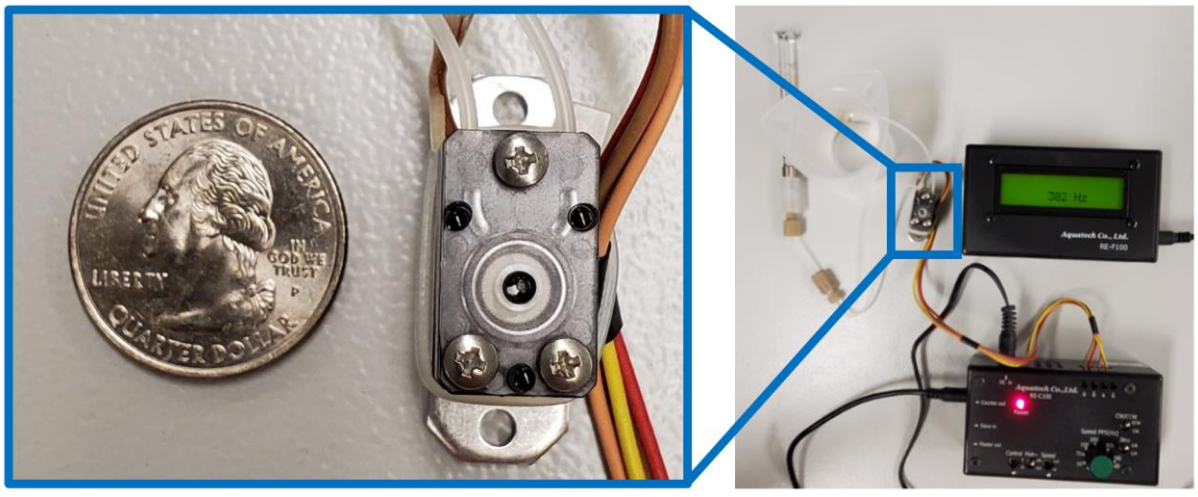

Figure 2: The miniature peristaltic pump in initial configuration with scale marker (inset) and associated hardware.

backpressure, pump speed, and chemistry of the biocide. In a flight system, the stepper motor would be driven by a small integrated circuit, replacing the system employed here for additional mass savings. Pump mass and volume are very small (~14 g, ~6 ml) allowing for multiple strategies for reliability and redundancy..

C. Multi-Piston Pump

The traditional technologies for controlled dispensing of small volumes of liquid in the laboratory are syringe pumps and piston pumps driven by integrated precision stepper motors. In such systems, external valving is required to control fill and dispense cycles, and to enable semi-continuous flow. These were considered at the beginning of the project, and are still of interest, but a more modern iteration of the piston pump was identified. It has multiple pistons operating out of phase to each other, with integrated valving, for "continuous" dispensing such that the pump doesn't require separate fill/dispense cycles. Such pumps have been adopted in a variety of high-performance laboratory instruments for pumping of sensitive or corrosive solutions.

The multi-piston pump selected for this work was manufactured by VICI Valco (Model M6, part # CP2-4841-F1), and is shown in Figure 3a. A schematic of the pump head is reproduced in Figure 3b. Four PTFE pistons are driven by a cam plate in aluminum oxide cylinders (each piston stroke is 25 µl, for 100 µl dosed per rotation). The pump is driven by a micro-stepping motor. A co-rotating valve plate controls liquid flow during operation, removing the need for separate valving and control circuitry. Further description of pump operation is available and in the inventors' patent[17] and in the manufacturer's literature. In the standard M6 pump, wetted materials are PTFE, PAEK, PTFE/carbon composite, and Viton. Expected pump lifetime with water is 10^6 rotations, or 100 L liquid dispensed. The pump head has dimensions of 1.5" (3.8 cm) diameter × ~3" (8 cm)" long, and the stepper motor with gear reduction (excluding power and control circuitry) is 2" (5 cm) × 2" (5 cm) × ~4" (10 cm) and a mass of 1.09 kg. As with the peristaltic pump, the piston pump could be fed from a flexible reservoir in a flight system.

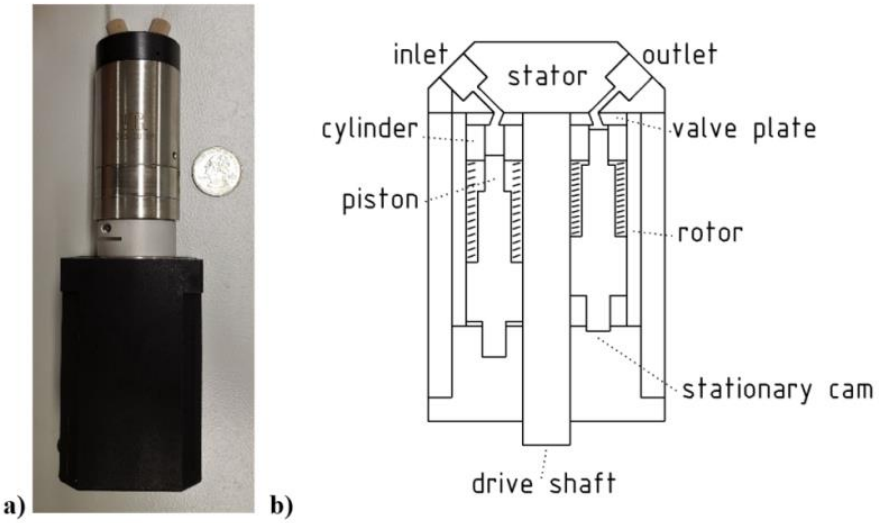

Figure 3. The multi-piston pump, a) with stepper motor and scale marker, and b) cross-sectional schematic.

