

# Interactions Between Copper and Chlorine Disinfectants: Chlorine Decay, Chloramine Decay and Copper Pitting

Caroline Kimmy Nguyen

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Dr. Marc Edwards, Chair  
Dr. Andrea Dietrich  
Dr. Peter Vikesland

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## ABSTRACT

Interactions between copper and chlorine disinfectants were examined from the perspective of disinfectant decay and copper pitting corrosion. Sparingly soluble cupric hydroxide catalyzed the rapid decay of free chlorine, which in turn, led to production of less soluble and more crystalline phases of cupric hydroxide. The catalytic activity of the cupric hydroxide was retained over multiple cycles of chlorine dosing.

Experiments with chloramine revealed that copper species could also trigger rapid loss of chloramine disinfectant. In copper pipes, loss of free chlorine and chloramine were both rapid during stagnation. Reactivity of the copper to the disinfectants was retained for weeks. Phosphate tended to decrease the reactivity between the copper pipe and chlorine disinfectants.

A novel, inexpensive and real-time test to monitor copper pitting corrosion was developed. In a normal pipe, it is not possible to measure the electron flow or *pitting current* from the pit anode to the cathode. But a new method was developed that can form an active pit on the tip of a copper wire, which in turn, allows the pitting current to be measured. Preliminary experiments presented herein have proven that this technique has promise in at least one water condition known to cause pitting. The method also quickly predicted that high levels of orthophosphate could stop pitting attack in this water, whereas low levels would tend to worsen pitting. Future research should be conducted to examine this technique in greater detail.

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# **CHAPTER 1: Review of Copper, Lead, Iron, and Nitrogen Interactions**

Caroline K. Nguyen, Marc A. Edwards\*  
Dept. of Civil and Environmental Engineering  
Virginia Polytechnic Institute and State University,  
407 Durham Hall, Blacksburg, VA 24061-0246

\*Corresponding author phone: 540-231-7236; fax: 540-231-7916; e-mail: [edwardsm@vt.edu](mailto:edwardsm@vt.edu)

## **ABSTRACT**

The chemical reactions of chlorine and chloramine can drive corrosion reactions with lead and copper plumbing materials, leading to premature failures and consumption of the disinfectant residual. Nitrogen species can also be involved in corrosion reactions with metals. These reactions are first discussed from the perspective of equilibrium for copper, lead, and iron metals, and chlorine and nitrogen species. Thereafter, current knowledge regarding the kinetics of the reactions is reviewed.

## **1.1 EQUILIBRIUM**

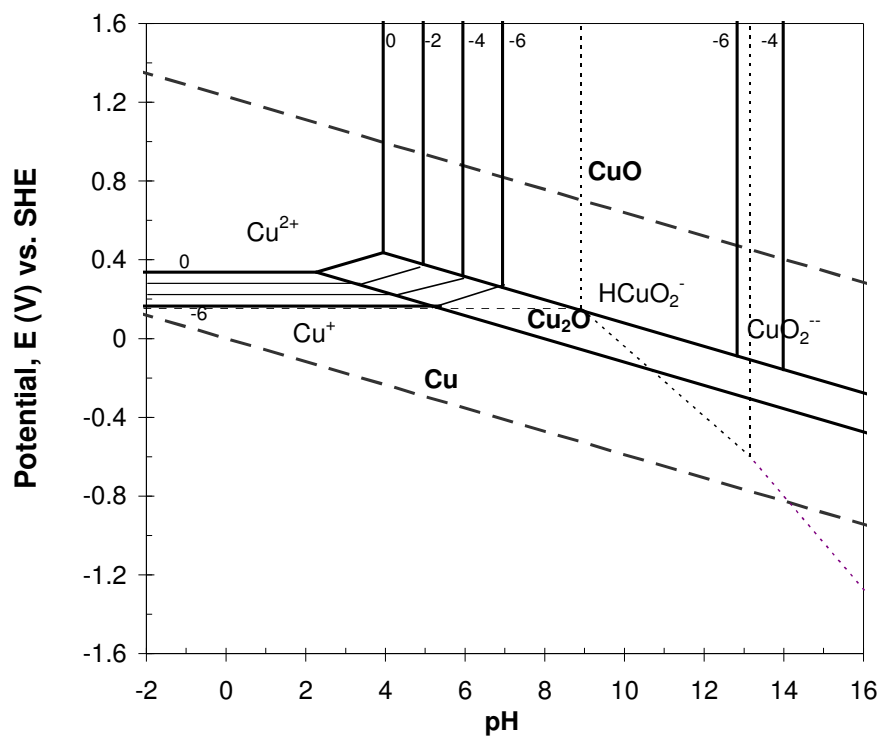
Potential-pH (pE-pH) or Pourbaix diagrams are useful in predicting chemical equilibrium in water. Pourbaix diagrams are developed from thermodynamic constants based on Nernst equations <sup>[1]</sup>.

To interpret potential-pH diagrams in the context of metallic corrosion, a few general rules have been established. Thermodynamically, a metal is completely immune to corrosion when the metal itself is the thermodynamically predicted stable species. Under such circumstances, the metal will not be eaten away, as in the common example of gold, which is immune to corrosion in normal waters. If the water chemistry is such that a soluble metal ion is the thermodynamically predicted stable species, and solid (e.g., rust) layers do not form, contact of the metal with the water will result in very rapid corrosion.

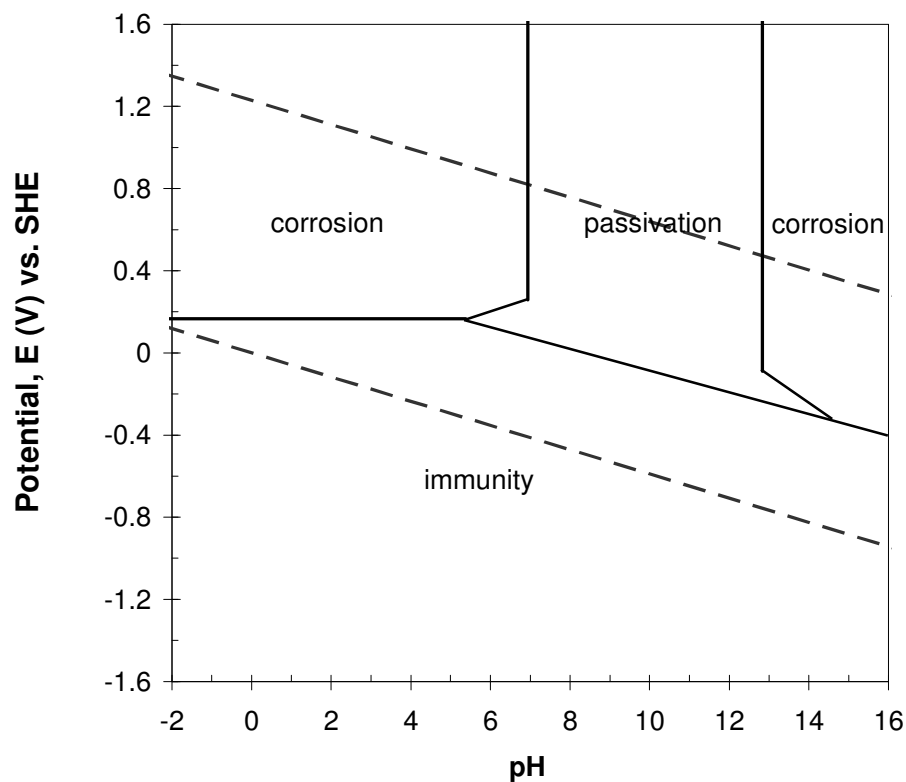
An obvious example is sodium metal, which reacts violently with water in a very rapid corrosion reaction.

The situation for metals in aerated water distribution systems is between the above extremes, as the metal itself is not stable thermodynamically, but the metal ions released during corrosion can form precipitates or rust layers on the pipe. To the extent this rust layer is a good barrier between the water and the underlying metal, the rate of corrosion can be reduced to very reasonable levels. This explains why iron pipes can last for decades or centuries to transport water, even though the thermodynamic destiny of iron metal in water is conversion to rust. If the scale layer is of low conductivity, impermeable, and durable, the kinetics of corrosion can be very low, whereas corrosion rates are high if the scale is a poor barrier. While Pourbaix diagrams cannot be used to predict if a given scale layer is a “good” or “poor” barrier in practice, if a solid “rust” layer is predicted to form, it is at least possible to dramatically slow the rate of corrosion. Combinations of pE and pH that lead to production of oxidized metallic solids are labeled “passive” in pE and pH diagrams. Finally, water itself is only stable between the two dashed lines (Figures 1-1, 1-2, 1-3, and 1-4), and pE and pH of water is therefore confined within these boundaries as long as water is present.

Regions of corrosion, passivation, and immunity for copper (Figure 1-2) have been derived from the pE-pH diagram (Figure 1-1) using the above rules. For copper, rapid corrosion is possible in areas where the soluble ions,  $Cu^{2+}$  and  $CuO_2^-$ , are stable at very low and very high pH, respectively. Passivation is possible at pE-pHs where oxides such as CuO are stable. When corrosion occurs in copper plumbing, copper ions ( $Cu^{2+}$ ) are released to the water either directly or after dissolution of scale (e.g., copper rusts). A typical  $E_{corr}$  for copper in potable water is between 0.32–0.47 volts vs. SHE at pH 7.0. Thus, Cu pipes are typically in the passivation region. Similarly, the Pb pipes in the same experiment had final  $E_{corr}$  between -0.23 V and -0.01 V vs. SHE, which is also in the passivation region.



**Figure 1-1.** Potential-pH equilibrium diagram for copper in water system at 25°C. Data from Pourbaix, 1966. <sup>[1]</sup>

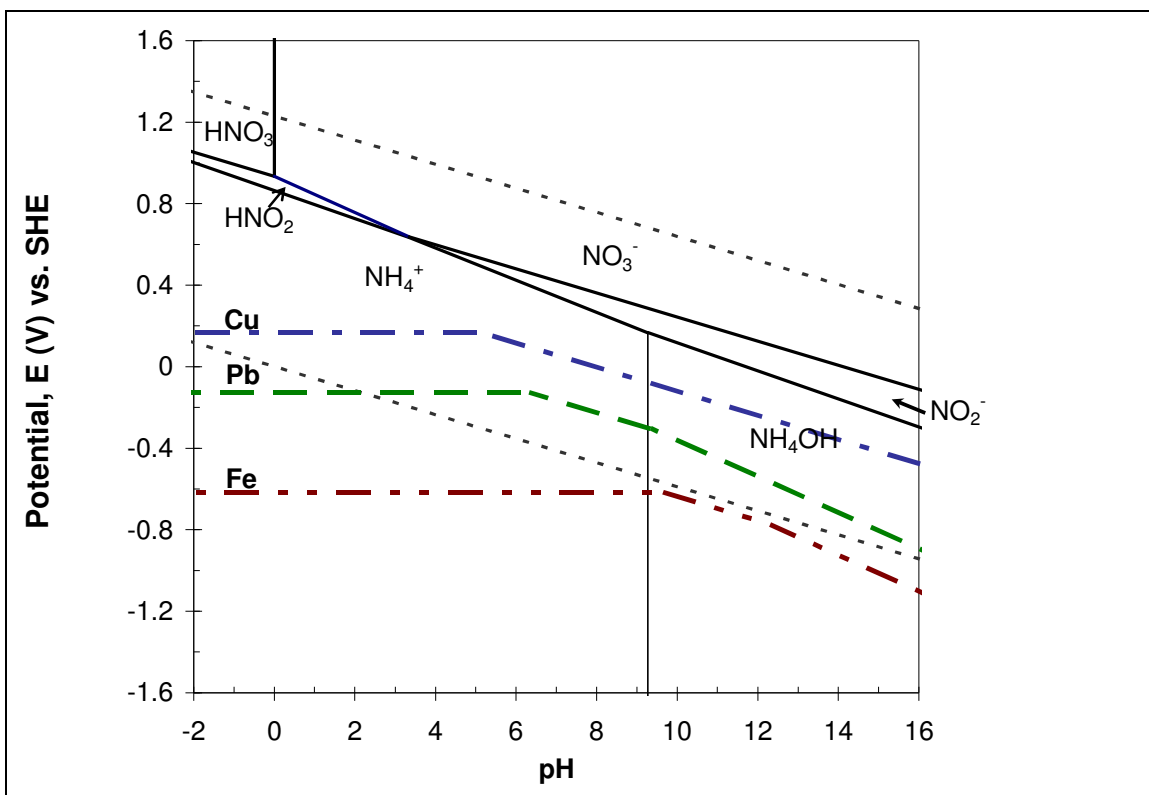


**Figure 1-2.** Regions of corrosion, passivation, and immunity for copper at 25°C.

Copper is immune to corrosion at potentials ( $E$ ) below approximately 0.06 volts (V) versus standard hydrogen electrode (SHE) at pH 7.0, whereas iron is not ever immune to corrosion in potable water (Figure A-1). The 0.06 V is consistent with a dissolved oxygen concentration less than  $10^{-51.8}$  mg/L  $O_2$  at this pH, so in aerated water copper is predicted to corrode. Lead is immune to corrosion only below about -0.17 volts versus SHE at pH 7.0, which corresponds to  $10^{-52.8}$  mg/L  $O_2$  at this pH (Figure A-2). As oxygen is consumed during corrosion in lead and copper pipes, the potential at the pipe surface would decrease until it reached these values, at which point corrosion would stop.

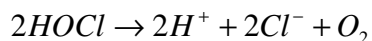
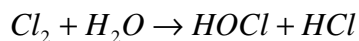
Superposition of these curves with the pE-pH diagram for nitrogen can predict reactions between the metals and nitrogen. For instance, at iron metal surfaces in the distribution system,  $E$  is expected to vary from -1 V to -0.5V along the  $Fe^0 \rightarrow Fe^{2+}$  line in Figure 1-3. At the boundary, the stable nitrogen species in the presence of iron is always ammonium ion ( $NH_4^+$ ) or ammonia ( $NH_3$ ), which forms  $NH_4OH$  in water. This is consistent with the observation of Westerhoff and James who found that nitrate ( $NO_3^-$ ) is converted to ammonia by iron metal at low DO <sup>[2]</sup>. Likewise,  $NH_3$  and  $NH_4^+$  are also thermodynamically favored in the presence of Cu and Pb, although the driving force for the reaction is weaker than with iron. As a result, under some circumstances, Cu and Pb can react with nitrate via corrosion to produce ammonia <sup>[2][3][4]</sup>.

In a given experiment, it is possible to directly measure the potential at the surface of the metal ( $E_{corr}$ ) using a reference electrode. The diagram can be used in conjunction with this measurement to predict the stable nitrogen species at equilibrium. For example, for a copper rust surface at pH 7.0 with an  $E_{corr}$  of 0.6 V vs. SHE, the stable nitrogen species is  $NO_3^-$  (Figure 1-3). Figure 1-3 predicts the stable nitrogen species in equilibrium with copper, lead, and iron metals under various circumstances.



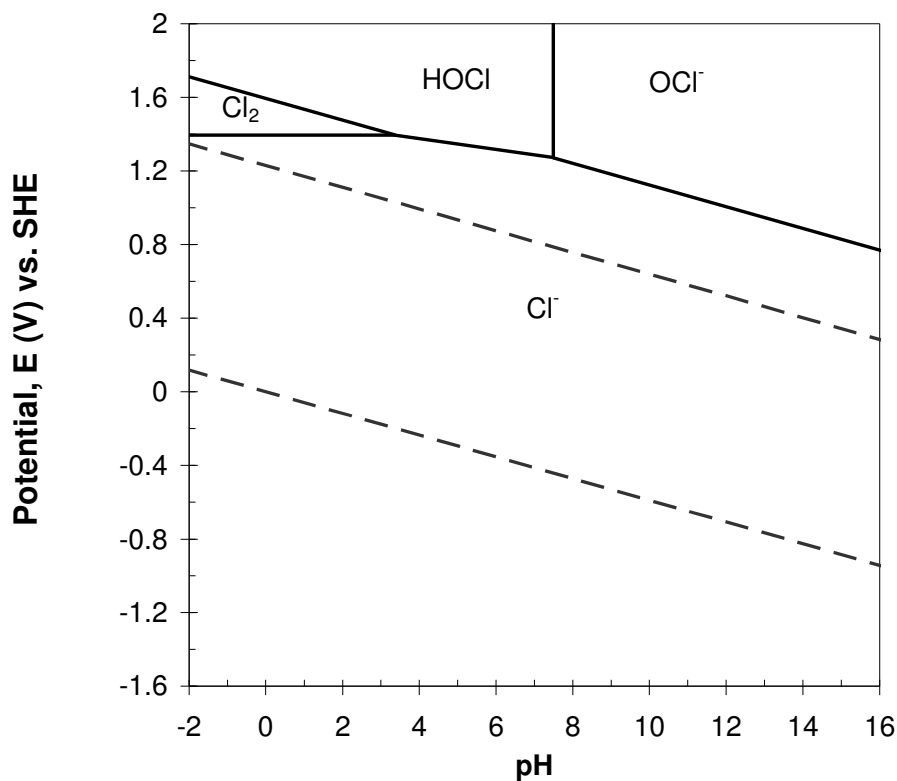
**Figure 1-3.** Potential-pH diagram for nitrogen-water system at 25°C with the lines indicating the potential at copper, lead, and iron surfaces. Drawn from data presented in Pourbaix, 1966. <sup>[1]</sup>

The pE-pH diagram for the common disinfectant free chlorine ( $\text{Cl}_2$ ,  $\text{HOCl}$ ,  $\text{OCl}^-$ ), assuming 1 mg/L as  $\text{Cl}_2$  for the species, highlights the fact that free chlorine is unstable in water and is thermodynamically destined to form  $\text{Cl}^-$  (Figure 1-4).  $\text{Cl}_2$  can even slowly react with  $\text{H}_2\text{O}$  to form oxygen through an autodecomposition reaction that produces oxygen:



The constants necessary to draw the chloramine pE-pH diagram are not yet available and are therefore not presented. However, chloramine is also inherently unstable in water and is also destined to decay to form  $\text{Cl}^-$ . A representative autodecomposition reaction for chloramine is:





**Figure 1-4.** Potential-pH diagram for free chlorine and water system at 25°C.

## 1.2 KINETICS

Loss of disinfectant, although not necessarily a public health hazard, could promote microbiological problems such as regrowth in the bulk water and in accumulated sediments <sup>[5]</sup>. The Surface Water Treatment Rule regulates maximum contaminant level goals (MCLGs) for viruses, *Legionella*, HPC, and *Giardia lamblia* accompanied by treatment technique requirements. Under this regulation, 95% of samples collected monthly throughout the distribution system must maintain a detectable disinfectant residual <sup>[5]</sup>.

