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CONTROL OF COPPER CORROSION OF HOUSEHOLD PLUMBING MATERIALS

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INTRODUCTION

The promulgation of the "Lead and Copper Rule" by the USEPA in 1991 has forced hundreds of water utilities nationwide to become concerned with controlling the uniform corrosion of copper plumbing materials. The exact extent of the problem is hard to quantify, but in the first round of monitoring by the large water systems (about 682), approximately 6 % exceeded the 1.3 mg/L action level according to an AWWA study. The highest copper levels for these utilities appeared to be in the southeastern and western regions of the United States, in utilities covering a considerable range of water qualities. The cuprosolvency problem apparently increases with decreasing utility size. When medium-sized water systems are included, large numbers of action level exceedences for copper occurred in the central and north-central midwest, implicating areas having hard and high alkalinity ground waters of approximately neutral pH. These water qualities are not those conventionally considered "corrosive".

Unfortunately, the regulatory monitoring data are of limited use for extracting details of copper chemistry behavior and understanding potential copper passivation strategies. Nonetheless, several interesting gross-scale trends have been discerned for large water systems. One example is that there is a poor correlation between 90th-percentile lead and copper levels. Another trend is that copper exceedences tended to be highest at very low alkalinities (<25 mg $CaCO_3$/L) and increasingly greater over 75 mg $CaCO_3$/L. Finally, no action level exceedences were reported for systems having a pH above approximately 8.

The data thus far suggest that cuprosolvency (copper solubility) will be a major concern across the United States, especially for smaller water suppliers that are less likely to employ corrosion control and use ground water sources. Further, the poor correlation between reported 90th-percentile lead and copper levels suggests that different control strategies for copper than those considered appropriate for lead may need to be developed or employed by affected utilities. Understanding how copper will respond to lead control measures and the results of other regulatory treatment requirements is therefore of considerable interest. Indeed, a response that effectively controls lead corrosion might exacerbate copper corrosion. Moreover, a utility must distribute aesthetically-pleasing water. A good example of the conflicts between control of corrosion of iron mains and reducing copper corrosion rates has been given for a study in Vancouver, BC.

In attempting to address some of the data gaps for cuprosolvency control by utilities, a variety of experimental systems have been constructed and operated in USEPA laboratories. During these experiments, some perplexing data was generated that appeared to either contradict some "conventional wisdom" on copper corrosion, or showed unexpected sensitivities to important water chemistry variables and experimental system operational protocols. These observations provided the motivation to begin

exploring the "cuprosolvency" (copper solubility) issue in detail. The initial results of this ongoing research are reported in the new U. S. Environmental Protection Agency publication[1].

An accurate equilibrium model for cuprosolvency provides utilities and consultants with a useful and practical tool for reliably selecting and applying corrosion control programs that will work over the long term. A sound theoretical and practical understanding of the important factors affecting cuprosolvency greatly obviates the need for complicated, costly, and sometimes misleading bench-top and pilot-plant experimental studies. Small and medium-sized water systems frequently lack the technical sophistication as well as the mechanical and financial resources needed to conduct elaborate "demonstration" studies. For water systems able to conduct experimental treatment evaluations, an accurate model for cuprosolvency reduces the need for including fundamental tests (*e.g.* pH and carbonate concentration effects) in their evaluations. Utilities may then concentrate on determining the need for additional experimental evaluations of inhibitor treatments or investigation of other unusual chemistry characteristics of particular water systems.

A better understanding of roles of pH and DIC (dissolved inorganic carbon) in cuprosolvency greatly improves the accuracy of regulatory "desk-top" corrosion optimization evaluations, thereby providing a better assessment of long-term treatment impacts than those ascertained over a short time-frame (*i.e.* weeks, months). Finally, an accurate solubility model for copper allows many utilities to achieve the requirements of the Lead and Copper Rule without the need to conduct the treatment studies.

A newly-emerging indirect constraint on copper corrosion control in drinking water is by wastewater effluent guidelines and limits that are becoming increasingly stringent. Ironically, ambient corrosion of domestic, commercial and institutional plumbing systems is now becoming a "contaminant" of wastewater that is becoming difficult to control to an adequate degree through normal waste treatment processes. The development of an accurate model for copper solubility allows the evaluation of treatment alternatives for optimizing the control of cuprosolvency beyond drinking water regulatory requirements, to achieve adequate levels at the end of wastewater treatment.