III. Experimental Methods

A. Flow Rate Measurement

Two methods of flow rate measurement were identified that required minimal technical effort to implement. In the first case, an analytical microsyringe with a volume of 5 to 100 µl Hamilton, depending on the volume of the test) is connected to the outlet of the dosing system with the precision graduated barrel serving as a measuring cylinder. This allows for the measurement of average flow rate over a given time period. After connecting tubing is purged of air, the syringe is temporarily disconnected to allow removal of any liquid with its plunger. While this technique is primitive, it is more easily employed than gravimetric methods (using an analytical balance), which require complicated apparatus to minimize evaporation effects.

In the second case,, a microfluidic flow meter with flow range of +/− 8,000 nl/minute (Sensirion part # SLG-0150) is used to measure the instantaneous flow. Full resolution is available at ~10 Hz sampling rate with +/− 40

nl/minute error in the range of interest. The sensor operates by measuring thermal transport by the flowing liquid as it transits a fused silica capillary tube with integrated heating and temperature sensing elements. Both this instrument and the syringe-based technique will be used to characterize the various dosing systems under different operating conditions, and to test for performance degradation by comparison before/after long-term operation with concentrated Ag^+ solution.

B. Measurement of Dosing System Flow Profiles

The flow profiles of the three dosing systems with deionized water were characterized using the Sensirion flow meter, which was plumbed to the dosing system outlet with fluoropolymer tubing and thermoplastic fittings. $AgNO_3$ solution was not used here given the potential of plating or particulate formation, which could clog the meter's capillary. However, operation of the flow meter with $AgNO_3$ solution is of interest, as it would eliminate the need to flush the dosing systems with deionized water prior to its use.

For the capillary dosing system, the solenoid valve was energized by manually making and breaking the electrical circuit. The syringe reservoir was pressurized to 20 psi (140 kPa), and the laboratory temperature was ~26.8 °C, corresponding with a predicted flow rate of ~0.93 µl/minute.

The miniature peristaltic pump was driven by 1/8 micro-stepping at 37.5 pulses/ second (corresponding to 0.825 rotations/minute) giving a nominal 1.0 µl/minute flow rate.

The multi-piston pump was operated at ~0.010 rpm (a minor correction factor was applied, as given by the pump manufacturer) corresponding to a nominal 1.0 µl/minute average flow rate.

C. 7-Day Continuous Operation Test

A preliminary test of the dosing systems' reliability and compatibility with the concentrated $AgNO_3$ solution, as called for by the Direct*INJECT* approach. The dosing systems' inlets and outlets were plumbed to 30 ml polypropylene reservoirs using fluoropolymer tubing and thermoplastic fittings (the syringes used with the capillary dosing system, described above). The inlet reservoir for the capillary dosing system was pressurized to 20 psi (140 kPa) with a regulated high-purity N_2 supply. In the other cases, the reservoirs were capped with syringe tops, which were vented by piercing with a needle, in order to keep pressure at ambient level . A layer of Parafilm was placed under the caps to limit evaporation of water while allowing for equilibration of air pressure. Foil shield were used to minimize photo-reduction of the Ag^+, and a spray shield was used with the capillary dosing system to protect laboratory workers in the event of a leak or catastrophic failure of a pressurized component.

An $AgNO_3$ solution was made by dissolving 3.78 g of the salt (>99.99% purity, Sigma-Aldrich) in 60 ml of deionized water, resulting in a 40 g Ag^+ / liter solution. 20 ml of this solution was pipetted into the inlet reservoirs of the three dosing systems. The room temperature was not monitored. The pumps were operated as described above for 7 days, except the solenoid valve of the capillary dosing system was here controlled with a digital timer relay, with a 50% duty cycle and 20 second cycle period. Operation of the systems was confirmed regularly by visual observation of the liquid levels in the inlet and outlet reservoirs.

D. Materials Compatibility Observations

After the 7-day continuous operation, the visible components of the three dosing systems, including polypropylene inlet and outlet reservoirs, fluoropolymer flow tubing, and silicone peristaltic tubing, were visually inspected for any apparent discoloration or other degradation.

E. Ag^+ Loss During Continuous Flow-Through

After the 7-day continuous operation tests, described above, the Ag^+ concentrations of the biocide concentrate solutions in the inlet and outlet reservoirs of each of the three dosing systems were compared using a combination ion-selective electrode. A 60 µl aliquot from each reservoir was diluted in 6 ml deionized water in 12 ml polypropylene tubes (in triplicate). The samples were stirred at 200 rpm using a magnetic cross, with the combination ion-selective electrode (ThermoFisher Orion 9616BNWP with Optimum Results B filling solution) inserted into the tube.

IV. Experimental Results and Discussion

A. Ultra-Low Flow Rate Measurement

The syringe method was used successfully in preliminary experiments to check dosing systems operation and average flow rate, and to confirm the accuracy of the Sensirion flow meter using a totalizing function included in the

data acquisition software (data not shown). As shown in the following sections, the flow meter was successfully used to characterize the flow profiles of the dosing systems over their operating cycles.

