

Investigations of Copper Corrosion at Willmar, Minnesota

Part 1: The Problem and the Search for Effective Treatment Alternatives

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From recent specialty conferences and published literature, it appears clear that the magnitude of the problem nationally was unexpected until the results of monitoring at the state level became available. To make matters worse, neither the literature or active researchers in the field of drinking water can offer generally effective alternative methods for control of copper corrosion, even in hard waters. This is leading to the marketing of costly 'remedies' whose effectiveness is not universal and, often, has not been confirmed. As a result, state regulatory agencies are unable to offer effective alternative remedies for compliance with the problem of copper corrosion.

Background for Copper Corrosion Study Program

Because studies cited in the USEPA 1987 Criteria Document have determined that *"acute copper intoxication is associated with higher exposure levels among a wide variety of populations"*, USEPA established a Maximum Contaminant Level Goal (MCLG) of 1.3 milligrams per liter for copper in drinking water. The concentration of copper is to be determined on samples withdrawn from the consumer's tap after 6 hours of storage (static conditions) in the (copper pipe) plumbing system. Under the USEPA *Lead and Copper Rule* (56 FR 26460, promulgated June 7, 1991), monitoring for both lead and copper by public water systems in Minnesota began in 1992.

Following completion of the first round of the Minnesota copper/lead monitoring program, public water systems in Minnesota were found to be exceeding 'action exceedance levels' more frequently with respect to copper than with respect to lead. Moreover, the Minnesota Department of Health, Section of Drinking Water Protection, Public Water Supply Unit, reported that all copper exceedances were observed in water systems utilizing ground water. Overall, 129 community public water systems exceeded the limit of 1.3 mg Cu/l applied to 'first draw' samples taken from household taps.

A second round of copper/lead monitoring was conducted in 1993. The results appeared to be substantially the same as those observed in the first round of sampling. However, some water utilities had started to apply chemical additives to their finished water in an effort to reduce copper corrosion. The efficacy of these additives appeared to

be mixed. Even where reductions in copper levels were observed, copper concentrations remained near the 1.3 mg Cu/l "copper action level".

Characterization of Minnesota Ground Waters

Minnesota ground waters are characteristically hard (5 to 9 meq/l; 250 to 450 mg CaCO₃ equivalent/l) and similarly high in alkalinity as a result of equilibration with calcium carbonate. Sulfate and chloride concentrations vary widely, while nuisance levels of iron and manganese are frequently present. As a result, iron and manganese removal is commonly practiced. Because the waters are highly buffered by the carbonate system, pH reactions are generally neutral, ranging from 6.8 to 7.7 prior to aeration. The presence of iron and manganese indicate that reducing conditions commonly prevail in Minnesota ground waters.

Aeration of Minnesota ground waters characteristically results in the release of carbon dioxide, increasing pH and thereby causing supersaturation of the water with respect to calcium carbonate (positive calcium carbonate saturation indices). Since the ground waters are normally cool, oxygen solubility in fully aerated waters may be in the range of 9 (@ 20 °C) to 12 (@ 7 °C) mg O₂/l.

Observed Levels of Copper In Minnesota Household Tap Sampling

Two seasonal series of monitoring of 'first draw' tap samples (5255 sites) conducted by the Minnesota Department of Health in 1993/1994 yielded average copper concentrations of 0.24 mg Cu/l (July to October) and 0.28 mg Cu/l (January to April), respectively. The maximum copper concentration reported was 7.0 mg Cu/l.

Assessment of Willmar Municipal Utilities Data

Water Supply System Data for Willmar Municipal Utilities are given in Table 1. Raw and finished water alkalinities are very high at both plants. At 8 to 9 meq/l, alkalinity is two to four times greater than many hard Midwestern ground waters. Similarly, the hardness is about five times greater than what has been described as by an AWWA Committee (Elwood Bean, 1972) as 'ideal' for finished water (1 meq/l).

Aeration is used to increase raw water pH from 7.5 to 8.1. This is the key corrosion control treatment provided to limit lead and copper corrosion. The solubility of both metals decrease significantly with pH. Because Willmar's water is *supersaturated* with respect to calcium carbonate solubility (has a *positive* Langelier Saturation Index), any increase in pH above that currently maintained in the finished water (8.1) is likely to initiate precipitation in the mains. Otherwise, increasing the pH values to 8.5 or even 9 should remediate the corrosion problems. This could be done if Willmar's water was softened by lime precipitation. Alternately, pH *decreases* during distribution as a result of the acid production from the microbial process of nitrification.

Treatment for iron and manganese removal is consistently effective at Willmar through the use of potassium permanganate and greensand filters. Finished water residual color is the result of natural organic matter rather than iron or manganese residuals.

USEPA-Identified Treatment Approaches for Copper Corrosion Control

Four methods have been cited by USEPA for optimum copper corrosion control treatment (OCCT):

- pH/alkalinity adjustment -- to decrease solubility of carbonates, oxides,
- calcium adjustment -- to increase calcium carbonate supersaturation,
- polyphosphate addition -- to cause formation of phosphate films on piping,
- silicate addition -- to cause formation of silicate films on piping.

