

Chemistry of Ionic Silver and Implications for Design of Potable Water Systems

Dean L. Muirhead¹

Barrios Technology, Houston, Texas 77058

Amy Button-Denby²

Jacobs Technology, Houston, Texas 77058

Christopher M. Smyth³

Oceaneering Space Systems, Houston, Texas 77058

and

Jason Nelson⁴ and Michael R. Callahan⁵

NASA, Lyndon B. Johnson Space Center, Houston, Texas 77058

Ionic silver (Ag^+) at approximately 400 $\mu\text{g/L}$ is proposed as an ingestible biocide for potable water systems in future human spacecraft. This paper investigates the underlying chemistry of the silver ion at potable concentrations and its interactions with other solutes and surfaces. This chemistry evaluation will elucidate ionic silver behavior in potable water systems and enable design optimization to minimize ionic silver depletion during long duration crewed and uncrewed segments of missions. Ionic silver can be lost from the water phase to the water-solid interface via adsorption as the cation and oxidation-reduction reactions with passivation defects. The adsorption and oxidation-reduction reactions of heritage piping materials used on spacecraft – stainless steel 316L, titanium, Inconel 718, and Teflon flex hoses – are considered. Conceptual models of adsorption isotherms and pH adsorption edges are applied to understand the role of pH and the surface-to-volume ratio of pipes and tanks on the partitioning of ionic silver between the aqueous and the solid phase during aging. The effect of repeated exposure-aging to an Ag^+ -containing solution of two passivated alloys (316L and Inconel 718) is evaluated to determine if an equilibrium concentration of ionic silver in the potable range is attainable for a given alloy and surface-to-volume ratio. Aging unpassivated and passivated 316L reduced the ionic silver depletion rate relative to first time exposures, but the same beneficial effect was not observed for Inconel 718.

Nomenclature

$\text{Ag}^+(aq)$	= silver ion in aqueous phase	K	= equilibrium constant
$\text{Ag}^+(ads)$	= silver ion in adsorbed phase	K_{sp}	= solubility product
$\text{Ag}(s)$	= elemental silver	pH	= negative logarithm of hydrogen ion activity
AgNP	= silver nanoparticle	PP	= polypropylene
aq	= aqueous phase	$PTFE$	= polytetrafluoroethylene
D	= diameter	PZC	= point of zero charge
DI	= deionized (water)	s	= solid phase
ISS	= International Space Station	S/V	= solid surface area to liquid volume ratio
JSC	= Johnson Space Center		

¹ Principal Engineer, JETS Contract, 16441 Space Center Blvd.

² Project Manager, JETS Contract, 2224 Bay Area Blvd.

³ Project Engineer, JETS Contract, 16665 Space Center Blvd.

⁴ Water Technology Engineer, Crew and Thermal Systems Branch, Mail Stop EC3, 2101 NASA Pkwy.

⁵ Water Technology Lead, Crew and Thermal Systems Branch, Mail Stop EC3, 2101 NASA Pkwy.

I. Introduction

IONIC silver (Ag^+) is currently being investigated as an alternative to iodine for potable water disinfection in spacecraft water transport and distribution systems. Employing ionic silver is advantageous over iodine because it would provide antimicrobial biocide throughout the pipe system; currently the iodine biocide must be removed upstream of the potable water discharge, which leaves a downstream segment of the potable water dispenser without biocide.

The history and future of biocides for spacecraft applications has previously been summarized at this conference.¹ An electrolytic silver generation system was designed and tested for the Apollo missions,² but sodium hypochlorite was ultimately employed as the biocide. Silver biocide has heritage in the Russian segment of the International Space Station (ISS), in combination with pasteurization, and was used for microbial control in the Mir Space Station in the 1980s. Iodine is the principal biocide on the US Segment of ISS.

Despite the advantages of ionic silver as a low-mass and low-consumable disinfectant, a number of challenges must be overcome before ionic silver can supplant iodine. Reliable methods to inject, monitor, and control ionic silver concentrations within a biocidal range must be refined. Both passive and electrolytic dosing methods, along with in-line monitoring requirements for ionic silver concentrations are under development.³

One challenge of using ionic silver as a biocide is understanding and controlling the reactions between ionic silver and wetted surfaces. The silver deposition rate on some nonmetallic surfaces such as polytetrafluoroethylene (PTFE) and polypropylene (PP) is minimal, but ionic silver readily reacts with metallic surfaces.^{4,5} The deposition rates of silver ions on passivated alloys commonly employed in space applications have been summarized and modelled,^{5,6} and another paper summarized nine published investigations of silver interactions with alloys, and the important role of the surface to liquid volume ratio (S/V) on silver depletion was noted.⁷ The transformations between silver ions and silver deposited on metal alloys is complex, and depends on many physical, chemical, electrical, and geometric conditions of the heterogeneous, multiphase (gas-liquid-solid) system.

The objective of this paper is to define the important physical and chemical parameters and processes that dictate the stability of aqueous silver ions ($\text{Ag}^+(\text{aq})$) in contact with wetted surfaces of metals. The effects of critical system variables, including S/V, wetted surface material and roughness, and water quality are considered. Understanding the behavior of ionic silver in future potable water systems will enable design optimization to eliminate loss of ionic silver during storage and transport of potable water. This paper also reviews relevant literature on the adsorption of silver in the natural water cycle, and the relationship between water quality and ionic silver stability. Finally, this paper examines whether aging of surfaces by constant exposure to potable ionic silver concentrations can enable a steady state concentration of potable silver to be maintained with a given S/V ratio. If aging alone is unsuccessful at reaching a steady state biocidal concentration of ionic silver, manipulations of water quality parameters such as pH and additional cations are proposed to minimize the depletion rate of ionic silver to metal surfaces. The effectiveness of the aging surface preparation concept based on adsorption isotherms has been tested on unpassivated 316L coupons, and in passivated stainless steel 316L and Inconel 718 pipes, and the results are included here. Finally, alternative materials with higher silver compatibility, e.g., non-metallics, are being considered in parallel studies to help minimize and/or eliminate the issue of silver loss.

II. Primary Water System Operational Modes

Upcoming human missions beyond low Earth orbit will require the ability to satisfy water system requirements under two distinct operational scenarios, as outlined in Figure 1. The requirements for daily, occupied operations ("Day to Day") and long-term unoccupied durations ("Year to Year") pose different challenges that must be solved in a single system, and the system must also enable smooth, reliable transitions between the scenarios. A framework for the major aspects of silver chemistry in a potable water purification system is shown in Figure 2. Elements of this framework are discussed in the following sections of this paper.