In flight systems, built in flow measurement may be useful to confirm nominal system operation at the cost if additional fluidic connections. A similar flow meter to the aforementioned, with a metal-free, inert flow path is also available (Sensirion part # LG16-0150D). However, it is unclear if the apparently poorly supported fused silica capillary tube employed could survive vibrational loads during launch. A more robust in-line flow measurement may need to be developed for use in flight systems. Alternatively, nominal operation could be confirmed by in-line measurement of the biocide concentration or electrolytic conductivity.

B. Measurement of Dosing System Flow Profiles

The flow profiles at ambient pressure for the capillary dosing system, miniature peristaltic pump system, and multi-piston pump system are shown in Figures 4, 5a, and 6a, respectively. Minute differences in flow profiles were observed with the peristaltic and multi-piston pump systems between pumping into ambient and 3 psi (20 kPa) backpressure, shown in Figures 5b and 6b, but otherwise operation did not seem to be negatively affected. Future experiments will investigate the range operation of the various dosing systems at other than the nominal 1.0 µl/minute rate employed here.

The capillary system shows rapid flow initiation with solenoid valve energization, steady flow as the valve remains open, and a slight spike in flow that rapidly decays as the valve diaphragm is pushed against its seat. The starting and ending anomalies are trivial to the overall operation of the dosing.

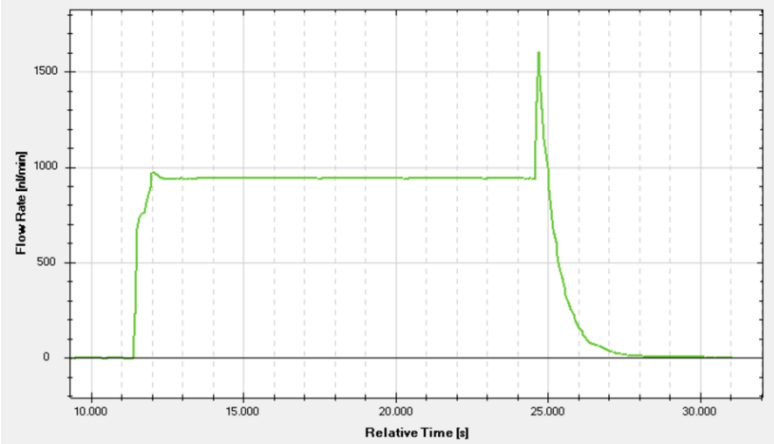

Figure 4. Flow profiles for capillary dosing system, showing valve opening, normal flow, and valve closing.

The miniature peristaltic pump shows pulsatile flow with a period of ca. 70 seconds, corresponding to the rotational period of the ring roller. The shape of the flow profile is believed to correspond to the geometry of the peristaltic tube/ring roller system. A secondary experiment showed that the transient negative flow rate observed in the peristaltic pump was not sustained when pump operation was stopped at that position when pump outlet was pressurized (data not shown), suggesting that the tube was still appropriately occluded there.

The multi-piston pump system's flow cycle period corresponded to ca. 13 seconds. Its profile may be the result of reduction gearing in the stepper motor drive system or other mechanical interface.

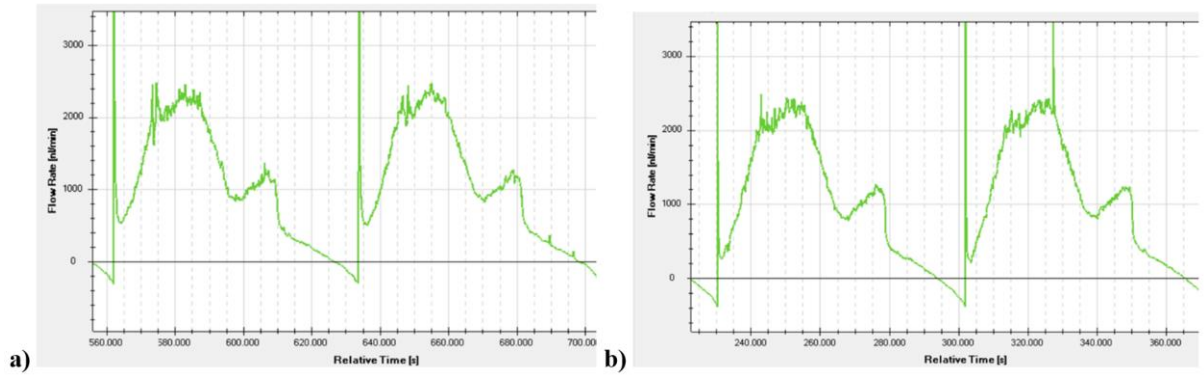

Figure 5. Flow profiles for micro-peristaltic pump, a) into ambient and b) 3 psi (20 kPa) backpressure.

