

# Investigation of Silver Biocide as a Disinfection Technology for Spacecraft – An Early Literature Review

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**An ideal spacecraft water disinfection system should prevent or control microbial growth, inhibit or prevent biofilm formation, and prevent microbial-induced corrosion. In addition, any biocides in the disinfection system should be chemically compatible with materials used in the water storage and distribution system, have minimal maintenance requirements, especially for long-duration missions, and should be safe for crew consumption at levels appropriate for biocidal control. Silver ion is a proven broad spectrum biocide. There has been an increased interest in the biocidal function of silver, both due to its potential to control biocide resistant species and due to advances in silver and nanosilver microbial control technologies. NASA is considering silver as the future biocide for exploration. In order to select and design a successful silver biocide delivery system to meet NASA's requirements, it is essential to understand the advantages and disadvantages of moving to a silver disinfection system. To enhance the knowledge of silver biocides in spacecraft water systems, this paper provides a first compilation of review data related to: (1) Silver as a biocide technology; (2) Options and concepts for silver biocide delivery; and (3) Silver biocide compatibility.**

## Nomenclature

<i>AgNPs</i>	= silver nanoparticles
<i>ATV</i>	= Automated Transfer Vehicle
<i>DNA</i>	= deoxyribonucleic acid
<i>EDTA</i>	= ethylenediaminetetraacetic acid
<i>EMU</i>	= Extravehicular Mobility Unit
<i>EPA</i>	= Environmental Protection Agency
<i>FEP</i>	= perfluoroelastomer
<i>ISS</i>	= International Space Station
<i>IX</i>	= ion exchange
<i>LBC</i>	= low biocide concentration
<i>NASA</i>	= National Aeronautic and Space Administration
<i>PWD</i>	= potable water dispenser
<i>RNA</i>	= ribonucleic acid
<i>ROS</i>	= reactive oxygen species
<i>SWEGs</i>	= Spacecraft Water Exposure Guidelines

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TEM = transmission electron microscopy  
 UV = ultraviolet  
 WHO = World Health Organization

## I. Introduction

SILVER is a proven broad spectrum biocide. There has been an increased interest in the biocidal function of silver, both due to the advancement of silver and nanosilver biocide technologies and the potential to address antimicrobial resistance in clinically relevant organisms. The National Aeronautics and Space Administration (NASA) is interested in adopting silver biocide as a replacement for iodine (I<sub>2</sub>) for long duration exploration missions. Although iodine has been successfully used on the International Space Station (ISS), it can have adverse effects on the thyroid and must be removed before being consumed by astronauts. Currently, iodine removal is achieved through the use of additional hardware. The iodine removal hardware increases the overall complexity and mass of the disinfection system. Silver ion (Ag<sup>+</sup>) is an effective biocide at concentrations that can be directly consumed by the crew. Silver is the biocide of choice used by the Russian Space Agency. If silver can be an acceptable biocide for future missions, this will allow for water to be standardized and shared across international spacecraft platforms and mission architectures. In general, an ideal biocide should have no adverse effect on humans, inhibit microbial growth and biofilm formation, and reduce microbial-induced corrosion in the water storage and distribution systems. In order to move to a silver-based biocide system in future spacecraft, it will be essential to have a firm understanding of the biocidal mechanisms of silver, its fate and behavior in spacecraft water systems, and the advantages and disadvantages of proposed silver delivery systems. This paper presents a literature review of silver as it relates to its potential application as a biocide in spacecraft water systems.

## II. Overview of Water Treatment Technologies

### A. Types of Contaminations

The three types of pathogenic microorganisms that are of main concern in terrestrial water systems are: protozoa, bacteria, and viruses.<sup>1</sup> Their characteristics are shown in Table 1. For spacecraft systems, these general classes of microorganisms are also a concern. ISS water quality has been evaluated for compliance with potable water requirements, set by the ISS Medical Operations Requirements Document (ISS MORD), which specifies limits for bacterial counts, coliform bacteria, fungal count, and parasitic protozoa (e.g. *Giardia* and *Cryptosporidium*).<sup>2,3</sup> For bacteria, the types of organisms typically isolated from spacecraft and terrestrial water systems include: *Burkholderia cepacia*, *Cupriavidus metallidurans*, *Methylobacterium fujisawaense*, *Pseudomonas aeruginosa*, and *Sphingomonas paucimobilis*.<sup>3,4</sup>

**Table 1. Pathogenic microorganisms in water.**

Type (Examples)	Characteristics
<b>Protozoa</b> ( <i>Amoebae</i> , <i>Giardia lamblia</i> , <i>Cryptosporidia</i> )	<ul style="list-style-type: none"> <li>• Animal single-cell organisms, 1-15 microns in size.</li> <li>• Contaminate water through animal and human feces.</li> <li>• Form cysts, which lead to acute gastrointestinal diseases in human.</li> <li>• A single cell can cause an infection.</li> </ul>
<b>Bacteria</b> ( <i>E. coli</i> , <i>Salmonella</i> , <i>Vibrio cholerae</i> )	<ul style="list-style-type: none"> <li>• Single-cell organism, 0.5 – 5 microns in size.</li> <li>• Contaminate water through animal and human feces.</li> <li>• Propagate quickly in warm environments and, particularly in water, become dangerous when mixed together with human and animal feces in the drinking water.</li> </ul>
<b>Viruses</b> (Hepatitis A, Norwalk virus, Rota virus, Polio virus)	<ul style="list-style-type: none"> <li>• An infective agent, 0.02-0.2 microns in size.</li> <li>• Can only propagate in living cells since they do not possess their own metabolism.</li> <li>• Contaminate water through animal and human feces near populated areas where wastewater can get into drinking water.</li> </ul>

## B. Types of Treatments

In terrestrial drinking water systems, different water treatment technologies are available and generally matched to the types of water sources, quality, and flow rate of the water to be treated. Factors to be considered are: turbidity, chemical loading, processing rates, presence of viruses, bacteria and protozoa, and final water quality requirements.<sup>5</sup> Often, adsorption using active carbon and ion exchange (IX) through resins are used to reduce chemical contaminants and improve the taste of the water. Various filtration techniques remove suspended solids that are bigger than their pore size and can be effective to separate particles, bacteria and protozoa. but removal of viruses from water is a challenge due to their extremely small sizes. Ultraviolet (UV) devices and chemical biocides kill microbes of all sizes, but they do not improve the taste or appearance of the drinking water. Typically, chemical biocides, such as chlorine, are supplied as a residual biocide to inhibit microbial re-growth in the downstream of the distribution system.

In US spacecraft systems, treated water is typically ground supplied, and/or generated on demand within the vehicle, e.g., as a by-product of energy generation through fuel cells. In either case, the water is generally near or equivalent to deionized water. When water is recycled, as is now the case on the International Space Station (ISS), it is treated using activated carbon, ion exchange resin, and high temperature catalysis. Whether ground supplied, produced, and/or recycled, all potable water is treated with a biocide, prior to storage and distribution, to ensure that microbial control and overall potability are maintained. For US spacecraft systems, the different biocides that have been used have generally relied on iodine (the current biocide system for ISS). On occasion, chlorine was used in the Apollo command module and silver was used in an Extravehicular Mobility Unit (EMU) loop on the space shuttle and when transferring water to the Russian segment on ISS which has historically made use of silver biocide.

## III. Biocidal Activity of Silver Ion and Nanosilver

Though the antibacterial function of silver compounds is well known, their biocidal mechanisms are not completely understood. This is likely due to the versatility of the silver biocides that compounds the already complex nature of the interaction between biological organisms and their environment. Many studies have been conducted and are available in the literature on the biocide effects and interactions of silver with microorganisms. For reference, several published literature reviews are listed here to provide a general insight on the subject, including the Case Study by the Environmental Protection Agency<sup>6</sup> and a literature review published by WHO.<sup>7</sup> An extensive literature search is yet to be conducted for the microorganisms of interest in spacecraft water systems. However, some useful information can be found in the work in references 4, 8, and 9.

