# Investigation of Silver Electrochemistry Water Disinfection Applications

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McGill University
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Robert Niven
McGill Environmental Engineering Masters Candidate

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#### 1. INTRODUCTION

Modern water treatment technologies have been responsible for dramatic improvements in human health. However, in recent decades, their safety and applicability have been called into question. In an effort to provide safe, appropriate, effective and affordable water treatment alternatives, new and old technologies are being re-examined. Silver electrochemistry is being explored as a viable water treatment technology. This paper will analyze the municipal, consumer, industrial and socioeconomic development applications of silver electrochemistry. A comparison will be made with existing methods and recommendations will be provided for the uses of silver as a viable alternative to modern water treatment technologies.

# 2. BACKGROUND

The disinfectant properties of silver have been known for centuries (Laubusch 1971). History is full of examples in which silver has been used for its purification properties. According to Russell (1994), Aristotle advised Alexander the Great to boil water and store it in silver vessels to prevent waterborne diseases. Pioneers that crossed America placed silver coins in their water barrels. Vikings would line the hull of their ships with strings of silver and copper to prevent growth of algae and barnacles. Notably, modern ships still use silver and copper for the same purpose (Laubusch 1971). Although most early civilizations did not fully comprehend the antibacterial properties of silver, it was widely understood that adding silver to water increased clarity, reduced odor and improved taste. Until recently, silver water purification techniques had fallen out of favor for more fast acting methods such as chlorination.

Silver electrochemistry methods were reexamined in the 1960s when NASA developed an electrolytic silver ionizer to purify drinking water in the Apollo spacecraft. NASA now uses silver for the CO<sub>2</sub> chemsorption process on board the Challenger space shuttles and the international space station (NASA 2004). Today silver is used to prevent infections in burn patients, to prevent blindness in newborns, to make bacteria-free cosmetics, to disinfect water storage containers including swimming pools, to control Legionella bacteria in hospitals and to improve the performance of drinking water filters.

Recent research has also shown that silver may be used as an alternative to conventional municipal water and wastewater treatment processes.

#### 3. PHYSICAL PROPERTIES AND ABUNDANCE

Silver is a soft, noble, malleable metal. Table 1 outlines the physical properties of silver. It is stable in air and water but is highly reactive with sulphur compounds (Silver Inst. 2004). Its ore, Argentite, accounts for a large proportion of global mining activity. In 2003, 859.2 Moz of silver were produced. Silver can be extracted in its pure form, although 70% of silver is extracted as a byproduct of zinc, lead, gold and copper mining (Silver Inst. 2004). Mexico is the world's largest silver producer, ahead of Peru and Australia. Electronics, alloys, solders and brazing products account for the majority of silver demand. Water disinfection products account for a small proportion of the total silver industry.

Table 1: Physical Properties and Abundance of Silver (adapted from CRC 1997)

| Measure                   | Value  |  |  |
|---------------------------|--|--|--|
| Atomic Number             | 47   |  |  |
| Atomic Weight             | 107.868                                      |  |  |
| Oxidation States          | $Ag^+, Ag^{2+}, Ag^{3+}$ (unstable)          |  |  |
| Common Mineral Form       | Argentite, Ag <sup>2</sup> S                 |  |  |
| Total Content in Soils    | 0.03 – 0.9 mg/kg                             |  |  |
| Soluble Content in Soils  | 0.01 – 0.05 mg/kg in 1 N NH <sub>4</sub> AOC |  |  |
| Content in Sea Water      | 0.04 μg/kg                                   |  |  |
| Content in Fresh Water    | 0.13 μg/kg                                   |  |  |
| Content in Marine Animals | 3-10  mg/kg                                  |  |  |
| Content in Humans         | Blood: $< 2.7 \mu\text{g/L}$                 |  |  |
|                           | Bone: 1.1 mg/kg                              |  |  |
|                           | Liver: $<5-32 \text{ ng/g}$                  |  |  |
| Content in Animals        | 6 μg/kg                                      |  |  |
| Content in Plants         | 0.01 - 0.5  mg/kg                            |  |  |
| Content in Common Foods   | 0.07 – 20 mg/kg                              |  |  |
| Essentiality              | Plants: no                                   |  |  |
|                           | Animals: no                                  |  |  |

# 4. DISINFECTANT AND HEALTH PROPERTIES

Disinfection is the process of controlling microorganism and particulate levels to decrease the health risks to humans. Waterborne health risks (Table 2) include cholera, typhoid, diarrhea, intestinal worms, trachoma, schistosomiasis and legionella disease

(UNICEF 2004). Four main classifications of microorganisms are of concern in water disinfection: bacteria, protozoa, viruses and helminthes.

