

Investigations of Copper Corrosion at Willmar, Minnesota

Part 3: Results of Pilot Plant Column and Copper Pipe Test Loop Studies

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Copper Corrosion Studies Using Pilot Columns and Copper Pipe Test Loops

For evaluation of the effect of additional treatment on bacterial growth and copper corrosion rates, four pilot columns were installed at the the Willmar, Minnesota Southwest Water Treatment Plant. The size and contents of the columns and design parameters are indicated on Figure 8 (Pilot Plant Column Studies).

Effect of Ammonium Ion Removal on Copper Corrosion

Column 1, a 6' length of 6" diameter acrylic plastic, was filled with 4 feet of cation exchange (softening) resin as part of an effort to reduce the concentration of ammonium ion entering the copper pipe corrosion test loop. The cation exchanger influent was chloraminated Southwest plant finished water. Approximately, 20 percent of the influent flow by-passed the exchange column so that the water entering the copper pipe test loop would contain sufficient ammonium ion to ensure the continued formation of a chloramine residual.

The use of cation exchange to achieve a reduction in ammonium ion was intended to make it possible to determine whether there was a relationship between the rate of copper corrosion and the activity of nitrifying organisms in the copper pipe test loop. In practice, the reduction of ammonium ion to less than 1 mg N/l would be adequate to ensure that total oxygen depletion did not occur due to nitrification in the distribution system and household plumbing.

Effect of Removal of Organic Matter on Copper Corrosion

The second treatment column contained five feet of bituminous-base granular activated carbon (Calgon Filtrasorb). At a surface loading rate of 2 gpm/sf, this depth of GAC provided an empty bed contact time (EBCT) of 18.5 minutes. Under these operating conditions, TOC reductions should continue for several months. Treatment for the removal of dissolved organic matter, as measured by TOC and indicated by color, was intended to make it possible to determine whether the removal of organic ligands would decrease copper solubility and thereby reduce the rate of copper corrosion.

Fabrication of Copper Pipe Corrosion Test Loops

Three identical copper pipe corrosion test loops were fabricated using hard copper pipe and soldered joints (Figure 9). These test loops were fabricated to simulate the plumbing in a typical Willmar household. Each test loop held several liters of water for testing. During treatment, water passed through the loops under continuous flow conditions. Valves at the influent and effluent ends of the test loop allowed isolation (static conditions) of the water in the loop for various test periods. At the end of the test period, samples were withdrawn for analysis for copper, ammonium ion, dissolved oxygen and temperature. The first copper pipe corrosion test loop received water with reduced ammonium ion and hardness. The second loop received GAC-treated water which was both low in TOC and chloramine residual. A third test loop received the chloraminated Southwest plant finished water and served as a comparative control.

Visual Indication of Slime Growth

Two treatment columns were filled with the same plastic packing material used in the Willmar aeration towers. These two columns were intended to serve as *visual indicators* of the development of attached bacterial slime on the plastic packing and column walls. One of these treatment columns received the GAC-treated (reduced TOC) water while the other received the treatment plant finished water directly. This was intended to provide a side-by-side comparison of microbial growth in reduced TOC (GAC-treated) and normal plant effluent. After over a month of continuous operation, visible development of organism growth (brown slime) was evident in both columns.

Results of Column and Copper Pipe Test Loop Studies

The treatment column effluents from the *GAC post-adsorber* and the *cation exchange resin* were each passed through their respective copper pipe test loops on a continuous basis for forty days. Periodically, the copper pipe test loops were isolated by valves on each end of the loop. The water within each loop was then allowed to remain static for periods ranging from 6 to 25 hours. At the end of these periods, water was withdrawn from each pipe loop and analyzed for *copper ion*, *ammonium ion*, *dissolved oxygen* and *chloramine residual*.

Southwest plant finished water was run through a parallel copper pipe test loop as a *control* against which the GAC and cation exchange effluents could be compared. The averages of 28 sequential copper pipe corrosion test studies are given in Table 4.

Copper ion was found to dissolve readily in all test loop studies within eight hours. The average copper ion concentration observed in the 28 *control* replicates slightly exceeded 2 mg Cu/l.

Effect of Removal of Organic Matter on:

a. Copper Corrosion

Initially, the *GAC post-adsorber* effluent appeared less corrosive to copper corrosion than the Southwest Plant water (control) in that, for the first ten days, copper ion averaged *0.85 mg Cu/l* in the static test loop tests as opposed to *1.65 mg Cu/l* in the control test loop. Thereafter, copper concentrations progressively increased in the copper pipe test loop provided with GAC-treated water until they exceeded the copper concentrations observed in the control.