### A. Silver and its Physicochemical Properties

The physicochemical properties of silver compounds are important factors that influence their biocidal effect. These properties include composition, solubility, size (and dispersibility), morphology (shape and crystal structure), surface area, as well as, its electrical, magnetic, and optical properties. In nature, silver metal ( $\text{Ag}^0$ ) and silver ion ( $\text{Ag}^+$ ) forms are the most common states. The most abundant silver compounds in the environment are silver sulfide ( $\text{Ag}_2\text{S}$ , Argentite), silver nitrate ( $\text{AgNO}_3$ ), and silver chloride ( $\text{AgCl}$ , Cerargyrite). The Earth's crust contains 0.08 ppm of silver, while urban soil contains about 0.3 ppm silver.<sup>10</sup>

Solubility determines the dissolution of the silver compounds and release rate of silver ions into the environment. It is an important factor that influences the bioavailability of silver and its biocidal efficiency. A list of silver compounds and their solubilities are shown in Table 2. The solubility of these compounds in water also reflects the strength of the covalent bonds between silver and other elements, which determines its biocidal efficiency. For instance, the electronegativity values, by Pauling's scale, of Ag, sulfur (S), chlorine (Cl), oxygen (O), and fluorine (F) are 1.93, 2.58, 3.16, 3.44, and 3.98, respectively. Based on these differences in electronegativity, the Ag-S bond is less polar than the Ag-Cl bond, and very stable in water. As a result, the solubility product ( $K_{sp}$ ) of  $\text{Ag}_2\text{S}$  is about  $10^{-49}$ , the  $K_{sp}$  of  $\text{AgCl}$  is about  $10^{-10}$ , and that of  $\text{AgOH}$  is about  $10^{-8}$ . On the other hand,  $\text{AgF}$  is highly soluble in water, with a solubility of 182 g/100 mL at 15.5°C.<sup>11</sup> This is consistent with one of the main biocidal mechanisms of silver, i.e., the strong interaction of silver with the thiol ( $-\text{SH}$ ) group of the biological systems.

### B. Bioavailability

Exposure to a biocide requires contact between the biocide and the surface of an organism via the environmental media. For internal exposure to occur, the biocide must penetrate the organism's cellular walls, membranes, or other barriers. Bioavailability of silver is likely a function of its form, the chemical makeup of the environment, and the organism.

**Table 2. Solubility product constants for various silver compounds.**<sup>12,13</sup>

Silver compound	Formula	Solubility product constant (K <sub>sp</sub> ) at 25°C
Silver	Ag	Insoluble
Silver sulfide (α-form)	Ag <sub>2</sub> S	6.69 x 10 <sup>-50</sup>
Silver sulfide (β-form)	Ag <sub>2</sub> S	1.09 x 10 <sup>-49</sup>
Silver arsenate	Ag <sub>3</sub> AsO <sub>4</sub>	1.03 x 10 <sup>-22</sup>
Silver iodide	AgI	8.51 x 10 <sup>-17</sup>
Silver phosphate	Ag <sub>3</sub> PO <sub>4</sub>	8.89 x 10 <sup>-17</sup>
Silver bromide	AgBr	5.35 x 10 <sup>-13</sup>
Silver chromate	Ag <sub>2</sub> CrO <sub>4</sub>	1.12 x 10 <sup>-12</sup>
Silver oxalate	Ag <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	5.40 x 10 <sup>-12</sup>
Silver carbonate	Ag <sub>2</sub> CO <sub>3</sub>	8.46 x 10 <sup>-12</sup>
Silver chloride	AgCl	1.77 x 10 <sup>-10</sup>
Silver sulfate	Ag <sub>2</sub> SO <sub>4</sub>	1.20 x 10 <sup>-5</sup>
Silver bromate	AgBrO <sub>3</sub>	5.34 x 10 <sup>-5</sup>
Silver nitrate	AgNO <sub>3</sub>	Highly soluble
Silver fluoride	AgF	Highly soluble

Increasing Solubility

The biocidal nature of silver is attributed to the physicochemical properties of the silver ion. The biocide function of silver metal or silver nanoparticles (AgNPs) is due to the presence of silver oxide on the metal surface.<sup>14</sup> It should be mentioned that if AgNPs adhere to an organism's external surface and release silver ions, the concentration of silver ions in the immediate vicinity of the organism might be higher than that in the surrounding medium. This "local" silver concentration is more relevant than the overall silver concentration, but it is challenging to measure. From the results of toxicity tests, the release rate of silver ions generally decreases with increasing particle size, due to the surface-volume relationship. Release of silver ions from nanosilver is also enhanced in oxidative conditions. The bioavailability and toxicity of AgNPs for bacterial and mammalian cells increases with increasing concentration of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).

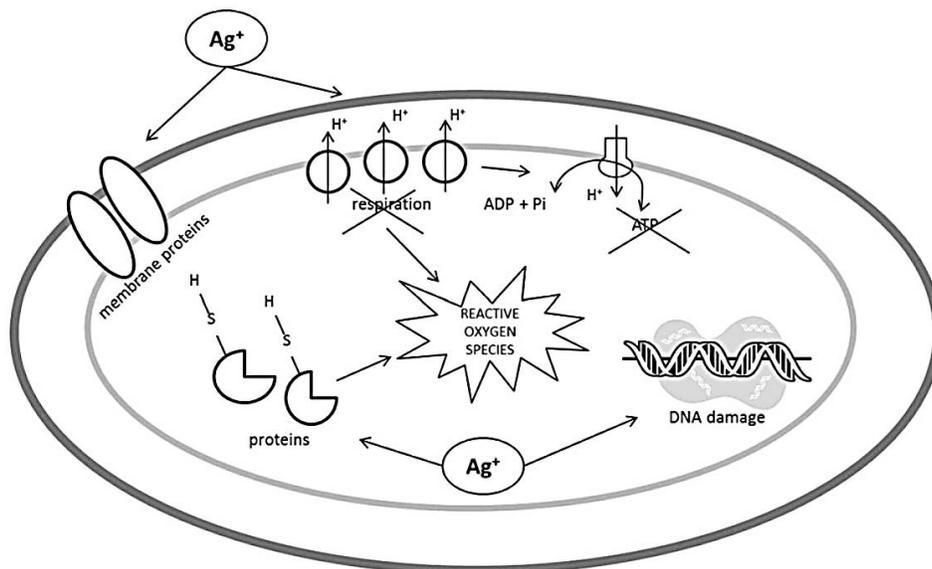
In addition to the concentration of Ag<sup>+</sup>, different attributes of an organism can influence bioavailability of silver biocides. The type of organism, its structure, and its physiology are key determinants of its biocide uptake mechanism. Whether the organism is prokaryote (a microscopic single-celled organism without a distinct nucleus or other specialized organelles) or eukaryote (an organism consisting of a cell or cells with a distinct nucleus), its cell size, cell wall or membrane construction, type of circulatory system, respiratory physiology, and other major aspects of its physiology can play important roles in the biocide uptake process. Similarly, the properties of water, including trace inorganic and organic matter content, will play important roles in changing the bioavailability of silver. This likely happens through aggregation of AgNPs and complexing of nanosilver or silver ions with organic or inorganic materials to form larger particles or insoluble precipitates.