Table 2: Waterborne Disease-Causing Organisms (Metcalf & Eddy 1991)

| Organism                           | Disease                | Remarks                       |  |  |
|------------------------------------|------------------------|-------------------------------|--|--|
| Bacteria                           |                        |                               |  |  |
| Escherichia coli                   | Gastroenteritis        | Diarrhea                      |  |  |
| Legionella pneumophila             | Legionellosis          | Acute respiratory illness     |  |  |
| Leptospira                         | Leptospriosis          | Jaundice, fever               |  |  |
| Salmonella typhi                   | Typhoid fever          | Fever, diarrhea               |  |  |
| Salmonella                         | Salmonellosis          | Food poisoning                |  |  |
| Shigella                           | Shigelloisis           | Bacillary dysentery           |  |  |
| Vibrio cholerae                    | Cholera                | Heavy diarrhea, dehydration   |  |  |
| Yersinia enterolitica              | Yersinosis             | Diarrhea                      |  |  |
| Viruses                            |                        |                               |  |  |
| Adenovirus                         | Respiratory disease    |                               |  |  |
| Enteroviruses (67 types, including | Gastroenteritis, heart |                               |  |  |
| polio, echo, etc.)                 | anomalies, meningitis  |                               |  |  |
| Hepatitis A                        | Infectious hepatitis   | Jaundice, fever               |  |  |
| Norwalk agent                      | Gastroenteritis        | Vomiting                      |  |  |
| Reovirus                           | Gastroenteritis        | -                             |  |  |
| Rotavirus                          | Gastroenteritis        |                               |  |  |
| Protozoa                           |                        |                               |  |  |
| Balantidium coli                   | Balantidiasis          | Diarrhea, dysentery           |  |  |
| Cryptosporidium                    | Cryptosporidiosis      | Diarrhea                      |  |  |
| Entamoeba histolytica              | Amebiasis              | Diarrhea, bleeding            |  |  |
| Giardia lamblia                    | Giardiasis             | Diarrhea, nausea, indigestion |  |  |
| Helminths                          |                        |                               |  |  |
| Ascaris lumbricoides               | Ascariasis             | Roundworm infestation         |  |  |
| Enterobius vericularis             | Enterobiasis           | Pinworm                       |  |  |
| Fasciola hepatica                  | Fascioliasis           | Sheep liver fluke             |  |  |
| Hymenolepis nana                   | Hymenolepiasis         | Dwarf tapeworm                |  |  |
| Taenia saginata                    | Taeniasis              | Beef tapeworm                 |  |  |
| T. solium                          | Taeniasis              | Pork tapeworm                 |  |  |
| Trichuris trichiura                | Trichuriasis           | Whipworm                      |  |  |

Silver is a particularly effective bacteriostat (prevents the growth or reproduction of bacteria). Silver ions use three main mechanisms to control bacterial growth.

- a) Remove hydrogen atoms from sulfhydryl groups (-SH) on bacteria and viruses. Sulphur atoms then join and block cellular respiration and electron transfer.
- b) Inhibit DNA replication by interfering with DNA unwinding.
- c) Alter the bacterial membrane with enzyme mechanisms.

Silver poses no toxic effects to humans (USEPA 2001, WHO 1993); however, extreme cases of overexposure will lead to a cosmetic blue discoloring of the skin called Argyria (USEPA 1992).

#### 5. PRACTICAL APPLICATIONS

Recent changes to environmental standards and fundamental research discoveries have positioned silver electrochemistry as an emerging technique in the water treatment sector. Selected silver ion-based technologies in the consumer, industrial, municipal and socioeconomic development sectors have been described below to exhibit the emerging influence of silver in the water treatment field.

#### 5.1. CONSUMER PRODUCTS

The list of consumer products that are incorporating silver electrochemistry is steadily expanding. Samsung has recently released a line of washing machines, air conditioners, air purifiers and refrigerators that use the *Silver Nano Health System<sup>TM</sup>* technology (Samsung 2004).

Electricity is passed through the electrodes to generate Ag+ ions 2nd stage • Tap water then flows through the mechanism carrying the Ag+ ions to the tub Ag+ ions disinfect the 3rd stage 5th stage Ag+ ionized Aa+ ions act to water is prevent bacteria from released during . clinging onto the clean the wash and clothes and block their rinse cycle propagation in the tub

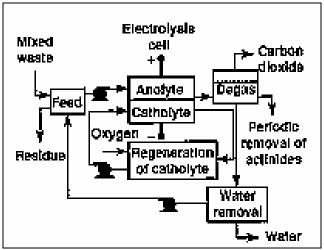
Figure 1: Silver Nano Health System<sup>TM</sup> Technology (Samsung 2004)

The Samsung's *Silver Nano Health System<sup>TM</sup>* technology uses a silver anode assembly to release silver ions into a bypass stream that is blended into the water supply to achieve better bacterial control than conventional systems. The slow acting but long lasting bacteriostatic effect of silver is well suited for these products.