OXIDATION REACTIONS OF COPPER

Because of the positive cell potentials for copper metal oxidation, copper pipe in water containing oxidizing agents will continue to corrode until either all of the oxygen is depleted, or until precipitated oxide films arrest the rate of corrosion. There is some evidence that the overall transformation from Cu^+ to Cu^{2+} is essentially the rate-limiting factor, with Cu^+ existing in reversible equilibrium with the Cu metal at the pipe surface.

In drinking waters, the oxidizing agents (electron acceptors) that will cause the corrosion of metallic copper are predominantly dissolved oxygen and aqueous chlorine species. These reactions may be composed of several intermediate steps, any of which can be rate-controlling. Many studies have documented (to some degree) the impact of dissolved oxygen or aqueous chlorine species on copper oxidation and dissolution rates. Free chlorine species (i.e. HOCl , OCl^-, Cl_2) have not been conclusively shown to affect the equilibrium solubility of copper, other than by influencing the valence state of the copper by its presence or absence.

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[1] Schock, Michael R., Lytle, Darren A., and Clement, Jonathan A. Effect of pH, DIC, Orthophosphate and Sulfate on Drinking Water Cuprosolvency. EPA Office of Research and Development, Cincinnati, Ohio, 1995. In press.

Oxidants may have several other potential impacts on the observed copper levels in the water and the nature of the passivating solids on the pipe. The effect of chlorine on the oxidation rate of the copper metal might be alteration of the crystalline characteristics and porosity of the oxide corrosion product film produced at the pipe surface. For example, by reducing the formation of a protective $Cu_2O(s)$ underlayer through maintaining a high E_H level, or by indirectly influencing scale structure and conductivity through chloride formation as the chlorine is reduced. However, many of the apparent effects of chlorine on copper solubility may merely result from accelerated corrosion kinetics (rates), rather than changes in equilibrium conditions.

Copper plumbing can be exposed to a wide environment of E_H-pH conditions. This environment evolves as oxidation and reduction reactions occur through corrosion and deposition processes for different lengths of stagnation times, and in different diameters of pipes. Therefore, all three normal copper valence states (metal, +1, +2) could reasonably occur under drinking water conditions either geographically or with time. The relative stabilities of Cu(I) and Cu(II) species in aqueous solution depend very strongly on the nature of anions or other ligands present in the water.

Solubility Chemistry of Copper (I) and Copper(II)

Because the immune region for copper corrosion extends well above the minimum E_H for water stability, water does not corrode copper in the absence of oxygen or other added oxidants. With the addition of electron acceptors to the solution (e.g. HOCl , O_2), either or both of the oxide solids Cu_2O (cuprite) or Cu(OH) may form. The equilibrium solubility of cuprous copper, $S_{T,Cu(I)}$, may be described as the sum of the concentrations of all dissolved cuprous species:

$$S_{T,Cu(I)} = [Cu^{+}]+[CuCl^{\circ}]+[CuCl_2^{-}]+[CuCl_3^{2-}]+[Cu_2Cl_4^{2-}]+[CuNH_3^{+}]+[Cu(NH)_3^{+}]$$

in which [ ] (brackets) indicate concentration in mol/L. The total solubility may then be computed by standard techniques. Under relatively anoxic drinking water conditions, such as many well waters, pH and chloride concentrations are the dominant controls on copper solubility. Metastable solid formation and the rate of the oxidation reaction are important in governing copper levels at the tap. Ammonia forms strong complexes, but little research has been done to determine its significance in drinking water.

Under oxic conditions, copper(II) aqueous speciation is dominated by hydroxide, carbonate, and hydroxycarbonate complexes. Weak complexes are formed with sulfate, orthophosphate and chloride. Strong complexes are formed with ammonia, but the high concentrations of carbonate, bicarbonate and hydroxide usually swamp out any expected impact on the speciation. Generally, copper(II) solubility is given by the equation:

$$S_{T,(OH,CO_3)} = [Cu^{2+}]+[CuOH^{+}]+[Cu(OH)_2^{\circ}]+[Cu(OH)_3^{-}]+[Cu(OH)_4^{2-}]+2[Cu_2(OH)_2^{2+}]+3[Cu_3(OH)_4^{2+}]+$$
$$[CuHCO_3^{+}]+[CuCO_3^{\circ}]+[Cu(CO_3)_2^{2-}]+[CuCO_3OH^{-}]+[CuCO_3(OH)_2^{2-}]$$