Monochloramine ( $\text{NH}_2\text{Cl}$  or chloramine) is commonly cited as being much more stable in water than free chlorine ( $\text{HOCl}$ ,  $\text{OCl}^-$ ). For instance, a recent study examined chlorine and chloramine decay as a function of temperature and found that warmer temperatures accelerated chlorine loss. Over a period of 120 hours, 71% of the free chlorine was lost

at 20°C and 90% was lost at 30°C. Chloramine decayed significantly slower than free chlorine, as only 26% and 32% was lost over 120 hours at 20°C and 30°C, respectively [6]. As a general rule, the water industry would not be startled by chloramine losses as high as 32% in 5 days, but losses of more than 50% in a day are highly unusual. Even considering reactions with iron and manganese oxide scales that can catalyze decomposition, the decay rate is relatively low [7].

Despite the studies demonstrating the low rate of chloramine loss compared to chlorine decay, certain conditions promote greater chloramine dissipation; in fact, very high rates have been noted to occur in the distribution system [3][8][9]. In the Edwards study, it was even determined in a head-to-head test that chloramine could decay more quickly than an equivalent amount of free chlorine. Powell et al. [9] made a similar suggestion based on experiences with an existing system. If the monochloramine residual were lost more rapidly than a free chlorine residual, this would be problematic given that free ammonia from chloramine decay can cause problems with nitrification, lower pHs, organic carbon production and enhanced re-growth relative to free chlorine [3].

### ***1.2.1 Factors contributing to disinfectant decay***

Currently not much is known about chloramine and chlorine decay in copper pipes in practice. These reactions have been implicated in copper pitting corrosion [3][10][11][12].

Free chlorine decays more quickly in the presence of light and increased temperature. Greater ionic strength accelerates the free chlorine decay; furthermore, no specific catalytic effect was seen by the addition of sodium hydroxide, carbonate, or chloride beyond the increased ionic strength [13][14][15]. However, Lister still noted that the decomposition rate of NaOCl, commonly added as the source of free chlorine, increases with increasing pH [13]. It is thought that HOCl reacts with  $\text{SO}_3^{2-}$ ,  $\text{I}^-$ ,  $\text{Br}^-$ , and  $\text{NO}_2^-$  [16], and chlorine decay can be catalyzed by metallic oxides [13] or metal catalysts such as nickel, manganese, cobalt, platinum, iridium, and rhodium [17]. Soluble cupric hydroxide complexes are another established catalyst for chlorine decay [14]. Catalysis is believed to proceed through an unstable Cu(III) complex, although the specific chemical form is

uncertain <sup>[13][14][18]</sup>. Very rapid free chlorine decay has been noted for around a 1:1 molar ratio of iron-copper solid catalyst <sup>[19]</sup>; however, no work has demonstrated whether or not chloramine is similarly affected by this catalyst. When free chlorine decays chloride ions are formed <sup>[13]</sup> (Table 1-1), but free chlorine can also decay to form chlorate as well <sup>[13][15]</sup>. Oxygen is produced as a result of chlorine decay.

Various species contribute to the catalytic disappearance of chloramine, a common disinfectant that is 180,000 times less reactive than free chlorine based on rate equations of water containing disinfectant, phosphate buffer, and nitrite <sup>[20]</sup>. The stability of chloramine residual is enhanced at higher concentrations of ammonia and lower concentrations of nitrite ( $\text{NO}_2^-$ ) <sup>[20]</sup>. However, the presence of phosphate and natural organic matter (NOM) can increase the rate of chloramine decay <sup>[20]</sup>. Looking at  $[\text{PO}_4^{3-}]$  ranging from 620 mg/L P to 4,340 mg/L P, a trend of phosphate contributing to chloramine decay was small but significant – over 5 days 3.2% chloramine decay could be seen from each additional 1 mg/L P <sup>[20]</sup>. In addition, Song et al. <sup>[21]</sup> determined that reactions with NOM are the dominant pathways for chloramine decay in potable water during the first 24 hours, whereas autodecomposition of chloramine dominates at later times (Table 1-1) <sup>[5][22]</sup>. Wilczak <sup>[23]</sup> asserted that pH is the most important factor that controls chloramine autodecomposition rate; chloramine decay rates double for each decrease of 0.7 pH units <sup>[24]</sup>. Similar to chlorine, any acid can catalyze the reaction of chloramine with  $\text{NO}_2^-$ ,  $\text{I}^-$ ,  $\text{SO}_3^{2-}$  (sulfite),  $\text{Br}^-$ , and  $\text{CN}^-$  <sup>[20]</sup>.

When chloramine decays, ammonia and chloride are formed as a result of either autodecomposition or reactions with pipe corrosion products (Table 1-1). The ammonia formed can be biologically utilized to form nitrite and nitrate (Table 1-1). Under rare anaerobic conditions in the water system, anaerobic microbes can convert the nitrate to nitrogen gas in the denitrification process. Metals, such as copper, iron, and lead, can also react with the nitrate and nitrite that is formed as a result of chloramine decay to reform ammonia (Table 1-1).



**Table 1-1.** Summary of key reactions and when they are favorable.

Equation #	Reaction Description	Overall Reaction	Ref.
1.1	Release of ammonium through chloramine decay (autodecomposition).	$3NH_2Cl \rightarrow N_2 + NH_3 + 3Cl^- + 3H^+$	[5]
1.2	Ammonium and nitrite conversion to nitrate by AOB and NOB. *	$NH_3 + O_2 \xrightarrow{\text{bacteria}} NO_2^- + 3H^+ + 2e^-$ $NO_2^- + H_2O \xrightarrow{\text{bacteria}} NO_3^- + 2H^+ + 2e^-$	[5]
1.3	Release of ammonium through reaction of chloramine with corrosion of products at pipe surfaces.	$\frac{1}{2}NH_2Cl + H^+ + Fe^{2+} \rightarrow Fe^{3+} + \frac{1}{2}NH_4^+ + Cl^-$	[5]
1.4	Thermodynamic chloramine oxidation of nitrite to nitrate.	$NH_2Cl + NO_2^- + H_2O \rightarrow NH_4^+ + NO_3^- + Cl^-$	[20]
1.5	Free chlorine decay.	$NaOCl \rightarrow NaCl + \frac{1}{2}O_2$	[13]
1.6	Free chlorine decay with copper(II) catalyst.	$2OCl^- \xrightarrow{Cu(II)} 2Cl^- + O_2$	[14]
1.7	Free chlorine reaction with nitrite.	$OCl^- + NO_2^- \rightarrow Cl^- + NO_3^-$	[16]
1.8	Cu(I) regeneration by disproportionation.	$Cu^0 + Cu^{2+} = 2Cu^{1+}$	[29], [30]
	Cu(I) reaction with nitrate to form NO.	$3Cu^+ + NO_3^- + 4H^+ = 3Cu^{2+} + NO + 2H_2O$	[29]
	Nitrous oxide formed can be reduced at the copper cathode.	$NO + 3e^- + 3H_3O^+ = NH_2OH + 3H_2O$ $NH_2OH + \text{oxygen} \rightarrow \text{peroxonitrite (ONOO}^-)$	[29] [20]
1.9	Nitrate reduced by Pb to nitrite.	$NO_3^- + Pb \rightarrow NO_2^- + PbO$	[22]
1.10	Nitrite then reduced further by Pb to N <sub>2</sub> or NH <sub>3</sub> (depending on pH).	$2NO_2^- + 3Pb + H_2O \rightarrow N_2 + 3PbO + 2OH^-$ $NO_2^- + 3Pb + 2H_2O \rightarrow NH_3 + 3PbO + OH^-$	[22]

\* Ammonia-oxidizing bacteria (AOB) and nitrogen-oxidizing bacteria (NOB)

### 1.2.2 Nitrate and Nitrite

Nitrate and nitrite in potable water can be a health concern, arising from nitrogen sources such as agricultural runoff, sewage contamination, and ammonia addition for secondary disinfection; however, total nitrogen in surface waters is usually below 0.1 mg/L <sup>[25]</sup>.

Work has therefore been done to develop processes to treat water and wastewater containing concentrated nitrate. For instance, in Uchida's work <sup>[22]</sup>, nitrate was reduced by lead metal at an increasing rate with increased temperature.

The current primary maximum contaminant levels (MCLs) under the Safe Drinking Water Act (SDWA) for nitrite ( $NO_2^-$ ), nitrate ( $NO_3^-$ ), and the sum of nitrite plus nitrate are 1 mg/L  $NO_2^-$ -N, 10 mg/L  $NO_3^-$ -N, and 10 mg/L  $NO_2^- + NO_3^-$  as N, respectively.

Compliance is measured at the entry point to the distribution system; however, subsequent nitrite and nitrate formation as a result of nitrification within the distribution system is not identified in compliance monitoring <sup>[5]</sup>. A survey of 40 utilities using chloramine disinfectant determined that nitrite and nitrate produced as a result of chloramination could increase 0.05 to 0.5 mg/L as N. At a high chloramine dose of 4 mg/L as  $Cl_2$  and a common mass ratio of  $Cl_2:NH_3$  of 4:1, 1 mg/L free ammonia can form from chloramine decay. If this was converted quantitatively to nitrite, as much as 1 mg/L  $NO_2^-$ -N could form. Thus, the authors concluded that changes in the nitrite and nitrate levels, as long as they were not near the regulatory MCLs prior to the distribution system, would not be significant enough to exceed regulatory requirements <sup>[5][26][27]</sup>. Biological nitrification occurs through nitrifying bacteria which are pH-sensitive; the optimal pH for *Nitrosomonas* is between approximately 7.0 and 8.0 and for *Nitrobacter* is between 7.5 and 8.0.

Copper is recognized as an efficient catalytic reducer of nitrate <sup>[28]</sup>. In the presence of a copper metal cathode and the addition of  $6.0 \pm 1.2$  mg/L copper ions in a closed-loop system, electrolytic reduction converted nitrate to nitrite and then to ammonia <sup>[28]</sup>. Paidar attributed the beneficial effects of copper ions to the slow continuous deposition of copper onto the cathode surface, forming new active sites to sustain electrocatalytic

activity autonomous of the electrolysis duration. He also determined that cupric ions decreased the nitrite concentration more rapidly than when cupric ions were absent. In addition, in hot-water heaters containing aluminum protector rods, a form of pitting corrosion called Rosette corrosion occurs between copper metal and nitrate <sup>[12]</sup>. Specifically, Rosette corrosion occurs under circumstances of high nitrate and high sulfate concentrations compared to other anions in the water. It is believed that nitrate reacts with the copper to form ammonia, which in turn promotes corrosion.

### **1.3 CONCLUSIONS**

Relatively little is known about chloramine decay, chlorine decay, and reactions of nitrate in copper pipes. The current theory is that chloramine is stable in water, despite rare data demonstrating the contrary result. Work has been done investigating the effects of plumbing materials including polyethylene, PVC, iron, and cement on monochloramine demand. A conclusion was drawn that these materials do not rapidly react with chloramine. However, potential reactions between copper pipe and chloramine were not examined <sup>[31]</sup>. Portions of this work attempted to determine when chloramine can decay rapidly in copper pipe by examining fundamental and practical reactions of significance.

### **1.4 ACKNOWLEDGEMENTS**

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## **CHAPTER 2: The Role of Silica and Chlorine in Cupric Hydroxide Aging**

Kim A. Powers, Marc A. Edwards\*, Caroline K. Nguyen  
Dept. of Civil and Environmental Engineering  
Virginia Polytechnic Institute and State University,  
407 Durham Hall, Blacksburg, VA 24061-0246

\*Corresponding author phone: 540-231-7236; fax: 540-231-7916; e-mail: [edwardsm@vt.edu](mailto:edwardsm@vt.edu)

### **ABSTRACT**

Fundamental reactions between dissolved silica and cupric hydroxide solids were investigated at pH 7-10.5 and 0-30 mg/L Si. Silica sorbed strongly to cupric hydroxide surfaces with a sorption density ranging from 0-0.77 M Si/ M Cu depending on solids age and initial silica concentration – sorption density was not a strong function of pH if the silica was present in excess. At all pH values studied, sorption of silica to  $\text{Cu}(\text{OH})_2$  slowed its aging to CuO as noted by color changes, solubility and XRD patterns. Chlorine concentrations between 5-65 mg/L hastened transitions from  $\text{Cu}(\text{OH})_2$  to a new solid phase that was at least partly CuO at pH 6 and pH 7 with concurrent loss of free chlorine. The latter reaction was unanticipated and is deserving of additional research, because it would be expected to influence copper pipe corrosion in the presence of chlorine, as well as degraded drinking water quality from free chlorine loss and copper release.

### **2.1 INTRODUCTION**

Cupric hydroxide solubility can control copper removal from industrial wastewaters and the concentration of copper leached to drinking water from plumbing materials (1-5). The latter problem is a key cause of waterborne illness as manifested by gastrointestinal upset (6,7) and is a significant source of copper to the environment via wastewater treatment plant effluent (8,9). Previous research has demonstrated that several factors control cupric hydroxide solubility including pH and temperature. In addition, the

transition of relatively soluble cupric hydroxide [Cu(OH)<sub>2</sub>] to less soluble tenorite [CuO] and other solids tends to decrease soluble metal leaching with pipe age (3-5,10,11).

The rate of transition from cupric hydroxide to tenorite is slowed at lower pH, lower temperature, and by the presence of constituents such as natural organic matter (NOM) (5,12). Other chemicals present in drinking water are suspected to influence the rate of transitions from Cu(OH)<sub>2</sub> to other solids, since high levels of copper release are sustained for decades in some waters (consistent with persistent soluble cupric hydroxide scale), while insignificant levels of copper are observed a few days after installation in other waters with similar alkalinity, temperature, and pH (5,13).

Silica and chlorine are two important constituents in water that commonly contact copper pipe – their impact on the transition from cupric hydroxide to other solids has not been previously studied. Silica is commonly present in untreated drinking waters at 1-45 mg/L or can be added to water as a corrosion inhibitor (14,15). Silica sorbs strongly to iron and aluminum hydroxides and interferes with their aging to more crystalline phases (14,16,17,18), so it is logical to expect that similar reactions might be important for cupric hydroxide. Chlorine is the most common disinfectant added to drinking water, and while there is no reason to suspect it might influence aging, some previous practical research demonstrated that dosing of free chlorine led to marked reductions in copper release to drinking water under some circumstances (19). While these benefits of chlorine are commonly attributed to elimination of microbes that accelerate corrosion (19), it was deemed advisable to confirm the assumption that chlorine does not directly influence the chemistry of scales such as Cu(OH)<sub>2</sub>.

## **2.2 MATERIALS AND METHODS**

### ***2.2.1 Rate of base addition and copper solubility***

The rate of base addition had significant impacts on the persistence of soluble copper in dilute nitrate solutions. To study this effect explicitly, sodium hydroxide base was added to 0.5 L solutions containing 0.5 mM cupric nitrate and 1 mM sodium nitrate using three



approaches including 1) adding 815  $\mu\text{L}$  of 1 M NaOH in a single step, 2) dosing 50  $\mu\text{L}$  of 1 M NaOH every five minutes for forty-five minutes, and 3) addition of 400  $\mu\text{L}$  0.1 M NaOH every 20 minutes for four hours, with two final doses of 600  $\mu\text{L}$  every 20 minutes to reach pH 7. The total titration time to pH 7 varied from 0 minutes to 5 hours.