Many ligands exist for silver ions, including inorganic ligands (chloride, bicarbonate, thiosulfate), simple organic ligands (amino acids and ethylenediaminetetraacetic acid, EDTA), and complex polydispersed organic ligands (humic and fulvic acids). Among sulfide (S<sup>2-</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>), Cl<sup>-</sup>, phosphate (PO<sub>4</sub><sup>3-</sup>), and EDTA, S<sup>2-</sup> is the most effective ligand in reducing AgNP toxicity to nitrifying bacteria.<sup>15</sup> Silver binds very strongly with sulfide (S<sup>2-</sup>) and only forms relatively insoluble AgCl with the chloride anion (Cl<sup>-</sup>). The abundance of Cl<sup>-</sup> favors the formation of soluble silver chloro complexes. In seawater, the high ionic strength and high Cl<sup>-</sup> content can lead to the formation of nanosilver clusters, and/or the formation of soluble silver chloro complexes; either process can dominate depending on the water chemistry, presence of organic matter, and AgNP surface treatment.<sup>16</sup>

### C. Biocidal Activity of Silver Ion

Silver ions are highly toxic to all microorganisms, probably due to poisoning of the membrane respiratory electron transport chains and components of DNA replication.<sup>17</sup> Silver ion affects the function of membrane-bound enzymes, such as those in the respiratory chain.<sup>18</sup> It has been shown that after Ag<sup>+</sup> treatment, DNA loses its replication ability and proteins become inactivated.<sup>19</sup> The antimicrobial action of Ag<sup>+</sup> is closely related with its interaction with the thiol group in enzymes and proteins. Recent work showed that Ag<sup>+</sup> treatment promotes reactive oxygen species (ROS) production, which results in an enhanced antibacterial effect, as ROS are highly toxic oxidants that cause damage to proteins, DNA, RNA, and lipids.<sup>20</sup> An illustration of some proposed antimicrobial

mechanisms of silver is shown in Figure 1. Detailed discussion on the mechanism of the antimicrobial actions of the silver ion can be found in references 21 and 22.



**Figure 1. Antimicrobial effects of Ag<sup>+</sup>: Interaction with membrane proteins, blocking respiration and electron transfer; inside the cell, Ag<sup>+</sup> ions interact with DNA, proteins, and induce ROS production.** Reprinted by permission from: Nature/Springer/Palgrave.<sup>21</sup>

#### D. Uptake and Biocidal Activity of Nanosilver Biocide

Bacteria readily take up nanosilver, which is consistent with its well-known antibacterial properties. It has been shown that only oxidized AgNPs function as biocide (reduced nanosilver is easily oxidized).<sup>14</sup> The antimicrobial effect of nanosilver is likely due to a combination of nanosilver, which can anchor to and penetrate the cell wall, and the silver ions that are chemisorbed on the surface.

Nanosilver can anchor and penetrate the cell wall of gram-negative bacteria. It has been suggested that this could increase its permeability and result in uncontrolled transport of materials. It has also been proposed that the antibacterial mechanism of nanosilver involves the formation of free radicals that damage the membrane. Furthermore, others have proposed a synergistic toxic effect in which nanosilver is adsorbed to the bacterial cell wall surface and silver ions move into the cells and produce ROS. Experimental results have provided strong support to the anchoring function of nanosilver. Pal and his coworkers evaluated the toxicity of nanosilver with various different shapes along with AgNO<sub>3</sub>. It was found that truncated triangular nanoparticles (with [111] facet) exhibited the strongest antibacterial activity. Transmission electron microscopy (TEM) showed that many triangular nanoparticles adhered to the cell surface.<sup>23</sup> Though not a conclusive study, the mechanism of AgNPs as a disinfectant has been summarized in some references.<sup>24</sup>

#### E. Human Exposure and Toxicity

Due to the long history of silver usage as a biocide and lack of known toxic effects, silver is generally considered safe to humans at the effective biocidal level. However, the growing use of nanosilver and silver colloid products has raised some concern recently. Some highlights on human exposure are summarized below and more detailed information can be found in references 6, 7, and 25.

The degree to which silver exposure leads to absorption, distribution, metabolism, or excretion in humans depends on particle properties and the route of exposure. The major route of silver exposure is through the inhalation of silver dust typically generated in various manufacturing processes. Other routes include dermal absorption, e.g., contact with jewelry, photographic, pharmaceutical, and/or wound care products. Exposure can also occur via oral ingestion, especially when incorporated into smoking deterrent products, such as chewing gum or throat lozenges. Once taken into the body, silver can subsequently cross biological barriers to accumulate in tissues, including lungs, liver, kidneys, stomach, brain, and blood. In animal studies, elevated silver concentrations of silver have been found

in the lungs and blood following exposure through inhalation. Whether silver can cross the blood-brain barrier in humans is controversial. No evidence to date indicates that AgNPs, even those as small as 1–2 nm, can penetrate the blood-brain barrier in mammals. When ingested, exposures to nanosilver appear to result in lower relative absorption and subsequent dose compared to other exposure pathways. Silver has been demonstrated to cross the intestinal barrier following ingestion exposure. Limited animal study data suggests that silver can be excreted slowly through feces and to a lesser extent, through urine. The limited data for nanosilver suggests that particle characteristics, including surface modification, affect whether nanosilver is absorbed or excreted following ingestion. In spacecraft, the exposure route of highest concern is through oral ingestion.

Silver has been used as the primary drinking water biocide in some of the international space systems, including the Russian Mir Space Station and the Russian Segment of the International Space Station. NASA is considering the use of silver as the primary potable water biocide for future exploration missions. A critical review of studies examining the exposure-related health effects of silver and silver compounds<sup>26</sup> concluded that, the most notable adverse health effect is argyria and/or argyrosis, the blue-gray discoloring of skin; metallic silver has minimal effect on the human body and soluble silver compounds are more likely to produce argyria and argyrosis. These types of studies, in addition to various animal studies, Environmental Protection Agency (EPA) and World Health Organization (WHO) guidelines, have been used to develop the Spacecraft Water Exposure Guidelines (SWEGs).<sup>25</sup> The SWEGs have been established for exposures of 1, 10, 100 and 1000 day class missions. Allowable concentration of silver in the drinking water may change slightly depending on mission duration. The exposure concentrations decrease accordingly as the mission duration increases. For 1, 10 and 100-day missions, the SWEGs are set at 5.4 (rounded to 5), 7.5 and 0.6 part per million (ppm) per day, respectively. For 1000-day class exploration missions, the maximum allowable silver concentration is set at 0.360 ppm per day, rounded to 0.400.

#### **F. Resistance to Silver Biocide**

There are not many studies on the biocidal resistance to silver. For the studies performed, most were not considered long enough to create resistance. However, bacteria are the most adaptive organisms known and have been shown to develop resistance to the spectrum of bactericidal agents, including antibiotics and heavy metals. Many metal resistance mechanisms in bacteria are recognized.<sup>27</sup> Bacteria can generate cell surface proteins that bind heavy metals, producing a barrier to metals entering the cell. Other metal detoxification proteins are produced in the cytoplasm of bacteria and other organisms. These proteins are products of single genes that can easily be amplified to develop increased metal resistance. Bacteria also can exclude silver that has reached the cell's interior through efflux pumps. These pumps are able to bind to the silver ions and transport them to the cell surface where they are ejected. Plasmids that encode resistance for metals, including silver, have been isolated from bacteria.<sup>28</sup> Development of resistant strains can be expected when the exposure continues for several years. Such was the case in the extended study of the effects of silver/copper disinfection on *Legionella* in a hospital water system.<sup>29</sup> A detailed review on the bacterial resistance to silver can be found in references 30 and 31. Possible resistance mechanisms are proposed, but experimental work failed to produce strong support for them. A thorough understanding of silver resistance is yet to be achieved.

To cope with silver resistance, the following recommendations have been made: (1) Identify a different disinfectant that will complement the silver biocide system and alternate them on a regular basis, (2) employ a method to periodically eliminate the entire bacterial population, (3) where applicable and possible, drain, clean and shock the water system with an appropriate disinfectant. Terrestrially, such shock chemicals have included: chlorine, ozone, and/or another aggressive disinfectants. As it is often difficult to completely sterilize the system, it is generally recommended to use strategies 1 and 3 in combination.<sup>32</sup> In spacecraft systems, the following multi-barrier strategies have been used: periodic system draining for returned vehicles, system flushing or “shock” with high concentrations of biocide, especially prior to first use, point-of-use filtration, and high temperature sterilization. High concentrations biocide “shock”, however, cannot be considered as a strategy against biocide resistance, unless a different biocide is used.

### **IV. Silver Dosing Systems: State-of-the-Art**

For potable water biocide applications, the silver ion supplied should be sufficient to maintain the microbial integrity of the water without exceeding the exposure limits for the crew throughout the mission. For long duration missions, silver losses can be expected as water is consumed and reprocessed for use. In addition, losses of silver biocides can also occur due their reactions with wetted materials of construction, and other interactions, such as adsorption and/or uptake by microbes and organic and inorganic materials in the system. These losses might be

appreciable especially during missions with long periods of dormancy. To meet requirements for exploration, an effective and robust silver dosing/delivery system will be needed.

