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Effects of materials surface preparation for use in spacecraft potable water storage tanks

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ABSTRACT

Maintaining a safe supply of potable water is of utmost importance when preparing for long-duration spaceflight missions, with the minimization of microbial growth being one major aspect. While biocides, such as ionic silver, historically have been used for microbial control in spaceflight, their effectiveness is sometimes limited due to surface reactions with the materials of the storage containers that reduce their concentrations below the effective range. For the Multi-Purpose Crew Vehicle, the primary wetted materials of the water storage system are stainless steel and a titanium alloy, and ionic silver has been chosen to serve as the biocide. As an attempt to understand what processes might reduce the known losses of silver, different treatment processes were attempted and samples of the wetted materials were tested, individually and together, to determine the relative loss of biocide under representative surface area-to-volume ratios. The results of testing presented here showed that the materials could be treated by a nitric acid rinse or a high-concentration silver spike to reduce the loss of silver and bacterial growth. It was also found that the minimum biocidal concentration could be maintained for over 28 days. These results have pointed to approaches that could be used to successfully maintain silver in spacecraft water systems for long-duration missions.

1. Introduction

As human spaceflight progresses beyond low-Earth orbit to long-term exploration missions, the need to maintain an adequate supply of high quality potable water becomes imperative. During spaceflight, water accounts for a significant portion of the daily mass intake of crewmembers; this critical life support element is used for food preparation, drinking, and oxygen generation [1–4]. Controlling microbial growth is an essential aspect of maintaining water quality and mitigating crew health risks. In addition to negatively affecting crew health, microbial growth in a potable water system can lead to corrosion and other issues with material compatibility [1,5]. The current bacterial acceptability limit for potable water on the United States Operating Segment (USOS) of the International Space Station (ISS) is 50 colony-forming-units per mL (CFU/mL) [6]. If this limit is exceeded, then consumption of the water is halted until remediation has been successfully completed.

While numerous means of control can be implemented to ensure low microbial levels, maintaining residual biocide in the water storage system is one of the simplest and most effective; maintaining this biocide is important as complete sterilization of the water storage system prior to loading is often not attainable. The USOS currently uses molecular iodine for microbial control in potable water. This biocide selection was based largely on the successful use of molecular iodine in the potable water system of the Space Shuttle. While effective at controlling microbial growth, iodine must be removed from the water prior to consumption due to potential side effects. These side effects include accumulation in the thyroid as well as taste and odor issues that could lead to diminished water consumption [7,8]. For these reasons, molecular iodine is not an ideal biocide for long-term exploration missions.

Metals have long been known to possess antimicrobial properties, with the biocidal mechanism being related to oxidative stress, protein dysfunction, or membrane damage [9]. Ionic silver (Ag^+) is one of these species that possesses bacteriostatic and bactericidal properties [10,11]. Suggested mechanisms of action on microbial cells include inhibition of cell wall and protein biosynthesis [12–14], DNA replication [15], and interference with transport channels [16]. More specifically, Ag^+ has been shown to deplete total cellular thiols in *Escherichia coli*, including glutathione, which is used in oxidant defense [17]. Ionic silver is also

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known to attack iron-sulfur clusters of dehydratases, thereby inactivating them for further reactions until the clusters are rebuilt [18].

Currently, Ag^+ is used in the water systems in the Russian Segment (RS) of the ISS [7,8,10,19]. Silver provides effective microbial control at low levels and does not pose a significant health risks unless it is routinely consumed at high concentrations. Therefore, the need for biocide removal prior to consumption is eliminated if the concentration is maintained within the potable range [20]. The maximum allowable silver concentration at the point of consumption has been defined as 0.4 mg/L [5,20]. This level of silver has been shown to effectively inhibit microbial activity in water systems. As such, Ag^+ was selected as the biocide for the U.S. water storage system on future long-term exploration missions [21].

When stored in metallic tanks, silver biocide solutions can lose their efficacy over time due to interactions between the silver ions and the storage container walls [1,5,19,21,22]. This effect was observed during Automated Transfer Vehicle (ATV) launch campaigns, in which the European Space Agency (ESA) was tasked with providing potable water containing silver biocide to the ISS [22,23]. Petala and coworkers found that exposure of metallic surfaces to potable water containing silver led to almost total depletion of the silver after 7 days [22]. Atomic Force Microscopy (AFM) analysis of 316L stainless steel coupons before and after the exposure indicated that silver was being deposited as a thin film or islands rather than as large particles. More importantly, X-ray Photoelectron Spectroscopy (XPS) analysis of the 316L stainless steel and Ti6Al4V titanium alloys after exposure to the silver showed that the bound silver was in the form of silver oxide. In this composition, the silver no longer functions as an effective biocide. More extensive testing of silver deposition on different grades of stainless steel coupons confirmed that, regardless of passivation or pretreatment processes, potable levels of silver were not stable in contact with the surfaces. These results reinforce the fact that the materials used in the design of the water storage systems in new exploration vehicles using silver as a biocide must be given careful consideration.