Interestingly, as soon as pH 7.0 was achieved, soluble copper was  $9 \text{ mg/L} \pm 0.8$  in all cases, but the ratio of  $[\text{OH}]:[\text{Cu}]$  in the solid ranged from 1.2-1.8 before aging. However, when base was added over a 5 hr time period, the soluble copper after 50 hrs was 6 mg/L, but was below 1.5 mg/L in the other 2 solutions, confirming that the rate of base addition had long-term impacts on copper solubility. All experiments in this work used the 45 minute titration approach described above since the solid formed was most consistent with that characterized previously by Hidmi (10).

### ***2.2.2 Sorption of silica to copper***

The role of silica (0-30 mg/L) and pH in copper solubility and aging at  $20^\circ\text{C}$  was assessed experimentally by using techniques described elsewhere (5,10). To eliminate concerns of silica leaching from glassware, plastic Nalgene bottles were used for reactors and for storage of reagent grade stock solutions. pH measurements were made using a pH meter and a combination electrode using Standard Method 4500- $\text{H}^+$  B.

Cupric hydroxide solids were preformed by dosing 350  $\mu\text{L}$  1 M NaOH to a 3.5 L solution of 0.5 mM  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  and 1 mM  $\text{NaNO}_3$  every 5 minutes for 45 minutes. The solids that formed were aged for two hours at pH 7 while stirring at 250 RPM using a 2-inch stirbar. Soluble copper after this time was always between 5-6.5 mg/L at pH 7, and the only solid that could be identified by XRD (Table 2-1) was  $\text{Cu}(\text{OH})_2$  consistent with results of others (10).

Thereafter, aliquots of this suspension were collected and dosed with a desired level of silica from a fresh stock solution of  $\text{Na}_2\text{SiO}_3$  (8000 mg/L as  $\text{SiO}_2$ , pH 12.8) along with a predetermined dose of 1 M HCl to maintain constant  $\text{pH } 7 \pm 0.1$ . This approach minimizes but does not eliminate the likelihood of forming polymeric silicates (20). pH

was then adjusted to a target value between 7 to 10.5, and the solution was mixed on an orbital stir-plate at 100 RPM. The pH was maintained within  $\pm 0.20$  units of the target during the first eight hours and  $\pm 0.3$  units during the remainder of the experiment (up to 40 days). Although the experiment was not conducted in a glove box, plastic lids minimized CO<sub>2</sub> dissolution.

### ***2.2.3 Measurements for determination of silica sorption density***

The sorption density (moles Si /mole copper in the solids) was measured after 8 hours, 168 hrs (1 week), and 500 hrs (2.5 weeks) of reaction time with the silica. 10 mL of sample was collected from each bottle for total copper measurements and immediately acidified to 2% HNO<sub>3</sub>. 50 mL of sample water was also passed through a 0.45  $\mu$ m pore size nitrocellulose filter. The filtrate was collected and analyzed for soluble species, and the filter with the solids was dissolved after acidification in 20 mL nanopure water containing 2% HNO<sub>3</sub>. Visual observations and mass balances confirmed that dissolution of captured solids was complete for copper but not always for silica. Copper and silicon in the total, filtrate, and digested filter samples were measured using Inductive Coupled Plasma Emission Spectroscopy (ICP-ES).

### ***2.2.4 Zeta potential, x-ray analysis, and free chlorine***

A Malverne ZetaSizer 3000HS was used to measure zeta potential and the instrument performance was checked by comparison to standard solutions. Representative solids were collected for analysis using X-Ray diffraction using a Scintag instrument, and free chlorine was determined using Standard Method 4500-CLG.

## **2.3 RESULTS AND DISCUSSION**

### ***2.3.1 Reaction of silica with cupric hydroxide***

#### ***2.3.1.1 Sorption density***

It was initially considered possible that the silica was reacting with cupric hydroxide by forming a new solid such as:



The molar ratios of Cu:Si in solid samples collected in this work ranged between three and a half to forty-three, which is well above the one to one ratio for diopside if it formed quantitatively. Thus, a solid such as diopside did not form exclusively, although both cupric hydroxide and some  $\text{CuH}_2\text{SiO}_4$  might both be present. Considering the Si:Cu ratios in the solid and assuming that only cupric hydroxide and diopside were present, the concentration of diopside could have been no greater than 2-29 % of the total copper. The solids were also analyzed by x-ray diffraction, and no patterns out of the ten possible Cu:Si solids in the standard database (including diopside) matched the solid peaks in this system (Table 2-1). Because the solids were initially cupric hydroxide and no CuSi solids were identified by x-ray diffraction after silica addition, all further discussion assumes the solids present are actually cupric hydroxide with silica sorbed to the surface in a monomeric or polymeric form.

The sorption density of silica on the pre-formed  $\text{Cu(OH)}_2$  could be calculated based on measurement of soluble copper and silica remaining in water, or based on the ratio of silica to copper captured on the filter. Both approaches were in good agreement in this work, with exceptions occurring at three weeks when mass balances indicated that a significant fraction of the particulate silica was not recovered from the filter paper. All sorption density data that follows is based on the difference between the total copper and silica prior to filtration, and measurements of total copper and silica in the filtrate as per the logic and approach used for silica sorption to iron elsewhere (20).

Silica sorbed very strongly to the surface of cupric hydroxide (Figure 2-1). Between pH 7 and pH 10.5, the sorption density was between 0.30-0.77 M Si/ M Cu for solutions initially containing 30 mg/L as  $\text{SiO}_2$ , and unlike data for iron and aluminum (14,16,17), the sorption density is a relatively weak function of pH (Figure 2-1) for initial silica at 30 mg/L. As initial silica concentrations increased from 0 to 15 mg/L at pH 9.2, the sorption density increased from 0-0.32 M Si/ M Cu and increased steadily with initial silica

concentration. Consistent to trends reported for  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  surfaces, sorption density generally increased with reaction time and  $\text{SiO}_2$  concentration.

#### 2.3.1.2 *Sorption and zeta potential*

In the sorption experiments, zeta potential varied from +45 to -30 mV depending on the pH and silica concentration – as pH and silica concentration increased the zeta potential decreased (Figure 2-2). Thus, silica sorption converts positively charged sites on the cupric hydroxide surfaces to neutral and negatively charged sites, presumably through surface complex formation. Like silica, the presence of high concentrations of chlorine had some effect on the zeta potential. At lower pH values the zeta potential is slightly lower in solutions with 65 mg/L chlorine than solutions without chlorine; but at pH 9, the zeta potential is slightly greater. When 10 mg/L of silica is added along with chlorine in these solutions, the zeta potential seems to be controlled by silica and not chlorine.

#### 2.3.1.3 *Transition time of $\text{Cu}(\text{OH})_2$ to $\text{CuO}$*

For iron hydroxide solids, the transition of ferrihydrite to goethite is normally complete in 24 hours, but in the presence of silica can take one to two weeks (18). Observations of color changes in 32 experiments for this work demonstrated that silica played a similar role in the transition from  $\text{Cu}(\text{OH})_2$  to tenorite (1). That is, when cupric hydroxide ages in the laboratory at 20°C, it changes color from the more soluble light blue cupric hydroxide to the much less soluble brown tenorite phase (10). This transition occurs in a few hours at pH 9 but requires a few days at pH 7 (5, 10). However, when greater than 10 mg/L  $\text{SiO}_2$  is added to water with cupric hydroxide at pH 7 or pH 9.2 (Figure 2-3), this transition never occurred. Even when the pH is raised to 10, the cupric hydroxide solids remained blue for over one year when 30 mg/L silica was present (Figure 2-3), whereas the transition to tenorite was complete in a few hours when silica was absent. At a fixed pH of 9.2, solutions without silica were brown immediately, but the transition in solutions with 7.5 mg/L as  $\text{SiO}_2$  took 600 hours and solutions containing greater than or equal to 10 mg/L as  $\text{SiO}_2$  did not change color in a year (Figure 2-3). Analysis of XRD patterns of representative solids confirmed that the transition of blue to brown solids in the experiments without silica corresponded with disappearance of cupric hydroxide,

$\text{Cu}(\text{OH})_2$ , and the appearance of tenorite,  $\text{CuO}$  (Table 2-1). If silica was present, only weak peaks XRD were observed, with no strong signal of either  $\text{Cu}(\text{OH})_2$  or  $\text{CuO}$ .

#### *2.3.1.4 Effects on Solubility, Particle Size and Deposition to the Plasticware*

The transition of cupric hydroxide to tenorite is often associated with a significant decrease in copper solubility. At pH 7, soluble copper levels are usually higher at 10-30 mg/L  $\text{SiO}_2$  when compared to 0-5 mg/L  $\text{SiO}_2$ , which might be expected to result in a longer time period for soluble copper to drop below the 1.3 mg/L level (the EPA Action Limit for copper in drinking water) in practical situations within home plumbing (Figure 4). Measurement of free cupric ion at pH 7 in standard solutions using an ion specific electrode indicated that addition of 30 mg/L silica did not significantly change the concentration of free copper in a standard solution at pH 7.0. This supports the idea that silica was causing higher solubility short-term by hindering the transition of cupric hydroxide to tenorite. At pH 9.2, there was little effect of silica on copper solubility, despite the fact that the blue solid cupric was maintained for long time periods. However, the dosing of free chlorine causes a rapid drop in soluble copper, which is consistent with the formation of a less soluble tenorite phase.

Particle size, unlike copper solubility, was greatly influenced by the concentration of silica at pH 9.2, consistent with reported effects in experiments starting with pre-formed iron hydroxide (20). Although the size of most particles was above the Malvern's upper detection limit of 3 microns, the general visual trend was that the higher the silica concentration, the larger the particles. Moreover, the blue solids in systems with silica tended to remain suspended much longer than in the systems where tenorite was confirmed to form after one half hour settling, and only a small fraction of the solids in the presence of silica attached to the walls of the plastic reactors whereas the majority of the tenorite solids did attach.

#### *2.3.2 Reaction of chlorine with cupric hydroxide*

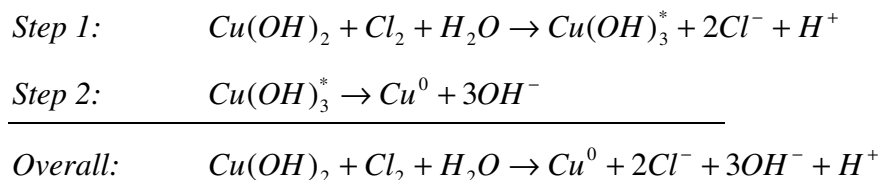
The initial assumption was that free chlorine would not react with preformed cupric hydroxide. In the absence of cupric ion (Figure 2-5), chlorine decays slowly in solution

as expected, although it is known that factors such as light and heat could accelerate decomposition (21). If cupric species are present, however, the chlorine decayed rapidly in solution at pH 7 and pH 9, and a significant portion of the decay occurred before the first sample could be collected (Figure 2-5). Interestingly, the ability of the solid to catalyze chlorine decay after consecutive doses of chlorine to the targeted amount was not lost (Figure 2-6). The presence of sorbed silica decreased the rate of free chlorine decay in the presence of  $\text{Cu}(\text{OH})_2$ .

QA/QC testing confirmed that, while cupric ions had a slight positive influence on the DPD test for chlorine (Standard Method 4500 CLG) used in this experiment (22), the observed chlorine decay was not a measurement artifact. Moreover, as chlorine decayed the color of the  $\text{Cu}(\text{OH})_2$  solids immediately ( $< 10$  minutes) changed from blue to brown (23) and some tenorite was detectable via XRD. This proved that the observed chlorine decay was not due to simple catalysis of chlorine autodecomposition, since the  $\text{Cu}(\text{OH})_2$  solids themselves were obviously altered (23,24,25).

A more thorough review of the literature suggests several possible reactions that might be operative (23). For instance, cupric ion could react with free chlorine to form a cupric hypochlorite solid (24). While the solubility and color of this solid was not revealed in a literature search, if it did form, it could explain the complete loss of chlorine observed in the two experiments but not the complete loss of blue  $\text{Cu}(\text{OH})_2$  [i.e., complete conversion to  $\text{Cu}(\text{OCl})_2$ ]. A second possibility is that chlorine is an oxidant for the conversion of copper (II) to a copper (III) species which could be less soluble (24); however, stoichiometric considerations indicate that only 28% of the cupric solid could have been oxidized at the lower chlorine dose, and the redox reaction could have consumed only 27% of the 65 mg/L free chlorine (at the higher dose tested) when it was actually completely consumed. Moreover, the reactivity should have decreased upon multiple doses, if the  $\text{Cu}(\text{III})$  was stable. Another possibility is that cupric hydroxide or cupric solids catalyzed chlorine autodecomposition (25), and that the chlorine simultaneously catalyzed  $\text{Cu}(\text{OH})_2$  aging to another solid such as tenorite. However, both proposed catalytic reactions had to occur simultaneously, since both reactants were consumed. The

most probable established explanation is that the cupric hydroxide solid catalyzes for the chlorine decay (28). Catalysis is believed to proceed through an unstable Cu(III) complex, although the specific chemical form is uncertain (28,29,30,31). A hypothetical reaction pathway consistent with the data is:



#### 2.3.2.1 Reactions with Cu pipes in pure water and applied potential

To further examine the reaction pathway described above with an unstable Cu(OH)<sub>3</sub> intermediate, pure water containing 10<sup>-3</sup> M NaCl at pH 7.0 was recirculated at a flowrate of 1 gpm through a ¾” sample of copper pipe. The coupons were polarized to 1.5 V vs. Ag-AgCl using a potentiostat. The potential for conversion of Cu(II) to Cu(III) at pH 7.0 is +0.52 V (32). When polarized to 1.5 V, the released copper solids turned brown much more rapidly than when polarized to only 0.3 V. Assuming Cu(III) was formed above 1.0 V, this is indirect evidence that unstable Cu(III) leads to more rapid formation of CuO.

#### 2.3.3 Practical implications

Silica in water, either naturally present or added as a corrosion inhibitor, can be expected to sorb to Cu(OH)<sub>2</sub> surfaces and dramatically slow transitions to other solid phases such as tenorite. This probably explains why, in rare cases when very high concentrations of particulate copper are released to drinking water near pH 9.2, the copper solids occur as “blue water” from Cu(OH)<sub>2</sub> (19) and not as “brown water” from the thermodynamically favored tenorite phase. It is noteworthy that silica was initially hypothesized to be a key contributor causal factor in blue water propagation (26), and this work directly supports the idea that tenorite should rapidly form from Cu(OH)<sub>2</sub> at higher pHs if silica is below about 5 mg/L as SiO<sub>2</sub>. It remains to be seen whether the silica is involved in helping to mobilize the high concentration of Cu(OH)<sub>2</sub> particles from copper pipe in the first place, but the fact that tenorite solids attached strongly to the plasticware whereas blue Cu(OH)<sub>2</sub>

coated with silica remained unattached suggests that meaningful differences in adhesion and durability are likely.

The specific mechanism of the reaction between  $\text{Cu}(\text{OH})_2$  and free chlorine is not readily apparent, but it has obvious importance in maintaining residual disinfectant, disinfection of biofilms on copper or brass plumbing, and control of copper leaching. In practical circumstances where copper leaching is decreased after dosing free chlorine (19), a presumption that the mode of action is through microbial inactivation is probably overly simplistic, since it is now clear that chlorine causes important abiotic reactions with preformed  $\text{Cu}(\text{OH})_2$  that might control the aging of  $\text{Cu}(\text{OH})_2$  to  $\text{CuO}$ . Other biocides that have been tested such as heat, oxidants and even antibiotics might also be expected to also abiotically influence transitions between solid phases that are important to corrosion. It is also very understandable why maintaining a residual free chlorine in new copper plumbing is occasionally difficult during disinfection, since the sources of chlorine demand obviously go well beyond direct oxidation of copper metal to cupric species (27). It would be interesting to determine if similar disinfectant-consuming reactions occurred between  $\text{Cu}(\text{OH})_2$  solids and chloramines and chlorine dioxide, which are becoming increasingly popular in drinking water.