In new plumbing systems, copper(II) solubility is generally controlled by a poorly-crystalline form of cupric hydroxide, $Cu(OH)_2$. This scale ages, and after some time becomes either CuO (cuprite) or $Cu_2CO_3(OH)_2$ (malachite), depending on pH and the dissolved inorganic carbon concentration. Below about pH 7.5, orthophosphate reduces copper(II) solubility. The effect is particularly strong in the pH range of 6.5 to 7, and is fairly consistent with the hypothesis of the formation of a solid of approximately the composition of $Cu_3(PO_4)_2 \bullet 2H_2O$. Orthophosphate also appears to interfere with the normal formation of cupric oxide, cupric hydroxide, and malachite, at low DIC concentrations.

Little research has been done on the effect of sulfate on copper solubility in potable water. Results of this ongoing research project so far suggest that sulfate plays a major role in the increase of soluble copper(II) through the formation of a metastable basic cupric hydroxide solid, such as $Cu_4(OH)_6SO_4 \cdot 2H_2O$. This effect appears to be particularly strong above pH 8.

PRACTICAL CONSEQUENCES OF REDOX POTENTIAL ON CUPROSOLVENCY

In water supplies maintaining oxidizing disinfectant residuals, copper oxidation and dissolution into the water will take place until both that residual and dissolved oxygen are depleted. However, copper levels will stop climbing after saturation equilibrium is reached with a passivating solid (e.g. $Cu(OH)_2$). The profile of copper concentration versus time in oxidizing systems will depend upon the water chemistry and the relative stabilities of copper(I) and copper(II) aqueous species. The copper concentration in the water may continue to rise for many hours, perhaps substantially beyond the "overnight standing" period normally used for sampling, depending on the operative kinetics in a given system. Complexation of either copper(I), copper(II), or both, will be important in these systems.

In undisinfected water systems having low levels of dissolved oxygen, such as many closed ground water systems, complicated copper versus time profiles may result, as the initial small quantity of oxygen is consumed. This behavior is consistent with the observation of short-term copper concentration maxima, followed by decrease in concentration, reported in several studies. Copper(I) aqueous speciation and solid reactivity are extremely important in these systems. Different parts of a distribution system, particularly ones fed by a combination of different water sources (such as multiple wells or a mix of wells and conventionally-treated surface water), may exhibit different stagnation profiles.

For the anoxic systems, the use of aeration for VOC, radon or iron removal may cause increased copper levels, because copper(II) solids are virtually always more soluble than copper(I) solids. Unanticipated violations of copper corrosion action levels may result from the installation of any new oxidation processes for water treatment. In contrast, for oxic systems, proper aeration may strip DIC from the water and increasing pH, both favorable effects in reducing copper(II) solubility.

Significant variability in copper levels from site to site in the same water system will likely be found in water after the normal number of hours of stagnation found in most sampling programs. This results from the interaction of aqueous complexation and oxidation chemistry of copper, plus effects of the existence or development of passivating films in the pipe. Examination of copper concentrations in experimental coupon cells and pipe loop systems after various standing times frequently show almost linear increases in concentration extending far beyond the 6-16 hour standing time requirement of regulatory sampling.

SIGNIFICANCE OF pH AND DIC IN CUPROSOLVENCY CONTROL

The relationship between DIC and copper(II) solubility is very complex. DIC can play several significant roles, depending upon its concentration, other water chemistry factors, age of plumbing, water flow amount and pattern of use.

This research has shown conclusively that trends in copper concentrations resulting from uniform corrosion are predictable for a range of appropriate water qualities. Given that field conditions frequently do not reflect equilibrium conditions, some discrepancy between the model predictions and the results of normal tap water monitoring programs is completely understandable. Nonetheless, using a comprehensive equilibrium solubility chemical model, water quality objectives for copper corrosion control by pH and DIC adjustment can be predicted without the necessity of complicated experimental and field studies.