#### 5.2. INDUSTRIAL APPLICATIONS

There is a specialized demand for silver electrochemistry-based technology in the industrial waste water treatment sector. *Mediated Electrochemical Oxidation* (MEO) units have proven to be valuable means of treating radioactive hazardous wastewater at ambient temperatures in very specific industrial processes (DWPF 1989). The US Defense Department (DWPF 1989), Chevron (Clarke & Foller 1990), Battelle Pacific Northwest (Molton et al 1988) and the Lawrence Livermore National Laboratory (Farmer et al 1992) have developed MEO processes to treat mixed wastewater streams containing radioactive, inorganic, organic and biological contaminants. Their chief benefit is the low temperatures required to effectively remediate hazardous wastes. However, the most sophisticated models are limited by low destruction rates. Typical destruction rates range from 3 to 12 L/day (Sequeira 1994).

Figure 2: Schematic of the MEO Process (Sequeira 1994)



The silver redox reaction is driven by electrolysis (Sequeira 1994). At the anode Ag<sup>+</sup> is oxidized to Ag<sup>2+</sup>. The opposite cathodic reduction is provided by the reduction of nitric acid, HNO<sub>3</sub>. Dissolved organics are converted into basic CO<sub>2</sub> and H<sub>2</sub>O components at ambient temperatures in the aqueous phase. Other metals including iron (II) may be used, although silver (II) provides the optimal results (Sequeira 1994).

Oxidation Anodic Oxidation: 
$$Ag^+ \leftrightarrow Ag^{+2} + e^-$$
 (1)

Reduction Cathodic Reduction: 
$$HNO_3 + 2H^+ + 2e^- \leftrightarrow HNO_2 + H_2O$$
 (2)

Nitric acid is regenerated by nitrous acid and oxygen.

$$2HNO_2 + O_2 \leftrightarrow 2HNO_3 \tag{3}$$

In the absence of organics, silver (II) complexes with nitrate.

$$Ag^{+2} + NO_3^- \leftrightarrow AgNO_3^+ \tag{4}$$

Examples of the destruction of Ethylene Glycol and Benzene (Sequeira 1994).

$$10 \text{AgNO}_3^+ + (\text{CH}_2\text{OH})_2 + 2 \text{H}_2\text{O} \leftrightarrow 10 \text{Ag}^+ + 2 \text{CO}_2 + 10 \text{HNO}_3$$
 (5)

$$30 \text{AgNO}_3^+ + \text{C}_6 \text{H}_6 + 12 \text{H}_2 \text{O} \leftrightarrow 30 \text{Ag}^+ + 6 \text{CO}_2 + 30 \text{HNO}_3$$
 (6)

# **5.2.1. APPLICATIONS**

Historically, hazardous waste has been incinerated or stored. Incineration of radioactive material produces volatile radionuclides including PuO<sub>2</sub>(OH)<sub>2</sub> and UO<sub>2</sub>(OH)<sub>2</sub>. Ion exchange technologies were used in conjunction with MEO processes at ambient temperatures to remediate mixed radioactive waste. Due to the intense public concern over the release of radionuclides into the environment, the MEO process is a feasible alternative that satisfies public scrutiny. As such, MEO processes have an integral role in the US Defense Department strategy to remediate the radioactive waste produced from over 30 years of US nuclear testing.

# 5.3. MUNICIPAL APPLICATIONS

Chlorine is the principal drinking water disinfectant due to its low cost, efficacy and simple application. Since its introduction as a water disinfectant in 1908, there have been countless lives spared from waterborne diseases including cholera and typhoid. The use of chlorine in drinking water has saved more lives than penicillin and antibiotics combined (Shuval et al 1995), although in 1974, Johannes Rook discovered that chlorine

formed toxic Disinfection By-Products (DBPs) with organic matter in drinking water leading to rectal and bladder cancer (Rook 1974). Recent epidemiological evidence has linked DBPs with other adverse health effects including reproductive development and other disinfectants such as chlorine dioxide, chloramines, bromine and ozone (Batterman et al 2000).

As a temporary measure, regulatory agencies such as the USEPA and the WHO have both imposed 100 μg/L DBP *Maximum Contaminant Levels* (MCL) in water supplies (USEPA 2001, WHO 1993). Germany and France responded by outlawing all chloramine drinking water disinfectants (Pedahzur et al 1995). The US and Canadian governments have acknowledged the necessity of finding alternate water disinfection techniques. In 1992, the United States-Canada International Joint Commission chose to "... sunset the use of chlorine and chlorine containing compounds" with the aim to "virtually eliminate persistent chemicals" from the Great Lakes ecosystem (Sullivan 1992 pp 9-10).