Considering the long history of silver ion as a biocide and the renewed interest in silver, there are surprisingly few publications on silver ion delivery methods. However, a patent search proved to be fruitful. The following section provides a short review on silver delivering/dosing systems.

## **A. Silver Coated Filtrating Media**

Metallic silver was one of the first silver biocides considered for water treatment. To increase the contact surface, silver can be used to coat filtrating media, such as sand and activated carbon. A number of patents, cited and summarized below, provide details on the application of coating media with silver as a means of dosing silver as part of a water treatment system.

### *1. Silver Coated Sand*

In US patent 1642089 (1927), Schreier described a method to coat sand particles with silver, and use it as a filtration medium to sterilize liquid for human consumption.<sup>33</sup> A formula for preparation of the silver coating is the following: 7 parts by weight of 0.1 normal solution of silver nitrate are diluted with 3 parts of distilled water. Then 0.3 parts of a 40% formaldehyde solution is added into the mixture. Afterwards, 4.7 parts of 0.1 normal ammonia solution are added and mixed under agitation. This solution is mixed with washed and cleaned quartz sand while stirring. After a short time, the liquid and the grains darken. The amount of sand or its grain size was not specified in the patent. No example is given in the patent.

In US patent 1,988,246 (1935), one of the early patents on the “oligodynamic action” of silver biocide, Krause introduced a two-step process for water sterilization.<sup>34</sup> First, the contaminated water (with B. Coli, half million communities per cubic cm) was filtered through silver coated quartz sand; the sand (300 grams) was coated with 30 grams of silver by wetting it with silver nitrate solution and then heating in a muffle furnace at 400°C. The quartz sand was placed in a suction-filter and 5 liters of contaminated water were passed through per minute. The filtration did not completely filter out the bacteria and still contained 15,000 bacilli per cubic cm. Second, the water was left to stand in a container and, after 10 hours, complete sterility was ensured. Though not specified, the sterilization was likely achieved by the action of silver ion released from the silver coated sand. This setup was used to process 1500 liters of water and achieved “total” sterilization, as shown in the examples.

### *2. Activated Carbon with Impregnated Silver*

Activated carbon is one of the most used filtration materials. It can be impregnated with an aqueous AgNO<sub>3</sub> solution. After the water is evaporated and the product is heated to a higher temperature, the AgNO<sub>3</sub> will be converted to metallic silver. This procedure often results in an impregnation that is not very uniform, due to the premature reduction of AgNO<sub>3</sub> by carbon and the formation of large silver crystals.

In US patent 3,294,572 (1966), Piccione *et al.* disclosed a method to prepare a more uniform silver impregnated carbon.<sup>35</sup> First, the activated carbon was soaked in a strongly acidic solution of AgNO<sub>3</sub>, then the slurry was heated at 70 to 80°C to evaporate water until the carbon was just wet; then, it was transferred to a flask and heated at higher temperature (up to 500°C) in a nitrogen atmosphere to form metallic silver.

Silver impregnated active carbon, when properly prepared, has the potential for widespread use in sterilization and purification of liquid; yet, due to organic substances accumulated on the surface of the material, these filter materials can be rapidly spent, and their applications are limited. US patent 4,045,553 (1977) disclosed a process to restore the sterilization and purification properties of these materials through periodical treatment with steam.<sup>36</sup> The surface fouling of activated carbon filtering materials is similar to heterogeneous catalyst deactivation, though possibly in a less complicated manner.<sup>37</sup> It is not surprising that similar techniques are used for the regeneration of these materials.

## **B. Silver Compounds with Various Solubilities**

The use of solutions of silver compounds, as a source of silver ions, has been suggested. In some cases, the compounds are more toxic than silver ion itself; but mostly, it is difficult to dissolve at a rate sufficient to reach, but not exceed, the required silver biocide concentration. Nevertheless, different silver compounds have been incorporated into water filtration systems.

### *1. Silver Chloride, Silver Oxide, and Silver Sulphocyanate*

In US patent 1,473,331 (1923),<sup>38</sup> H. Bechhold disclosed filters and filtering systems to prevent or retard microbial infection by impregnating filtering masses, with insoluble or low solubility noble metals or their compounds. The suitable filtering materials include diatomaceous earth, cellulose, and clay. The filtering systems, having beds or layers of sand, gravel, or coke, were utilized for filtration on a large scale. They retained micro-

organisms for a certain time, yet the microorganisms can grow through the pores of the filters, so the filtered water would become contaminated within a few days. To prevent microbial growth through, disinfectants were used, including silver, silver chloride, silver oxide, and silver sulphocyanate. Excellent results reported when activators, such as gold and platinum, were also used. As an example, a diatomaceous earth filter material was impregnated with 2% silver and a small fraction of platinum. Water contaminated with B. Coli was passed through filters with and without metal treatment. The untreated filtrate remained sterile for only two days, while the treated filter supplied sterile water for a significantly longer duration. A similar effect was obtained when silver chloride was used as the disinfectant with gold as the activator.

For these systems to achieve effective filtration and disinfection, the impregnation method is considered important. The impregnation process should ensure a uniform distribution and limit the leaching of disinfectants within the filtering mass. For example, a filter was first treated with vaporized ammonium chloride, which precipitated uniformly in the pores of the filter. Then, the filter was treated in the vacuum with a silver nitrate solution to allow  $\text{AgNO}_3$  to penetrate into all pores.  $\text{AgCl}$  was precipitated and fixed into the filtering mass in uniform distribution. Another method was to soak the filter with a salt of low osmotic pressure, and then bring it into a solution of higher osmotic pressure. The two will react without forming a semi-permeable membrane that leads to uniform impregnation of disinfectant throughout the filter. For instance, a filter is first soaked with a diluted solution of  $\text{AgNO}_3$  and brought into a solution of sodium chloride (with higher osmotic pressure). The filter will be uniformly impregnated with  $\text{AgCl}$ .

### 2. Silver Chloride, Silver Sulfide

In US patent 2,595,290 (1952),<sup>39</sup> D. H. Quinn discloses the purification of water by means of a two-step processes: the first step is mechanical filtration, preferably using a ceramic filter of fine porosity, such as described in patent US 2,566,371;<sup>40</sup> in the second step, which combines adsorptive and chemical treatment, the water is passed through a three component system: a granular mass comprising an admixture of adsorptive granules, granules of an ion exchange synthetic resin, and granules coated with a bactericide of very low water solubility.

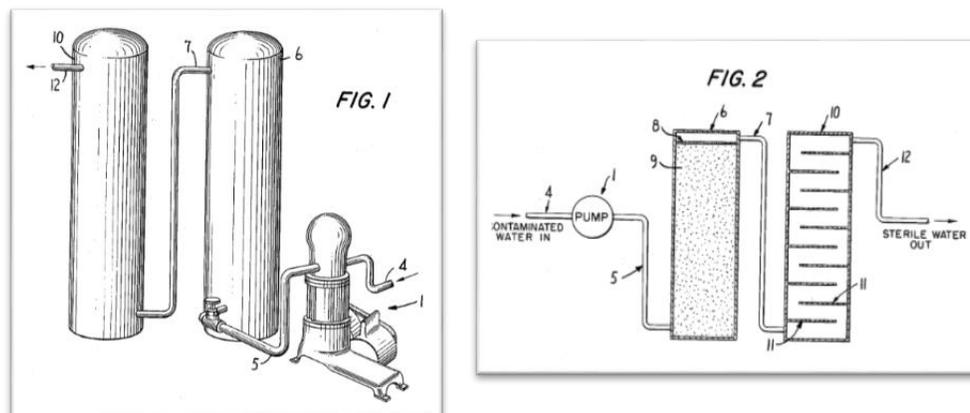
In the first step, mechanical filtration is used to remove solid particles and bacteria from the water. In the second step, the combined adsorption and chemical treatment, each one of the three components provides a complimentary function. The adsorptive granules act by capillary action to remove impurities such as chlorine, bacterial toxins, and others that impart objectionable odors and taste. For this function, both activated carbon and silica gel can be used, with activated carbon being the preferred material. The ion exchange granules act chemically on similar impurities. The combination makes the process more effective. For the final step, a slightly soluble bactericide is used to coat a certain portion of granules. This step renders the water in the apparatus sterile for an extended period.