III. Primary Atmospheric Boundary Conditions: Open or Closed System

A critical condition affecting the chemistry of ionic silver in solution is whether or not the potable water will be open or closed to the habitat's atmosphere. Upstream treatment processes and the gas permeability of pipe materials determine the water's concentrations and composition of dissolved gases. The pH of water decreases with increased atmospheric carbon dioxide (CO_2) partial pressure. Similarly, dissolved oxygen concentration, $\text{O}_2(\text{aq})$, in water increases with atmospheric oxygen partial pressure in accordance with Henry's Law. Both CO_2 and O_2 can react with deposited silver in complicated pathways discussed below. Unless specifically noted, the water systems discussed in this work are assumed to be open to the atmosphere of ground conditions, but it is critical to note that spacecraft CO_2 concentrations are typically an order of magnitude higher. The working assumption is that the upstream spacecraft

water source is essentially deionized (DI) water. This could have implications in the success of an integrated silver biocide system because DI water is poorly buffered, and variable water quality could affect ionic silver stability. Open

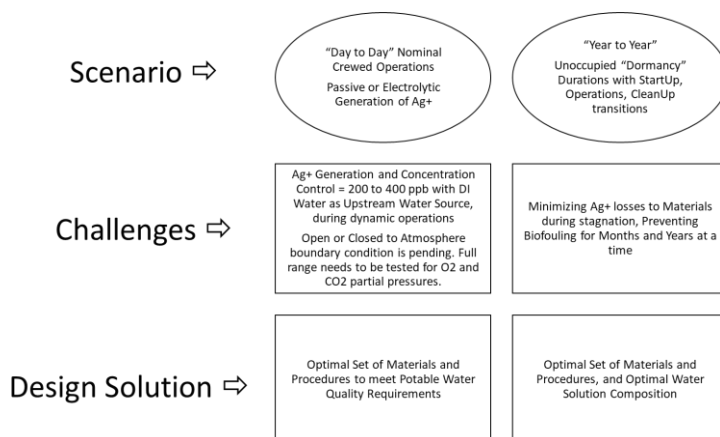


Figure 1. "Day-to-Day" and "Year-to-Year" Operations of Potable Water Systems beyond Low Earth Orbit.

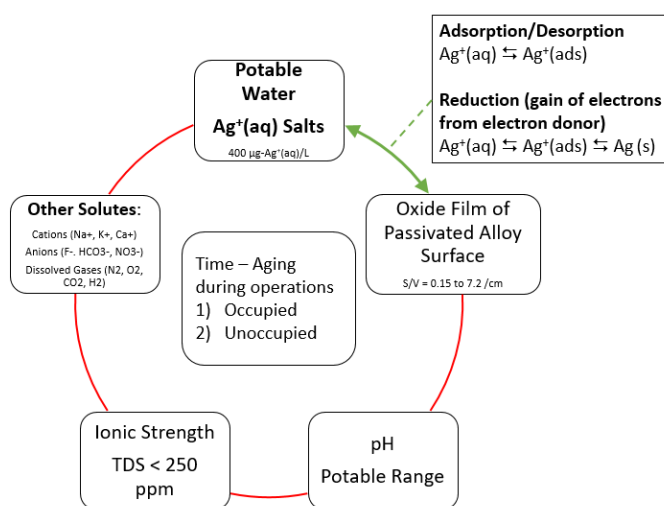


Figure 2. Framework of Silver Chemistry in Potable Water Systems.

systems are therefore expected to have a lower pH and different reactivity between ionic silver and wetted surfaces than closed systems. The role of dissolved oxygen concentration on the silver depletion rate is poorly understood, and will also depend on reactions between oxygen and the wetted pipe material (see Equation 1 as an example). Future testing across the full range of O₂ and CO₂ partial pressures from open to closed spacecraft levels is planned.

IV. Chemistry of Silver in Aqueous Solution

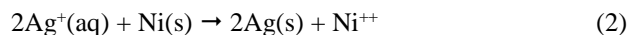
Silver is a Group IB transition metal with unique properties. As a noble metal, its lowest energy state is elemental silver with a zero charge in the solid phase, Ag(s). The most common ionic form of silver in aqueous solutions is the Ag⁺(aq) oxidation state with a charge of +1. The silver cation is electroactive. As a cation, Ag⁺(aq) is attracted to ligands and surfaces with a negative charge, such as sulfur, nitrogen, or oxygen anion constituents of bacterial cell walls. This type of charge-based attraction is known as nonspecific adsorption, since all cations are attracted to a negative surface.

The oxidative dissolution of ionic silver from silver nanoparticles (AgNPs) or silver surfaces proceeds according to the following chemical reaction⁸



Hence, both the pH and dissolved oxygen content of water determines the relative amounts of ionic silver that can be provided by ‘bulk’ elemental silver. Nanoparticles with diameters in the range of 3 to 100 nm are typically used to achieve an adequate ionic silver concentration in solution because of the large elemental silver surface area.

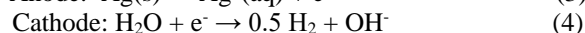
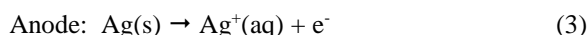
The silver ion undergoes galvanic replacement (redox) reactions⁴ with less noble metals of unpassivated alloys and oxygen vacancies in passivated alloys (elemental iron, nickel, chromium). As an example, when the redox reaction between Ag⁺ ions and Ni(s) proceeds to completion, 1 mole of Ni⁺⁺ replace 2 moles of Ag⁺ (Equation 2). This corresponds with 0.27 grams of Ni⁺⁺ replacing 1.00 grams of Ag⁺ in acidic solutions in which Ni(OH)₂ is soluble.



Steric hindrance does not limit silver ion reaction rates due to its monatomic structure. The silver ion is highly polarizable, meaning that its electron cloud will reorient in response to electrical fields in the vicinity of surfaces to enhance adsorption and other reactions. Ag⁺(aq) does not readily undergo hydrolysis (form complexes of the form Ag(OH)_n) in the potable pH range.

The variable solubility of different silver compounds has been summarized.⁷ Silver chloride is a well-known insoluble silver salt with a K_{sp} value of 1.8×10^{-10} . Silver fluoride and silver nitrate are highly soluble and are a simple source of ionic silver in potable water systems. Insoluble silver carbonate (K_{sp} = 8.5×10^{-12}) has also been proposed as a source of ionic silver, with evidence that the carbonate anion can enhance the biocidal effectiveness of ionic silver.⁹

When silver ions are electrolytically generated in a closed system, the pH increases as Ag(s) is converted to Ag⁺(aq), which is due to the generation of OH⁻ at the cathode.¹⁰



Other silver species associated with silver electrodes are the silver oxides Ag₂O and AgO, generation of which depends on the potential and pH of the electrode-water system.¹¹ In an electrolytic ionic silver generation system open to the atmosphere, the pH is buffered at a pK value of 6.3 of the carbonate system. In contrast, the pH of biocide water with 400 ppb Ag⁺(aq) is calculated to be 8.5 in a closed system absent of dissolved CO₂.