#### 5.3.1. ALTERNATIVE DISINFECTANT CRITERIA

New methods must be non-toxic, long lasting, effective, and economically feasible. Faust and Aly (1999) have established criteria for a potential alternative disinfectant:

- a) Ability of the disinfectant to control the kinds and numbers of organisms present within the  $Contact\ Time\ (C_T)$  available, the range of water temperatures encountered, and the anticipated fluctuations in composition and condition of the water being treated.
- b) Dependable availability of the disinfectant at reasonable cost and in a form conveniently, safely, and accurately applied.
- c) Ability of the disinfectant, in concentrations employed, to accomplish the desired objectives without rendering the water toxic or objectionable, aesthetically or otherwise, for the purposes it is intended.
- d) Ability of the disinfectant to persist in residual concentrations as a safeguard against recontamination such as in potable-water distribution systems.
- e) Adaptability of practical, duplicable, quick and accurate assay techniques for determining the disinfection concentration, for operating control of the treatment process, and as a measure of disinfecting efficiency.

Emerging physical treatment methods, including UV radiation, Ultrasonic treatment and membranes, satisfy many of the Faust and Aly (1999) criteria, however they do not provide any significant residual effect which is critical in systems with an extensive distribution network or long storage times. Alternative chemical disinfectants including; chloramines, chlorine dioxide, bromine, titanium dioxide and potassium permanganate are limited by low efficacy, high costs and often produce toxic DBPs (Batterman et al 2000).

Promising results of silver electrochemistry experiments suggested that silver has an important role as a safe chlorine alternative in drinking water disinfection (Shuval et al 1995, Batterman et al 2000, Pedahzur et al 2000). Two prominent applications of silver electrochemistry have been proposed for municipal drinking water treatment. In both applications, silver was combined with hydrogen peroxide (HP/Ag) to form a powerful virucidal and bacteriostatic agent. The application of the HP/Ag formula was evaluated to complement non-toxic treatment processes or existing toxic treatment processes.

# **5.3.2. COMPLEMENT NON-TOXIC TREATMENT**

Important research was conducted at the Hebrew University of Jerusalem on the application of a *Hydrogen Peroxide/ Silver Ion* (HP/Ag) water disinfection technique to complement non toxic water treatment processes (Shuval et al 1995, Pedahzur et al 2000 and Liberti et al 2000). The aim of the research was to determine the safety, efficacy, bacteriostatic (*E. coli*) and virucidal (*MS-2 phage*) mechanisms and applications of combined HP/Ag systems.

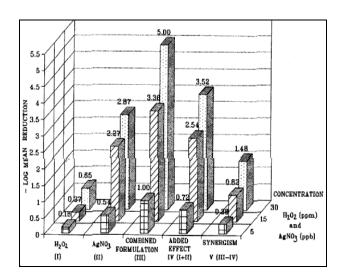
#### 5.3.2.1. TECHNICAL ANALYSIS

The human toxicology of hydrogen peroxide and especially silver has been well researched. According to the EEC, WHO, and the USEPA silver and hydrogen peroxide pose no harmful effects to humans (Pedahzur et al 1995). The USEPA has not set any drinking water MCL standards for hydrogen peroxide (USEPA 2001). The USEPA has set the silver MCL at  $100 \mu g/L$  (USEPA 2001). Considering the optimal dose for silver and hydrogen peroxide is respectively 30ppb and 30ppm, the HP/Ag system is expected to pose no adverse effects to humans. France, Germany, Switzerland and Australia have

all approved HP/Ag products for drinking water disinfection (Pedahzur et al 1995, Shuval et al 1995).

Research suggested that the HP/Ag system was a safe and effective bacteriostat and virucidal agent with a long residual effect that did not offer any disagreeable appearance, odor or taste (Shuval et al 1995, Pedahzur et al 2000 and Liberti et al 2000). Most importantly the system did not produce any DBPs or other toxic substances. Unexpectedly, early research discovered that HP and Ag provided a synergistic effect. In some cases, it was found that the combined system was between 100 and 1000 times more effective at controlling *E. coli* bacteria growth than the sum of the individual chemicals (Pedahzur et al 2000).

Figure 3: Synergistic Disinfectant Effect of the HP/Ag System (Pedahzur et al 1995)



The major disadvantage of the technique was the long Contact Time ( $C_T$ = 900) required to treat drinking water supplies. Using typical 30ppm HP and 30ppb Ag concentrations, a 3 log reduction of *E. coli B* and MS-2 phages required 77 and 802 minutes respectively (Liberti 2000). The same reduction using 1 ppm chlorine required 15 minutes and 2 minutes, respectively (Liberti 2000). The other shortfalls of the system were that the bactericidal effect is very slightly pH and temperature dependent and efficacy was reduced when the water had high TOC, TSS and metal contaminant levels (Liberti 2000). Optimal disinfection results were achieved at ambient temperatures with clarified water at pH 6-9 (Pedahzur et al 1997).

Multiple theories had been proposed for the biological and chemical toxic mechanisms of silver and hydrogen peroxide (Thurman & Gerba 1989, Pedahzur et al 2000). Further microbiological research is required to validate any one of the theories. However, there are some common understandings. The common theories can be considered in a chemical and biological context.