In new plumbing or at high pH, where cupric solubility is controlled by either cupric hydroxide or cupric oxide, DIC complexes dominate copper speciation above pH 7.5, resulting in increased cuprosolvency. The solubility enhancement effect is strongest in the DIC range of 0 to 20 mg C/L, but the predicted soluble copper at equilibrium is still below about 1 mg/L.

DIC serves to control the buffer intensity in most water systems. Therefore, sufficient DIC is necessary to provide a stable pH throughout the distribution system for corrosion control of copper (and lead). In treatment practice, the increase in DIC to ensure pH control through buffering will probably need to be offset by increasing pH to maintain lowered cuprosolvency.

Possibly offsetting the solubility enhancement of copper(II) by carbonate complexes is the possibility that moderate DIC levels would logically accelerate the formation of passivating $Cu_2CO_3(OH)_2$ (malachite) films in the pH/DIC region where it would be thermodynamically stable. Thus, enhancement of conditions that would hasten the formation of $Cu_2CO_3(OH)_2(s)$ (malachite), CuO(s) (tenorite), or both, relative to cupric hydroxide, would result in a net lower copper(II) solubility, even with the existence of some additional carbonate complexation.

In the region of pH from approximately 8.5 to 10, this solubility model developed occasionally predicts slightly lower copper(II) solubility than has actually been observed in some well-controlled pipe loop and precipitation studies. The discrepancies are most likely the result of formation constant errors, inadequacies of understanding copper(II) aqueous complexation with hydroxide and carbonate, or the presence of metastable copper solids associated with anions other than carbonate or hydroxide.

SIGNIFICANCE OF pH AND ORTHOPHOSPHATE IN CUPROSOLVENCY CONTROL

Because cupric hydroxide solubility has been shown to be a better estimate of cuprosolvency tendencies in many water systems than previously presented models based on $Cu_2CO_3(OH)_2$ (malachite) equilibrium, orthophosphate in sufficient dosage is now predicted by the models to have an ability to further reduce copper levels in the pH range of approximately 6.5 to 7. The necessary dosage is hard to quantify, but the calculations suggest that 3-5 mg PO_4/L orthophosphate may be necessary to achieve substantial improvements in cuprosolvency over the DIC/pH system at approximately pH 8, but perhaps only 1-3 mg PO_4/L at approximately pH 7. More investigation is still needed to ascertain objectively and consistently if any synergistic cuprosolvency reduction effect exists from the use of blended phosphates rather than orthophosphate, as has been suggested by one research project.

IMPLICATIONS FOR CONTROLLING HIGHEST COPPER EXPOSURES

The distinct aging process noted for recrystallization and development of cupric hydroxide, cupric oxide, and cupric orthophosphate films raise an important caution for determining the highest exposures to copper in drinking water. While the Lead and Copper Rule was specifically intended to bias the sampling site selection towards locations with high relative risks for lead exposure, these sites do not generally correspond to commensurately high risks for copper exposure, which include: newest construction and remodeling, areas with unstable pH, and dead ends.

Changes in solubility of copper as pipes age, and films build up, has been indicated in several studies and by practical experience. This investigation has shown how such a phenomenon may have a firm chemical basis that has heretofore been unappreciated. In practice, when attempting to predict the impact of different water treatment scenarios on cuprosolvency, a fruitful strategy may be to apply different solubility models depending on the general age of the plumbing systems involved. For example, for older neighborhoods where $Cu_2CO_3(OH)_2$ (malachite) and CuO (tenorite) have had sufficient time to form an integral part of the passivating film, a better prediction of pH, DIC and orthophosphate dosing impacts would be obtained using their solubility constants to predict copper levels and success of different hypothetical control strategies. Conversely, for areas predominantly of new construction, a "cupric hydroxide model" would be more applicable.

SIGNIFICANCE OF THE "CUPRIC HYDROXIDE MODEL" FOR DEMONSTRATION STUDIES

Utilities may encounter some complications in projecting pipe loop or coupon leaching cuprosolvency data obtained in demonstration studies to behavior across the whole distribution systems. In the absence of significant concentrations of orthophosphate, this research indicates that for the short timeframes of most experimental studies conducted to satisfy Lead and Copper Rule requirements (6 months to 2 years in most cases), cupric hydroxide will usually be the most important solid phase, rather than CuO(s) (tenorite) or $Cu_2CO_3(OH)_2(s)$ (malachite). Both pH and DIC effects will be magnified in the experimental systems, relative to significantly aged piping in the distribution system.