## **2.4 ACKNOWLEDGEMENTS**

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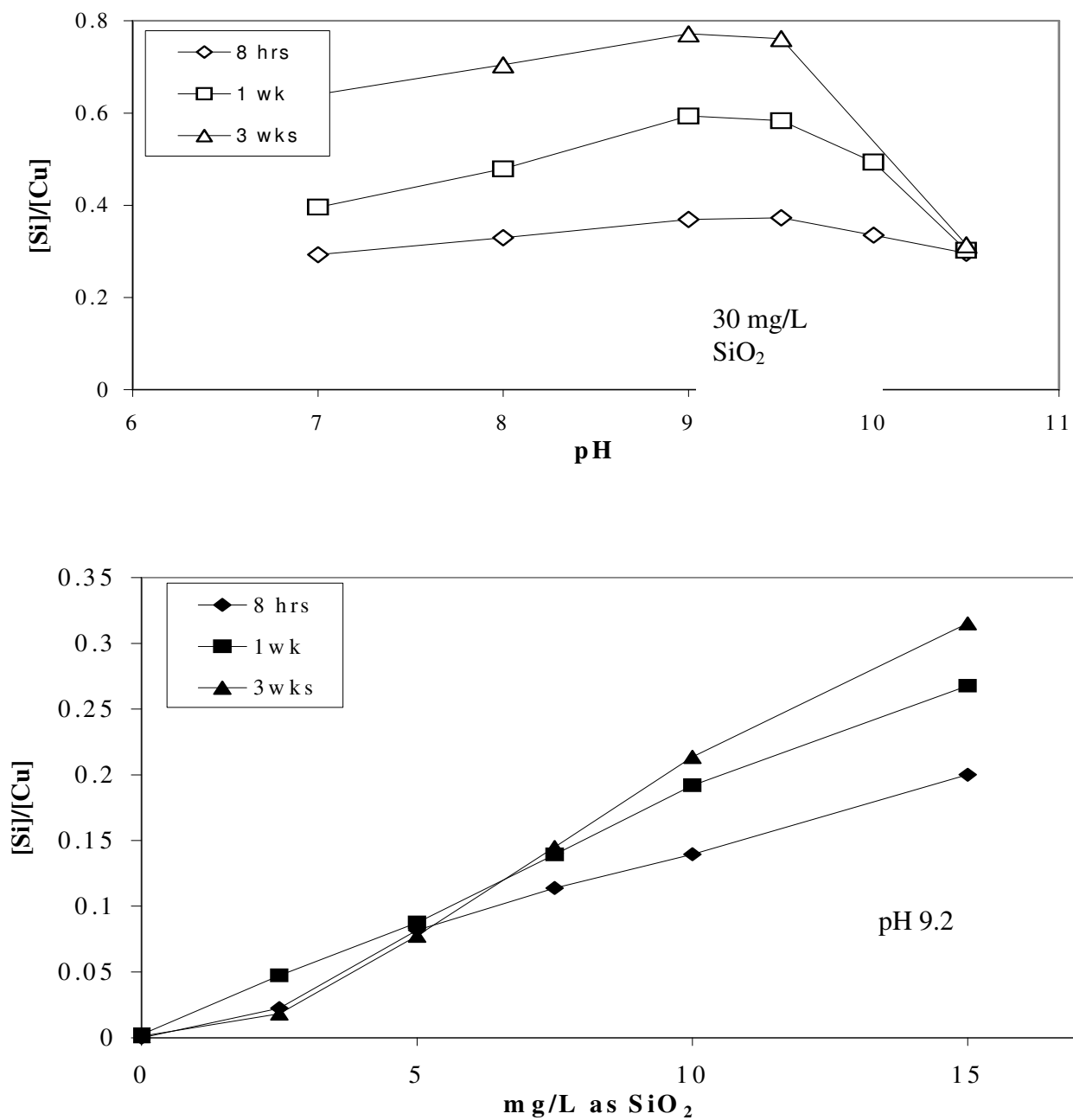
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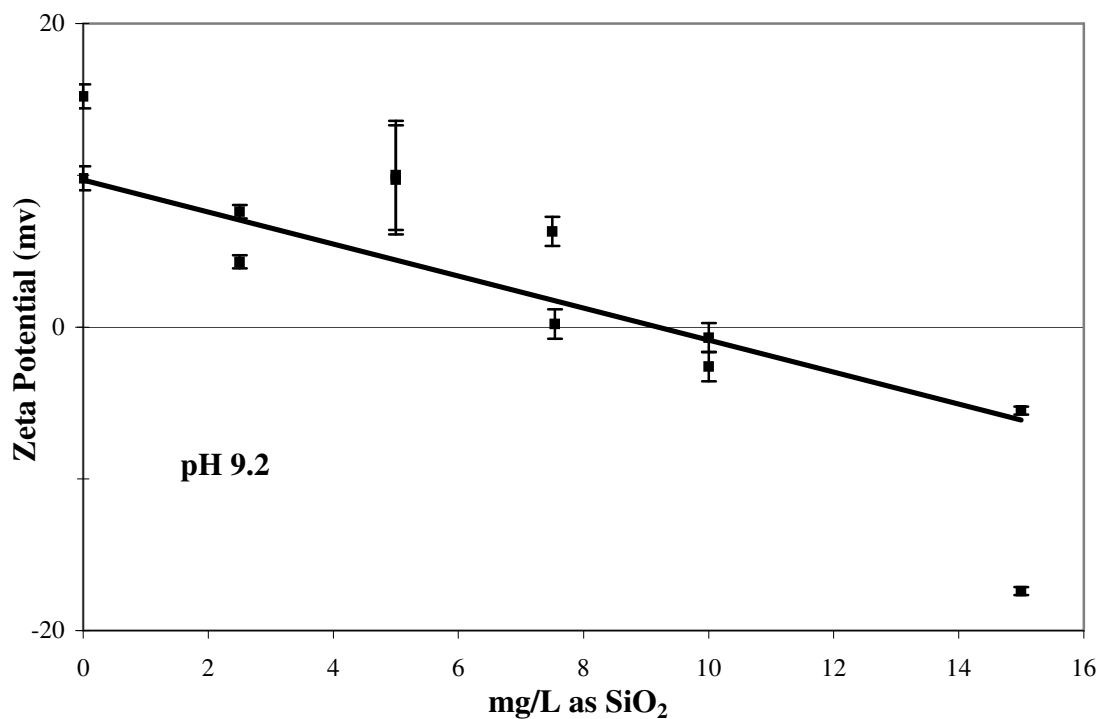
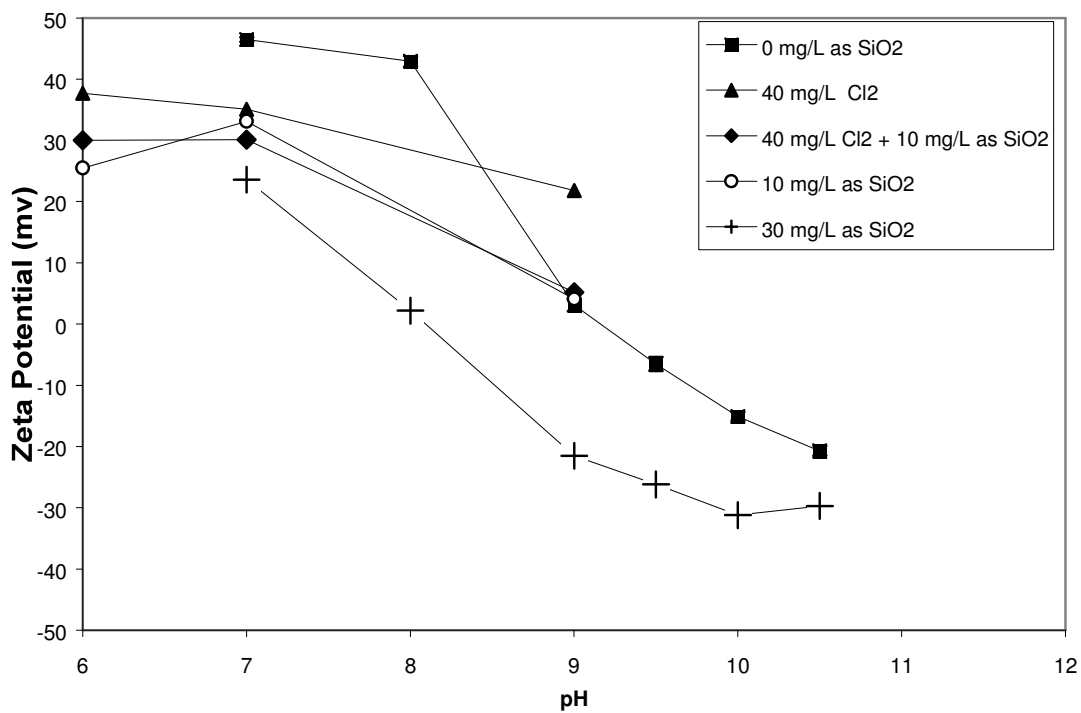
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**Table 2-1.** Solids identified in experiments by x-ray diffraction (XRD).

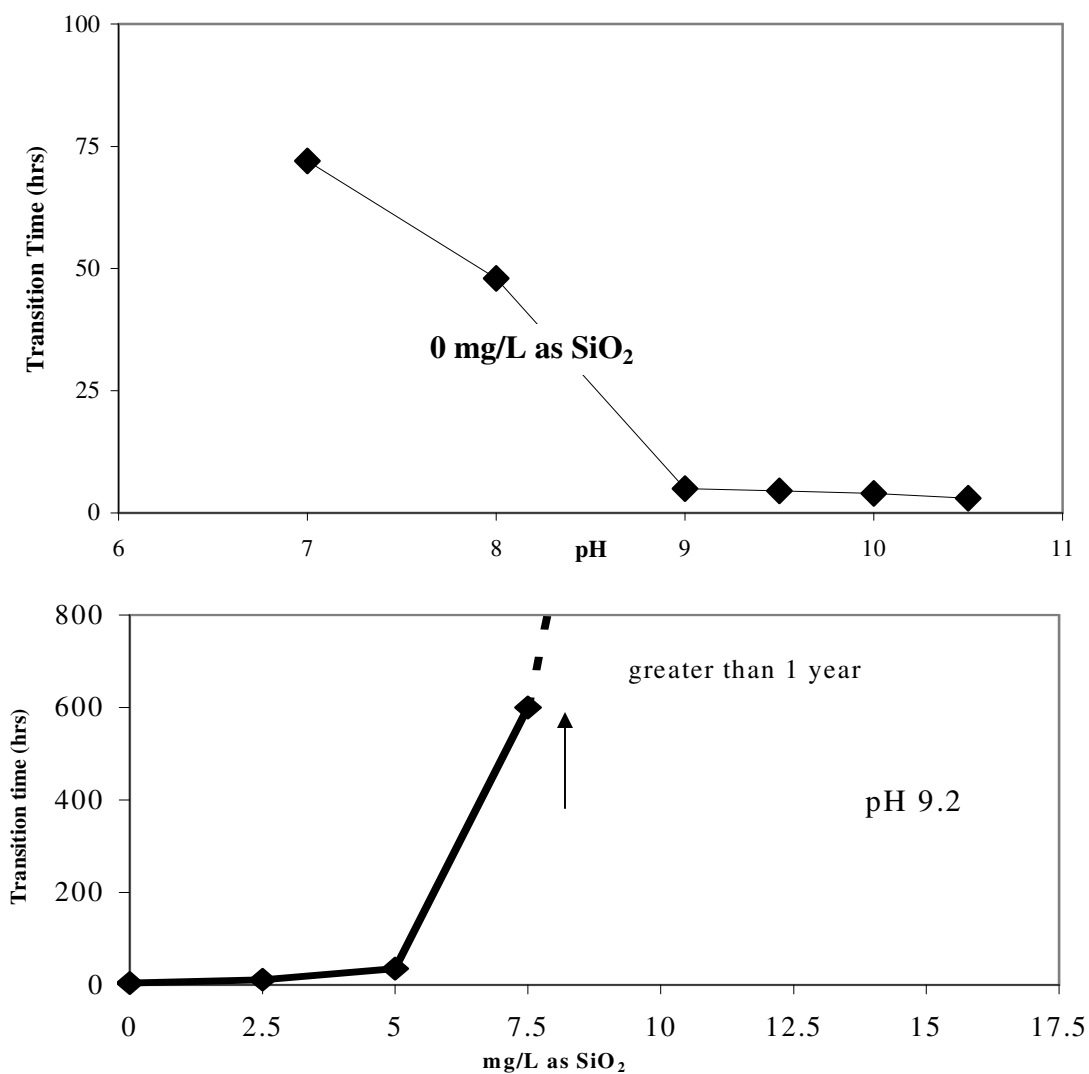
<b>Solid Description</b>	<b>Color</b>	<b>Identification</b>
Preformed Cu(OH) <sub>2</sub> , pH 7, aged 0.5 hrs	blue	Cu(OH) <sub>2</sub>
Slow titration (5 hrs), pH 7, aged 8 hrs	blue	no Cu(OH) <sub>2</sub> , unidentified peaks
0 mg/L as SiO <sub>2</sub> , pH 9.2, aged 8 hrs	brown	CuO
10 mg/L as SiO <sub>2</sub> , pH 9.2, aged 8 hrs	blue	no Cu(OH) <sub>2</sub> , unidentified peaks
30 mg/L as SiO <sub>2</sub> , pH 9.2, aged 8 hrs	blue	no Cu(OH) <sub>2</sub> , unidentified peaks
Preformed Cu(OH) <sub>2</sub> , pH 7, aged 8 hrs	brown	CuO
65 mg/L Cl <sub>2</sub> , pH 7, aged 8 hrs	brown	CuO
65 mg/L Cl <sub>2</sub> + 10 mg/L as SiO <sub>2</sub> , pH 7, aged 0.5 hrs	green	CuO
65 mg/L Cl <sub>2</sub> + 10 mg/L as SiO <sub>2</sub> , pH 7, aged 8 hrs	brown	CuO



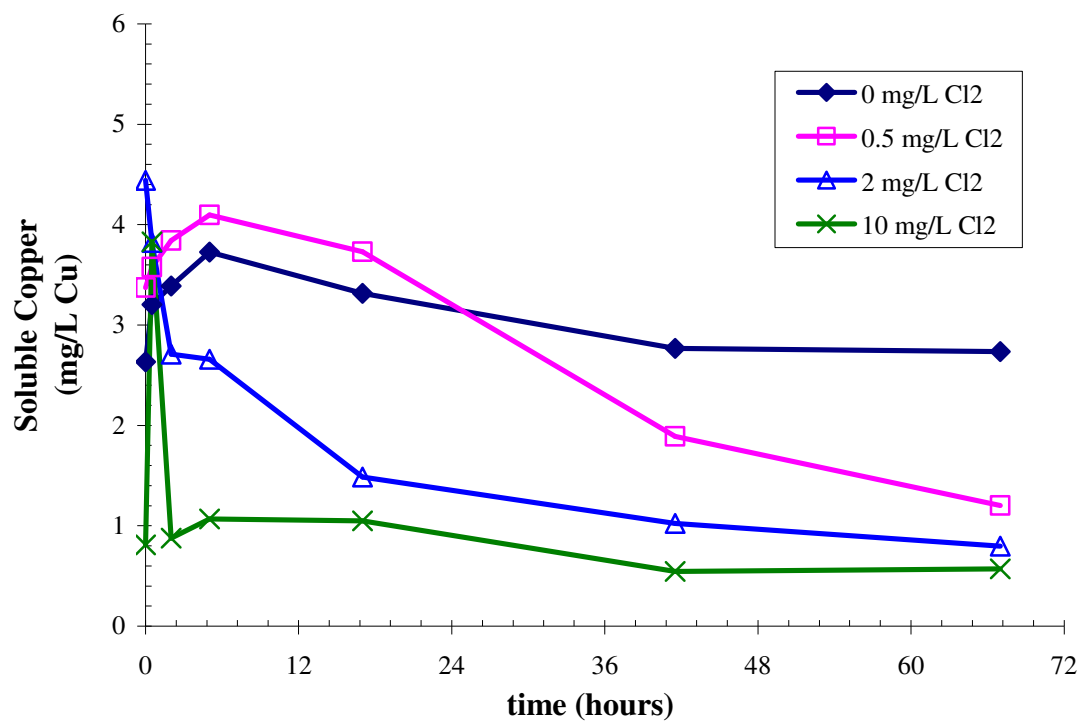
**Figure 2-1.** Sorption density of cupric hydroxide waters with varying pH (above) and silica concentration (below).