Pedahzur et al (1997) assessed the chemical context of HP and Ag toxicity. Three chemical interactions were observed: stabilization of HP by silver to limit HP breakdown; interference of HP in silver efflux from cell walls; and interference of Ag with HP cellular detoxification. Furthermore, the Ag/HP pair, unlike the Cu/HP interaction did not produce active hydroxyl species that follow a Fenton Redox reaction or Haber-Weiss cycle.

Therman and Gerba (1989) studied the biological effects of the HP/Ag system. It was found that silver and hydrogen peroxide interfere with electron transport, DNA replication, and the cell walls of viruses and bacteria. Silver has a particularly high affinity for sulfhydryl groups on bacterial cell membranes. By binding to sulfhydryl groups on cell walls, bacterial respiration is prevented. Since protein denaturation of viruses is more difficult than sulfhydryl oxidation, the virucidal effects of silver are limited. Hydrogen peroxide is a much stronger virucidal agent. Hydrogen peroxide acts on viruses by inactivating nucleic acid within the viral capsid. The synergistic results indicate that the toxic processes for silver and hydrogen peroxide are metabolically related and potentiate similar responses (Pedahzur et al 2000).

#### 5.3.2.2. APPLICATIONS

The HP/Ag water disinfection method has promising large scale water disinfection applications. On its own, the HP/Ag treatment technique is limited by the slow contact time required to treat drinking water. The method may be used for distribution systems where the time between treatment and point of use is over 900 minutes or for water storage facilities such as those found in ships (Pedahzur et al 2000). Pedahzur et al (2000) recommended that ideally the system may be used as a secondary treatment method to complement another non-toxic disinfection method with fast contact time but low residual effect such as UV and membrane technologies. The combined treatment system

would fulfill the Faust and Aly (1999) criteria for optimal water disinfection, however, the cost of treating water would certainly increase. UV radiation and membrane methods are more costly to operate in most applications, due to their inherent high energy requirements.

### 5.3.3. COMPLEMENT EXISTING TREATMENT

Batterman et al (2000) were the first to discover a second important application of silver electrochemistry that may also have fundamental implications on municipal water supply disinfection. In response to the growing demand for non-toxic water disinfectants, Batterman et al (2000) have engineered a method using the HP/Ag system to dramatically decrease the toxicity of chlorine treatment by quenching the formation of DBPs.

#### **5.3.3.1. TECHNICAL ANALYSIS**

Batterman et al (2000) proposed that hydrogen peroxide had the dominant role in the DBP quenching process. Hydrogen peroxide reduced chlorine to form non-toxic chlorides (Baxendale 1952). At equilibrium, the system strongly favored chloride formation (Batterman 2000).

$$Cl_2 + H_2O_2 \leftrightarrow 2Cl^2 + 2H^+ + O_2 \tag{7}$$

The rate of chloride formation was given by the simplified equation:

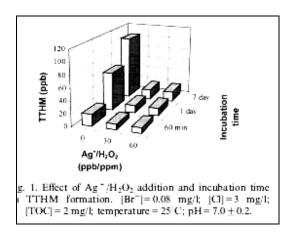
$$([Cl^{-}]^{2}[H^{+}]^{2})/[Cl_{2}] = K^{0}_{1}/K^{0}_{2}$$
(8)

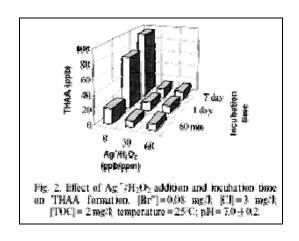
where  $K_1^0$  was the simplified chloride generation reaction rate (to the right), and  $K_2^0$  was the simplified reverse reaction rate (to the left). For experimental pH ranges between 5 and 9, which are also commonly used in water treatment processes, the  $[H^+]^2$  is very small ( $10^{-10}$ - $10^{-18}$ ). Experimental results suggested that  $K_1^0$  was greater than  $K_2^0$ . In consideration of the equilibrium equation for chloride formation, the concentration of chlorides was much larger than chlorine. Batterman et al (2000) suggested that the concentration of chlorine is essentially negligible at equilibrium which resulted in the strong quenching action of the HP/Ag system on DBP formation.

The research indicated that the HP/Ag system quenches the formation of *Trihalomethanes* (THM) and *Haloacetic acids* (HAA), the major DBP carcinogenic classes (Batterman et al 2000). HP/Ag was added after a 10 minute chlorination period.

Essentially, all of the DBPs were formed within the 10 minute chlorination period. A 30ppm HP and 30ppb Ag dose appeared to halt nearly all DBP formation. Following the HP/Ag treatment of ground, surface and mixed waters, THM and HAA levels were found to decrease on average by  $72 \pm 9\%$  and  $67 \pm 11\%$ , respectively. The quenching effects were shown to be only slightly affected by temperature and pH. Batterman et al (2000) suggested that the process may be optimized by reducing DBP organic precursors, reducing the elapsed time before HP/Ag addition and selecting the lowest effective chlorine dose.