Because of the slow oxidation rate relative to diffusion rates, it is unlikely that copper concentrations are at "equilibrium" when samples are taken from experimental pipe rig systems operated to allow "overnight" standing times, unless the systems have been operated long enough that the passivating films are well-developed, perhaps for years.

When orthophosphate dosing is tested, overestimates of its effectiveness could be obtained for distribution system areas having old copper plumbing with well-developed passivating films. The experimental systems may also be very sensitive to minor dissolved oxygen, chlorine residual, sampling, and stagnation time fluctuations, because of the highly non-equilibrium nature of copper behavior in the 6-16 hour time period.

OTHER IMPORTANT APPLICATIONS OF EQUILIBRIUM CUPROSOLVENCY MODELS

In addition to the applications to drinking water corrosion control, the solubility model has considerable application to several other important environmental research areas, namely:

- aqueous speciation of copper in relation to aquatic toxicity
- estimation of the impact of domestic and institutional plumbing corrosion on wastewater loading
- estimation of the feasibility of various wastewater effluent guidelines for copper
- estimation of copper removal from wastewater by hydroxide or carbonate precipitation

HYDRAULIC FRACTURES AS SUBSURFACE ELECTRODES: EARLY WORK ON THE LASAGNA PROCESS

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INTRODUCTION

Fine-grained sediments present the greatest obstacle to in situ remediation at many contaminated sites. Where fine-grained sediments are continuous, discharges from wells are slow and contaminants are recovered at negligible rates. In contrast, at sites underlain by interbedded sand and silt or clay, volumetric discharges from wells can be significant as water is readily recovered from the more transmissive sands. The rate of recovery of contaminants can be rapid as the sands are flushed during initial operations, but the clay interbeds act as persistent sources of contaminants so that concentrations can be maintained at small but serious values for many years.

Hydraulic fractures filled with coarse-grained sand provide high permeability layers that increase fluid flow primarily by reducing the large losses of hydraulic head in the vicinity of a well (1,2). These features have been shown to increase the discharge from wells by an order of magnitude or more (2). Nevertheless, current applications of hydraulic fractures are designed to improve the recovery and removal of contaminants from the subsurface by advective processes. Effects related to adsorption, preferential flow and other processes can result in mass transfer limitations that require a large number of pore volumes of fluid to be moved through porous material before it is remediated using hydraulic flow alone.

Electrokinetics is an effective method of inducing the movement of water, ions, and colloids through fine-grained sediments. In this process, typically a direct current is applied to the sediment, inducing osmotic movement of water away from a positively charged anode and toward a negatively charged cathode (3). Ions and colloids migrate toward the electrode with a charge opposite from the one that they carry (3,4). In addition, electrolysis of water results in a decrease in pH at the anode and an increase at the cathode (4). The acidic conditions at the anode and the basic conditions at the cathode will propagate into the region between the electrodes, potentially forming a sharp discontinuity in pH (4,5).

Based on the results of laboratory tests and limited field applications (7), electrokinetics has been shown to be a promising method of recovering ionic and water-soluble contaminants. However, the process is not without problems. Acidic conditions and electrolytic decay can corrode some anode materials. Sharp discontinuities in pH induced within the soil mass by electrokinetics could result in a deposition front where minerals are precipitated in soil pores, markedly reducing permeability and inhibiting recovery. It may be possible to mitigate problems related to pH by circulating a buffering solution across the electrodes (7).

Another drawback to conventional electrokinetic remediation is that it requires contaminants to migrate from their initial location to an electrode and then up to the groundsurface. In some cases, the migration path could be long or there could be stagnant zones between wells where the rate of migration is particularly slow, both of which result in incomplete remediation of the contaminated zone. Moreover, sharply convergent electrical fields can result in heating and potential losses in the vicinities of electrodes, just as convergent flow paths result in head losses in the vicinities of wells. Electroplating, or pH-related deposition can cause contaminants to be removed from solution prior to arrival at the ground surface.

Recent investigations have shown that it may be possible to address some of the shortcomings of electrokinetics by degrading contaminants in situ. Our colleagues have developed a solid compound (8), which slowly releases oxygen, that can be injected into