V. Chemistry of Silver Depletion

A. Adsorption Mechanisms

The adsorption of metal ions, such as Ag⁺, onto metal oxide surfaces can occur via several mechanisms. The silver ion can be captured within the diffuse double layer (as a diffuse ion with waters of hydration), as an outer-sphere complex bound to the functional groups of the surface (as an ion pair), and as an inner-sphere complex bound by a covalent bond with the functional groups of the surface.¹² A variety of active sites are present on the surface of metal oxides, some of which preferentially react with certain cations. Adsorption of cations (adsorbate) on metal oxides (adsorbent) can be caused by two distinct types of interactions between ions and functional groups of surfaces: electrostatic (nonspecific, physical) adsorption and chemisorption (specific).¹³ The types of adsorption typically associated with metal ions and metal oxides are summarized in Table 1, and specific and nonspecific adsorption pathways are described for each proposed adsorption mechanism.

B. Adsorption of Ag⁺ on Metal Oxides

Adsorption losses of ionic silver to traditional wetted spacecraft alloy materials is a major concern in a silver biocide system. In this paper, we focus on legacy alloy pipe materials used for pipes on the ISS because the structural reliability and operational lifetime in highly ionizing conditions is known. The combination of alloys with ionic silver may provide unique toxic effects to bacteria and biofilm prevention, as compared to plastic pipes. Stainless steel 316L (¼-inch pipes and bellows tanks), unalloyed titanium (½-inch pipes), Inconel 718 (bellows tanks), and Teflon flex hoses (¼-inch and ½-inch pipes) have been most widely employed for wetted pipes on the ISS. Of these, Teflon hoses adsorb the least amount of ionic silver. The focus of this paper is on 316L and Inconel 718. A wide range of adsorption losses on the alloy materials has been presented in the literature and summarized. In general, passivated alloys are able to maintain potable concentrations of ionic silver if the surface to volume ratio is less than 1 cm⁻¹, but the ionic silver concentration loss rate typically exceeds 10% per day when the S/V ratio exceeds 1 cm⁻¹.⁷

Table 1. Nonspecific and Specific Adsorption of Cations.

	Nonspecific “Physical” Adsorption	Specific “Chemisorption” Adsorption
Effect of Surface Charge	Ion adsorbs to surface of opposite charge, little adsorption takes place on neutral or similar charges.	A coulombic correction factor is used to quantify effect of surface potential and long range electrostatic forces on adsorption.
Effect of pH	Adsorption is dominant at pH values above the point of zero charge, PZC, of the metal oxide surface.	Adsorption to reactive functional groups is decreased at low pH due to competition by protons with the cation.
Effect of Ionic Strength	Electrostatic interactions are attenuated by high ionic strength. Effect is small.	Adsorption is insensitive to ionic strength of water.
Effect of Competing Cations	Adsorption of one metal ion does not significantly affect adsorption of another metal ion.	Adsorption sites tend to be metal ion specific, but competition between similar metal ions can occur for adsorption sites.
Effect of Anions	Anion adsorption is dominant at pH values below the PZC of the metal oxide.	Specific anions precipitate and/or alter the surface chemistry by increasing value of PZC.
Diffusion of Ion into Adsorbent	Diffusion of ions into porous, permeable, and microchannels is another potential loss of aqueous ions.	Chemical reactions can occur within pores of adsorbent.

One way to understand the role of the S/V ratio of pipes on the silver loss rate is to consider the interaction of the ionic silver (adsorbate) with the wall surface (adsorbent) as a function of the S/V ratio. For a pipe section (without end caps), the relationship between inner diameter (D) and S/V is simply $S/V = 4/D$. Figure 3 shows the nonlinear relationship between ionic silver concentration (y-axis represents moles of adsorbate and/or oxidizer relative to moles of adsorbent) and the S/V value of pipes, tanks, or coupons (x-axis represents ratio of adsorbent and/or reductant to adsorbate). As reference, a ¼-inch pipe (0.22-inch internal diameter) – the smallest traditional pipe diameter used in the ISS Water Recovery System – has a S/V of 7.2 cm^{-1} . A large tank (57 liters) has an S/V on the order of 0.15 cm^{-1} when the bellows is fully expanded and liquid volume is a maximum. Thus, a pipe with an S/V of 7.2 cm^{-1} has 48 times more adsorbing sites (quantity of adsorbent) for a given volume of water than a tank with S/V of 0.15 cm^{-1} .

Traditional adsorption studies utilize the concept of isotherms to show the equilibrium between concentrations of the adsorbate dissolved in the water phase and the amount of the adsorbate on the surface (adsorbent). Figure 4 shows a range of isotherms that are possible. Isotherms are linear at low concentrations of adsorbate (ionic silver) and transition to either a Freundlich or Langmuir isotherm at higher adsorbate concentrations. In the worst case, an adsorbate precipitates on the wetted surface, which significantly depletes the $\text{Ag}^+(\text{aq})$ and makes it difficult to maintain potable concentrations. An isotherm representing more than a monolayer of adsorbate, in the form of surface-clusters (surface site saturation), is known as a surface precipitation isotherm.¹⁴ The surface-clusters themselves can become new adsorption sites.¹⁵ In the case of metal ions surface precipitating on metal oxides, the result can be a complete coating of the original oxide surface with a new surface with new properties.¹⁶ Surface precipitation is normally associated with cation adsorption on amorphous oxides. In the case of the electroactive silver ion in a passivated metal pipe, the surface precipitation is complicated by an additional process of “surface reduction” of ionic silver to elemental silver.

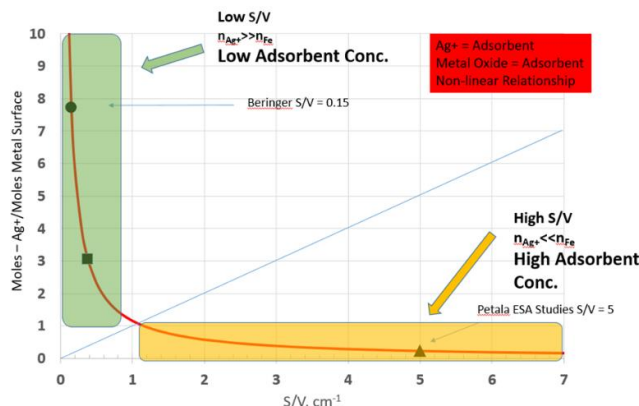


Figure 3. Molar Ratio of Ionic Silver to Surface Metal for 316L at 400 ppb $\text{Ag}^+(\text{aq})$.