Figure 4: Quenching Efficacy of HP/Ag System (Batterman et al 2000)





#### 5.3.3.2. APPLICATIONS

Batterman et al (2000) concluded that the HP/Ag quenching technique could complement a conventional chlorination process to achieve the 1998 USEPA 80 µg/L trihalomethanes MCL. The implications of such a finding will allow municipal water suppliers to continue using chlorine for its cheap, effective and now safe disinfectant properties. As an added benefit, the HP/Ag system has no known toxic effects and was proven to provide effective, long-lasting and synergistic bacteriostatic and virucidal control (Pedahzur et al 2000). The combined chlorine, silver and hydrogen peroxide disinfectant system satisfies the five Faust and Aly (1999) disinfectant criteria.

#### 5.4. SOCIOECONOMIC DEVELOPMENT APPLICATIONS

Of the many applications for sophisticated silver electrochemistry the potential application with the greatest rewards is in providing safe, effective and economical water treatment methods to developing nations. According to UNICEF (2004) 1.1 billion people do not have access to potable water and the vast majority of these people live in Africa and Asia. With the number likely to climb dramatically in the near future, there is an urgent need for appropriate water treatment technologies for developing countries (UNICEF 2004). Schumacher (1975), a pioneer of developmental economics, criticized the implementation of advanced technology in developing nations. It has been found that when certain water disinfectant technologies are implanted in developing countries, they tend to sit idle due to insufficient resources, lack of operating expertise, and/or prohibitive maintenance costs. Alternately, indigenous technologies are often too rudimentary and rarely achieve satisfactory disinfection (Schumacher 1975). Schumacher (1975) recommended the use of *Intermediate* technologies that are more advanced than indigenous methods but more practical than sophisticated alternatives. The United Nations Environment Program has acknowledged the need for intermediate technologies in development. It has encouraged decision makers in local and national governments and other organizations to implement environmentally sound intermediate technologies (UNEP 2004).

#### 5.4.1. ZENON ENVIRONMENTAL CASE STUDY

Many examples can be found to demonstrate the inappropriateness of Hi-Tech solutions in developing countries. Zenon Environmental is a Canadian manufacturer of a revolutionary membrane technology called ZeeWeed® that is used for municipal and industrial water treatment (Zenon 2004). In 2002, they rightfully saw the need to improve the water quality in Quang Dien District, Vietnam. Quang Dien is one of the poorest regions in Vietnam where many of the 2000 residents have experienced severe adverse health effects that were directly linked to poor water quality. The three most common illnesses were eye disease (27%), diarrhea (31%) and dysentery (15%) (Zenon 2004). Their current water supply was a shallow polluted well; no water treatment was in place. In 2003, a team of engineers built a ZeeWeed® system for the community (Zenon 2004).

In less than a year, the system had malfunctioned and it no longer provides a safe drinking water supply to the local population (Hortop, 2004). The system failed because there was a lack of maintenance personnel and repair components.

Figure 5: Zenon ZeeWeed® Technology and Existing Water Well (Zenon 2004)





#### 5.4.2. SILVER BASED CERAMIC FILTERS

Historical uses of silver for disinfection over the last 200 years, suggest that silver may be used in Low-Tech applications. Small modifications to modern silver electrochemistry methods have proven that silver may act as an effective intermediate technology in water treatment for developing countries. The United Nations Environment Program (2004) has listed silver-treated ceramic water filters as an appropriate technology for water purifications in developing countries and regions affected by natural disaster.

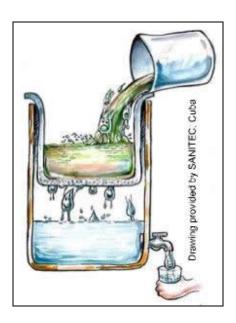
A non-governmental organization, Potters for Peace, has developed a family sized ceramic filter using colloidal silver called the Filtron (PFP 2004). Filtron filters are used in households throughout Central and South America, Africa and Asia and by emergency relief organizations including the International Red Cross and Doctors Without Borders. Laboratory studies indicate that the filter is capable of removing 99.98% of most waterborne diseases (PFP 2004). However, field studies indicated that the filters provide less than ideal disinfection results. An average of 20% of families had filtered water with more than 2.2 CFU/100 mL, which exceeded the 0.0 CFU/100 mL WHO (1993) water standard target (Hwang et al 2002). The discrepancy is mainly due to cracks in the filter incurred during transportation and non-standardized fabrication methods (Lantagne 2001). Ongoing efforts are being made to improve the field performance of the

technology. The cost of the Filtron filter is approximately 4 USD (Lantagne 2001). A Swiss company, Katadyn Inc., manufactures high quality plastic models available for 159 USD.

#### 5.4.2.1. TECHNICAL ANALYSIS

Manufacturing the filter requires simple, locally-available materials and methods. The filter is 31cm in diameter, 24cm high and holds 7.1 L of water (PFP 2004). Both sides of the filter are brushed with 0.32% Microdyn colloidal silver solution to give it its disinfectant properties. The pore size of the filter is 1  $\mu$ m. It rests inside a 20L clay or plastic receptacle with a spigot for accessing the treated water.

