

FINAL REPORT ON COPPER/SILVER DISINFECTION SYSTEM

For
Ted Kuepper, REM
Pacific Research Group
Global Water, Inc.

By

W. Craig Meyer
Professor of Geology
Pierce College
Director - The Center for Environmental Technology

and

Nicolai S. Reeve, Daniel D. Williams, Jasmine M. Diaz, Hector E. Borjas and Carmen P. Torres
Pierce College Student Project Team

June 17, 2013

INTRODUCTION

In the previous progress report we explained the development of: 1) methods to use the ionizing equipment and 2) methods of water analysis necessary to determine the results of water treatment using the Cu/Ag ionizing system. This final report presents the results of our tests of this system using the methods presented in our preliminary progress report.

The following questions regarding performance of the system were tested and the results are presented here. They are:

- 1) Is the proper silver concentration slaved to changing copper concentrations in water passing through the ionizer?
- 2) How well do the UF membranes serve as a disinfection method?
- 3) Does a Cu/Ag residual prevent secondary bacterial regrowth and how long does treated water remain free of bacterial recontamination?
- 4) How well does Cu/Ag ionization serve as a primary disinfection method?

COPPER/SILVER TRACKING

No test to measure silver was made available by the manufacturer of the ionization unit (Clearwater). They assert that it is not necessary to measure silver levels since their proprietary alloy coordinates the ionization of both metals. Thus, only one of the metals needs to be evaluated to confirm the concentration of both. Therefore, if the copper levels are adequate for disinfection, the silver levels will also be adequate. For example, if an effective copper ion residual of 300 ppb is obtained in treated water, an effective residual of silver ion (≈ 50 ppb) should also be present. This is convenient since there is no simple test kit specific to silver and measurement of this element requires use of Atomic Absorption (AA) or Inductively Coupled Plasma (ICP) spectrophotometry.

To test the claim that silver is slaved to copper ionization and need not be measured, we ran distilled water through 5 cycles of ionization and measured copper and silver ion concentrations. Table 1 presents this data for cycles 1, 3, and 5. Since our ICP spectrophotometer is not operational at this time, we sent cycles 1,3 and 5 to a commercial laboratory to measure copper and silver concentrations.

Table 1: Copper Levels of Samples Sent for ICP Determination of Dissolved Copper and Silver

Cycle	Cu (ppb)	Ag (ppb)
1	787	14
3	1084	9
5	1375	8

As indicated in table 1, the silver concentrations did not reach levels adequate for dependable disinfection and did not cycle up with the increasing copper concentrations produced by multiple passes through the ionizer. As a result, it is probable that any ionic disinfection of water is due to the copper concentrations produced by the ionizing system.

WATER DISINFECTION BY ULTRA FILTRATION

The principle behind disinfection by ultra filtration lies in the fact that a bacterium is a particle with an average size of approximately 2 microns. A filter membrane with pores smaller than this should effectively screen out bacteria from water passing through. Testing of the filter membranes supplied by the Pacific Research Group was conducted according to the following protocol.

A source of contaminated water was developed using chicken stock as a nutrient according to the method presented in our earlier preliminary report. The bacterial count (cfu/ml) was allowed to reach 10^4 or greater before use for testing. A five gallon batch of contaminated water was placed in a sterile plastic bucket to serve as our water reservoir. As a control, samples of unfiltered water were collected from this reservoir and analyzed at the start of each test run. To test the

ultra-filter, the contaminated water in the reservoir was pumped through the membrane with a ¼ hp centrifugal pump into another sterile plastic bucket. After the entire five gallon volume had passed through the filter membrane additional samples were collected for analysis to determine the effect of filtration. Pressure and flow rate were monitored along with water chemistry (Temperature, pH, TDS, Alkalinity, Ca Hardness, and Cu concentration) for all samples. Bacterial levels were determined by Heterotrophic Plate Count (spread plate method) according to standard methods.

Small UF Filters

The Pacific Research Group provided several filter units for testing. The first were short (36 inches) units of indeterminate origin... no brand name, operations manual, or performance expectations were available. Three separate tests of this filter were conducted at a flow rate of 1.7 gallons per minute (gpm). The pressure proved variable throughout each run, but never exceeded 20 psi. Table 2 presents the results of these tests.