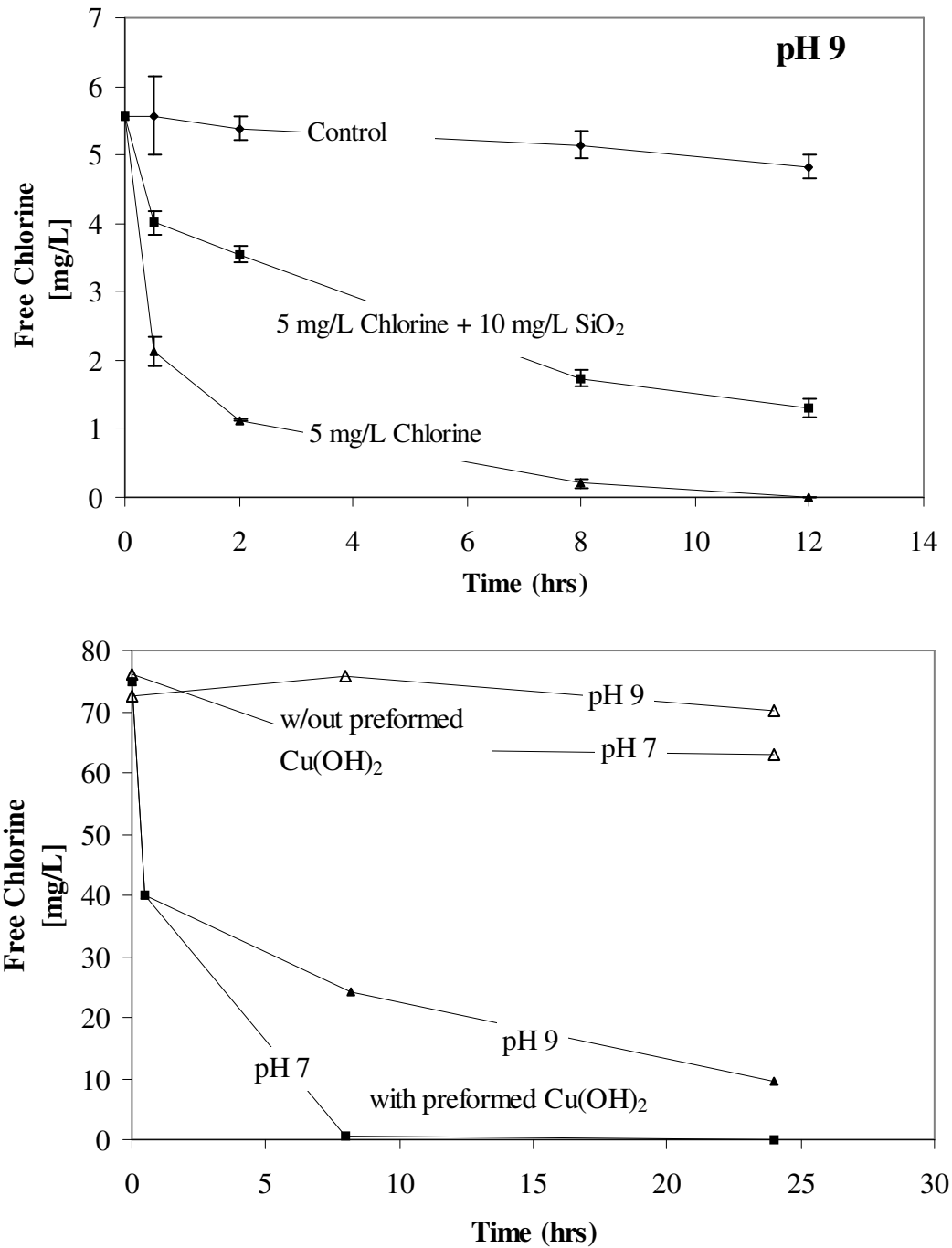
**Figure 2-2.** Zeta potential versus pH for waters initially containing cupric hydroxide at pH 7, with a dose of chlorine and/or silica, before final pH adjustments. Measurements were made in fresh solutions.



**Figure 2-3.** Transition time from blue  $\text{Cu}(\text{OH})_2$  to brown  $\text{CuO}$  solids is plotted for varying pH when  $\text{SiO}_2$  is absent (above). This transition did not occur between pH 7 and 10.5 if the silica concentration was 30 mg/L. At pH 9.2, the time of transition was a strong function of silica concentration (below).

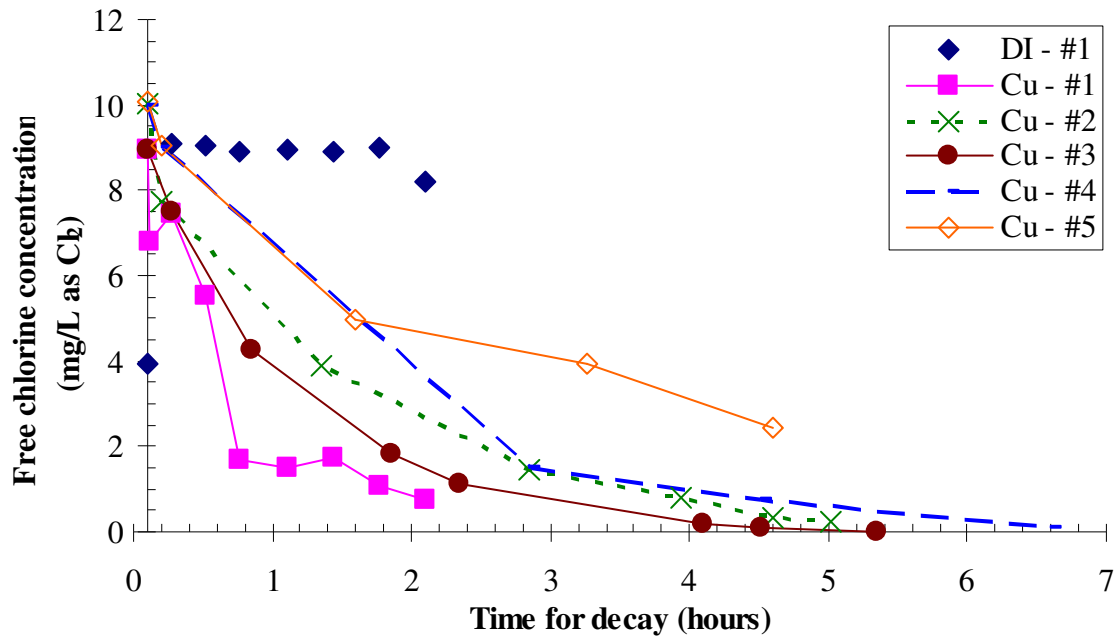


**Figure 2-4.** Soluble copper concentration for samples at pH 7 containing initially 0-10 mg/L as  $\text{Cl}_2$  and cupric hydroxide. The data points show that with increasing chlorine concentration, soluble copper concentration of the solution decreases.



**Figure 2-5.** Total chlorine versus time at pH 7 for solutions containing chlorine with and without cupric hydroxide (above). The decline of free chlorine over time for cupric hydroxide solutions at pH 9 with and without chlorine and silica (below).





**Figure 2-6.** Chlorine decay after each additional spike. While the chlorine decay in the DI water stayed level throughout the experiment, the first spike of chlorine into the copper nitrate solution resulted in a rapid decay of free chlorine. The second and third spikes decayed similarly. The fourth and fifth spikes decayed over a slightly longer period of time.

## **CHAPTER 3: Chemistry of Rapid Chloramine Decay in Water Contacting Copper and Lead Plumbing**

Caroline K. Nguyen, Marc A. Edwards\*  
Dept. of Civil and Environmental Engineering  
Virginia Polytechnic Institute and State University,  
407 Durham Hall, Blacksburg, VA 24061-0246

\*Corresponding author phone: 540-231-7236; fax: 540-231-7916; e-mail: [edwardsm@vt.edu](mailto:edwardsm@vt.edu)

### **ABSTRACT**

When held stagnant in relatively new copper pipes, chloramine and free chlorine disinfectants decay rapidly. In the presence of soluble and insoluble cupric, species, free chlorine decay is most rapid in the presence of cupric hydroxide solid surfaces, whereas chloramine decay (as  $\text{Cl}_2$ ) was slightly increased by cupric. In copper pipes, which have a virtually unlimited supply of metallic copper ( $\text{Cu}^0$ ) while in service, chloramine and free chlorine decayed almost completely during overnight stagnation even after months of exposure. The rate of this reaction was unaffected by extra ammonia, but it was slowed by the addition of phosphate or aluminum which presumably formed barriers between the water and reactive surface sites on the pipe. Experimental results are consistent with a chloramine decay path via  $\text{Cu}^{1+}$  formed by reaction between  $\text{Cu}^{+2}$  and  $\text{Cu}^0$ .

### **3.1 INTRODUCTION**

Chloramines are usually highly persistent and therefore well-suited to maintain disinfectant residuals to consumers' tap. For instance, Nowlin et al. (2001) investigated temperature effects and found 32% loss of monochloramine ( $\text{NH}_2\text{Cl}$  or chloramine) in 5 days at  $30^\circ\text{C}$  while the loss for free chlorine ( $\text{HOCl}$ ,  $\text{OCl}^-$ ) was 90% under the same conditions. Nowlin found no condition where chloramine decayed at the same rate or slower than free chlorine. Even when considering higher rates of decay in the presence of iron and manganese scales on pipes, rates were not fast enough to cause more than

50% chloramine loss in a day under normal conditions encountered in water distribution systems (Valentine, 1998).

Increasing ammonia and decreasing nitrite concentration create more stable conditions for monochloramine in bulk solution (Margerum et al., 1994). Factors that have been found to accelerate decay include decreasing pH, increased phosphorus, and greater amounts of natural organic matter (NOM). Specifically, Thomas found that chloramine decay rates double for each decrease of 0.7 pH units (1987). Furthermore, any acid can catalyze the reaction of chloramine with  $\text{NO}_2^-$ ,  $\text{I}^-$ ,  $\text{SO}_3^{2-}$  (sulfite),  $\text{Br}^-$ , and  $\text{CN}^-$  (Margerum et al., 1994). Margerum et al., looking at 620 mg/L P to 4,340 mg/L P, found that over 5 days 3.2% more chloramine would be lost for every additional 1 mg/L P. Reactions with NOM were determined to be the dominant pathway for chloramine decay during the first 24 hours of the decay process in real waters, whereas autodecomposition of chloramine dominates later or in the absence of NOM (Song et al., 1999; Vikesland et al., 1998; Duirk et al., 2005).

Despite studies demonstrating the low rate of chloramine loss compared to chlorine decay, certain conditions are known to promote rapid chloramine decay; in fact, very high decay rates have been noted to occur in real distribution systems (Edwards et al., 2005; Murphy et al., 1997; Powell, 2004). In Maui water, it was even determined in a head-to-head test that chloramine decayed more quickly than an equivalent amount of free chlorine. The high purity and low salt content of the Maui water may have been a factor, along with the warmer temperature and high levels of bacteria. The Powell et al. (2004) observation that chloramine decayed faster than free chlorine was also based on practical experience. To our knowledge, these are the first data to suggest that a monochloramine residual can be lost more rapidly than a free chlorine residual under at least some practically relevant circumstances.

If circumstances arose such that chloramine disappeared faster than chlorine, chloramine use would be problematic, given the problems with re-growth created by free ammonia. The ammonia can cause problems with nitrification, lower pHs, assimilable organic

carbon production and enhanced re-growth (Edwards et al., 2005). It is also believed that the reactions causing chloramine decay are directly involved in leaching excessive lead and copper to drinking water under at least some circumstances (Murphy et al., 1997; Edwards et al., 2005).

This research was initiated to systematically examine factors that might dramatically accelerate the rate of chloramine disappearance in copper pipe, thereby explaining some problems that occur as a result of rapid chloramine decay in premise plumbing in buildings and homes (Edwards et al., 2005). Preliminary screening tests first evaluated a wide range of factors that might contribute to chloramine loss, whereas longer term confirmation tests were conducted using real pipes and synthesized potable water.

## **3.2 MATERIALS AND METHODS**

### ***3.2.1 Chemicals and materials and NOM***

In all experiments, the target chemicals were added as reagent grade sodium or chloride salts. The standard recipe consisted of 4.2 mg/L  $\text{CuCl}_2$ , 13.7 mg/L  $\text{NaNO}_3$ , and  $5 \times 10^{-4}$  M NaCl in distilled and deionized water at pH 7.0 at 25°C. Natural organic matter (NOM) used in experiments was rinsed Aldrich humic. Before use in experiments, the chlorine demand of the humics was met by dosing 0.43 mg/L  $\text{Cl}_2$  per mg/L TOC. This gave a residual of nearly 0 mg/L  $\text{Cl}_2$  after 24 hours. The target total chlorine concentration was either 5 mg/L or 10 mg/L as  $\text{Cl}_2$  at various stages of experimentation, and chloramine was created by dosing bleach ( $\approx 6\%$  NaOCl) and  $\text{NH}_4\text{OH}$  at pH 8 at a ratio of 4:1 mg  $\text{Cl}_2$  to mg N. Total and free chlorine were measured using the DPD colorimetric test per standard method 4500-Cl G (AWWA et al., 1998), and pH was adjusted using HCl or NaOH. In the tests designed to examine low dissolved oxygen (DO) and metallic Pb and Cu, 125-mL plastic bottles were filled to capacity to eliminate atmospheric effects after purging with nitrogen gas.

### **3.2.2 Screening Experiments in Well-Mixed Conditions**

Preliminary screening tests examined effects of pH, NOM, and cuprous ion on chloramine decay in 1-L plastic containers with liquid volume of 500 mL. The contents were mixed at 200 rpm with 1-inch Teflon stirbars and 2 g of Cu powder or Pb granule metal was added as indicated. Afterwards, an end-over-end mixer was used in some tests to promote better mixing, in which case 0.2 g Cu and Pb metal granules were added to 100 mL water.

A mixture of soluble and insoluble copper solids were formed by adjusting the pH of 4.2 mg/L  $\text{CuCl}_2$  or 2 mg/L  $\text{Cu}^{2+}$  in water to pH above 10, maintaining that pH for 40 minutes, and then decreasing the pH back to 7.0 at the start of the experiment. Raising the pH to 10.0 briefly in this way decreased the soluble copper from 2 mg/L  $\text{Cu}^{2+}$  to 1.0 mg/L  $\text{Cu}^{2+}$ , versus the situation obtained when dosing the copper directly to water at pH 7.

### **3.2.3 Stagnant pipe rig test**

The most interesting effects of chemistry on chloramine decay were selected for long-term testing in pipes. The basic test water contained 4.2 mg/L  $\text{CuCl}_2$ , 13.7 mg/L  $\text{NaNO}_3$  (10 mg/L  $\text{NO}_3^-$ ),  $5 \times 10^{-4}$  M NaCl, and 4 mg/L total  $\text{Cl}_2$  in distilled-deionized water at pH 7.0 and 25°C. In addition, phosphate, ferric ion, and aluminum at the concentrations of 3 mg/L P, 1 mg/L Fe, and 1 mg/L Al, respectively, were added to investigate the effects of each constituent on disinfectant decay (Table 3-1). These constituents present in real drinking water are known to form coatings on pipes in practice. A 1.25 inch long coating of 50:50 Pb:Sn solder was applied to one end of the 1.5 foot pipe section (0.811 inch inner diameter) by dipping it into molten solder. The water in the pipes was changed Monday, Wednesday, and Friday each week but sat stagnant at all other times. After week 12, pre-chlorinated NOM at a concentration of 0.3 mg/L TOC was added to all pipes except for the control to examine whether the NOM formed a coating on the pipes that reduced the rate of chlorine and chloramine decay over the following 6 weeks of testing (Marshall et al., 2004).

Another set of copper pipe rig tests examined whether higher levels of ammonia reduced the rate of reaction between chloramine and copper pipe. The basic recipe consisted of 13.7 mg/L NaNO<sub>3</sub>, 5×10<sup>-4</sup> M NaCl, and 4 mg/L total Cl<sub>2</sub> at pH 7.0 and 25°C. Ammonia concentrations were varied between 0–4 mg/L N. The reaction stoichiometry and measurements using the DPD colorimetric test per standard method 4500-Cl G (AWWA et al., 1998) suggested that monochloramine was the dominant chlorine species present in all cases, except that for the condition in which no ammonia was added for which total chlorine was equal to the free chlorine.

A limited number of tests were conducted using 4 inch lengths of 0.98 inch inner diameter pure lead pipe for comparison to the copper. The same waters were used in the tests using lead pipe. Tubes made of pure glass were also tested to illustrate decay in the presence of a relatively non-reactive surface.

**Table 3-1.** Description of variations in water chemistry examined in the tests with pipe sections using chlorine and chloramine disinfectant.