Figure 6: Filtron Filter



The filter uses two mechanisms to disinfect the water. The first is by filtration; any harmful microorganisms or particles larger than 1 µm are removed from the water. These would include most bacteria, and all protozoa and helminthes. Viruses and some bacteria would not be trapped.

The second mechanism is by colloidal silver induced bacteriostatic action. Colloidal silver is composed of silver particles held in suspension in clusters between 10<sup>-9</sup> and 10<sup>-6</sup> m wide (Lantagne 2001). The same toxic mechanism for controlling bacteria growth is used in the Filtron filter as in modern silver electrochemistry techniques. Silver inhibits bacteria multiplication by reacting with sulfhydryl (-SH) groups in the bacterial cells,

producing structural changes in bacterial cell membranes and interacting with nucleic acids (Russell 1994).

#### 5.4.2.2. APPLICATIONS

The Filtron filter provides a critical service to areas where water quality is poor and where the water supply infrastructure is lacking. Ideally, the filter should not be used for long-term water purification in urban areas. Currently, the best possible drinking water quality is achieved from well-run water treatment plants with piped service to households. The Filtron filter is a viable interim solution for disaster relief in urban areas until the water supply is returned. For areas without any foreseeable access to piped drinking water supplies, the Filtron offers a cheap and effective intermediate water purification technology (PFP 2004). Filters should be regularly inspected for cracks and replaced every one to two years to avoid loss of biocidal action. The lifetime of the filter may be extended by intermittently scrubbing the inside of the filter and pre-filtering the raw water with a cloth. Lantagne (2001, p.72) concluded that, combined with an "education component for the users, the PFP filter is an effective and appropriate technology that improves both water quality and human health".

# 6. CONCLUSION

The recent surge of research in silver electrochemistry has shown that it is a viable alternative or complement to traditional consumer, industrial, municipal and socioeconomic water treatment technologies. The consumer products industry has shown confidence in silver chemistry by introducing a line of health and hygiene products based on the bacteriostatic properties of silver (Samsung 2004). Industry has found that silver can provide a unique wastewater treatment service that is both effective and reduces harmful emissions. The most significant research has taken place in the field of municipal drinking water treatment. Silver may perform an important role in fundamental changes to the municipal drinking water treatment process. The greatest need for water treatment innovations is in developing nations or areas inflicted with natural disasters. Potters for Peace (2004) have developed a simple silver treated ceramic filter that provides an affordable and effective water treatment technology to the world's most needy. In light of

the recent discoveries in silver electrochemistry, it will likely play an integral role in the future of water disinfectant innovations.

#### 7. REFERENCES

- 1. Batterman, S., Zhang, L., Wang, S., (2000). Quenching of Chlorination Disinfection By-Product Formation in Drinking Water by Hydrogen Peroxide. Wat. Res., 34, 5, pp. 1652-1658.
- 2. Baxendale, J. (1952). Decomposition of Hydrogen Peroxide by Catalysis in Homogeneous aqueous solution. Advances in Catalysis. 4, pp. 35-39.
- 3. Clarke, R., Foller, P. (1990). *Electrochemical Hydrogen Technologies*. Wendt, H., Ed., Amsterdam: Elsevier.
- 4. [CRC] (1997). The Handbook of Trace Elements. CRC Press, Boca Raton, FL.
- 5. [DWPF] "Defense Waste Processing Facility. (1989). *Process Description: Overview of DWPF Process.* DPSOP 257-8, Part 2, Item 100, Rev. 5, pp. 1-6.
- 6. Farmer, J., Wang, F., Lewis, P., Summers, L. (1992). *Lawrence Livermore Lab. Report*. UCRL-JC 109633; Electrochem. Soc.
- 7. Faust, S., Ally, O. (1999). *Chemistry of Water Treatment* (2<sup>nd</sup> ed.). Boca Raton: Lewis Publishers.
- 8. Hortop, S. (2004). *Personal communication*. Zenon Environmental Inc.
- 9. Hwang, R., Murcott, S., Miller, B. (2002). *ThinkCycle*. Banglore.
- 10. Lantagne, Daniele (2001). *Investigation of the Potters for Peace Colloidal Silver Impregnated Ceramic Filter*. Cambridge, MA
- 11. Laubusch, E.J. (1971). *Water Quality and Treatment* (3<sup>rd</sup> ed.). New York: McGraw-Hill Book Company.
- 12. Lenntech (2004). *Swimming Pool Treatment* (Online). Retrieved: October 6, 2004, from: www.lenntech.com/water-disinfection/swimming-pool-treatment.htm
- 13. Liberti, L., Lopez, A., Notarnicola, M., Barnea, N., Pedahzur, R., Fattal, B. (2000). *Comparison of advanced disinfecting methods for municipal wastewater reuse in agriculture*. Wat. Sci. Tech., 42 1-2, pp. 215-220.
- 14. Metcalf & Eddy, Inc. (1991). Wastewater Engineering: Treatment, Disposal, and Reuse: Third Edition. New York: McGraw-Hill, Inc.