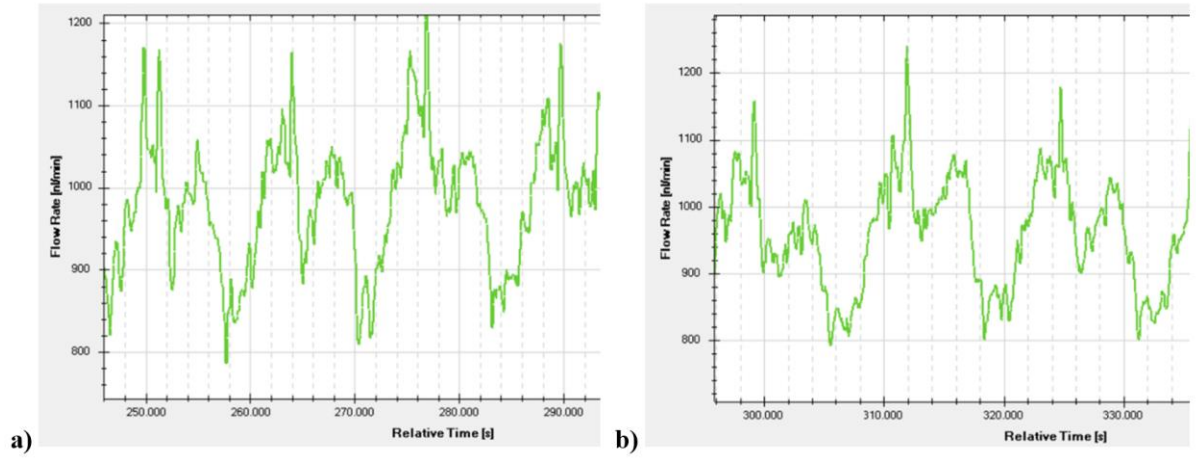

Figure 6. Flow profiles for multi-piston pump, a) into ambient and b) 3 psi (20 kPa) backpressure.

C. 7-Day Continuous Operation Test

The experimental setups for continuous operation of the dosing systems are shown in Figure 7, with the dosed volume of $AgNO_3$ solution visible in the outlet reservoirs on the right side in each case. The capillary dosing system dosed ca. 5 ml, due to its 50% duty cycle, while the pump systems both dosed ca. 10 ml, corresponding to 0.25 and 0.5 crew-year of potable water consumption, respectively. These results provide preliminary evidence of dosing system reliability, but extended duration operation and characterization with the flow meter is necessary for greater confidence and to investigate any degradation in performance. After the 7-day test, the dosing systems were restarted

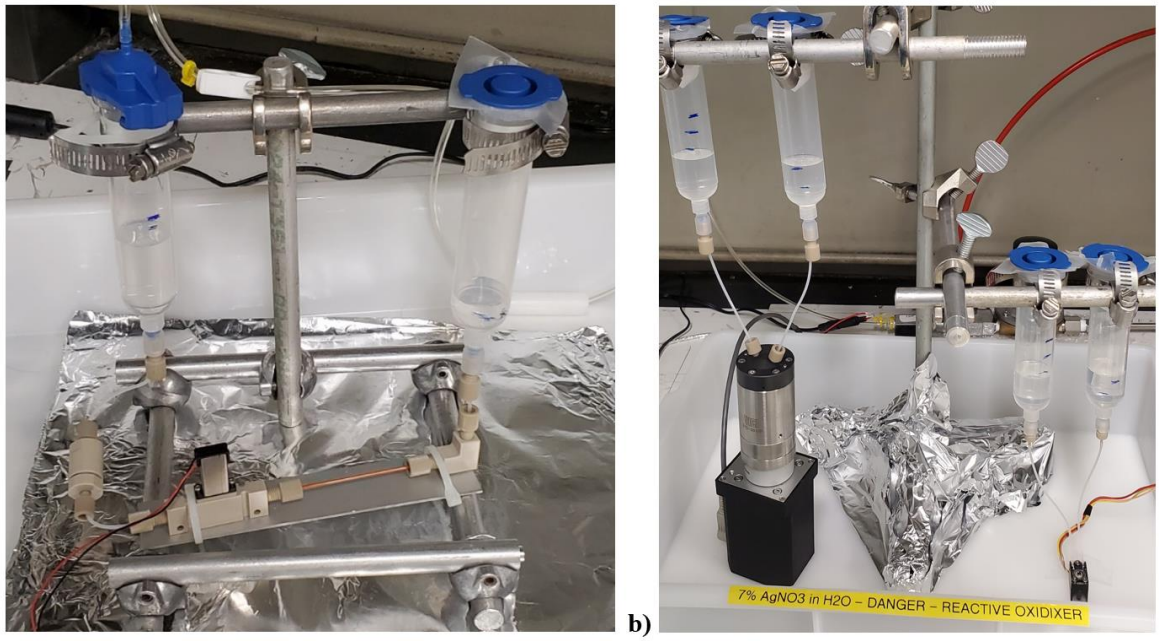

Figure 7. Experimental setups for long-duration dosing system experiments, a) the capillary dosing system and b) the multi-piston pump (left) and micro-peristaltic pump (right). Inlet and outlet reservoirs are on the left and right, respectively, in all cases. Light-shielding foil and the spray shield for the capillary dosing system are not shown.

and continued operation was confirmed in all three cases. Cursory inspection showed that the solenoid valve of the capillary dosing system still sealed when closed after 30,000 cycles with short-term exposure to the $AgNO_3$ solution. Further experiments will be necessary to confirm this after longer exposure and to determine if damage results in a significant leak rate when the valve is closed.

D. Materials Compatibility Observations

No discoloration of any visible components of the systems was observed after 7-day exposure. However, concealed surfaces were not investigated, and these may be subjects of future investigation. In addition, controlled mechanical testing to determine if the combined effects of stress/wear and chemical exposure on relevant materials properties may be useful, particularly in highly-stressed components or those subject to cyclic loading. However, the concentrated AgNO3 solution was observed to discolor a high-density polyethylene bottle after extended exposure. As such, further experiments with relevant grades of the material may be useful, particularly concerning the COTS pistons typically with the polypropylene syringes employed here.