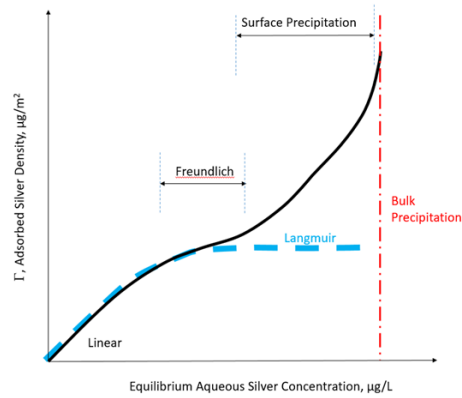


Figure 4. Adsorption Isotherms for Equilibrium between Aqueous Silver and Adsorbed Silver.

Finally, bulk precipitation can occur, which becomes favorable at an upper solubility limit that is dependent on adsorbate and pH. Similarly, if the adsorbed layer can act as an adsorbent (substrate) for additional adsorption of silver ions, then instead of adsorption leveling off (slope of isotherm approaches horizontal) it can continue to rise indefinitely (slope approaches vertical), resulting in a new wetted material made from the adsorbate. In the case of ionic silver, bulk precipitation can occur at alkaline pH values ($\text{pH} > 8$), and silver oxide (Ag_2O) becomes less soluble in water. In addition, the ionic silver reduction reaction can continue on elemental silver and on the Ag_2O that has accumulated on the wetted surface, which results in significant ionic silver depletion similar to bulk precipitation.

It is useful to explore the driving mechanisms behind the seemingly inverse relationship between silver ion concentration and S/V ratio in order to understand limitations in using small diameter metallic legacy materials such as stainless steel, titanium, and nickel-based alloys. One question of interest is why all 400 ppb of Ag^+ is lost with an S/V of 5 cm^{-1} , but negligible $\text{Ag}^+(\text{aq})$ is lost with an S/V of 0.15 cm^{-1} as reported in the literature.⁷ The concept of isotherms can also explain the pseudo-inverse relationship between ionic silver concentration in solution and S/V by tracking how ionic silver adsorbs to a surface when first wetted with ionic silver solution.

The steady state concentration of ionic silver in contact with a given alloy is reached when the equilibrium pathway line (dashed line in Figure 5) intersects the adsorption isotherm. The value of S/V determines the slope of the equilibrium pathway in Figure 5. Hence, the S/V value determines the concentration at which the equilibrium pathway line will cross the isotherm. This approach assumes that the residence time is sufficient in the vessel so that the system has reached equilibrium, which is valid when the residence time exceeds the time required to reach equilibrium, such as during long term storage of potable water in a pipe. Based on a mass balance of silver partitioning between the bulk phase and the surface, the slope of the equilibrium pathway line is the inverse of the S/V (slope = V/S). Low S/V correlates to low adsorbent quantity, high (vertical) slope, and a high equilibrium concentration of $\text{Ag}^+(\text{aq})$ in water. High S/V represents high adsorbent relative to adsorbate, low (horizontal) slope, and a low equilibrium concentration of $\text{Ag}^+(\text{aq})$ in water. The rate of procession from the initial condition (400 ppb $\text{Ag}^+(\text{aq})$) to the equilibrium condition is limited by kinetics and the flow regime.

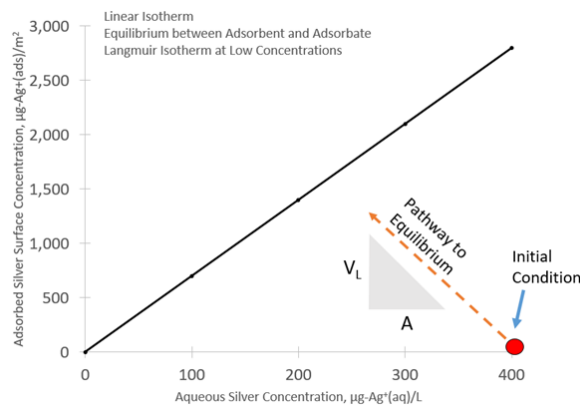


Figure 5. Pathway of a 400 ppb Silver Concentration to Equilibrium with Adsorbed Silver.

Figure 6 demonstrates that adsorption losses are negligible when S/V is low (e.g., in a water tank), while adsorption losses are significant if the S/V is high (e.g., in a small pipe, $\sim 5 \text{ cm}^{-1}$). Figure 7 summarizes the equilibrium concentration of Ag^+ in water over a large range of S/V, thereby rationalizing the complete (negligible) adsorption loss of 400 ppb ionic silver when the S/V is greater (less) than 4 cm^{-1} (0.15 cm^{-1}).

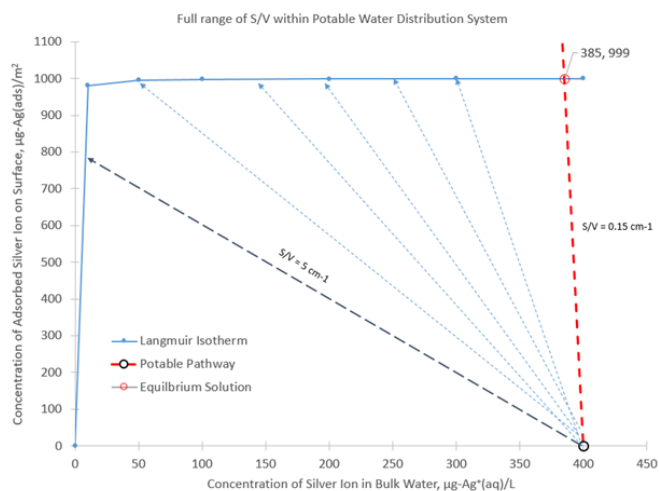


Figure 6. Langmuir Isotherm for a Range of S/V Values.

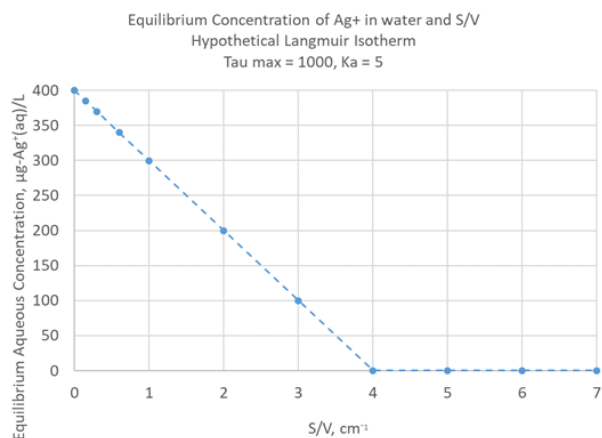


Figure 7. Equilibrium Concentrations of Ionic Silver and S/V Values.