- 15. Molton, P., Fassbender, S., Nelson, J., Cleveland, J. (1988). *Proc.* 13<sup>th</sup> Ann. *Environ. Qual. R&D Symp.*, Battelle Pac. Northwest Haz. Waste RD&D Center, Richland, WA.
- 16. Muller, G., Kempf, T., Goethe, H., and Herman, R. (1977). *Drinking Water Preservation For Life Boats*. Forum Staedt Hyg., 28, 33.
- 17. [NASA] National Aeronautics Space Agency (2004). *Atmospheric Carbon Dioxide Removal: Silver Oxide* (Online). Retrieved: Nov 18, 2004 from: http://marsoweb.arc.nasa.gov/About/Education/SpaceSettlement/teacher/c ourse/ag2o.html
- 18. Pedahzur, R., Katzenelson, D., Barnea, N., Lev, O., Shuval, H., Fattal, B., Ulitzur, S. (2000). *The efficacy of long-lasting residual drinking water disinfectants based on hydrogen peroxide and silver*. Wat. Sci. Tech., 42, 1-2, pp.293-298.
- 19. Pedahzur, R., Shuval, H., Ulitzur, S. (1997). Silver and Hydrogen Peroxide as Potential Drinking Water Disinfectants: Their Bactericidal Effects and Possible Modes of Action. Wat. Sci. Tech., 35, 11-12, pp 87-93.
- 20. Pedahzur, R., Lev, O., Fattal, B., Shuval, H. (1995). *The Interaction of Silver Ions and Hydrogen Peroxide in the Inactivation of Escherichia-Coli: A Preliminary Evaluation of a New Long Acting Residual Drinking Water Disinfectant*. Wat. Sci. Tech., 31, 5-6, pp 123-129.
- 21. [PFP] Potters for Peace (2004). *Ceramic Water Filter Project* (Online). Retrieved: November 15, 2004 from: http://www.potpaz.org/pfpfilters.htm
- 22. Rook, J. (1974). Formation of haloforms during chlorination of natural waters. J. Water Treat. Exam. 23, pp. 234-243.
- 23. Russell, A.D., Hugo, W.B. (1994). *Antimicrobial Activity and Action of Silver*. Progress in Medicinal Chemistry. Volume 31.
- 24. Samsung. (2004). *Samsung Silver Wash Technical Information* (Online). Retrieved: November 15, 2004 from: www.samsung.com/Products/WashingMachine/technicalinfo/index.htm
- 25. Schumacher, E.F. (1975). *Small is Beautiful: Economics as if People Mattered*. New York: Harper & Row Publishers.
- 26. Sequeira, C. (ed). (1994). *Environmental Oriented Electrochemistry*. Amsterdam: Elsevier Science.

- 27. Shuval, H., Fattal, B., Nassar, A., Lev, O., Pedahzur, R. (1995). The Study of the Synergism between Oligodynamic Silver and Hydrogen Peroxide as a Long-Acting Water Disinfectant. Water Supply, 13, 2, pp 241-251
- 28. Sullivan, J. (1992). *Chlorine: Public Health Savior or Hazard?*. Environmental Engineer. 29, pp 9-10.
- 29. [Silver Inst.] The Silver Institute (2004). *Supply and Demand* (Online). Retrieved Nov. 2, 2004 from: http://www.silverinstitute.org/supply/production.php
- 30. Thurman, R., Gerba, C. (1989). *The Molecular Mechanisms of Copper and Silver Ion Disinfection of Bacteria and Viruses*. CRC Critical Reviews In Environmental Control, 18, 4, 295-315
- 31. [UNEP] United Nations Environment Program (2004). *maESTro Directory* (Online). Retrieved Nov. 2, 2004 from: www.unep.or.jp/maestro2/index.asp.
- 32. [UNICEF] United Nations Children's Fund (2004). *Water Statistics* (Online). Retrieved Oct. 15, 2004 from: www.childinfo.org/eddb/water/current.htm.
- 33. [USEPA] United States Environmental Protection Agency (2001). *Drinking water standards*. Office of Water, U.S. Environmental Protection Agency, Washington D.C.
- 34. [USEPA] United Stated Environmental Protection Agency, (1992). *R.E.D. Facts:* Silver. Office of Prevention, Pesticides And Toxic Substances, U.S. Environmental Protection Agency, Washington D.C., H-7508W
- 35. [WHO] World Health Organization, (1993). *Guidelines for Drinking-Water Quality*, 2<sup>nd</sup> Edition. World Health Organization, Geneva.
- 36. Zenon Environmental Inc. (2004). *Water for Humanity*. Retrieved October 8, 2004 from: http://www.zenon.com/WFH.shtml.