To determine whether the initial result was an aberration, the test using the GAC-treated water was repeated twice (22 April; 2 May). Each time, the copper pipe test loop was cleaned, disinfected and placed back in service. For approximately a week after 22 April, copper ion concentrations again showed a marked reduction (averaging *1.1 mg Cu/l*) as compared with the control pipe loop (averaging *2.1 mg Cu/l*). However, thereafter, copper levels in the pipe loop receiving GAC-treated water again increased to levels exceeding those observed in the control. Once more, after the May 2 cleaning, copper levels in the test loop receiving GAC-treated effluent declined significantly. In this case, the beneficial effect lasted for only a few days.

These consistent results led to speculation that the removal of organic matter on GAC initially resulted in a decrease in the rate of copper corrosion in clean pipe. However, since little chloramine residual was present to retard organism growth, the progressive accumulation of biological film on the pipe surface was thought to have ultimately offset this advantage.

b. Nitrification

The average results shown in Table 4 indicate that little nitrification took place on the surface of the GAC medium. Whereas the *ammonium ion* in the Southwest Treatment Plant effluent averaged *2.6 mg N/l*, the GAC column effluent averaged *2.4 mg N/l*. This indication was confirmed by a dissolved oxygen depletion of 1.1 mg O/l in the GAC column effluent. This depletion would be consistent with the oxygen requirement for nitrification of 0.2 mg N/l of ammonium ion.

c. Chloramine Residual

As indicated earlier, the copper pipe corrosion test loop receiving GAC-treated water had virtually no chloramine residual (Table 4). However, the extensive depletion of chloramine from the Southwest Plant finished water (control) during storage in the copper pipe corrosion test loop was unexpected.

Chloramine is consistently maintained at approximately 2.8 mg Cl/l in the Southwest Plant finished water. After contact with the copper pipe corrosion test loop for periods ranging from 6 to 25 hours, the applied chloramine residual is reduced, on the average, to 0.3 mg Cl/l . It appears that, in as little as 12 hours, chloramine is almost totally depleted in the copper pipe test loop.

In summary, *GAC treatment* initially *retarded* copper corrosion rates. This effect was initially thought to be due to reduced concentrations of dissolved organic matter. However, the removal of the chloramine residual may have decreased the copper oxidizing capacity of the water stored in the copper corrosion test loops. Moreover, the absence of a disinfectant residual may have permitted colonization of the internal surface of the copper pipe with microorganisms which were able to accelerate copper corrosion rates. These results may have implications for those Willmar consumers using GAC cartridges in under-the-sink treatment units.

Removal of Ammonium Ion on Cation Exchange Resin

Corrosion rates in the copper pipe loop receiving water treated by cation exchange resin almost exactly replicated the values shown in the control loop (Table 4). Since cation exchange did not appear to have a beneficial effect on copper corrosion, these studies were not pursued.

However, the study results confirmed the effectiveness of cation exchange for near-complete removal of *ammonium ion* (Table 4). Even with the blending of 30 percent of Southwest Plant water, the ammonium ion concentration in the cation exchange column effluent was less than 1 mg N/l , a *63 percent overall reduction* from the plant influent concentration.

Both *dissolved oxygen* and *chloramine* concentrations in the copper pipe corrosion test loop series were comparable to the control. These replicate results would tend to confirm the accuracy and reproducibility of the test methods employed in the study. It also indicates that ammonium ion removal, in itself, did not reduce copper corrosion rates.

Overall, these tests demonstrated that ammonium ion can be very effectively removed from Willmar well water using cation exchange (softening) resin. Ammonium ion removal would subsequently lower *nitrite* and *nitrate* in the distribution system. It would also control microbially-mediated *dissolved oxygen depletion*.

Rate of Copper Corrosion

The effect of increasing residence time in the copper pipe corrosion test loops is indicated by the 28 studies conducted using *Southwest Plant finished water (control)*. Plotted on Figure 10, copper concentrations averaged 1.6 mg Cu/l when the static retention time in the test loop was 6 to 7 hours. Retention for 17 to 25 hours resulted in increases in copper concentrations to an average of 2.5 mg Cu/l .

Copper corroded most rapidly over the first six hours of contact, exceeding the 'copper action level' within that time. While progressively slower, copper corrosion continued with time, apparently approaching some steady-state concentration.

These 'control' results allow for comparison with the rates observed when *GAC-treated water* was applied to the copper pipe corrosion test loops (Figure 10). In parallel studies, copper concentrations in corrosion test loops receiving GAC-treated water averaged about 1 mg Cu/l after 6 to 7 hours of contact. This was 38 percent lower than the control. At the longer retention times, however, copper concentrations also increased to an average of 2.5 mg Cu/l .

A difference in the two sets of results is evident from the range of copper concentrations observed in the longer duration pipe loop studies. The corrosion test loop receiving Southwest Plant finished water exhibited copper

concentrations in the range of 1.9 to 3.3 mg Cu/l (13 tests) whereas the GAC-treated water produced copper concentrations ranging from 1.0 to 3.7 mg Cu/l. This broader range of copper concentrations (lower 'low' and higher 'high' values) indicates that different mechanisms of corrosion may have influenced corrosion rates.