For long-term exploration missions beyond low-Earth orbit, NASA has developed the Multi-Purpose Crew Vehicle, MPCV (previously known as the Crew Exploration Vehicle, CEV, or Orion). The MPCV crew module (CM) will be mated to a service module (SM) that will be built by ESA. The SM will house the majority of the consumables for the life support system, including water, nitrogen, and oxygen [24]. The water tanks in the service module of MPCV will be of a bellows configuration [24] and will consist of a Ti6Al4V titanium alloy for the outer shell and 316L stainless steel for the internal bellows. Based on the known adsorption of silver on these materials [22,23], it is important to understand how the wetted materials in the MPCV water storage system will affect the stability of the residual biocide and what processes potentially reduce biocide loss. A possible option for reducing losses is to spike the tanks with a high concentration ionic silver solution to eliminate any microbial growth and also to passivate the surfaces towards further silver adsorption. In preliminary studies, we attempted to shock 316L stainless steel and Ti6Al4V with ~500 mg/L Ag^+ solution in the presence of high bacterial concentrations [25]. These tests produced some puzzling results but seemed to indicate that pretreatment of the materials could help to reduce biocide losses in subsequent exposures, suggesting the need for more comprehensive testing, particularly for the Ti6Al4V surfaces. Here, we will describe more recent testing conducted in our laboratory that has provided insight into approaches that may reduce the adsorption of silver biocide on the MPCV tank materials.

2. Materials and methods

2.1. Biocide preparation

Ag^+ solutions were prepared gravimetrically in 1-L brown Teflon bottles. Stock solutions were prepared by dissolving the appropriate mass of silver (I) fluoride (>99.9% purity, Aldrich) in Milli-Q water (Millipore) and diluting to 1 L. This water contains less than 10 μg/L total organic carbon and has a resistivity of 18.2 MΩ-cm at 25 °C. The solutions were stored in a refrigerator at 4 °C until use.

2.2. Test vessels

In order to minimize the possibility of contamination during bacterial testing, sterile polypropylene urine cups were used as test vessels for all testing, even if they did not include bacteria. Prior to the start of testing, a high concentration Ag^+ solution was added to the cups for 24 h in order to determine what, if any, losses to the walls of the containers would occur. The loss of silver was less than 5%, but this result dictated the use of control cups during all further testing.

2.3. Materials used

Two materials were used for the testing described here: 316L stainless steel washers and Ti6Al4V coupons. The 316L washers were obtained from Alabama Specialty Products, Inc. (Munford, AL, USA). The dimensions of the washers were 1.25 inch diameter × 0.125 inch thick with the inner hole possessing a diameter of 0.375 inch. These washers were passivated in the clean room at Johnson Space Center using the standard Type VI process as described in AMS 2700E. The Ti6Al4V stock (per AMS 4928) was obtained from California Metal and Supply (Santa Fe Springs, CA, USA) and cut into coupons with dimensions of 0.7 inch × 0.5 inch × 0.12 inch. All washers and coupons were cleaned and degreased by 3 cycles of sonication in methanol for 1 h and then water for 1 h followed by drying in an oven at 50 °C.

2.4. Exposure of materials to silver solutions

To accurately mimic the conditions in the SM water tanks, specific surface area-to-volume (S/V) ratios were targeted during testing. For the 316L stainless steel, this ratio was 0.61 cm^2/mL, while an S/V ratio of 0.15 cm^2/mL was targeted for the Ti6Al4V alloy. One of the testing conditions required both materials to be exposed in the same test vessel. For these tests, a small Teflon spacer was used to position the 316L washer material to maintain representative S/V ratios. To achieve the appropriate S/V ratios, 30 mL of solution was used for all tests unless otherwise indicated. All test points were sampled from individual test vessels, i.e. aliquots were not continually removed from the same test vessel.

After positioning the coupons in the test vessels and adding biocide solution, the vessels were loosely capped and placed on the laboratory bench for the duration of testing. The temperature in the laboratory during this testing was consistently 20 °C ± 1 °C. Initial testing did not show significant effects from the presence of light, so no further effort was made to cover the urine cups during testing.

In order to account for biocide losses to the container as opposed to the materials being tested, a cup containing an equal volume of biocide as that being used for the materials testing was prepared and treated the same as the sample cups during all further testing.

2.5. Bacterial testing

Bacterial testing used a consortium of water organisms commonly found in archive water samples from the potable water systems on the ISS [6,26]. To prepare cultures, ~70–80 mL of water obtained from a Milli-Q water purification system was autoclaved and then inoculated with 1 colony of each of the bacteria. The cultures were allowed to grow statically for 24 h at room temperature. Earlier growth experiments had provided insight into the concentration of each of the organisms after 24 h of growth, and final bacterial concentrations were determined through standard dilution and plating methods.

For testing with 316L or Ti6Al4V, the test materials were placed in the sterile urine cups and appropriate volumes of the bacterial consortium