Figure 8 demonstrates how the equilibrium concentration of Ag^+ increases as a wetted surface is repeatedly exposed to batches of potable water with initial Ag^+ concentrations of 400 ppb. In this plot the hypothetical surface has been exposed six times to 400 ppb Ag^+ water. As described above, the ionic silver will follow the pathway line to equilibrium based on a mass balance on silver partitioned between the water phase and the solid phase. The solution is initially poured into a pipe that has never been exposed to an aqueous Ag^+ solution, which corresponds with an initial adsorbed silver density of zero (bottom red data point, on the x-axis). Each time the liquid in the pipe is removed and refilled with a new batch of solution, less and less ionic silver adsorbs on the wetted surface, until equilibrium is reached (where the equilibrium line intersects the isotherm line). Repeated exposures to freshly prepared solutions containing 400 ppb Ag^+ are accompanied by a corresponding increase in both the density of adsorbed silver and the equilibrium Ag^+ concentration. The equilibrium isotherm theoretically increases until the equilibrium Ag^+ concentration reaches 400 ppb (top, gold circle). However, if surface precipitation/reduction occurs, the solution may never be able to reach an equilibrium concentration above a critical value of S/V. This "aging" concept is discussed further in section VI of this paper.

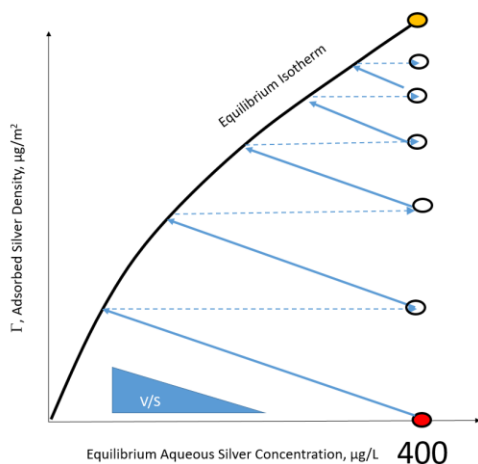


Figure 8. Aging of a Material to Reach the Target Equilibrium Concentration.

C. REDOX Reactions

For ionic silver solutions in contact with a passivated alloy, galvanic replacement of silver ions with less noble metal ions is possible for any surface sites or accessible sites that have not been oxidized by the passivation process. These sites are known as defects, such as oxygen vacancies. Many surface passivation processes applied to metallic alloys form a thin surface oxide layer that protects the underlying alloy from corrosion. In the case of stainless steel 316L, the oxide film is mostly comprised of Cr_2O_3 and is typically on the order of 1-10 nm thick.¹⁷ At the interface between the surface oxide and the underlying alloy, a nickel-rich layer can form.¹⁸ Galvanic replacement of ionic silver with ionic nickel via defects can be monitored by measurement of aqueous ionic nickel in solutions with a low enough pH to support nickel hydroxide ($\text{Ni}(\text{OH})_2$) solubility.

Redox reactions are a feasible explanation for major depletion of 400 ppb ionic silver at S/V values greater than 1 cm^{-1} . For example, if the real surface area, accounting for surface roughness, is assumed to be 3 times the planar area and the percent of oxidization of all sites is 96% (96% of all surface sites are oxidized), the resulting equilibrium concentration of ionic silver after reacting with unoxidized sites is 4% of the total number of sites (assuming 10^{15} total sites per cm^2 of metal oxide surface), as shown in Figure 9.

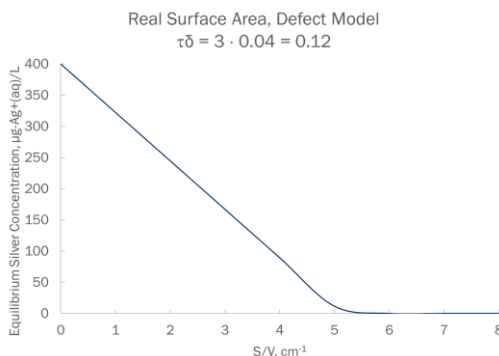


Figure 9. Equilibrium Concentration for Ionic Silver Oxidation Reduction Reactions with Oxygen Vacancies.

D. pH Effects on Adsorption

As described above, ionic silver can be lost to surfaces by way of adsorption to the surface as the cation, and also by way of redox reactions at defect sites on passivated surfaces. Silver ion loss reactions are all affected by the other water quality parameters in Figure 2. The pH affects the silver ion concentration most significantly; specifically, a low pH ($\text{pH} < 5$) inhibits ionic silver adsorption, and a high pH ($\text{pH} > 8$) favors adsorption. The pH effect is due to changes in the surface functional groups of the hydroxylated metal surface, which become protonated at lower pH values. At a critical pH for a given metal oxide, known as the point of zero charge (PZC), the net surface charge becomes zero. At pH values above the PZC, the net surface charge is negative and susceptible to cation adsorption.

Alloys with PZC values greater than the pH of the potable water, such as Al_2O_3 with a PZC of 9.1, or MgO with a PZC of 12.4, would have positive surface charges when in contact with potable water at pH 5.5. The pH of the potable water can depend on the source of the ionic silver, and the allowed pH limits for spacecraft potable water are between 4.5 and 8. Each metal oxide on passivated alloys will also have a minimum allowable water pH to prevent corrosion by acidic solutions.

The effect of pH on redox-based losses of ionic silver is not well known, but in general, a lower pH accelerates redox reactions. The pH of the potable water discussed in this work is important because it determines not only the water chemistry, but also the surface chemistry and net electrical charge of wetted materials such as passivated alloys. As in all cases, the system designer is constrained by the potable water quality requirements and the alloy surface's requirements to prevent corrosion.

It has been shown that the metal ion adsorption rate onto a wetted oxide surface is highly pH-dependent. In many systems, the cation adsorption rate rapidly increases from negligible to nearly saturated over 1-2 pH units. The pH at which the concentration of adsorbed cations is 50% of the initial adsorbed cation concentration is known as the "pH adsorption edge." For example, the pH adsorption edges of Ag^+ on amorphous $\text{Fe}(\text{OH})_3$ depended strongly on the concentration of adsorbent relative to a constant $0.4 \mu\text{M Ag}^+$, where the adsorption edge occurred at a pH of 5.5 when the wetted S/V was $243 \text{ m}^2/\text{L}$ (2430 cm^{-1}), at a pH of 7.0 when the S/V was $16 \text{ m}^2/\text{L}$ (160 cm^{-1}), and at a pH of 9.0 when the S/V was $1.6 \text{ m}^2/\text{L}$ (16 cm^{-1}).¹⁹ The commonly observed shift of the pH edges to higher pH values with lower S/V ratios (lower adsorbate/adsorbent ratios) has been explained by the shift to low affinity (weak binding) surface groups as the dominant adsorption sites at lower S/V ratios. At high values of S/V, high affinity (strong binding) surface sites dominate the adsorption due to the low ratio of adsorbate/adsorbent.²⁰

The pH edge effect on percent adsorption could explain the inverse relationship between equilibrium Ag^+ concentration and S/V. Figure 10 shows, in theory, that at a pH of 5.5 and a S/V of 0.15 cm^{-1} (representing a full liquid volume water tank) minimal silver adsorption will occur, while complete adsorption is possible in water tanks and small pipes (S/V of 5 cm^{-1}). Based on the data trend in Figure 10, the maximum allowable pH required to maintain a steady state concentration of potable levels of ionic silver (e.g., 400 ppb) will decrease as the S/V ratio increases from 0.15 cm^{-1} to 5 cm^{-1} . Future experiments will measure the true Ag^+ adsorption-pH edges as a function of pipe diameters (S/V values) for the required potable concentrations of ionic silver ($\sim 400 \text{ ppb}$) present at a potable pH ($\text{pH} > 4.5$).