The coating itself is applied to only a few of the filter granules, because the coated granules have little adsorptive capacity. Carbon granules or siliceous material, such as fine sand, can be used as silver carrier material. The loading of the bactericide should be sufficient for a long lasting effect. Bactericide can also be used in granular form, if suitable mechanical properties are achieved, rather than being applied to surface of the carrier granules. The preferred bactericide for these applications is silver chloride, however the use of silver sulfide and other compounds are suggested in the patent. When using more soluble compounds are used, such as silver chloride or silver oxide, careful control of the amount of the compound dissolved may be required to ensure silver concentrations to not exceed the limits for drinking water. Moreover, some compounds that may be applied, e.g., silver thiocyanate, are extremely toxic. Thus, processes incorporating these types of compounds would likely require an additional step to removal of excess biocide. On the other hand, other compounds which may be considered, such as silver sulfide, are extremely insoluble. So, measures may be required to ensure sufficient silver ion concentrations can be achieved to establish complete sterilization.

### 3. Silver Bromide

Pall *et al.*,<sup>41</sup> in US patent 3,257,315 (1966), claims to supply silver ions to water, intended for human consumption, in an amount sufficient to obtain complete sterilization without exceeding the toxic concentration limit and with enough silver supplied to the water to serve as a reserve after sterilization, to prevent further contamination. The inventors claim that both concentration control and subsequent contamination elimination can be achieved in one step. The silver source used is  $\text{AgBr}$ , in a "surface condition," and the contact time should be sufficient to dissolve enough  $\text{AgBr}$  to ensure a silver ion concentration of 10 to 50 ppb, preferably at least 20 ppb. To achieve the large surface area of  $\text{AgBr}$ , it can be mixed with a filter media with large surface area, such as sand, charcoal, diatomaceous earth, among other examples, to form a filtration bed or column, through which water can be flowed. Similarly, the  $\text{AgBr}$  can be made into tablets, with suitable extender and binder. These tablets can then be placed in the water, inside a water permeable container preventing solid particles of  $\text{AgBr}$  from escaping.

In the example of this patent, AgBr was coated on sand at 550°C with stirring to ensure uniform coating. The coated sand was placed in a tower as shown in Figure 2. Water is pumped into the bottom of tank (6), and emerges with 10 to 50 ppb silver at outlet (7), passing to the bottom of storage tank (10) and emerging finally from the system in purified and sterilized condition. The water is retained for sufficient time to allow sufficient silver ion to dissolve in tank (6) and to kill all bacteria in tank (10). For example, contaminated water containing *E. coli* was passed through the bed, slowing at room temperature, to ensure a contact time of 20 minutes and was passed through a retention tank with a retention time of 2 hours. The water emerging from the bed was tested, and found to be completely sterile. The concentration of silver in the water emerging from the retention tank was 17 ppb.



**Figure 2. Illustration of a combination pump and sterilization unit (left) and its cross-sectional view of the sterilization unit from US patent 3,257,315.<sup>32</sup>**

### C. Silver-Containing Ion Exchanger

Ion exchange technology is currently being used in the iodine biocide system in the US segment of the ISS. In these systems, a selected ion exchange resin is loaded with biocide through exposure high concentration biocide solutions. The selectivity of the resin is based on an interplay of weak charge interactions, ion size and concentration. When the loaded resin is exposed to solutions with different ion strength and/or affinity, the biocide bound to the resin is exchanged and released into the bulk solution. The rate of release can be predicted with reasonable certainty in simple water solutions under stable environmental conditions.

Four types of silver loaded ion exchanger have been disclosed in the patents the authors identified. Ion exchange resins have been used to serve as higher surface media for metallic silver, or provide silver through cation ion exchange process, or mediate silver ion release through chelating function of resin sites. Silver ion exchange resin have also been incorporated into composites to improve their structure integrity and release properties.

#### 1. Anion Exchange Resin

G. P. Ham in US patent 2,434,190 (1951)<sup>42</sup> discloses the preparation of a “silvered” anion exchange resin. An anion exchange resin, in the sodium form, may be treated with a  $\text{AgNO}_3$  solution to load the resin with silver ions. The resin is then treated with a reducing agent such as potassium metabisulfite to form metallic silver. The incorporation of the “silvered” anion exchange resin enhances the resistance to bacteria of elastomers, such as those used in vehicle tires, rubber insulation, and water hoses.

#### 2. Cation Exchange Resin

W. Juda, in US Patent 2,692,855 (1954),<sup>43</sup> discloses a cation exchange resin in a silver ion form for disinfection of water. For example, a cation exchange resin in the hydrogen form may be treated with a silver salt solution to exchange silver ions for hydrogen ions, thereby producing a resin for disinfecting water. However, it is necessary to minimize release of silver ion to a safe level by passing water first through a cation exchange resin in the hydrogen form to demineralize the water.

#### 3. Chelating Resin

G. L. Marchin and J. L. Lambert,<sup>44</sup> in US patent 5,366,636 (1994), disclosed a method that uses a chelating resin containing an iminodiacetate acid group at the metal chelating sites (Trade name Chelex by Bio-Rad™), in order to minimize the release of silver ions to a safe level. The resin composition contains less than 1 silver ion for every two iminodiacetate groups. The silver ions are retained within the resin bead while effectively killing microorganisms and/or removing iodide from the water. As a comparison, silver sulfonic acid resin and silver-zeolites have also

been prepared. Under the testing conditions described in the patent, after passing the Ag-Chelex resin, the free silver ion concentrations of eluates is  $0.9 \times 10^{-5}$  M using distilled water, and less than  $1 \times 10^{-6}$  M using tap water containing  $1 \times 10^{-5}$  M potassium iodide (KI), which correspond to 900 and 100 ppb silver ion, respectively. The Ag-sulfonic acid resin and Ag-zeolite releases 100 to 10,000 times more silver ion under the same test conditions.

#### 4. Inorganic Ion Exchanger-Based Biocidal Composite

Like ion exchange resins, silver containing inorganic ion exchangers have also been considered for biocidal applications. For example, zeolite particles of various sizes can be treated in a solution with silver ion at a pH that does not destroy the crystal structure of the zeolite.<sup>45,46</sup> Unlike polymer resins, inorganic ion exchangers lack structural integrity for long-term stable release. In addition to silver ion release, the dusting and loss of zeolite powder can also result in a large concentration variations in the silver elution.

US Patent 4,911,898 discloses zeolite particles,<sup>47</sup> incorporated into polymer articles made of Polyester or Nylon 6 to improve the mechanical properties of the ion exchanger. It is also mentioned that silver ion in the zeolite ion exchange should be kept below its saturation capacity. Otherwise, surface precipitation of insoluble species (such as  $\text{Ag}_2\text{O}$ ) will occur, which results in poor bactericidal performance. To avoid this, metal ions should be supplied from a dilute solution through repeated processes.

Another inorganic ion exchanger investigated was zirconium phosphate, a well-known inorganic ion exchange material.<sup>48</sup> Silver-modified zirconium phosphate (Ag-ZrP) has been studied as an antimicrobial agent,<sup>49</sup> as well as a photocatalyst.<sup>50</sup> In international patent application WO2011114976,<sup>51</sup> the inventors disclose a polyamide resin composition containing Ag-ZrP to achieve continuous long term silver ion release, at a concentration that is effective for antimicrobial treatment and safe for human consumption. The chemical composition of Ag-ZrP has the base formula:  $\text{Ag}_a\text{M}_b\text{Zr}_c\text{Hf}_d(\text{PO}_4)_3 \cdot n\text{H}_2\text{O}$ , where M represents an alkali metal ion, an alkaline earth metal ion, ammonium ion, hydrogen ions, or another oxonium ion; a, b, and c are positive numbers and their values are restricted by the total charge being neutral. The 3-D crystalline zirconium phosphate is the preferred structure for this application, due to its superior thermal and chemical resistance. Silver-substituted hexagonal zirconium phosphate, is claimed to exhibit excellent antibacterial properties, durability, and ion selectivity. In addition, the compound also exhibits superior properties during resin processing. Several silver-containing antibacterial agents were synthesized, blended with various resins, and made into plates and pellets. Various samples have been tested for their silver release properties. Some compositions provided sustained release up to 90 days with daily water replacement.