Table 2: Bacterial removal by 36 inch Ultra Filters

Test	1	2	3
Control (cfu/ml)	1.17×10^6	2.49×10^4	2.69×10^4
Filtered (cfu/ml)	2.71×10^4	4.63×10^4	1.27×10^4

As these results indicate, filtration with this unit was ineffective. In one case the plate count was higher after filtration (Test 2). These data suggest that the filtration membrane was damaged. The filter was disassembled and a number of membrane tubules were found to be broken. This would allow water to pass through unfiltered, accounting for the high flow rate at such moderate pressures and the lack of bacterial removal. Below is a photograph of the broken tubules that were revealed when the outer housing was removed.



Damaged Filter Tubules in Short Ultra filter

TORAY HFU 1010 Ultra Filter

When informed of the poor performance of the short filter, the Pacific Research Group provided another filter for testing. This filter, a 48 inch TORAY HFU model 1010, had been used in the test system on the golf course at Point Mugu Naval Station. It was tested using the protocol described earlier for the 36 inch filter membrane.

To allow us to determine whether the same efficiency of bacterial removal is sustained during multiple passes through the membrane the last two disinfection test runs were modified. After the first pass through the filter membrane (cycle 1), the volume of water was passed through the filter membrane for a second time (cycle 2) and a sample collected when this volume had been completely treated. The process was repeated a third time (cycle 3) and a final sample collected. Table 3 presents the results of these tests.

Table 3: Bacterial Removal by the Toray HFU 1010 Ultra Filter

Run	Cycle	HPC (cfu/ml)	Cu (ppb)	Flow (GPM)	Pressure (psi)
1	Control	4.0×10^5	99	5	10
	1	2.3×10^4	191	5	10
2	Control	6.8×10^3	76	5	5
	1	9.2×10^3	45	5	5
3	Control	1.5×10^6	160	5	5
	1	< 30	275	5	5
	2	< 30	313	5	5
	3	< 30	290	5	5
4	Control	4.6×10^4	57	5	5
	1	< 30	76	5	5
	2	5.8×10^3	95	5	5
	3	1.13×10^2	122	5	5

Though cycle 1 of runs 3 and 4 showed what appears to be effective bacterial removal after a single pass, the previous two runs (1 and 2) did not indicate similar bacterial reduction. The single filtration cycle of run 2 actually produced water with a higher bacterial count than the raw control. When cycles 2 and 3 for the later runs are examined the results become more confusing. The bacterial counts for cycles 2 and 3 of run 3 indicate effective bacterial removal but these cycles for run 4 are unacceptably high. A similarly confusing pattern is displayed by the copper levels which, in most cases, increase with succeeding cycles.

This variable performance suggests that the membrane was compromised. An operating manual obtained from the Toray Company presents the following instructions: 1) the operating pressure

of the unit should not exceed 40 psi; 2) for short term storage (<7 days) the storage solution should be sodium hypochlorite not to exceed 20 ppm Cl; 3) longer term storage should use a solution of 1 gram/liter sodium bisulfite . The operators of the Point Mugu unit, where this filter membrane had been used previously, indicated that it was common to run the system in excess of 60 psi and that a solution of bleach (sodium hypochlorite) was used for long term storage. The Cl concentrations of this storage solution were not available.

These facts suggest that membrane damage was probable. To test this, a membrane integrity protocol was obtained from the Toray company. This test determines the rate that air diffuses through the membrane at a set pressure. A pressure drop faster than the ideal rate of 0.3 kPa over 5 minutes indicates membrane damage while a drop of 3 kPa over 5 minutes indicates a broken membrane tubule. Our pressure test showed a loss of 1.8 kPa over 5 minutes. This is 6 times the ideal rate, but slightly over half what would be expected if a tubule has been broken. We interpret this to indicate that the membranes have been compromised by the overpressure and aggressive chemical storage, but that complete breakage of the tubules has not occurred.

Partial membrane damage could explain the erratic bacterial results obtained in our testing. If the membranes were only partially effective at removing the smallest particles a bacterial load will accumulate on the upstream side of the membrane. Leakage through the damaged membrane would increase with the concentration of accumulated bacteria. Under these conditions, when filtration ceased, there would be bacterial contaminants in the water on both up and downstream sides of the membrane. This would contaminate subsequent runs. In response to the poor results of runs 1 and 2, membranes were flushed with greater volumes of clean water for later runs. This would flush the bacteria on the downstream side of the membrane and explain the filtration results for cycle 1 of runs three and four.

Based on our experience with the membranes and the warnings presented in the operation manual provided by the filter manufacturer, it can be concluded that this technology is delicate and can be easily damaged by poorly monitored pressure variations and improper chemical treatment. Considering the need for regular filter cleaning (backwashing with air scrubbing), carefully monitored operating conditions and proper long and short term storage protocols, there is some question regarding the dependability of this technology when used in the rugged conditions that accompany field application for the military or disaster relief.