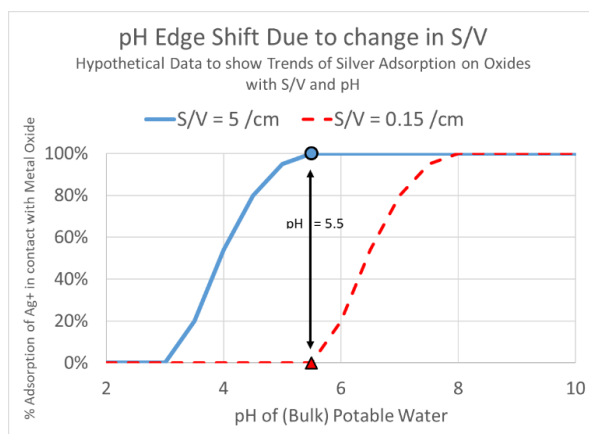


Figure 10. Hypothesized effect on Silver Adsorption based on the S/V shift in pH Adsorption Edge.

VI. Aging of Surface in Contact with Potable Ag^+ Concentrations

A passivated alloy surface consists of a thin film of oxide and hydroxide species of the metallic elements that comprise the alloy. Upon contact of the surface with a water solution, water molecules quickly react with the surface, resulting in amphoteric OH groups. The concentration of OH groups on metal oxides is on the order of 2 to $10 \text{ OH}/\text{nm}^2$. The surface will obtain a surface charge distribution that depends on the PZC value of the oxide film and the ionic strength and pH of the water solution.

As silver is deposited onto surfaces, either by redox or adsorption reactions, it covers the surface with elemental silver, $\text{Ag}(\text{s})$, and silver oxide, $\text{Ag}_2\text{O}(\text{s})$.⁴ If the elemental silver forms clusters, known as silver islands, the islands can provide a new negatively charged surface area conducive to adsorption of silver ions onto silver²¹ or onto the silver oxide layer.²² This surface transformation process from original surface to a new surface has been described by the surface precipitation model for other metal ions adsorbing and precipitating on metal oxides.¹⁴

Because silver is an ideal conductor of electrons from the substrate alloy to the silver ions in the water solution, the process of adsorption-redox reactions is expected to continue unless or until a sufficient charge imbalance builds up by an accumulation of the alloys metal cations (e.g., Ni^{++}). If the electron-donating alloy metals (e.g., $\text{Ni}(\text{s}) \rightarrow \text{Ni}^{++} + 2\text{e}^-$) are unable to diffuse from the unpassivated alloy to the water-solid interface (wetted surface), the resulting charge imbalance (buildup of positive charge in the unpassivated alloy) could slow the supply of electrons driving the process of ionic silver deposition by the oxidation reduction reaction ($\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}(\text{s})$).

To demonstrate these aging effects, tests were performed on coupons with low S/V and in pipes with higher S/V.

A. Unpassivated Stainless Steel 316L Coupon Test

A 400 ppb $\text{Ag}^+(\text{aq})$ solution was prepared by dissolving silver fluoride in ultrapure water with 18.2 M Ω resistivity. The potable water solutions had a pH of 5.5 ± 0.3 in the ambient lab conditions. Unpassivated 316L stainless steel coupons (2B finish, 0.105 inches thick) with a surface area of 38 cm² were immersed in 100 mL of solution within a closed polypropylene snap-cap container (coupon S/V = 0.38 cm⁻¹). Two coupons were used to provide a replicate for each test point. One container of potable water solution without a coupon served as a control and provided a measurement of container uptake, which was found to be less than 2% per week. Containers were stored in the dark at 22 ± 2 degrees Celsius under static conditions. Each container had an ambient air headspace of 30 cm³. The coupons were then regularly removed from the containers and placed in newly prepared potable water solution in new containers. Over time, the frequency of the replenishment increased from daily to weekly. The concentration of the total aqueous silver, as measured by inductively coupled plasma mass spectrometry, is shown in Figure 11 for both replicates. At 32 weeks of cumulative soak time, the weekly loss rate was less than 10% for both coupons.

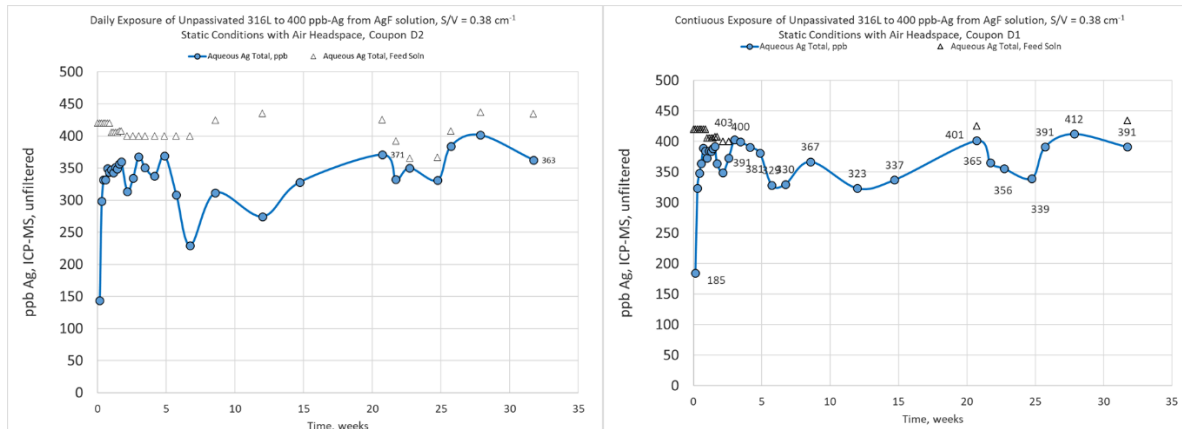


Figure 11 Aging of Unpassivated 316L Coupon, S/V = 0.38 cm⁻¹, with Exposure to Potable Water of 400 ppb Ag⁺ from AgF, Replicate 1 on Left, Replicate 2 on Right.