Condition #	Water Recipe
1	2 mg/L Cu <sup>2+</sup> , 10 mg/L NO <sub>3</sub> <sup>-</sup>
2	2 mg/L Cu <sup>2+</sup> , 10 mg/L NO <sub>3</sub> <sup>-</sup> , 3mg/L P
3	10 mg/L NO <sub>3</sub> <sup>-</sup> (No Cu <sup>2+</sup> )
4	2 mg/L Cu <sup>2+</sup> (No NO <sub>3</sub> <sup>-</sup> )
5	1 mg/L Fe, 10 mg/L NO <sub>3</sub> <sup>-</sup> (No Cu <sup>2+</sup> )
6	1 mg/L Al, 10 mg/L NO <sub>3</sub> <sup>-</sup> (No Cu <sup>2+</sup> )

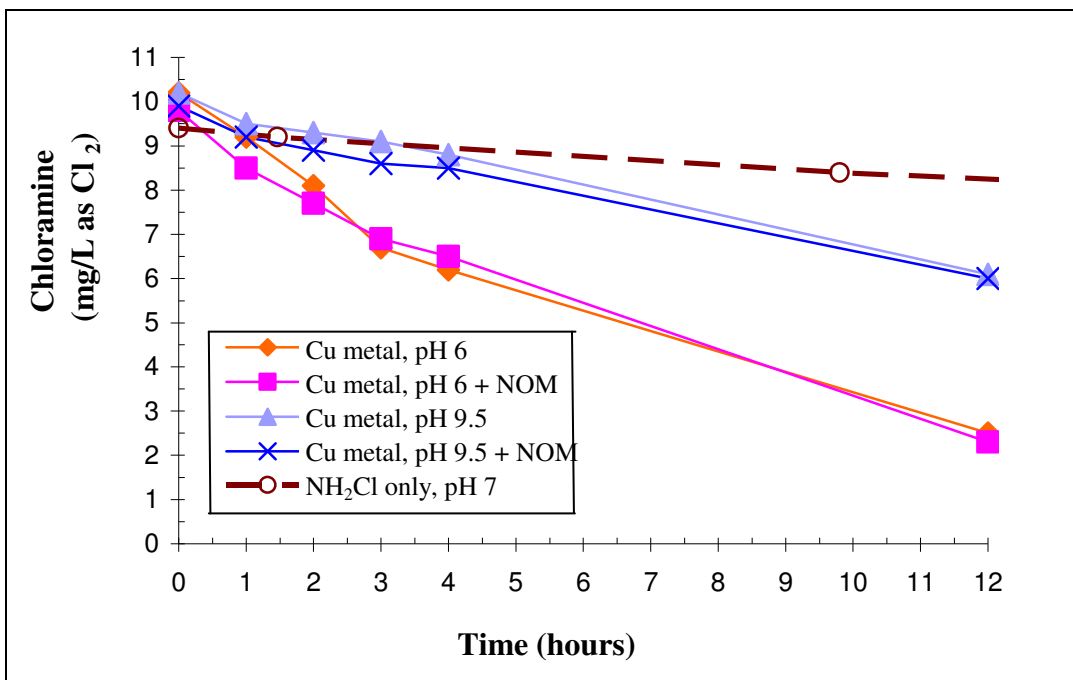
### 3.3 RESULTS AND DISCUSSION

#### 3.3.1 *Fundamental reactions under well-mixed conditions*

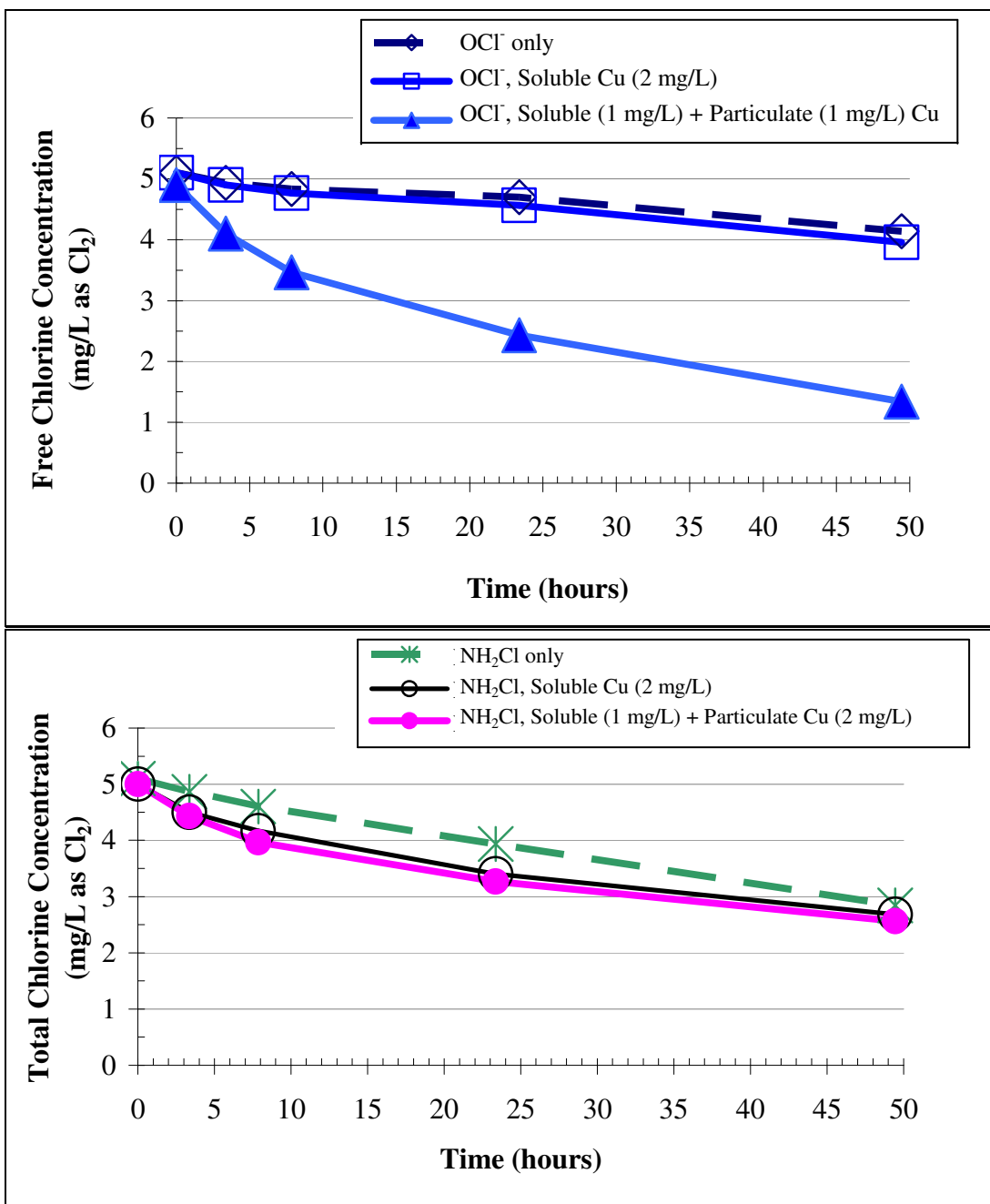
When metallic copper powder was present, the rate of chloramine decay very rapid, and relatively unaffected by NOM. This is in contrast to previous observations made in the absence of metallic copper, which found NOM increased chloramine decay rates (Margerum et al., 1994; Song et al., 1999). It is possible that meeting the chlorine demand of the NOM used in this test was the cause, or that the acceleration of decay due to NOM was nearly insignificant compared to the effect from metallic copper. The time it took for chloramine decay to 60% of the initial concentration was 2.5 times faster at pH

6 than at pH 9.5 (Figure 3-1), consistent with trends for chloramine decay in bulk water via autodecomposition and other reactions (Margerum et al, 1994; Valentine, 1998).

When copper was added to the water in a mixed form of sparingly soluble  $\text{Cu}(\text{OH})_2$  solid and soluble copper the rate of disinfectant loss increased (Figure 3-2). It was of interest to test whether soluble copper or the particulate copper species were involved. For the test, after passing the solution through a 0.45  $\mu\text{m}$  pore size filter, a solution with 2 mg/L soluble copper was produced. Removal of the particulate copper reduced the rate of free chlorine decay relative to that in the control. Thus, the decay is due to particulate cupric oxyhydroxides. In contrast, chloramine decay rates were the same in the presence of both soluble and insoluble forms of copper, and decay rates were only slightly higher than the controls.



**Figure 3-1.** Greater chloramine decay occurred with decreasing pH in the presence of copper metal, and no effect was observed for 4 mg/L of pre-chlorinated NOM. The water contained an initial target concentration of 10 mg/L as  $\text{Cl}_2$ , 0.2 g copper metal powder, 19 mg/L  $\text{Cu}^{2+}$ , 10 mg/L  $\text{NO}_3^-$ , and 4 mg/L TOC (as indicated) at pH 6 and 9.5 except in the solution specified as  $\text{NH}_2\text{Cl}$  only which contained chloramine in distilled-deionized water.

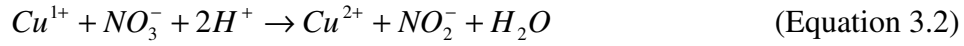
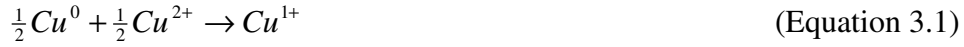


**Figure 3-2.** Free chlorine (upper) disappears more rapidly when particulate Cu is present in the water. Monochloramine concentration (lower), on the other hand, is affected by either soluble or particulate copper. Also of note is the greater chloramine decay compared to the free chlorine decay in the pure water. The experimental water was distilled, deionized water at pH 7. Samples labeled as soluble Cu or particulate Cu also have 2 mg/L total of soluble and/or particulate Cu(OH)<sub>2</sub>, formed by the process described in the methods section.

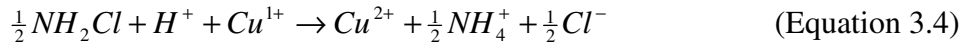
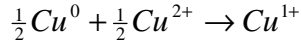
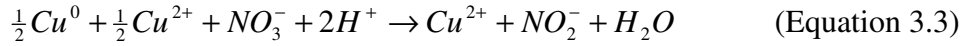
Other conditions at pH 7.0 were investigated to determine the effect of variations in bulk water chemical constituents relative to chloramine decay, and to provide insight to



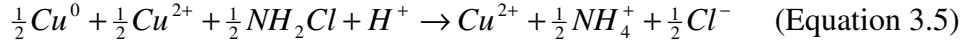
possible reaction pathways. One reaction mechanism of high interest was based on an observation of Filmanov (2004) regarding the role  $\text{Cu}^{2+}$  and  $\text{Cu}^0$  in forming reactive  $\text{Cu}^{+1}$ . Filmanov hypothesized that Cu metal in the presence of cupric ion formed cuprous ion ( $\text{Cu}^{+1}$ ), and the cuprous ion reacted with nitrate to form nitrite and other reactive species (Equation 3.2). The nitrite would react further with chloramine in this work (Equation 3.4). These reaction pathways explain why addition of  $\text{Cu}^{+2}$  would increase the rate of reactions in the presence of metallic copper, especially in the initial time period when low levels of  $\text{Cu}^{+2}$  would be present in water due to relatively slow corrosion and dissolution of  $\text{Cu}^0$  (Figure 3-3).

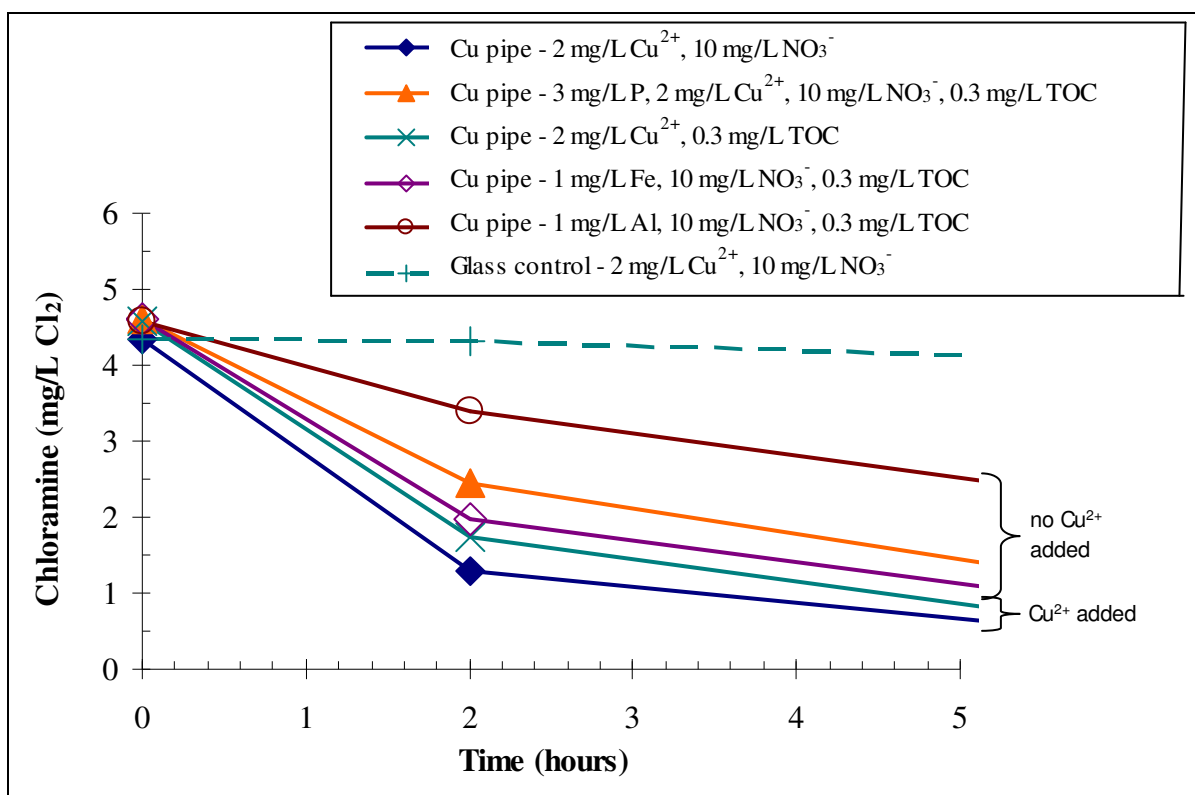


Overall reaction:



Overall reaction:

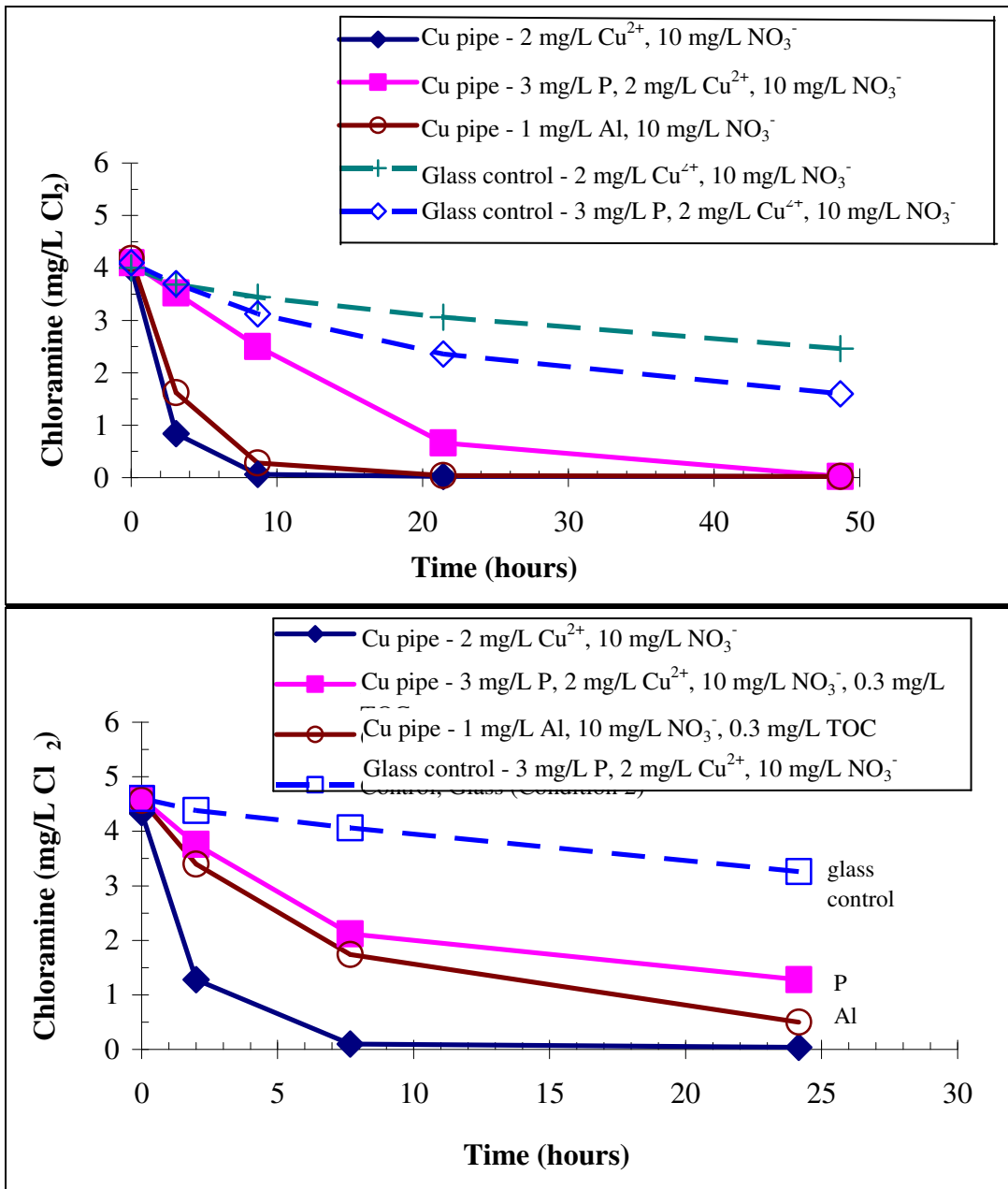




**Figure 3-3.** In copper pipes, the chloramine decay was more rapid when cupric ion was added to the water. These results demonstrate chloramine decay during the first 5 hours after 19 weeks into the experiment.