SHELF LIFE OF CLEAN WATER WITH Cu/Ag RESIDUAL

An advantage of the proposed Cu/Ag disinfection system is that it produces a residual concentration of Cu and Ag ions that should prevent recontamination of treated water. The literature reports a variety of copper and silver concentrations that are claimed to produce effective disinfection but there is general agreement that a copper ion concentration between 300 and 400 ppb meet this goal. Recommended Silver ion concentrations are more variable, from a minimum of 10 ppb to a maximum of 50 ppb (the Maximum allowed by EPA drinking water guidelines). For our experiments we chose a copper ion concentration of 350 ppb as our target residual. Based on the Cu/Ag tracking analyses reported earlier, this should produce a Ag concentration approximating 10 ppb.

Our tests were conducted according to the following protocol. Ten gallons of chlorine free tap water was divided into two five gallon sterile HDPE containers with covers. The water in one of the containers was run through the copper ionizing system to develop an initial copper concentration of 381 ppb and an estimated silver concentration of 10ppb. This would simulate a volume of treated water that would be stored on site for future use. No Cu/Ag ions were added to the other container (un-ionized) to serve as a control. Each day water samples were collected from each container and analyzed. Bacteria levels were determined by spread plate Heterotrophic Plate Count (standard methods). Copper levels were determined by the colorimetric method we developed and described in the previous project report. TDS and pH were determined with a Myron T2 meter and Alkalinity and Ca hardness were determined with a Taylor titration test kit.

Table 4: Comparison of Bacterial Development in Ionized and Un-Ionized Potable Water

	Un-Ionized		Ionized	
Day	Cu (ppb)	cfu/ml	Cu (ppb)	cfu/ml
1	22	>30	381	>30
2	30	>30	359	>30
3	30	>30	328	>30
4	38	>30	359	>30
5	15	1.1×10^3	336	>30
6	30	5.7×10^3	343	>30
7	15	2.08×10^4	328	>30
8	31	2.03×10^4	366	>30
9	15	2.0×10^4	313	>30
10	15	2.31×10^4	305	3.38×10^4
11	15	290×10^5	290	2.36×10^4

Bacterial levels and copper concentrations were the only parameters that showed significant variation from one day to the next, therefore they have been included in Table 4. The un-ionized water showed the expected exponential growth of bacteria over time starting at day five. The standard methods require a plate have more than 30 countable colonies (colony forming units per milliliter of water – cfu/ml) to be statistically valid. Consequently no specific numbers are presented for plates with fewer than 30 cfu. The EPA suggests that 500 cfu/ml is the maximum allowable for drinking water. Based on this criterion, the un-ionized water stayed potable for 4 days while the ion treated water remained potable for 9 days.

It might be asked why water with a residual copper level above 300 ppb should eventually develop a bacterial population. It is likely that this is due to the fact that bacteria populations develop resistant to copper and silver over time. When they are first added to the water, most but not all bacterial cells are killed. Some, however, due to natural biochemical variation, are resistant to the toxic effects of exposure to these metals. These cells reproduce and eventually produce a resistant population.

Based on these results it can be concluded that the copper ion residual (with accompanying questionable silver ion concentrations) will allow decontaminated water to remain potable during storage up to 9 days. To allow a margin of error, storage for more than a week should be discouraged. Storage vessels should be drained, cleaned and shocked with an oxidative biocide every week or so to remove any colonies of resistant bacteria that may form a biofilm on the submerged surfaces in the container.

COPPER/SILVER AS A PRIMARY DISINFECTANT

The use of Copper/Silver ions for primary disinfection has been widely reported in the literature. Though this is not the role played by these ions in the proposed system, it was thought appropriate to test its effectiveness as a primary disinfectant in our system.

Five gallons of contaminated water was produced by the method discussed earlier. This water was run through the ionizing system for two cycles which brought the copper ion concentration up to 458 ppb. Bacterial levels were determined by Heterotrophic Plate Count (spread plate method) according to standard methods. Bacterial levels and copper ion concentrations were determined at the start and after each cycle. Samples collected the first day were allowed to sit at room temperature for 24 hours and the bacterial levels and copper concentrations were measured again. This would respond to the possibility that since copper/silver ions work at the biochemical level it may take time for the ions to be assimilated to produce their disinfection effect. By examining the bacterial levels on day two we can account for such delayed effects.