#### D. Electrolytic Generators and Electrochemical Method

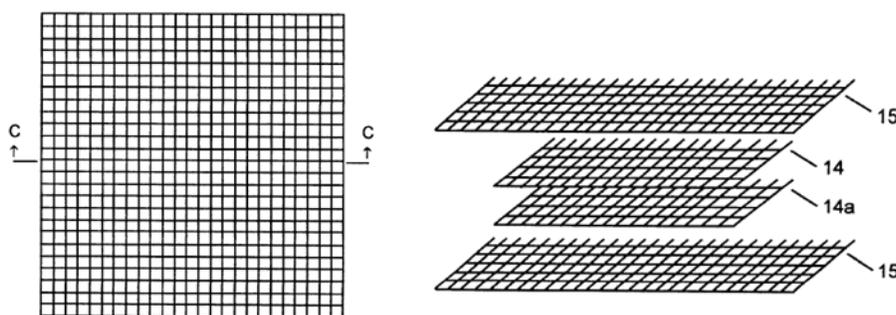
Another proposed method for silver dosing is via electrolytic processes. Electrolytic silver ion generators are usually composed of a negatively charged cathode and a positively charged anode made of the metal to be ionized. The electrodes are contained in a chamber or flow cell containing the water to be disinfected. A direct current (DC) power source provides a current that causes the metal, such as silver, in the anode to ionize and dissolve in the water. The concentration of metal ions in the water leaving the electrolytic cell depends on the current and water flow rate past the electrodes. Other factors that affect the ion release rate have been described and may need additional investigation to achieve a highly reliable dosing system. A description of some of the electrolytic dosing devices that have been investigated are provided below.

One of the earlier examples of silver dosing via an electrolytic method is given in US patent 2,046,467 (1936).<sup>52</sup> The patent describes a process to supply ionic silver to water by electrolysis. It also suggests that it is possible to remove excess silver from solution by introducing a less noble metal. A similar method was considered by NASA for its Apollo spacecraft water systems.<sup>53</sup> The developed units were small and self-contained, with a promised battery life of 9000 hours. Silver concentrations between 50 to 200 ppb were obtained, varying with the water flow rates. The device was shown to be effective against specified microbial challenges. However, loss of silver through interactions with wetted materials (aluminum) was an issue, and thick silver plating was used to address it. The device was never used on Apollo. NASA has also invested in electrolytic techniques such as the silver dosing method for the Space Station Internal Thermal Control System (ITCS) fluid. In 2001, Cole *et al.* proposed an electrolytic silver ion generator using a silver electrode system operated with pulsed polarity switching to minimize contamination buildup on the electrodes. Preliminary testing showed the device capable to rapid reduction of microbial populations in the ICTS fluid matrix.<sup>54</sup> Material compatibility problems and concerns of silver loss also existed in this design. Ultimately, a different biocide system was selected for this application. More recently, NASA began investigating electrolytic silver dosing devices for microbial control of potable water system being considered for long duration missions.<sup>55</sup> Early feasibility testing has been performed on the dosing device and feed-back control

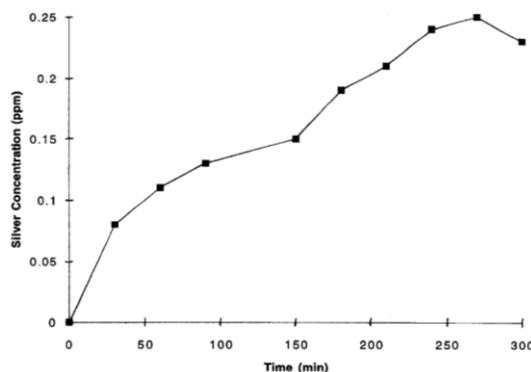
mechanisms. These tests continue to suggest the viability of the approach, but work is still needed to resolve issues of material compatibility, sensing, and electrode fouling.<sup>56</sup>

A different approach is offered in US Patent 6287450. The proposed device provides an electrochemical method where water is purified with silver released from an immersed galvanic cell. The galvanic cell has a silver anode, which is electrically connected to a cathode made from a metal with higher electrochemical potential, such as platinum and palladium. Figure 3 shows the top view and a cross-section view of the most preferred embodiment of the galvanic cell setup.<sup>57</sup> The figure depicts the layers of an anodic metal (14) positioned next to a cathodic metal (14a) sandwiched between two polyethylene or nylon layers forming a pouch.

In one of the examples, a strip of 2.5 cm by 5.0 cm silver metal and a 2.5 cm by 5.0 cm strip of platinized niobium expanded mesh was immersed in 200 mL of deionized (DI) water containing 5.25 ppm of sodium hypochlorite. The solution pH was 7.5. The silver and platinum strips were separated by a 0.5 mm thick polypropylene mesh and were electrically connected via a volt/ampere meter. The solution was agitated with a magnetic stirrer. The potential was 0.47 V and the current was 0.066 mA. The solution was analyzed for silver every 30 minutes using an atomic absorption spectrometer. The results are shown in Figure 4.



**Figure 3.** Most preferred setup for a galvanic cell from US patent 6287450. The left is the top view, and the right is the cross section view, taken at aspect line C-C.



**Figure 4.** A plot of the silver ion concentration as a function of time during the galvanic cell reaction between silver and platinum (US patent 6287450).

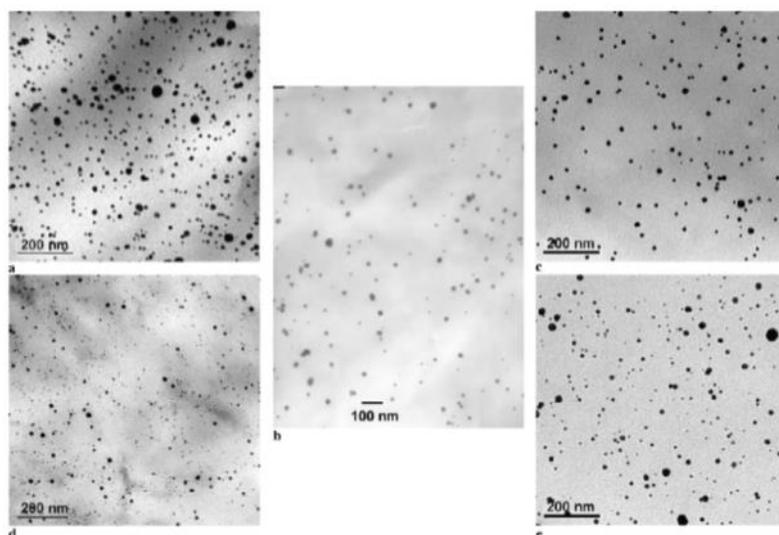
### E. Polymer Nanocomposites

One way to make metal ions available is by incorporating metal nanoparticles into a polymer matrix. In contact with an aqueous environment, polymer-embedded nanoparticles are known to release metal ions due to corrosion and dissolution.<sup>58,59</sup>

AgNPs release ions quite efficiently because of their large specific surface area. The generation of silver ions occurs on the surface of the particles. Traces of gold or platinum in the AgNPs improve the silver ion release because the Au/Ag or Pt/Ag galvanic couple results in an enhanced oxidation of the silver.<sup>60</sup> The polymer properties

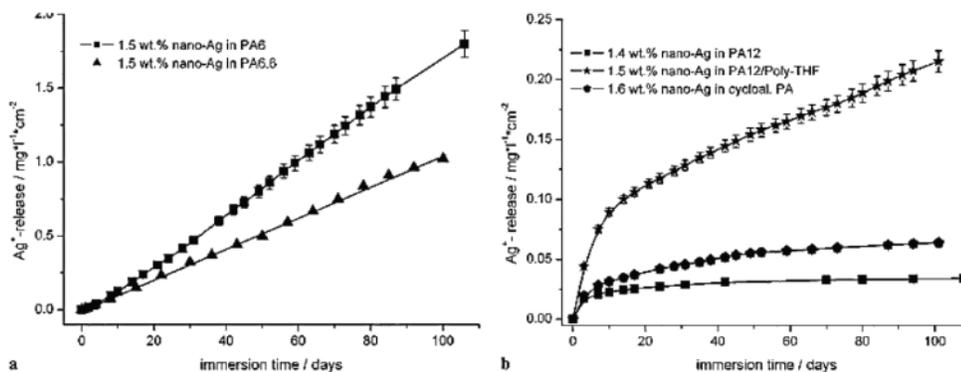
also influence the silver ion release. The silver ion release rate increases with decreased crosslinking of the polymer, decreased hydrophobicity of the polymer, and the decreasing crystallinity of the matrix.