E. Ag^+ Loss During Continuous Flow-Through

The Ag^+ losses between in the inlet and outlet $AgNO_3$ biocide concentrate solutions were found to be less than 5% during continuous operation for each of the three dosing systems. Loss levels during initial exposure to Ag^+ are expected to be somewhat larger as surface adsorption sites saturate, and these may be subjects of future experiments; similarly, losses during dormancy in the limited volume of the dosing systems (excluding reservoirs) may also be of future interest. The selection or development of suitably inert materials for storage reservoirs must be completed to enable long-term storage and operation.

V. System Design Considerations and Mitigation of Potential Failure Modes

While the Direct*INJECT* approach for biocide dosing is conceptually simple, issues such as chemical compatibility, long-term mechanical reliability, and potential gas bubble intrusion make practical system design considerably more involved than would be first expected. Additionally, dosing system compatibility with variable flow rates is also of concern. In the present work, we have completed a first look at some potential performance requirements and failure/malfunction modes as well as possible design solutions. This analysis should not be considered exhaustive or final, and more effort will be required as experimental data is gained and the system design progresses. General mechanical reliability will be investigated with extended-duration experiments, but further treatment is beyond the scope of the present work.

A. Dosing with Variable Flow Rates

While our initial experiments focused on demonstrating dosing system performance at a nominal 1.0 µl/minute injection rate, other capabilities are of interest. If WPA production rate varies significantly during wastewater processing, it would be desirable to maintain a constant Ag^+ concentration in the effluent by varying the dosing rate. In this case, a simple control system that adjusts dosing rate with production rate by measuring the potable water flow rate (open loop) or direct measurement of the silver concentration (closed loop) would be necessary. Alternatively, if the same dosing system is to be used with WPA systems of different production rates (e.g., with different crew sizes), it would be desirable to qualify said system over a range of dosing rates. The practicality of these approaches is discussed below, and will be the subject of future experimental work.

In the case of the capillary dosing system, average flow rate could be controlled by the adjustment of the effective duty cycle of the solenoid valve (by pulse-width modulation) and/or by adjusting the pressure level in the biocide reservoir. In the former case, solenoid lifetime could be reduced due to excessive cycling, and the instantaneous Ag^+ concentration of the effluent would vary (on the time scale of the pulse frequency). Varying the reservoir pressure could require a more complex pneumatic regulator and would induce cyclic stressing of the reservoir pressure vessel. If a constant dosing rate is acceptable, reservoir pressure or capillary geometry could be altered to suit a given application.

In the case of a pump-based dosing system, dosing rate can be varied by adjusting the pump speed. As dosing rate decreases, the frequency of the pump cycle decreases, and the period of the flow profile is spread out in time, resulting Ag^+ concentration of the effluent varying over a greater time period (and volume). Unless significant reverse-leakage occurs, it is expected that the total volume pumped in a cycle should vary little as pump speed is changed over the operational range, and average flow rate should vary linearly with pump speed. In the case of the miniature peristaltic pump system investigated here, minimal reverse-leakage is expected, as near-total occlusion of the pumping

tube is believed to occur. In the case of the multi-piston pump, minimal leakage should occur unless the piston seals are damaged. While average flow rate is expected to vary approximately linearly with pump speed, the relative "noisiness" of the flow profile may increase as pump speed is lowered. This is a result of volumetric "steps" corresponding to mechanical hysteresis effects and lash decreasing less significantly than the average flow rate does. However, these predictions regarding reverse-leakage and flow profile "noisiness" must be verified and quantified experimentally.

B. Introduction and Mitigation of Gas Bubbles

One area of potential concern for dosing systems based on volumetric control of liquid flow is the formation of gas bubbles in the biocide solution reservoir or further along in the flow path. In the case of the pressure driven capillary dosing system, the primary gas entry point would be at the syringe piston/barrel interface, which may be subject to blow-by, particularly under vibrational conditions, or due to slow cross diffusion of pressurant gas and water vapor over long periods caused by differentials in partial pressures. This issue could potentially be mitigated by improved piston seals or replacement with a hermetically sealed internal reservoir inside the pressure vessel, such as a non-metallic (PTFE, etc.) bellows, flexible bladder, or diaphragm constructed with a very-low permeability material. In the case of pump-driven dosing systems, air diffusion from the spacecraft cabin through the flexible reservoir walls could result in bubble formation, as has been observed with Contingency Water Containers, which employed thin FEP film for their bladders.[18] Similarly, loss of water by diffusion should be minimized to prevent dosing concentration errors and reduction in endurance. Such diffusion could potentially be minimized by selection of very-low permeability materials, increasing wall thickness, and/or by use of laminates with impermeable diffusion barriers.

If bubble formation in reservoirs cannot be prevented, various separation and trapping techniques are available. These can include geometric designs and hydrophobic porous membranes to separate bubbles using capillary forces. However, these introduce additional complexity and in some cases may result in significant evaporative loss of water; further research effort is necessary in this area. As such, prevention of gas intrusion is strongly preferred to bubble mitigation techniques, particularly in microgravity. In contrast, in systems for use on Mars or Moon surface habitats, separation of bubbles using buoyancy would be relatively straightforward.