B. Passivated Stainless Steel 316L and Inconel 718 Pipe Test

A similar aging test was conducted on two different pipe materials that had been passivated with a patented process involving a high temperature oxidation followed by a 50 ppm Ag^+ silver soak.²³ 400 mL of potable water were poured into the pipes and the potable water solution was replaced weekly to monitor silver depletion rates with time. The bottom end of each pipe was sealed with a welded plate of the same material, and the pipes were stored standing vertically. The open pipe end was covered with aluminum foil to maintain dark conditions on the liquid, but this did not seal the liquid surface away from the ambient lab air. An Inconel 718 pipe with a square cross section (2.5 cm internal side length, made from two bent plates welded together) with S/V of 1.4 cm⁻¹ and a seamless round stainless steel 316L pipe (3.5 cm inner diameter) with S/V of 1.2 cm⁻¹ were tested in replicate pipes. Results are not shown here for the Inconel pipe, as it continued to take up more than 90% of the aqueous silver per week, even after 26 weeks. The results for the 316L steel pipe are shown in Figure 12; during 26 weeks of cumulative soak time, the average-weekly loss rate relative to an average of 411 ppb Ag^+ was 8.5% for replicate 1 and 15% for replicate 2. A steady-state concentration of 400 ppb $\text{Ag}^+(\text{aq})$ was not reached after 26 weeks; the silver depletion rate was not reduced to zero. During the 6 months, an average cumulative total of 909 $\mu\text{g}/\text{L}$ of ionic silver was transferred from water phase to the 316L surface in replicate 1 and 1,618 $\mu\text{g}/\text{L}$ was transferred in replicate 2. These values correspond to 7.6 mg-Ag/m² adsorbed and/or reduced for replicate 1's surface and 13.5 mg-Ag/m² adsorbed and/or reduced for replicate 2's

surface. If the first time exposure loss of 420 $\mu\text{g-Ag/L}$ to surfaces is included, the total silver loading on surfaces becomes 11.1 mg/m^2 (103 $\mu\text{mole-Ag/m}^2$) for replicate 1 and 17.0 mg/m^2 (157 $\mu\text{mole-Ag/m}^2$) for replicate 2. No correction in surface area is made for roughness (real surface area) or porosity of the passivated 316L oxide layer.

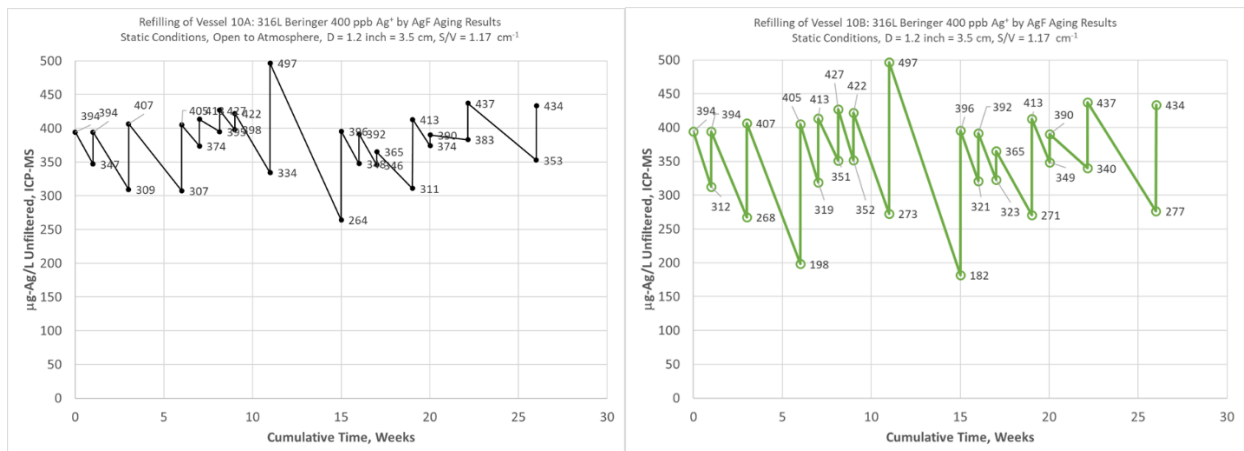


Figure 12 Aging of Beringer Passivated 316L Pipe, S/V = 1.2 cm⁻¹, with Exposure to Potable Water of 400 ppb Ag⁺ from AgF, Replicate 1 on Left, Replicate 2 on Right.

VII. Summary

This paper examined the chemistry and fate of ionic silver in aqueous-solid systems. The framework of processes reviewed provides a methodology and new terminology for evaluating the feasibility of using legacy metal alloy pipes and tanks to store and transport potable water with ionic silver as the biocide. Depletion of ionic silver to passivated metal surfaces can be explained by adsorption to the metal oxides, oxidation reduction reactions with the oxygen vacancies, and surface precipitation/reduction processes resulting in a new solid surface of silver and silver oxides. The difference in silver depletion between low values of S/V (tanks) with minimal ionic silver losses and high values of S/V (small diameter pipes) with major ionic silver depletion can be explained by a range of chemical aqueous-surface processes. For first time exposure of potable water to surfaces of different S/V values, a mass balance approach defining the surface as the adsorbent and the liquid volume's ionic silver as the adsorbate accounts for the S/V effect on the extent of silver depletion (Figure 7). Similarly, REDOX (galvanic) reactions of ionic silver with unpassivated metal sites is a feasible silver loss mechanism (Figure 9). For repeated exposure of metal oxide surfaces to ionic silver ("aging"), the presence of two types of adsorption sites: strongly binding and weakly binding, shift the pH adsorption edge to lower pH values at higher S/V values (lower adsorbate/adsorbent ratios). Thus, the pH required to maintain 400 ppb ionic silver concentrations in potable water is proposed to be a function of the value of S/V (Figure 10).

The chemistry of ionic silver of potable systems indicates minimization of ionic silver depletion rates by: 1) minimizing the surface to liquid volume ratio (S/V) of the entire water distribution system, 2) use of electropolished metals as the base material (e.g. 316L) to minimize real surface area prior to passivation, 3) supplemental passivation by aging or constant exposure of wetted surfaces to potable water with 400 ppb Ag⁺, 4) operating with lowest possible water pH subject to potable limits and material pH limits, and 5) addition of potable concentrations of multivalent cations (Ca⁺⁺, Mg⁺⁺, Zn⁺⁺) in the form of soluble salts to compete with silver ions for adsorption sites.