Damm and his coworker<sup>58</sup> generated silver nanoparticles *in situ* in different polyamides by a thermal reduction of silver acetate during melting processing of the polymers. To prepare composites with a theoretical filler concentration of 2 wt%, 980 g of the polymer pellets were premixed with 31 g of silver acetate and then processed in a co-rotating twin-screw extruder. The processing temperatures ranged from 170 to 270°C for different polyamides. Figure 5 shows the transmission electron microscopy (TEM) micrographs of different polyamide/Ag nanocomposites. The long-term silver ions release increases with growing maximum water absorption of the polymer as well as the growing diffusion coefficient of water in the polymer.



**Figure 5. TEM micrographs of polyamide/Ag nanocomposites.**<sup>58</sup>

The silver ion release tests were done by an indirect method. To investigate the silver ion release from the polyamide/Ag nanocomposites, rectangular silver specimens were immersed in distilled water. At defined times, the immersion liquid was exchanged completely. The concentration of silver ion in the solution was measured by anodic stripping voltammetry. This method is described briefly here, but more details can be found somewhere else.<sup>61</sup> Figure 6 shows the ion release behavior of the different silver nanocompositions. For hydrophilic polymers, plasticized by water, the silver ion release is a zero-order process (Figure 6a). For more hydrophobic polyamides, the silver ion release is governed by diffusion (Figure 6b).



**Figure 6. Cumulative silver ion release from the polyamide/Ag nanocompositions.**<sup>47</sup>

## V. Silver Biocide Compatibility Studies for Spacecraft Systems

When using silver ion as a biocide, the choice of materials for the water system is important because surface reactions can reduce the biocide concentration below their effective range. There have been several investigations on this subject (Table 3). Alloys, such as stainless steel, Ni-based alloy, and titanium alloy, have been studied to determine the effect of the material on silver depletion. Different surface conditions were also compared to identify treatments to reduce silver loss. These studies were designed to represent the silver concentrations in potable water (200 to 500 ppb), and the conditional water (up to 500 ppm). Different surface (S) to volume (V) ratios, corresponding to the S/V range for water storage tank and tubing components in water distribution system were also examined.

Callahan *et al.*<sup>62</sup> studied passivated stainless steel 21-6-9 tubing and Inconel 718 coupons using a solution containing 500 ppb silver ion, at S/V ratios 4.59 and 0.14. The effects of acid passivation and silver plating, using 3 ppm silver ion solution (for 24 hours), was examined. These data suggest that silver loss rates are slower at lower S/V ratios. Although surface passivation was shown to have an effect on the silver depletion rate, the challenge in consistent passivation of small tubing must be overcome to achieve reliable results.

Roberts *et al.*<sup>4</sup> also compared acid passivated stainless steel 21-6-9, 316L, and Inconel 718 coupons (acid passivated) for their effect on silver loss in 500 ppb silver ion solution, at an S/V ratio 0.14. This study also included testing to assess microbial efficacy using microbes commonly found in spacecraft water systems. Although all three metals showed silver loss greater than 10% in three days, significant variations were observed across different metal types. After 21 days, the residual silver concentration is about 12%, 30%, and 70% for Inconel 718, SS 316L, and SS 21-6-9, respectively.

Adam<sup>63</sup> further studied the effect of S/V ratio using acid passivated stainless steel 316L, acid passivated Inconel 718, and electropolished Inconel 718. Tests were conducted using 500 ppb silver ion solution and S/V ratios ranging from 0.2 to 8.2. This study clearly demonstrated that the silver depletion rate increases with increasing S/V ratio. In addition, it was shown that electroplating of Inconel 718 appeared to be an effective surface treatment to reduce silver depletion.

Beringer *et al.*<sup>64</sup> disclosed in US patent 8,685,257 some surface treatment methods to achieve long-term storage of silver biocide in potable water systems. Of the techniques explored, thermal oxidation at elevated temperature, such as 590°C for 2 hours, or with additional silver plating by immersion using 50 or 25 ppm silver ion solutions on Inconel 718 and stainless steel (E-Brite) coupons were shown to maintain a silver concentration about 0.35 to 0.39 ppm up to a year, at a low S/V ratio, corresponding to full water tank configuration.

Recently, Petala and her coworkers<sup>65</sup> studied several substrates, including Teflon, ethylene, propylene, rubber, stainless steel 316L with different surface treatments, stainless steel 15-5 pH, and Ti6Al4V in silver biocide solutions created by a silver ionization unit. Silver ion concentration of 0.5 ppm and 10 ppm were used. These concentrations correspond to the potable water and conditional water silver concentrations. A high S/V ratio of 5 cm<sup>-1</sup> was selected to intensify the silver deposition kinetics. It should be mentioned that a mineral-rich water formula, based on Russian ISS water, was used. All metallic samples resulted in complete or near complete depletion in the 0.5 ppm silver water, after 7 days of immersion. For the water with 10 ppm silver, the surface treatment had a greater impact on silver loss, with 316L passivated and electropolished surface resulting in much less silver loss (21%), compared to passivated 316L (95%). The XPS studies also showed that Ag metal is the silver form on 316L sample surfaces,<sup>66</sup> while oxidized Ag was present on the Ti6Al4V surface. The mechanism for the formation of the latter is yet to be determined.<sup>67</sup>

W. T. Wallace *et al.*<sup>9,68</sup> reported the effects of different surface treatments for Ti6Al4V and 316L on silver depletion using silver biocide solutions at different silver concentrations (0.4 ppm and higher). Both acid passivation and silver plating using high concentration (up to 500 ppm) silver solution can reduce silver loss rate for Ti6Al4V. In a related publication, M. Adami *et al.*<sup>69</sup> reported the results of a study of the silver biocide behavior in the Russian potable water delivered to the ISS by means of the European Automated Transfer Vehicle (ATV). The objective was to identify the cause of the silver ion concentration fluctuation/drop in sanitization and flight water during the water lifecycle from the producer to the ATV storage. The Russian ATV water, which is richer in minerals than the US water, is from the Regina Margherita water plant at the Societa Metropolitana Acque Torino premises. After the appropriate treatment with sodium fluoride (NaF), ionic and colloidal silver are added through an electrochemical process. Precipitates (e.g. AgCl) are removed using a 2-step microfiltration. Once produced, the water is transferred into on-ground Water Transport Tanks, made of passivated and/or electro-polished stainless steel 316L. Two important findings were reported: First, the chemical nature of the colloidal silver “nanoparticles” has been

clarified. They are actually micrometer sized colloidal particles of AgCl, likely with adsorption layers of ions. The colloidal particle sizes increase (from 1 to 3-5 micrometer), with increased silver concentrations. Second, analysis of 316L, cut from water tanks, showed that silver deposits on the internal 316L walls, irrespective of the surface treatment and that the deposition is not uniform, but localized on the spots rich in carbon. It was hypothesized that the organic carbon originated/associated with the 316L surface might play a role in the silver reduction.