The first, and most obvious, treatment requires the adjustment of pH and alkalinity. Lead and copper are known to corrode most rapidly in low pH, low alkalinity waters, such as in the soft waters of New England and the Southeastern United States. In Minnesota ground waters, however, pH and alkalinity are initially sufficiently high that corrosion rates would be expected to be moderated without further adjustment. Only very small additional increases in either pH or alkalinity can be accomplished without initiating large-scale precipitation of calcium carbonate (i.e., softening by precipitation).

The hard waters of Minnesota are also rich in calcium. The application of additional calcium salts (generally, lime), similarly, will result in calcium carbonate precipitation (lime softening). Therefore, neither of these two control methods offers a suitable option for most Minnesota ground waters.

By default, the optimal corrosion control option in Minnesota appears to be limited to treatment of the distributed water by the addition of a chemical 'inhibitor'. Since there are, at least, 200 commercially available variants of these compounds, Minnesota water utilities are currently faced with the need for complex evaluations of numerous proprietary chemical formulations.

Alternative Corrosion Control Treatment Options

Limited to the sole remaining option (addition of a sequestering agent) which has previously proven ineffective (and troublesome) in the control of iron and manganese in their distribution system, the City of Willmar authorized the implementation of a research program to identify and evaluate *alternative* strategies for the control of copper corrosion.

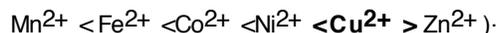
Nitrification and the Removal of Ammonium Ion

The City of Willmar, using a comprehensive distribution system monitoring program, had previously demonstrated the progress of nitrification (biologically-mediated conversion of ammonium ion to nitrite and nitrate accompanied by the stoichiometric depletion of oxygen) in their distribution system (Table 2). This process takes place as chloramine residuals are dissipated in the system permitting bacterial processes to proceed.

The City of Willmar had determined that there was sufficient ammonium ion in their well water sources ($\text{NH}_4^+ \approx 2$ to 3 mg N/l) to completely consume the oxygen (10-11 mg O/l) introduced during packed tower aeration. [One milligram of ammonium ion, expressed as N, will consume $64/14 = 4.57$ milligrams of oxygen through nitrification.] Preliminary indications were that both nitrification and copper corrosion proceeded simultaneously during water distribution, so that there might be a causal relationship between the two phenomena.

One of the alternative control options under investigation, therefore, was the removal of ammonium ion on cation exchange resin to assess the effect of reduced ammonium ion on nitrification and, possibly, copper corrosion.

The City of Willmar had also previously determined that their well water sources were also high in dissolved organic carbon, presumably, the result of refractory (persistent) humic and fulvic substances extracted from the rich Minnesota soil. Copper is known to be complexed more readily than most other metals by such organic ligands (Irving-Williams Series {organic complex stability sequence of the transition metals}):



Removal of Dissolved Organic Carbon on Granular Activated Carbon

A second alternative control measure investigated was the use of granular activated carbon post-adsorption for the reduction of the dissolved organic carbon content of the well waters. The effect that this treatment has on copper corrosion was observed using copper pipe test loops installed at the Willmar Southwest treatment plant.

Total Organic Carbon in Willmar Well Waters and Finished Waters

Previous analyses had indicated that TOC concentrations were high in the treated water from both treatment plants. Additional samples were collected as part of the present study. The results, presented in Table 3, indicate that the Southwest wells and finished waters are comparable and range from 2.8 to 4.2 mg C/l, averaging 3.7 mg C/l. TOC in the Northeast wells and plant finished water ranged from 4.8 to 5.6 mg C/l, averaging 5.2 mg C/l.

A comprehensive survey of 101 Missouri water supplies by the authors, first conducted in 1980 and repeated in 1989 for validation, indicates that Willmar's TOC concentrations are very high as compared with other hard, alkaline, Midwestern ground waters. Of the 101 Missouri water supplies analyzed for TOC, 16 were from shallow wells (<30 m) which averaged 1.2 mg C/l while 42 were from deep wells (>30 m) which averaged 0.18 mg C/l.

The substantial amount of organic matter derived from the Willmar wells may have several important influences on copper corrosion and organism growth in the Willmar water distribution system:

Organic Chelation

Since terrigenous humic compounds are typically 50 percent carbon (by weight), Willmar's Northeast well field may be yielding approximately 10 mg/l of humic substances. This concentration may be capable of complexing (and solubilizing) metals by chelation with their associated carboxyl and phenolic groups. The effect of copper chelation on solubility and the rate of copper solution may be only partially responsible for the high concentrations of copper observed in household plumbing, however.

Peptization

To further complicate matters, high concentrations of humic substances are known to peptize (disperse or stabilize) precipitates (such as calcium carbonate, iron oxide), thereby preventing deposits from accumulating on pipe surfaces. In contrast with observations made in other regions of the Midwest which supply high hardness well waters, few significant surface deposits were observed on the inside of copper pipe sections removed from Willmar households. The failure to establish such protective barriers may also contribute to the accelerated corrosion of copper.