If bubble formation cannot be prevented, or if bubble segregation is not practical, the consequences for dosing system performance depend on the mode of operation. In the case of the capillary dosing system, relatively small bubbles will pass rapidly through the system due to the viscosity of air being approximately $1/50^{th}$ that of water (this was confirmed in preliminary experiments). In the case of pump based systems, this is not so, and Ag^+ dosing will be temporarily disabled as the air bubble passes through the flow path at the typical liquid volumetric flow rate. In certain pump designs, trapped bubbles may block liquid flow, particularly in the absence of buoyant forces. For pump-based dosing systems, a sensor could be used to detect air in the supply tubing, and pump speed increased until the bubble has been passed. Such sensors can operate by optical or ultrasonic methods, and we have already confirmed detection with one COTS optical sensor (TT Electronics, part # OCB350L062) in preliminary experiments. However, this approach would increase component count and pump control system complexity.

In the case of the capillary dosing system, super-saturation of dissolved pressurant gas may occur as pressure decreases across with capillary tube, but this should be minimal and not result in appreciable bubble nucleation. In any case, the fraction of dissolved gas is so small that potential volumetric error is insignificant. For example, N_2 pressurant at 20 psig (140 kPa) and room temperature, as employed in this work, could theoretically produce at most ~2% by volume free gas. However, if a bubble train is introduced into the very narrow capillary tube, the "Jamin Effect" could potentially stop flow.[19] This occurs when a series of bubbles, each supporting a finite pressure difference due to capillary forces, sum to a very large total static pressure. It is unclear if this phenomenon is significant at relevant conditions, or what mechanism could produce such a bubble train in the capillary tube. Further analysis may be necessary regarding this topic, but in our early experiments, no such effect has been observed. Finally, a shaft in a vented chamber could be used to transfer pneumatic force from a seperate pressurant piston to the reservoir piston, preventing gas super-saturation and slowing bubble introduction across the piston seal.

C. Damage or Blockage due to Particulate

In order to minimize the potential of particulates (possibly due to impurities, material degradation, or chemical precipitation) formed in the reservoir from damaging or clogging dosing system components (peristaltic tubing, pump piston seals or valving, or capillary tubing), the use of inert filter frits is of potential interest. The risk of such particulate being present is currently unknown, so we chose to investigate if filter-based protection was practical at an early stage of development; elimination in the future may be desirable to reduce system complexity and leak risks. A PEEK frit filter with 10 μm pore size (described above) was selected for experimental investigation and inclusion in the present

capillary dosing system design. The filter is located before the solenoid shut-off valve, but it may be desirable to also place such a filter directly before the capillary tubing to protect it against particle intrusions and blockage. Because capillary forces in filter pores can resist wetting and de-wetting, pore size and material surface chemistry (with resulting surface tension) must be properly selected, particularly when bubbles are present. It was observed that water penetration through the dry PEEK (slightly hydrophilic) filter and bubble passage through the wetted filter both required only 1-2 psid (7-15 kPa), as predicted by theoretical calculations. Smaller pore size or greater material hydrophobicity would require greater pressure to re-wet the frit. The miniature peristaltic pump and multi-piston pump are self-priming, and both were able to wet and de-wet the filter by pulling a slight vacuum.

D. Pumping into pressurized systems

It is expected that the dosing point will be at slightly elevated pressure vs. ambient (~3 psi (20 kPa)) for the PWB inlet. In the case of the ISS PWB, this allows for the filling of a large bellows tank for storage of processed potable water that has been dosed with biocide. It is thus important that any dosing system employed should be able to supply biocide concentrate against the backpressure and seal against appreciable backflow from the PWB when not in use. In the case of the capillary dosing system, components have been selected to allow for large margins in pressure ratings, and the flow resistance presented by the closed solenoid valve and the capillary tube should prevent any appreciable backflow. In the case of the peristaltic pump, proper tuning of the tube occlusion should minimize any potential backflow; however, experiments are necessary to determine if the COTS pump examined here satisfies this condition through the full pump cycle. In the case of the piston pump, the PTFE piston has a compliant seal, minimizing the potential for liquid flow-by (rated service pressure up to 100 psi (700 kPa)). However, damage to the sealing surface by extended operation or by solution that has leaked past the seal and precipitated could potentially result in appreciable leakage due to backpressure at the pump outlet. Some alternative dosing pumps identified rely on very tight, but still positive tolerance between the ceramic piston and cylinder employed, and with these, leakage at even small backpressures can be of significant concern. It may be desirable to include a shut-off valve between the dosing system and the potable water bus to prevent leakage in the event of dosing system malfunction, at the cost of additional complexity.

E. Materials Compatibility in the Dosing System

As dosing system performance must be maintained for extended periods (potentially several years or decades), materials compatibility with the biocide solution is a key requirement. The concentrated biocide solution must not cause significant degradation of system components, including potentially sensitive elastomers such as in reservoir bladders, seals, valve diaphragms/seats, or peristaltic tubing. Other components should be constructed of highly inert thermoplastics, such as PEEK, polypropylene, polyethylene, or fluoropolymers, with known resistance to chemical attack. During selection of the three dosing systems described above, commercial material rating compatibility guides were taken into account, but such compatibility must be verified experimentally. At seals and elsewhere, evaporation could increase biocide concentration, and even result in solid precipitation, and consequent deleterious effects such as more rapid materials degradation must be considered.