### 3.3.2 Practical testing in Cu pipes with solder

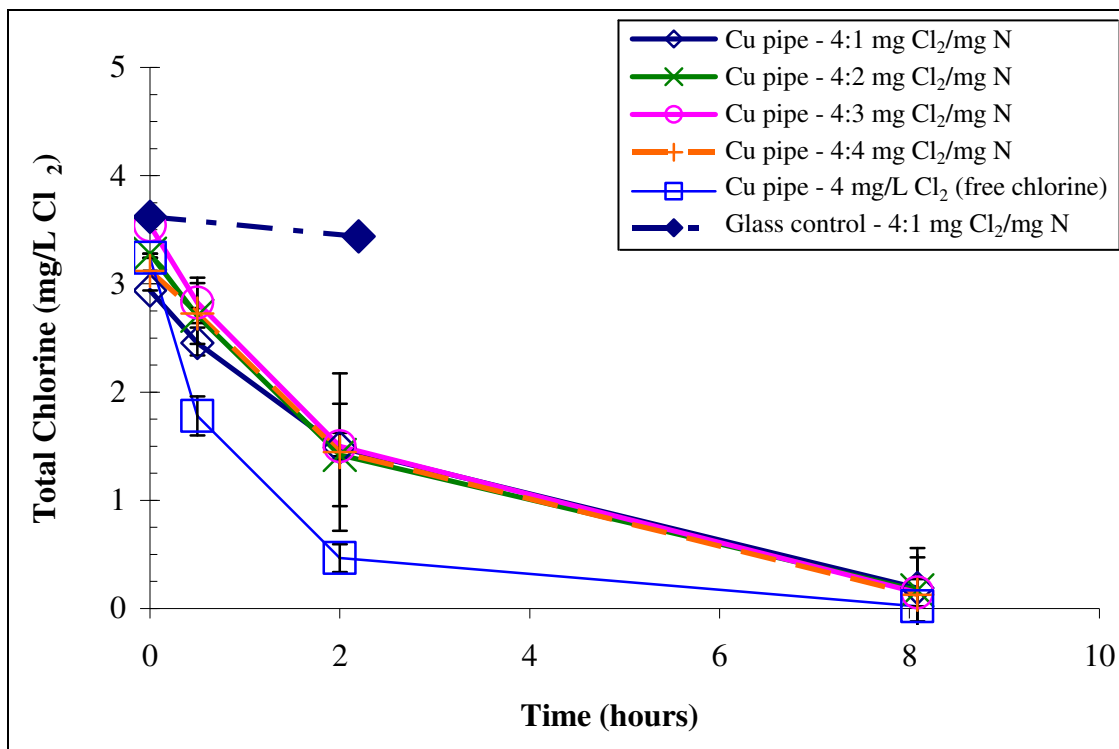
New Cu pipes were subjected to a range of water qualities selected after review of screening test results. At certain times, total chlorine was measured at various times of the experiment by removing an aliquot from the end of the pipe that did not have the lead solder, generating profiles of total chlorine versus time. In new Cu pipes both free chlorine and chloramine decay were so rapid, the disinfectant concentrations disappeared completely within 10 hours, except in the cases where phosphate was present. Even after 18 weeks exposure, during which NOM had been added to the bulk water for the last 6 weeks, chlorine and chloramine decayed rapidly, and was only decreased by the presence of Al and phosphate (Figure 3-4). Iron did not have a significant effect on chloramine decay.



**Figure 3-4.** The chloramine decay in Cu pipes between 7 weeks (upper) and 18 weeks (lower) did not slow significantly with aging, except in the case when Al was present. NOM was added to the bulk water during the last 6 weeks. Although data is not shown, the remaining waters tested had decay similar to that for the test water with only Cu<sup>2+</sup> and NO<sub>3</sub><sup>-</sup>.

Chloramine is frequently made at a 4:1 mg Cl<sub>2</sub> to mg N ratio at the treatment plant, but the ratio of Cl<sub>2</sub> to NH<sub>3</sub> naturally decreases as chloramine decays to Cl<sup>-</sup> and free ammonia. Higher ammonia concentrations will reduce the rate of chloramine autodecomposition

and can also decrease reactivity of chloramine with other species (Margerum, et al., 1994; Vikesland et al., 1998). In new copper pipes, the rate of chloramine decay was not significantly decreased by higher amounts of ammonia (Figure 3-5). Total ammonia (free and combined) was conserved in the pipes. This result supports the idea that chloramine decays by the reaction sequence noted in Equations 3.3 and 3.5, because the rate of chloramine decay is not affected by the presence of ammonia, whereas many other pathways of chloramine decay are impacted by the concentration of ammonia.



**Figure 3-5.** The chlorine disinfectant decay was more stabilized by the addition of nitrogen (4:1 mg Cl<sub>2</sub>/mg N); however, any further addition of nitrogen (from 4:1 through 4:4 mg Cl<sub>2</sub>/mg N) does not increase the stability of chloramine disinfectant in new Cu pipes. These results are averages of triplicates at each ratio condition and include 95% confidence error bars.

The authors have measured persistent chloramine residuals during stagnation in copper pipes in many field studies for systems both with and without phosphate inhibitors, and based on that data it is clear that the phenomenon of rapid chloramine decay does not always occur during stagnation. In this study, however, the rate of chloramine decay did not decrease in the copper pipes even after 18 weeks of aging, demonstrating that scales

forming on the pipe do not inherently reduce its reactivity. There is, therefore, interest in the circumstances that cause reduced reactivity between the pipe and chloramine in the water. This work clearly demonstrates that orthophosphate added to potable water as a corrosion inhibitor decreases copper corrosion rates and minimizes release of soluble  $\text{Cu}^{2+}$  ions to water, thereby reducing the reactivity of the copper to chloramine (Edwards, 2002). This is consistent with the reaction pathway described previously, as the presence of  $\text{Cu}^{2+}$  starts the chloramine decay reaction via formation of  $\text{Cu}^{1+}$ . Even if  $\text{Cu}^{2+}$  is not specifically added to the water, it is the expected soluble species released from the copper pipe naturally (Edwards, 1996). The aluminum coating formed on the pipe may reduce the reactivity of the copper surface, either by physically blocking access of chloramine to surface sites or by reducing release of  $\text{Cu}^{+2}$  from the pipe via dissolution reactions (Figure 3-4).

It was speculated that NOM might behave similarly to phosphate, in that it might form a coating on the copper that reduced the rate of chloramine decay, and that this effect might overwhelm the increased bulk water chloramine decay that would be attributed to the NOM. However, it did not happen during this experiment at a level of 0.3 mg/L NOM in the water. Another key factor is the purity of the bulk water (e.g., Vikesland et al., 2000). Specifically, in very pure water the rate of free chlorine decay is expected to be lower than that of monochloramine decay, since monochloramine decay via autodecomposition tends to be higher relative to chlorine.

Future research should examine whether other constituents present in natural waters, such as bicarbonate or silica, might create a scale on copper pipe that is less reactive with chloramine. But one practical implication of this work is that phosphate forms these scales.

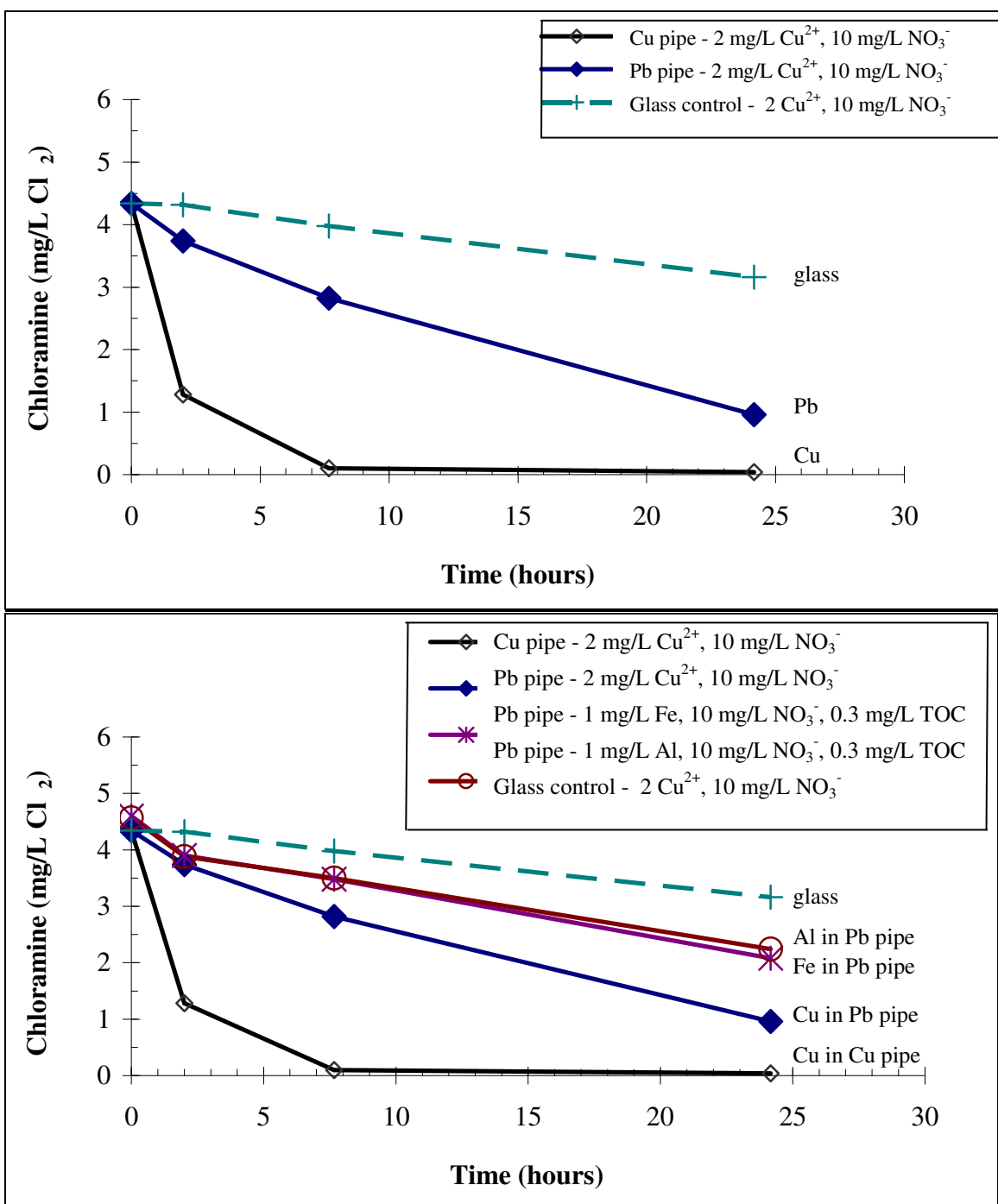
### **3.3.3 Reactions in Pb pipe rig**

The rate of chloramine decay in the pure lead pipes was also higher than the control but was about 8 times slower than the slightly smaller diameter copper pipes. For instance,

in the control water for copper, chloramine decayed to 50% of its initial value after about 2 hours, whereas it took about 16 hours for the same rate of decay in pure lead pipes (Figure 3-6). As was the case for copper pipes, aluminum, as well as iron, reduced the rate of chloramine decay; however, unlike results in copper pipes, phosphate did not significantly reduce chloramine decay rate (Figure 3-6). The time to decay to 50% of the initial chloramine concentration was about 1.7 times slower in the presence of aluminum or iron in Pb pipes, versus the condition when cupric ions were present. Metallic lead can reduce cupric to cuprous as per equation 3.1, and therefore, the same reaction pathway may be important for lead in the presence of cupric.

One interesting discrepancy was noted in the behavior of chloramine decay in the stagnant pure lead pipes versus lead granules mixed end over end. For instance, phosphate decreased reactivity with chloramine in pipes, but markedly increased reactivity for lead granules mixed end over end. This interesting experimental result was verified by repeating the test three times. The difference could be due to a scale or oxide layer forming on the Pb pipes and reducing reactivity with chloramine, as was observed for reactions between metallic lead and nitrate in other work (Uchida, 1998). In the case of end over end mixing with lead granules, fresh lead surfaces would be created, which remained very reactive with nitrate and presumably chloramine, but it is uncertain why phosphate would accelerate these reactions (Uchida, 1998). Very low amounts, below 0.07 mg/L N, of nitrite were determined to be created when either nitrate or ammonia were added to the Pb pipes. In addition, the pH increased to  $\text{pH } 9.5 \pm 0.4$  in the Pb pipes after 2 days of stagnation.

Another result seen in both Cu and Pb pipes was the effect of  $\text{Cu}^{2+}$  ion. When cupric ion was in the water with either of the pipe materials, the decay rates were slightly greater when compared to the condition when no cupric ion was added (Figure 3-6). The redox potential of lead metal is -0.13 volts, and therefore,  $\text{Cu}^{+2}$  could be reduced to  $\text{Cu}^{+1}$  or even  $\text{Cu}^0$  by reaction with the lead surface. Thus, the reaction between  $\text{Cu}^{+2}$  and metallic lead could start the same chloramine decay reaction sequence indicated in Reactions 3.1-3.5.



**Figure 3-6.** Chloramine in Pb pipe disappeared quicker than in glass, but Cu pipe with chloramine had the most drastic chlorine decay (upper). In lead pipes, chloramine decay was greatest in water containing Cu<sup>2+</sup> while the metals Al and Fe had a less significant effect (lower). These results are the chloramine concentrations in the pipe rig after 18 weeks.

### 3.4 CONCLUSIONS

Rapid loss of chloramine-chlorine residual in some waters that contact copper pipe suggests that utilities should carefully examine water for residual loss during stagnation in home plumbing. Rapid loss of residual could create a problem with re-growth of opportunistic pathogens. Practical measurements have shown that chloramine residual does not always decay rapidly in real copper pipes. Therefore, it is likely that natural reactions not reproduced in these tests can inhibit chloramine decay in at least some real systems. Longer aging and thicker scales, presence of silica, and presence of bicarbonate are likely factors to be examined in future research.

### 3.5 ACKNOWLEDGEMENTS

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## **CHAPTER 4: Development of a Novel Test to Monitor Copper Pitting**

Caroline K. Nguyen, Marc A. Edwards\*  
Dept. of Civil and Environmental Engineering  
Virginia Polytechnic Institute and State University,  
407 Durham Hall, Blacksburg, VA 24061-0246

\*Corresponding author phone: 540-231-7236; fax: 540-231-7916; e-mail: [edwardsm@vt.edu](mailto:edwardsm@vt.edu)

### **ABSTRACT**

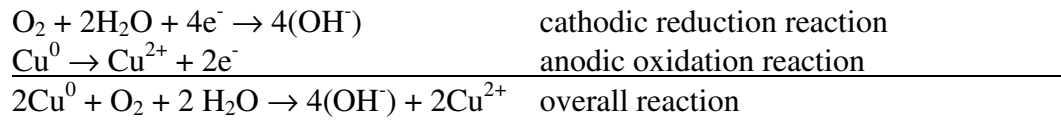
Although numerous attempts have been made to develop means of monitoring copper pitting corrosion, all existing methods have serious short-comings. A thorough evaluation led to development of a new method of tracking pitting corrosion that can provide a direct measure of pitting, real-time data, and is inexpensive. The technique demonstrates that copper pitting can in some waters by separation of anodic and cathodic areas by differential flow, and development of galvanic currents between cathodic and anodic areas. The measured galvanic current flow was sufficient to cause failure of a type M tube in a period of months. The effects of pH, chloride, phosphate, and natural organic matter (NOM) on galvanic pitting currents were consistent with current beliefs and expectations, and therefore, the method is likely to be useful in tracking pitting and in identifying remedial actions in at least some waters.

### **4.1 INTRODUCTION**

While copper is often among the most troublefree plumbing materials, the recent occurrence of copper pitting failures in certain areas of the U.S. with high chlorine and high pH has spurred studies to better understand and mitigate these problems.

Corrosion is the degradation of metal through chemical reactions with the environment, occurring via a coupled anodic and cathodic reaction. At the anode, the metal is corroded or oxidized, and the released electrons are transported to the cathode where they are consumed at the surface in a reaction with oxygen or chlorine (Equation 4.1).

(Equation 4.1)



For uniform corrosion, the corrosive attack proceeds evenly over most of the surface. Failure occurs via thinning of the metal, typically after much more than 50 years. In contrast, localized corrosion occurs when the anodic reaction is concentrated at a small location on the surface, as occurs during pitting, crevice, or galvanic corrosion. In a typical pit, a hole up to a millimeter in diameter is eaten through the metal at the anode causing failure. During this process, oxidized cuprous and cupric corrosion products accumulate and cover the developing hole (e.g, the pit) in a mound known as a tubercle. Other forms of non-uniform corrosion include crevice corrosion and galvanic corrosion.