Stimulation of Microbial Growth

Finally, it is not generally recognized that the organic substances derived from ground waters, although months or years old, may still be partially labile. This means that this organic matter may be more rapidly degraded by aerobic microorganisms once the water is brought to the surface and oxygenated through aeration. As evidenced by the presence of iron and manganese in the ground water, there is no oxygen present in the ground water up to the time it is withdrawn. This precludes any microbial activity by those organisms which require oxygen for their respiration.

Upon being withdrawn from the wells, Willmar's water is, first, aerated. From a chemical standpoint, aeration introduces oxygen and rapidly precipitates the dissolved iron present in the ground water. The iron oxides formed can subsequently be removed by filtration. Aeration also discharges carbon dioxide, markedly increasing the pH of the water. In some cases, hydrogen sulfide and methane are also among the gases stripped by aeration.

In some ground waters containing filamentous, iron-precipitating bacteria, a significant biological transformation is observed. The strictly anaerobic organisms withdrawn along with the ground water lyse (self-destruct) in the presence of oxygen. They are rapidly replaced by aerobic (oxygen-utilizing) heterotrophic organisms. If this is occurring in Willmar, it is not evident from direct observation, because filamentous, iron-precipitating bacteria are notably absent from the well waters.

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Part 2, "*Nitrification, Bacteria and Copper Corrosion in Household Plumbing*", of this series will present the results of

in-situ investigations of the progress of nitrification and copper corrosion in household plumbing. In addition, data will be presented on direct total bacterial cell counts and heterotrophic plate counts in the well water source, treated water, distributed water and after storage in a household plumbing system.

Table 1. Willmar Municipal Utilities - Water Supply System Data

Willmar, Minnesota - Public Water Supply ID No. 1340016
 Bart Murphy - Superintendent of Water (612) 235-4422

Water Sources: Southwest Wells, Northeast Wells
 Treatment Plants (2): Southwest Plant, Northeast Plant
 Treatment: Packed Tower Aeration, Permanganate Oxidation, Pressure Greensand Filtration, Chloramination, Fluoridation.
 Population Served: 22,000
 Water Production: 3.4 mgd (average); 6.9 mgd (peak)

Finished Water Characteristics:

pH: 8.1 Temperature: 5-15 °C
 Alkalinity: 400 mg CaCO₃ equiv./l (8.0 meq/l) - Northeast
 441 mg CaCO₃ equiv./l (8.8 meq/l) - Southwest
 Calcium: 150 mg CaCO₃ equiv./l (3.0 meq/l) - Northeast
 260 mg CaCO₃ equiv./l (5.2 meq/l) - Southwest
 Ammonium Ion: 3.0 mg N/l (NE); 2.8 mg N/l (SW)

Iron and Manganese Removal Effectiveness

Iron (Southwest): 1.67 mg Fe/l (Raw) 0.00 mg Fe/l (Finished)
 Manganese (Southwest): 0.109 mg Mn/l (Raw) 0.05 mg Mn/l (Finished)
 KMnO₄ Consumed: 1.6 mg KMnO₄/l (after 10 minute reaction time)

July-December 1992 - First Round Tap Monitoring Results

Lead: Min. < 5 µg Pb/l Maximum: 43 µg Pb/l 90% Value: 11 µg Pb/l
 Copper: Min. <50 µg Cu/l Maximum: 7.0 mg Cu/l 90% Value: 4.08 mg Cu/l

Corrosion Control Treatment: Aeration to increase pH from 7.5 to 8.1

Table 3. Results of Total Organic Carbon Analyses

Southwest Water Treatment Plant - TOC, mg C/l (West Wells)

19 March 1996	Raw: 3.6	Finished (Southwest): 3.8
19 March 1996		Finished + GAC: <0.5
22 March 1996	Raw: 3.8	Finished (Southwest): 3.5
22 March 1996		Finished + GAC: <0.5
22 March 1996	W-7: 3.9	
22 March 1996	W-8: 2.8	
22 March 1996	W-9: 3.9	
22 March 1996	W-12: 3.8	
22 March 1996	W-14: 3.8	
22 March 1996	W-15: 3.5	
22 March 1996	W-16: 3.5	
22 March 1996	W-18: 4.2	

Mean: 3.7

Northeast Water Treatment Plant - TOC, mg C/l (East Wells)

22 March 1996	Raw: 5.2	Finished (Northeast): 5.4
22 March 1996	E-10: 5.6	
22 March 1996	E-19: 5.2	
22 March 1996	E-20: 5.4	
22 March 1996	E-21: 4.8	

Mean: 5.2

Test of Effect of Lime Softening on TOC, mg C/l (Southwest Plant)

22 March 1996	Unsoftened: 3.8
22 March 1996	Lime Softened: 3.6

Total Organic Carbon In Willmar, MN Well Waters; GAC Effluent