In addition, exposure to reservoir walls and other dosing system components must not result in significant loss of biocide concentration. Such loss could result in reduced microbial control in the Potable Water Bus and potentially cause fouling of system components. In a previous report, concentration loss in plastic syringes with ~1.0 g/l Ag^+ (from AgF) solution was found to be minimal after 1-2 years.[6] From the standpoint of Ag^+ loss, it is likely that suitably inert materials can be found for long-term storage of our higher concentration solutions of AgF or $AgNO_3$ (~40 g/l Ag+). As the biocide solution is pumped from the reservoir into the Potable Water Bus, it flows through high surface area/volume ratio components such as valving, capillary tubing, peristaltic tubing, or connecting tubing that are potential adsorption sites. As average exposure time is short, such effects may be limited, particularly as adsorption might be rapidly saturated. For any dosing system of interest, minimal Ag^+ loss must be confirmed with experiments.

F. Biocide Compatibility in the Potable Water Bus

We must also consider materials compatibility and potential for increased microbial growth with the Potable Water Bus. The poor compatibility of Ag^+ with metals (due to auto-galvanic loss, rather than corrosion risks) has been addressed elsewhere. However, potential risks due to the counter-ion of the employed Ag salt (i.e. F^-, NO_3^-) must be investigated. A preliminary review of the corrosion literature suggests that sub-ppm concentrations of either species are not associated with significant corrosion risks in metal alloys typically used with spacecraft potable water systems or with degradation of chemically resistant thermoplastics. At much higher levels (>100 ppm), depending on pH and dissolved oxygen concentration, F^- has been found to damage the passive oxide formed on titanium, allowing for

significant corrosion.[20] In the future, a more exhaustive review could improve confidence that corrosion risks are insignificant. If inert barrier coatings or non-metallic materials are employed, counter-ion compatibility must be confirmed, but this is not expected to be of issue. Given that maximum local concentrations in the PWB will occur at the injection point (dosing system outlet), the "mixing zone" should be constructed out of highly compatible materials. Biocide compatibility at potable concentrations has been addressed in two previous NASA trade studies,[14,15] but further work may be necessary.

G. Biocide Compatibility with Crew Health and the Spacecraft Cabin

In the case of the Ag^+ biocides investigated here, health risks due to consumption of treated water should be insignificant. Counter-ion (F^- or NO_3^-) concentration would be much lower than the EPA limits for drinking water, or indeed the concentration employed in fluoridated municipal water. However, off-nominal release of concentrated biocide solutions stored in the dosing system reservoir may pose significant hazard to human health or equipment in the spacecraft cabin. At 40 g/l (Ag^+), AgF and $AgNO_3$ solutions are considered dangerous in cases of skin or eye exposure, ingestion, or inhalation, as they are corrosive, oxidizing, and potentially toxic. For both chemicals, negative effects depends strongly on dose and duration of exposure. In contextualizing these risks, it should be kept in mind that small amounts of AgF and $AgNO_3$ solutions at similar concentration are routinely used in dental, ophthalmological, and dermal procedures. Similarly, release poses risk of chemical attack of spacecraft equipment, including reaction with many organic materials. Mixing of concentrated AgF solution with any source of concentrated acid must be prevented, as this may potentially produce hydrofluoric acid (HF); however, limiting this risk should require only minor effort. It is expected that some degree of secondary containment will be necessary, particularly when pressurized reservoirs are used. This should not pose an excessive engineering challenge, and hazardous liquids are routinely used in spacecraft life support systems, e.g. the mixed-acid pretreatment solution employed in urine collection and storage.[21] The trade studies previously mentioned considered biocide compatibility with human health at highly-concentrated[15] and potable concentrations,[14,15] but again further work here would be helpful.

VI. Future Work

We plan on continuing long-term reliability and materials compatibility testing with concentrated $AgNO_3$ (and potentially AgF) solution. Periodically, dosing system flow characteristics will be measured to see if performance has degraded over time. We will also investigate the practicality of variable rate dosing and the flow rate ranges of the systems discussed in this work. In parallel, we will work on the design of reservoirs and other hardware to limit the possibility of gas infiltration and bubble formation, which may temporarily disable dosing as they pass through the non-reservoir components of the dosing systems.. We will continue to investigate and address other potential failure or malfunction modes, and mechanical reliability more generally. As we gain experience with dosing system operation and designs and requirements analyses mature, we will compare the relative merits of the various systems and select one to bring forward for continued development. Finally, we will continue to monitor the commercial market and literature for alternative dosing concepts.

VII. Conclusions

In this work, we have demonstrated the basic practicality of the Direct*INJECT* approach: dosing potable water with Ag^+ biocide by well-controlled injection of concentrated silver salt solution at very low (1 µl/minute) flow rates. We constructed or purchased three dosing systems based on pressure-driven flow through a robust micro-capillary tube with shut-off valve, a miniature peristaltic pump, and a multi-piston pump with integrated valving. We performed preliminary performance characterization of these systems and begun extended duration testing, starting with a successful continuous 7-day operation. We find that this approach has attractive attributes including minimal hardware and consumables mass, insensitivity to potable water chemistry, and potential for full control of dosing, making it suitable for in-line dosing and dosing directly into storage vessels.

Acknowledgments

We acknowledge the Advanced Exploration Systems – Habitation Systems Project for financial support.

References

[1]Peterson, L. J. and Callahan, M. R., "Overview of Potable Water Systems on Spacecraft Vehicles and Applications for the Crew Exploration Vehicle (CEV)," *37th International Conference on Environmental Systems*, SAE Technical Paper #2007-01-3259, 9-12 July 2007, Chicago, Illinois.