Table 5: Primary Disinfection with Cu/Ag Ions

Day	Cycle	HPC (cfu/ml)	Cu (ppb)	Flow (GPM)
1	Control	2.8×10^4	115	3
	1	3.0×10^3	244	3
	2	<30	454	3
2	Control	1.06×10^4	168	3
	1	4.85×10^4	336	3
	2	2.08×10^4	458	3

Again the results were confusing. On day one at 454 ppb copper/silver ion, the bacterial counts were reduced from 2.8×10^4 cfu/ml to less than 30. This is an excellent result. However, on day two the bacterial levels in all cycles had returned to essentially the same levels as the control. This is difficult to explain since the copper/silver ion levels were high enough to discourage re-growth according to our earlier experiments. If the bacterial population were resistant to copper/silver ions a day would be ample time for the population to grow from 30 survivors to the levels measured on day 2. Bacteria will develop resistance to metal toxicity and we have bacterial populations that have developed from populations that have been exposed to copper/silver ions chronically present in our tap water. It is, therefore, possible that the intense selection for resistance that resulted from the ion concentrations that were effective on day one

have allowed only the most resistant bacteria to produce the population on day two. If this is, in fact, the explanation for these findings it would have little effect on the proposed system. The water to be treated would not have been previously exposed to copper/silver and would not have developed resistance.

SUMMARY

It was originally anticipated that ultrafiltration followed by Cu/Ag ionization would provide a simple rugged technology that could be installed in the field and left to operate essentially unattended for the short periods of time needed for disaster relief or military field operations. Our results lead us to question this assumption.

Effective Ion Production

As presented in the first progress report, the ionizer is not able to produce an effective ion residual for all conditions of water chemistry. To be effective, the water being treated must have high enough TDS to produce conductivity sufficient to allow an electric current to pass between electrodes. The system was originally designed for swimming pools and fountains where the water chemistry is maintained within narrow limits with enough dissolved solids to allow for the necessary conductivity. It is most effective at TDS levels that approach the limits for potable water sources. In the field, where water may have a TDS of around 100 ppm or less, this ionizer is less effective and in very pure natural water such as snow melt or oligotrophic lakes, the unit may not be able to develop an effective residual. Therefore, attention must be paid to initial water chemistry when setting up a system in the field and water may have to be passed through the unit several times to develop the desired residual. When it is necessary to make multiple passes to obtain desired residuals, the volume of water produced over a given time period would be reduced.

When production of silver ions was measured, the concentration of silver ions did not develop to acceptable levels on the first pass through the ionizer and did not increase with increasing copper levels during multiple passes through the ionizer. This suggests that any bactericidal effect is being produced by the copper levels obtained. Our tests used water with a TDS comparable to natural waters (200 ppm) since it was assumed that this would be a characteristic of water most frequently encountered in field applications. It is possible that silver ion residuals may increase for waters with TDS near the maximum allowable range (TDS = 1000 ppm) but it does not appear that adequate silver ion concentrations will be obtained for water of average chemical characteristics.

The operation manual for the Clearwater ionization system indicates that the electrode is prone to scaling and should be cleaned on a regular basis. Cleaning involves washing the electrode in dilute acid and brushing the surface with a stiff fiber or wire brush. We found that at our limited

levels of use, the electrode would start to show the effects of scaling after a week of intermittent operation. This suggests that under continuous operation in the field there will be a need for frequent maintenance of the electrodes.

Membrane Filtration

The literature makes it clear that ultrafiltration can be an effective method to remove bacteria from water. These systems are, however, used in carefully controlled conditions in a water treatment plant or other specialty water projects. Conditions here are very different from those in the field as part of a disaster relief or military operation. We have learned that the membranes are quite delicate. The membranes we had to test were all damaged to some degree during prior field use. Some (the smaller units) had multiple tubule failures. The larger Toray HFU 1010 unit showed membrane degradation and though it appears that no tubules were severed, it was not able to perform adequate dependable water treatment. These membranes are susceptible to damage by rather small variations in operating pressure and improper chemical exposure during transfer and storage. Further, they blind off easily and require regular attention for filter cleaning by backwashing and air scrubbing. Use of these membranes will, therefore, require constant attention to keep them damage free and operational.

Effects of Cu/Ag Residual on Shelf Life

We found that clean water with a copper/silver residual concentration between 300 and 400 ppb remained free of secondary contamination for a period of 9 days. Our control, clean water with no added copper/silver residual, remained potable for 4 days. This suggests that a copper/silver residual developed by this system should be able to maintain potability for a period of time commensurate with normal use patterns.

Cu/Ag as a Primary Disinfectant

Copper/Silver ion seems to be effective as a primary disinfectant, but if bacteria have developed resistance to metal toxicity, the disinfection effect may be transient.