It is recommended that aging of materials be utilized by replenishing potable water solutions by flow or batch refilling in order to empirically measure if a steady state concentration of 400 ppb Ag⁺ can be obtained for the full range of expected S/V values. If 400 ppb Ag⁺ cannot be maintained by aging alone, the most promising approach to maintain it is to lower the pH of the solution to the lower water quality limit of 4.5, subject to the oxide's pH corrosion limit. Aging duplicate, passivated stainless steel 316L pipes (S/V = 1.2 cm⁻¹) reduced the ionic silver depletion rate relative to the first time exposure rate from 50% per week (first time exposure) to 15% per week (average over 26 weeks). Similarly, duplicate unpassivated 316L coupons (S/V = 0.38 cm⁻¹) exposed to potable water at 400 ppb Ag⁺ had average weekly silver loss rates of less than 10% per week for 32 weeks of cumulative exposure. The same beneficial effect was not observed when a similar pipe of passivated Inconel 718 (S/V = 1.4 cm⁻¹) was similarly aged. Future work will continue and expand on the aging experiments of the 316L surface to determine the maximum attainable equilibrium concentration of ionic silver as a function of S/V and pH.

References

- ¹ Steele, J. W., Wilson, M., Makinen, J., Ott, C. M., “Antimicrobials for Water Systems in Manned Spacecraft: Past, Present, Future,” ICES-2018-104, *48th International Conference on Environmental Systems*, Albuquerque, New Mexico, 2018.
- ² Albright, C. F., Nachum, R., and Lechtman, M. D., Garrett Airesearch Manufacturing Division, “Development of an Electrolytic Silver-Ion Generator for Water Sterilization in Apollo Spacecraft Water Systems,” Apollo Applications Program, Final Report 67-2158, June 1967.
- ³ Hicks, P., Nelson, J., and Callahan, M. R. “Initial Trade Study for In-line Silver Sensor for Spacecraft Potable Water Systems,” ICES-2019-315, *49th International Conference on Environmental Systems*, Boston, Massachusetts, 2019.
- ⁴ Petala, M., Tsiridis, V., Mintsouli, I., Pliatsikas, N., Spanos, Th., Rebeyre, P., Darakas, E., Patsalas, P., Vourlias, G., Kostoglou, M., Sotiropoulos, S., and Karapantsios, Th., “Silver deposition on stainless steel container surfaces in contact with disinfectant silver aqueous solutions,” *Applied Surface Science*, Vol. 396, pp. 1067-1075, 2017.
- ⁵ Petala, M., Tsiridis, V., Darakas, E., Kostoglou, M., “Longevity Aspects of Potable Water Disinfected by Ionic Silver: Kinetic Experiments and Modeling,” *Water*, Vol. 12, pp. 1-16, 2020.
- ⁶ Hanford, A. J., and Lange K. E., *Analysis Supporting Development of Silver Ion as a Water Biocide during Fiscal Year 2017*. JETS-Technical Memorandum, JE33-17-TAED-DOC-0041, 2017.
- ⁷ Li, W., Calle, L. M., Hanford, A. J., Stambaugh, I., and Callahan, M. R. “Investigation of Silver Biocide as a Disinfection Technology for Spacecraft: An Early Literature Review,” ICES-2018-82, *48th International Conference on Environmental Systems*, Albuquerque, New Mexico, 2018.
- ⁸ Fujiwara, K., Sotiriou, G. A., Pratsinis, S. E., “Enhanced Ag⁺ Ion Release from Aqueous Nanosilver Suspensions by Adsorption of Ambient CO₂,” *Langmuir*, Vol. 31, No. 19, pp. 5284-5290, 2015.
- ⁹ Swathy, J. R., Sankar, M. U., Chaudhary, A., Aigal, S., Anshup, Pradeep, T., “Antimicrobial silver: An unprecedented anion effect,” *Scientific Reports*, 4, 7161, DOI: 10.1038/srep07161, pp. 1-5, 2014.
- ¹⁰ Silva Martinez, S., Alvarez Gallegos, A., Martinez, E., “Electrolytically generated silver and copper ions to treat cooling water: an environmentally friendly novel alternative,” *International Journal of Hydrogen Energy*, Vol. 29, pp. 921-932, 2004.
- ¹¹ Delahay, P., Pourbaix, M., Rysselberghe, P. V., “Potential-pH Diagram of Silver,” *Journal of the Electrochemical Society*, Vol. 98, No. 2, 1951.
- ¹² Stumm, W. and Morgan, J. J., *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 1996.
- ¹³ Smith, K. S., “Metal Sorption on Mineral Surfaces: An Overview with Examples Relating to Mineral Deposits.” Reviews Volume 6, *The Environmental Geochemistry of Mineral Deposits*, Part A: Processes, Techniques, and Health Issues, Chap. 7, 1999, pp. 161-182.
- ¹⁴ Farley, K. J., Dzombak, D. A., Morel, F. M. M., “A Surface Precipitation Model for the Sorption of Cations on Metal Oxides,” *Journal of Colloid and Interface Science*, Vol. 106, pp. 226-242, 1985.
- ¹⁵ Bleam, W. F., McBride, M. B., “The Chemistry of Adsorbed Cu(II) and Mn(II) in Aqueous Titanium Dioxide Suspensions,” *Journal of Colloid and Interface Science*, Vol. 110, No. 2, pp. 335-346, 1986.
- ¹⁶ Stumm, W., *Aquatic Surface Chemistry: Chemical Processes at the Particle-Water Interface*, 1987.
- ¹⁷ Kerber, S.J., and Tverberg, J. “Stainless Steel Surface Analysis,” *Advanced Materials and Processes*, pp. 33-36, 2000.
- ¹⁸ Olsson, C. O. A., and Landoldt, D., “Passive films on stainless steels: chemistry, structure and growth,” *Electrochimica Acta*, Vol. 48, pp. 1093-1104, 2003.
- ¹⁹ Davis, J. A., *Adsorption of Trace Metals and Complexing Ligands at the Oxide/Water Interface*. PhD Thesis; Stanford University; Stanford, California, 1977.
- ²⁰ Dzombak, D. A., Morel, F. M. M., *Surface Complexation Modeling*, John Wiley and Sons, New York, 393 pages.
- ²¹ Liu, J., and Hurt, R. H., “Ion Release Kinetics and Particle Persistence in Aqueous Nano-Silver Colloids,” *Environmental Science and Technology*, Vol. 44, pp. 2169-2175, 2010.
- ²² Adegboyega, N., G., Sharma, V., K., Siskova, K., Zboril, R., Sohn, M., Schultz, B., J., Banergee, S., “Interactions of Aqueous Ag⁺ with Fulvic Acids: Mechanisms of Silver Nanoparticle Formation and Investigation of Stability,” *Environmental Science and Technology*, Vol. 47, pp. 757-764, 2013.
- ²³ Beringer, D. M., Steele, J. W., Nalette, T. A., “Long-Term Storage of Potable Water in Metallic Vessels,” United States Patent 8,685,257 B2, April 1, 2014.