**Table 3. Summary of the Silver Compatibility Studies.**

Study	Testing Material			Testing Condition		Silver Loss Rate	
	Composition	Geometry	Surface Treatments	Silver Solution	S/V (cm <sup>-1</sup> )	Quantitative	Qualitative
Callahan <i>et al.</i> , 2007	SS 21-6-9	Tube	passivated	0.5 ppm (AgF)	4.59	10-20%/day	high
			passivated & Ag plated	0.5 ppm (AgF)	4.59	10-20%/day	high
	Inconel 718	washer	passivated	0.5 ppm (AgF)	0.14	1.5%/day	med
Roberts <i>et al.</i> , 2007	SS 21-6-9	Coupon 10×10×1.5 mm	passivated	0.5 ppm (AgF)	0.14	3% 1 <sup>st</sup> day; 30% after 21 days	med
	Inconel 718	same	passivated	0.5 ppm (AgF)	0.14	>10% first day; 88% after 21 days	high
	SS 316L	same	passivated	0.5 ppm (AgF)	0.14	>10% 1 <sup>st</sup> day; 70% after 21 days	high
Adam 2009	SS 316L	washer	passivated	0.5 ppm (AgF)	0.2, 0.5, 1.0, 5.0, 8.2	90% loss: 411, 190, 180, 63 hours for S/V 0.2, 0.5, 1.0, 5.0	high
	Inconel 718	washer	passivated	0.5 ppm (AgF)	0.2, 1, 8.2	90% loss (days): 32.1 (0.2), 1.4 (1.0)	high
	Inconel 718	washer	electropolished	0.5 ppm (AgF)	0.2, 1, 8.2	90% loss (days): 108.3 (0.2), 17.7 (1.0), 0.5 (8.2)	med & high
Beringer <i>et al.</i> , 2014	Inconel 718	Test panels	thermal oxidized & Ag plated	0.35 ppm (AgF)	0.14	maintain about 1 year	low
	SS (E-Brite)	Test panels	thermal oxidized & Ag plated	0.39 ppm (AgF)	0.14	maintain about 1 year	low
Petala <i>et al.</i> , 2016, 2017, 2018*	SS 316L	Test Panels 76×12.7×1.6 mm	120 grit sanded passivated (P) passivated & electropolished (P&E)	Electrolytic Ag 0.5 ppm	5.0	near 100% loss for all samples after 7 days	high
	SS 15-5	same	thermal oxidized	0.5 ppm	5.0	100% loss after 7 days	high
	Ti6Al4V	same		0.5 ppm	5.0	100% loss after 7 days	high
	FEP & PTFE	same		0.5 ppm	5.0	> 60% loss after 7 days	high
	EPR	same		0.5 ppm	5.0	Near 100% loss after 7 days	high
*Russian water formula with high mineral content	SS 316L	Test Panels 76×12.7×1.6 mm	120 grit sanded passivated (P) passivated & electropolished (P&E)	Electrolytic Ag 10 ppm	5.0	Ag loss after 7 days: 316L P&E (21%) vs 316L P (94.75%) 316L (97%).	high
	SS 15-5	same	thermal oxidized	10 ppm	5.0	loss after 7 days: 78%	high
	Ti6Al4V	same		10 ppm	5.0	loss after 7 days: 100%	high
	FEP & PTFE	same		10 ppm	5.0	loss after 7 days: FEP 15%, PTFE 5%	med
	EPR	same		10 ppm	5.0	loss after 7 days: 60%	high
Wallace <i>et al.</i> , 2016, 2017	SS 316L	Washer	passivated	0.4 ppm (AgF) After 100 ppm for 24 hours	0.61	residual Ag at 28 days (ppb): 25 (control 350)	high
	Ti6Al4V	Panel 0.7×0.5×0.12 in	passivated by 20% HNO <sub>3</sub>	Same as above	0.15	residual Ag at 28 days (ppb): 225 (control 350)	med
	Ti6Al4V	Panel 0.7×0.5×0.12 in	Ag plated at 500 ppm	Same as above	0.15	residual Ag at 28 days (ppb): 325 (control 350)	low

## VI. Microbial Control during Dormancy

Maintaining biocidal activity during periods of extended unattended vehicle operations, commonly referred to as dormancy, is a challenge that must also be considered for future disinfection systems. For example, a major microbial contamination problem in the ISS potable water dispenser (PWD) unit occurred during a period of dormancy. Due to launch vehicle loading constraints, flight hardware was delivered to the launch site several months ahead of the actual launch date. The first PWD unit was required to be delivered 6 months prior to the launch of STS-126 at the Kennedy Space Center in November 2008. The PWD system remained unpowered and stagnant from the time of delivery until activation aboard the ISS. Although the final fluid disinfection treatment at the Johnson Space Center, using 20-30 ppm iodine, resulted in no detectable bacteria within the fluid lines at the time of disinfection, microbial growth occurred during the dormancy period and was identified shortly after activation when samples were drawn from the PWD for analysis.<sup>70</sup>

Future crewed missions beyond lower Earth orbit may include intermittent periods of dormancy. This has been identified as a critical problem for future missions, due to concerns of microbial growth or chemical degradation that would prevent water systems from operating properly when the mission begins. The mission requirement includes

the capability for life support systems to support crew activity, followed by a dormant period of up to one year, and subsequently for the life support systems to come back online for additional crewed missions. As such, it will be critical that the water system be designed to accommodate this dormant period.<sup>71,72</sup>

## **VII. Summary**

### **A. Biocidal Activity of Silver**

Silver ion is a powerful broad spectrum biocide that is relatively safe to humans. A complete understanding of the biocidal activity of silver is yet to be achieved, but there is a general agreement that silver ions demonstrate biocidal functions through a number of potential mechanisms. Spacecraft Water Exposure Guidelines have been set based on a variety of studies and should not exceed 0.400 ppm for 1000-day class missions. Silver resistance is a concern for spacecraft systems, especially for long-term applications. It may be important to take precautions to prevent the development of bacterial resistance to silver biocide through the use of a complementary biocide, alternating biocides on a regular basis, and periodically eliminating the entire bacterial population with a different biocide and/or sterilization by alternate means, e.g., ultraviolet radiation or heat.

### **B. Silver Ion Dosing Systems**

In order to introduce silver ion into the water system, several types of silver ion dosing systems have been reported in the literature: (1) silver-coated filtrating media, (2) silver-containing ion exchangers, (3) electrolytic silver ion generators and electrochemical methods, and (4) polymer/silver composites. In general, the dosing systems can be categorized into passive and active dosing systems. The passive systems, release silver ions through dissolution and/or exchange of silver compounds and/or complexes. For these systems, the release rate is considered to be a function of factors such as solubility, contact area, contact time, charge, ion size, temperature and solution chemistry. It is worth noting that activators, such as traces of gold and platinum, can be used to promote silver ion release to achieve “especially good” results. These dosing system options require additional development to ensure that efficient and highly reliable systems can be made available for spacecraft applications. In addition, the advantages and disadvantages of the various dosing approaches need to be better understood, traded, and ultimately down-selected for development into flight systems.

### **C. Silver Biocide Compatibility**

The choice of materials for the water system will be an important factor to ensure the success of silver as a biocide for spacecraft water systems. Due to the reactive nature of silver ion, its surface reactions on the wetted materials of construction can lower the silver below its biocidal effective range. Various studies have been conducted to investigate these surface interactions over conventional spacecraft materials, e.g., stainless steel, Inconel, Teflon and titanium, as well as, different surface treatments, e.g., acid passivation, silver plating, electropolishing and heat treatment. In general, more favorable results have been obtained at lower S/V ratios, with thermal oxidation, electropolishing and silver pre-treatment. Not surprisingly, some studies also indicated that some polymeric materials showed greater advantages over metallic surfaces. Additional work will be needed to establish a successful combination of materials and processing to mitigate the uptake of silver on time scales relevant to exploration-class missions.

## **Acknowledgments**

The authors would like to acknowledge funding from the Advanced Exploration Systems (AES) Life Support Systems (LSS).

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