[2]"MFSC Skylab Crew Systems Mission Evaluation," NASA Technical Memorandum X-64824, 1974, pp. 275-276.

[3]"Automated Iodine Monitoring System Development (AIMS)," NASA Contractor Report #144433, 1975.

[4]Shaw, L. A. and Barreda, J., "M. R., "International Space Station USOS Potable Water Dispenser Development," *38th International Conference on Environmental Systems*, SAE Technical Paper #2008-01-3259, 29 June - 2 July 2008, San Franscisco, California.

[5]Li, W., Calle, L., Handford, A., Stambaugh, I., and Callahan, M., "Investigation of Silver Biocide as a Disinfection Technology for Spacecraft – An Early Literature Review," 48th International Conference on Environmental Systems, ICES-2018-82, 8-12 July 2018, Albuquerque, New Mexico.

[6]Mudgett, P. D., Schultz, J. R., Packham, N. J., Veselka, D. J., Brasseaux, H. J., Jr., Rotter, H. A., and Sauer, R. L., "Potable Water Treatment and Transfer from Shuttle to *Mir*," *27th International Conference on Environmental Systems*, SAE Technical Paper #972461, 14-17 July 1997, Lake Tahoe, Nevada.

[7]Bobe, L. et al. "THE PERFORMANCE OF THE SYSTEM FOR WATER RECOVERY FROM HUMIDITY CONDENSATE (SRV-K) AND THE SYSTEM FOR URINE FEED AND PRETREATMENT (SPK-U) ON RUSSIAN SEGMENT OF THE ISS (MISSIONS 1 THROUGH 37)," *44th International Conference on Environmental Systems*, ICES-2014-307, 13-17 July 2014, Tucson, Arizona.

[8]Albright, C. F., Nachum, R., and Lechtman, M. D., "Development of an Electrolytic Silver-Ion Generator for Water Sterilization in Apollo Spacecraft Water Systems," NASA Contractor Report #67-2158, 1967.

[9]Slote, B. M., Salley, E., Carr, D., and Kimble, M. C., "Silver Ion Biocide Delivery System for Water Disinfection," *46th International Conference on Environmental Systems*, ICES-2016-136, 10-14 July 2016, Vienna, Austria.

[10]Hicks, P. M. and Nelson, J., "Preliminary Testing of Electrolytic Silver Ion Generation for Spacecraft Potable Water Systems," *2020 International Conference on Environmental Systems*, ICES-2020-371, 2020, Conference canceled).

[11]Beitle, E., "Task 1: Silver-based Microbial Check Valve for Spacecraft Potable Water Systems," Undergraduate Thesis, University of Arkansas, 2019. Available online at https://scholarworks.uark.edu/cheguht/148/.

[12]Irwin, T., Li, W., Diaz, A., Calle, L., and Callahan, M., "Silver Foam: A Novel Approach for Long-Term Passive Dosing of Biocide in Spacecraft Potable Water Systems – Update 2021," *International Conference on Environmental Systems*, ICES-2021-116, 12-15 July 2021 (virtual).

[13]Garcia Fernandez, R. E. and Beitle, R. R., Jr., "Dialysis-based Passive Biocide Delivery System: An Exploratory Analysis on the Development of a Silver Dosing Alternative for Spacecraft Potable Water Systems," *International Conference on Environmental Systems*, ICES-2021-383, 12-15 July 2021 (virtual).

[14]Steele, J., "Silver Biocide Chemical Dosing Trade Study," NASA Johnson Space Center Crew and Thermals Systems Division, Report #CTSD-ADV-1786, 2020.

[15]Abney, M. B. et al., "Assessment of Biocide Impacts on Life Support and Extravehicular Activity Architectures," *International Conference on Environmental Systems*, ICES-2021-116, 12-15 July 2021 (virtual).

[14]Anderson, M. S., Ewert, M. K., and Keener, J. F., "Life Support Baseline Values and Assumptions Document," NASA Technical Publication #2015–218570, Rev. 1, 2018.

[15]"About Ring Pump," Aquatech Co., Ltd., https://ringpump-aquatech.co.jp/english/ring_pump/about.html.

[16]Noma, H. (Takasago Fluidic Systems), Private Communication, 18 March 2021.

[17]Wolcott, D. K., and Marshall, G. D., "Pulseless, reversible precision piston-array pump," US Patent 6,079,313, 2000.

[18]Ungar, E. K., Pettit, D. R., and Lin, C. H., "Bubble Growth from Permeation of Cabin Air into FEP Water Bladders Stowed on the International Space Station," *47th International Conference on Environmental Systems*, ICES-2017-208, 16-20 July 2017, Charleston, South Carolina.

[19]Crane, M. D. and Smith, W. O., "The Jamin Effect in Cylindrical Tubes," *Journal of the American Chemical Society*, vol. 52, no. 4, pp. 1345-1349, 1930.

[20]Nakagawa, M., Matsuya, S., and Udoh, K., "Effects of fluoride and dissolved oxygen concentrations on the corrosion behavior of pure titanium and titanium alloys," *Dental Materials Journal*, vol. 21, no. 2, pp. 83-92, 2002.

[21]Carter, D. L. et al., "Operation of the Urine Collection and Pretreatment System in the ISS US Segment Waste & Hygiene Compartment (WHC)," *International Conference on Environmental Systems*, ICES-2021-35, 12-15 July 2021 (virtual).