While the data is limited, application of the cation exchange resin effluent yielded 1.8 mg Cu/l, exhibiting kinetics of copper corrosion similar to, but somewhat lower than, that of the control (2.1 mg Cu/l).

Removal of Microorganisms and Control of Nitrification in the Distribution System

In addition to the effects of pH and carbonate complexation on copper solubility, there are indications that microbial activity, principally, the activity of nitrifying bacteria, may play a role, directly or indirectly, in accelerating copper pipe corrosion.

Nitrification is an acid-producing reaction. The greater the activity of the nitrifiers, the lower the pH will become in a closed water distribution system. This effect is evident from the distribution system monitoring data of Table 2. During the March 1996 distribution system sampling, pH ranged from 7.0 to 7.9 as opposed to 8.1 to 8.4 in the Southwest Plant finished water.

Examples of the effects of nitrification were also strongly evident at specific points in the system. At distribution system sampling point #16 (Gary Faber), pH had declined to 7.0; temperature had decreased to 6.2 °C, and dissolved oxygen was totally consumed (0.0 mg O/l). Ammonium ion was virtually absent (0.19 and 0.12 mg N/l on two separate days). In addition, the chloramine residual had declined to 0.4 mg Cl/l. Other distribution system samples exhibited similar effects.

Copper corrosion notwithstanding, nitrification appears to be a precursor to anoxic conditions and water quality deterioration in the Willmar distribution system. Most significantly, nitrification is making it extremely difficult to maintain a bacteriostatic disinfectant residual throughout the distribution system. Transient levels of nitrite ion in excess of 1 mg N/l have been previously observed.

Impact of Granular Activated Carbon Treatment on Copper Corrosion

Two replicate tests using granular activated carbon post-adsorbers in the present study indicated that the removal of dissolved organic carbon (and color) from Willmar well water decreased copper corrosion for a short period. The short life of this effect was initially attributed to the loss of the bacteriostatic disinfectant (chloramine) residual. It was hypothesized that, subsequently, as a result of microbial growth, corrosion rates increased.

Subsequent studies of GAC post-adsorption and copper corrosion, conducted by the Willmar Water Department staff during July and August, 1996, provided extraordinary new evidence that *chloramine* is directly involved in the corrosion of copper pipe. This result explains the apparent benefit of GAC in reducing corrosion in the copper pipe corrosion test loops. In consuming the chloramine residual in the Willmar Plant finished water, GAC reduced the oxidizing agent which was actively corroding the copper pipe. Since comparable results have not been published in the waterworks literature, this work appears to be a significant contribution to the understanding of copper corrosion in drinking water distribution systems.

This discovery indicates that the installation of a GAC adsorption unit at the point-of-entry (POE) to a household or building may consume the oxidizing agent primarily responsible for the corrosion of the copper pipe.

Oxidation of Copper by Chloramine Disinfectant Residuals

The most recent corrosion test results (July-August 1996) from Willmar's continuing pilot plant studies using GAC post-adsorption followed by various dosages of chloramine provide strong evidence that the dosage of *chloramine* is the strongest factor influencing the corrosion of the copper pipe test loops. These results, presented in Figures 11 and 12, indicate that decreasing finished water chloramine to levels approaching 1 mg Cl/l should limit copper corrosion in household plumbing to less than the 1.3 mg Cu/l copper action level.

The principal barrier to decreasing the level of chloramine leaving the treatment plant is the loss (total consumption) of disinfectant during distribution. Under normal circumstances, low concentrations of chloramine will persist for hundreds of hours in finished water. However, when ammonium ion is present in excess, nitrifying organisms will oxidize the ammonium ion to nitrite ion and, ultimately, nitrate ion.

Nitrite ion, in particular, is a strong reducing agent. It combines rapidly with the chloramines to consume the residual in hours instead of days. This is the situation in the Willmar distribution system. High concentrations of ammonium ion in the well waters have resulted in the colonization of the distribution system with nitrifying organisms, possibly *Nitrosomonas*, which mediate the conversion of ammonium to nitrite ion.

In addition to the discoloration of poultry products, the presence of nitrite ion in a water distribution system may constitute a health threat (methemoglobinemia). Nitrite is therefore regulated at 1 mg N/l. For this reason alone, control of the activity of the nitrifying organisms is indicated.

Once the principal influence on copper corrosion was identified, the basic control strategy for Willmar reduced to the following:

- Reduce the concentration of chloramine applied as a distribution system residual.
- Control the loss of chloramine in the distribution system.
- Control the formation of nitrite during distribution.
- **Control the population and activity of nitrifying bacteria in distribution system.**

As a result of this assessment, a second phase of research was undertaken at Willmar, Minnesota. This study was directed at evaluating the technically and economically feasible alternatives for ammonium ion removal within the framework of the existing treatment process.