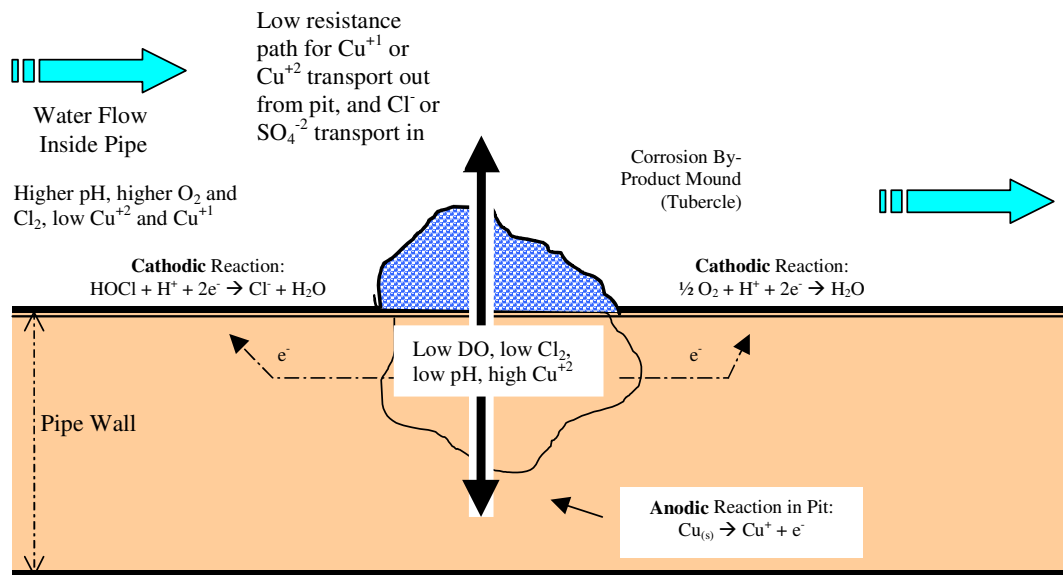
#### **4.1.1 Fundamental science of pitting**

A comprehensive review of copper pitting corrosion was conducted a decade ago (Edwards et al., 1993), and noteworthy changes in understanding are highlighted in the section that follows. The review that follows was focused on pinholes that grow from the inside of the pipe outwards (e.g., internal corrosion). The very different factors that cause leaks to grow from the outside of copper pipe inwards (e.g., external corrosion) are not addressed in this research.

A typical copper pit that might lead to a pinhole via internal corrosion is diagrammed schematically in Figure 4-1. The pit is the site of the anodic corrosion reaction which consumes the pipe wall, during which copper metal is converted into  $Cu^{+1}$  ions. In order to complete this reaction, the electrons released at the pit must be consumed by a cathodic reaction, and in normal cases of metallic pitting, electrons flow through the conductive metal to the pipe wall surface. The electron current ( $i$ ) through the metal driving pitting is termed the “*pitting current*” in this work, and it is directly proportional to the instantaneous rate at which metallic copper is being eaten away in the pit. Unfortunately, there is no way to directly measure this current in practice for real pits.

The electrons are then consumed at the cathode (at the pipe surface that is not undergoing visible attack) via reaction with  $O_2$  to produce  $OH^-$  or  $Cl_2$  to produce  $Cl^-$ . Thus, even though no visible attack is occurring at the pipe surface surrounding the pit, the cathodic reaction is critical to pit growth, and the importance of that reaction should not be overlooked. Indeed, in many instances the rate of pit growth is believed to be limited by the rate of the cathodic reaction. In addition, for every atom of metallic copper that corrodes in the pit anode releasing 1  $Cu^{+1}$ , 1 negative charge (e.g. 1  $Cl^-$ ,  $\frac{1}{2} SO_4^{-2}$ , or 1  $OH^-$ ) has to be transported into the pit from the water. Thus, the essential features of a pit include 1) the anodic reaction site, 2) the cathodic reaction site, 3) a pathway for  $Cl^-$ ,  $SO_4^{-2}$  or  $OH^-$  transport into the pit, and 4) a conductive pathway for pitting current flow.

The tubercle, a growing mound of corrosion byproducts that protrudes into solution, is often visible over the growing pit. The tubercle grows outward because  $Cu^{+1}$  and  $Cu^{+2}$  ions diffuse out of the pit and react with the higher pH water, creating a continuously forming precipitate. Alternatively, corrosion products such as  $Cu(OH)$  or  $CuCl$  that form in the pit occupy much more space than the original metallic copper, so pits also can be forced to protrude out from the tube due to the extra volume created. Within the pit, anodic reactions scavenge dissolved oxygen and  $Cl_2$  from the water, and hydrolysis of the copper [e.g.  $Cu^+ + OH^- \rightarrow Cu(OH)$ ] can remove  $OH^-$  from the water and drop pH to very low levels. Pourbaix predicted and observed that the pH in an active copper pit was about 3.5, for a case where the pH outside the pit was 7.9 (Pourbaix, 1971). The low pH enhances transport of soluble  $Cu^+$  ions from the pit.



**Figure 4-1.** Key reactions, locations, and elements of internal copper pitting.

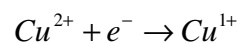
It was realized from the earliest dates that some potable waters allow pits to propagate (i.e., grow) and others will not. In many past studies of copper pitting, when “live” pits on a pipe were moved from a water that initiates/supports pitting to a water that does not, the pits were believed to rapidly die, and few if any pinhole leaks form. In such cases, pit death is believed to occur because:

- 1) a scale or barrier forms on the cathode surface that reduces the rate of the cathodic reaction, which in turn reduces the pitting current and slows the rate of pit growth
- 2) a scale or “cap” forms in the top of the tubercle that prevents rapid transport of anions into the pit

If the water does not have a natural tendency to stop pitting, pits can continue to propagate until a leak occurs. To greatly oversimplify previous research, many factors combine to determine whether pits grow in a given water including the pH, levels of oxidants ( $\text{O}_2$ ,  $\text{Cl}_2$ ), all anions (bicarbonate, sulfate, chloride, phosphate), natural organic matter (NOM), hardness ions ( $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ), and silicates. These factors can mutually interact and control the type of barriers (scale or corrosion by-products) that form over the anodic pit and cathodic pipe wall. Local flow conditions such as velocity, presence of scouring particulates or bubbles, or nearness to bends can play a critical role in pit growth. Microbes can also locally alter the types of barriers that are present and can

produce anions such as sulfides (from sulfate) that can catalyze the cathodic reaction. For all these reasons, it is not surprising that pitting is extremely complex, since water chemistry can vary significantly with time even in a given water supply. The complexity can also explain variability in pitting frequency for pipes exposed to the exact same water in the same house.

The above theory of pitting reflects thinking through about 1960 to 1970. At that time, the Lucey theory (1967-1972) of copper pitting was put forth and widely accepted. Lucey's experimental work was focused mostly on pitting corrosion occurring in copper tanks that occurred under stagnant or very low flow conditions. A cornerstone of the Lucey theory was that little or no pitting current existed. Instead, Lucey hypothesized that  $\text{Cu}^{+2}$  ions migrated into the pit from the bulk water, and removed the electrons directly within the pit by the following reaction:



In this way the pit could propagate without any pitting current or external cathode. This theory is unique relative to pitting for other metals, for which pitting via separate anodic and cathodic areas are key as per Figure 4-1.

A historical review of pitting literature that we have conducted in the last year revealed another oddity. Specifically, Lucey's theory came into acceptance despite the prior work of Bengough and May (1924) and May (1953), which unambiguously demonstrated that the pitting current existed. Moreover, May (1953) developed an active "artificial pit" that allowed the pitting current to be measured directly. The authors noted "that such a cell might form a valuable test for the rapid and direct demonstration of whether or not a given water would support pitting corrosion (May, 1953)." In other words, once an active pit was created, measurement of the pitting current in different waters would tell how fast the pit was growing, or if it had died.

It is further noted that the Bengough and May (1924) and May (1953) research was developed using pipes and flowing water conditions as occurs in home plumbing,

whereas the later Lucey theory was developed for a situation in which flow was very low or non-existent. Even so, in 1999 Sosa demonstrated that for conditions present in a pit, pitting currents did exist and were the key contributor to pit growth even under completely stagnant conditions. The Sosa work also repeated numerous experiments conducted by Lucey and demonstrated that alternative explanations existed for some of Lucey's key results. .

At first glance, the Sosa findings and re-examination may seem a step backwards, in that it questions the conventionally accepted theory of Lucey. However, it re-established that copper pitting is not fundamentally different from pitting of other metals, and it re-opened the possibility that pitting currents existed as per hypothesis based on earlier work in flowing potable water. As will be discussed in later sections, the latter point spurred additional research into a new and direct method of accurately measuring pitting.

#### ***4.1.2 Pitting initiation factors***

The previous discussion focused on reactions that occur once a pit is growing and did not address the questions of how pits get started in the first place or why they start in some instances and not others? In normal situations, at least for copper, it is believed that the corrosion reaction acts to prevent permanent separation of anodic and cathodic areas on the pipe surface. The differences in electrochemical potential between such areas tend to disappear naturally. This can occur, for example, if oxygen becomes locally depleted at cathodes, or cuprous and cupric ion build up in pits (anodes), thereby lowering the driving force for the overall reaction and current flow through the metal. Alternatively, higher pH at the cathodes might reduce the driving force for cathodic reactions, or deposition of positively charged colloids at cathodes provides a barrier to mass transfer. Regardless of the exact cause, even if the surface starts with distinct anodic and cathodic areas, the situation is only temporary because normal corrosion acts to oppose that separation. Corrosion is therefore relatively uniform during such circumstances. In contrast, waters that support pitting corrosion are conducive to situations that promote separation of anodic and cathodic areas on copper pipe.

A major impediment to progress and understanding is that pinhole leaks had never been successfully reproduced in the lab under conditions representative of their occurrence in practice until 2002. Until that time, attempts to improve understanding relied on work in real waters known to cause pitting (e.g. Smith and Francis, 1990), rendering it impossible to determine exactly what factors in the water were critical. Or, more frequently, very short-term electrochemical tests were conducted, and formation of micropits was tracked after forcing corrosion to occur at a high rate using electrochemical test cells. While the information gathered in those studies are useful, the conclusions could never be made with confidence in relation to fundamental understanding of pitting. Developing an ability to reproduce pits under scientifically reproducible conditions, without artificially applied potentials or currents, was essential to advance the science. This deficiency and barrier to progress was also noted by Bengough and May more than 80 years ago (1924).

None of the purported causes of copper pitting such as carbon films, surface imperfections, excessive flux, poor installation practice, electrical grounding and other factors, ever led to formation of real pits in copper pipes in the laboratory, even when the short term indirect electrochemical monitoring methods (e.g. forced currents via anodic scans, cyclic voltametry, electrochemical noise) suggested that pitting would occur. A failure to reproduce pitting with these initiating factors does not mean that the factors do not contribute to pitting in some instances, but it did illustrate that the earlier understanding is not as complete as some had believed (Sosa et al., 1999). The null results from the above tests also forced certain proponents of various theories to admit that they had never actually reproduced pitting either and that the listed “causes” for pit initiation were theory and not fact. It was then believed by some that the failure to reproduce the problem pointed to a microbial cause for pitting, but intensive research on the subject funded by the International Copper Association did not lead to either formation of pinholes or definitive results.

A breakthrough in understanding came when the important role of flow was reconsidered. According to the widely accepted Lucey theory, pitting had to be worst under nearly stagnant conditions, because it was only under that circumstance that cupric



ions could diffuse back into the pit and remove electrons without a pitting current. If the assumption that low flow would maximize pitting was wrong, that could be a possible reason for widespread failures to reproduce pits in the lab.

In 2004, it was shown that if water had a combination of: 1) low NOM, 2) aluminum residuals (above 50 ppb as Al), 3) free chlorine (above 2.5 mg/L as Cl<sub>2</sub>), 4) higher pH (above pH 8.2), 5) low chloride (less than 30 mg/L), and 6) frequent flow, fully penetrating leaks in copper tube would form (Rushing et al., 2004; Marshall et al., 2004; Marshall et al., 2005). In fact, under laboratory conditions using synthesized water with the right combination of the above factors, 8 leaks were formed in a 1-foot section of type M copper tube in 12 months. The tubes used no flux or even joints of any kind, and they were not connected to any electrical devices, so that grounding was not a concern. In some cases the copper surface was polished to a mirror-like finish to remove surface imperfections, and while pitting was of slightly lesser intensity, the polished copper tube did not perform significantly better than tube off-the-shelf. The water used was filtered, sterilized, carried large amounts of disinfectants, and contained no carbon, phosphorus or nitrogen source to support a high concentration of microbial growth. Levels of bacteria on the pipe were confirmed to be much lower than would be present in a typical distribution system, and therefore, it is highly unlikely that bacteria were a significant contributor to the problem. Consequently, for this one water recipe at least, copper pinholes were proven to be caused exclusively by a reaction between potable water and a normal copper tube. No other factors are necessary (Marshall, 2004).

Flow was critical in the attack (Marshall, 2004 and 2005). Specifically, the degree of pitting increased with more flow, and the worst condition was continuous flow. In pipes exposed to the exact same water but with flow only 5 minutes or less per day, no pitting could be detected. Pitting clearly initiated at 40 minutes or higher flow duration per day and the severity increased with flow duration. Thus, for this type of pitting at least, the conventional Lucey theory was incorrect. Ironically, we later found that the oldest work of Bengough and May (1924) and May (1954) noted “pitting in stagnant conditions was

necessarily a slow process and that water movement was essential before the rate could increase.”

Recent experiments using the Marshall pitting water showed that velocity is critical as well. That is, a 2 ft/sec velocity in pipes leads to pitting, but a 7 ft/sec velocity using the same water may not. Thus, there might be an “optimally bad” flow rate required to increase the likelihood of pitting. Marshall also noted that pitting was worst on the area of straight copper coming immediately after a bend in the plastic fittings. She hypothesized that both the turbulence at the copper surface near the pipe entrance and less turbulence on the surface further into the pipe played an important role in development of separate cathodes and anodes. In a later section, we exploit this hypothesis in developing a new method of initiating pits on the tips of wires, which in turn, allows us to develop a new way of tracking pitting.

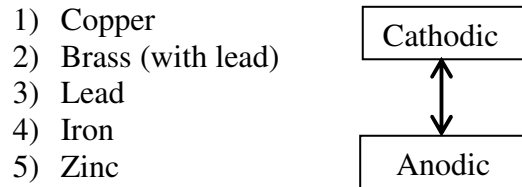
It was recently shown that the combination of chloramine, high pH, aluminum, and no NOM can also cause pitting, but that was in a “real” water. Nationally, we think that these two modes of attack explain about 30% of the failures which are occurring, and many of the outbreaks. However, we have only isolated one recipe for pinhole leak development, and we expect that many others will be eventually found important (Table 4-1). For instance, our previous research gathered very strong circumstantial and scientific evidence that growth of sulfate reducing bacteria (SRB) caused pinhole leaks in Florida and in other areas of the US (Jacobs et al., 2000). We also have seen many instances where corrosion is likely caused by a phenomenon known as gaseous cavitation (Novak et al., 2005). It has also been established with certainty that manufacturing/installation defects and other types of microbes can at least contribute to pinhole leaks in at least some waters, especially for Type III soft water pitting corrosion (Edwards et al., 2002). At this stage, it is important to remain open-minded to all reasonable possibilities regarding the causes for failures encountered in practice.

**Table 4-1. Summary of suspected inside-out pitting mechanisms.**

Probable Pitting Mechanism	Scientific Certainty	Cause	Characteristic water	Possible factors in water reducing the frequency of failure	Characteristic Location of Worst Pitting
Sulfide attack	Nearly 100%	Direct corrosion	Any raw water with sulfides or SRB	NOM, higher pH, molybdenum (inhibits SRB), phosphate	Near colonies of SRB
Cl <sub>2</sub> -Al-high pH	100%	Aluminum deposits cause non-uniform attack	pH > 7.8 Cl <sub>2</sub> > 2.5 ppm Cold water	NOM, phosphate	Pipes in frequent flow and at locations with highest residual
Chloramine-Al	100%	Same as above	Same as above, but seems to be hot water	Lower temperatures, lower velocity of water in pipes	Both hot and cold, but hot water recirculation lines worst impacted
High Cl <sub>2</sub> -High pH	Strongly suspected	Chlorine oxidant and non-uniform attack	pH > 8.5 Chlorine > 0.5 Cold water	Unknown	Pipes with frequent flow and close to treatment plant.
Gaseous Cavitation	Strongly Suspected	Bubble impingement	Dissolved gas supersaturation, hot and cold	Surfactants such as polyphosphates and NOM might reduce gaseous cavitation.	Near bends and flow constrictions
Particle/Water Erosion Corrosion	Suspected	Non-uniform wearing of pipe	Both hot and cold, although hot is more susceptible	Lower velocity of water, colder temperatures, lower turbidity	Near bends.
Deposition Corrosion	Suspected	Concentration cells caused by varied oxidant access to surface	Lines or mounds of deposits other than copper	Filter particles from water, reduce oxidant concentration (i.e., GAC may reduce Cl <sub>2</sub> )	Deposits often preferentially found on pipe bottom or outside of bends.
Other microbial	Strongly Suspected	Concentration cells caused by bacteria	Low alkalinity and poorly buffered water, lack of disinfectants	Low concentrations of AOC, phosphate, fixed N or K limit regrowth	Farthest reaches of treatment plant.

#### 4.1.2.1. Galvanic and deposition corrosion

When two dissimilar metals are electrically connected, the anodic and cathodic reactions are created. For common materials used in water supplies, the galvanic series defines the anode or cathode in galvanic connections:



As a result, lead and leaded-brass are expected to be anodic compared to copper, thus releasing more lead ions into the water than copper when electrically connected. This becomes an important issue because of the danger of lead leaching (Jones, 1992; Reiber, 1991; Shrier et al., 1995).

Another important, yet unappreciated, aspect of the galvanic phenomena is deposition corrosion. Deposition corrosion, which could also be categorized as pitting or crevice corrosion, can occur when soluble ions from a cathodic metal are present in the drinking water in a pipe. For example, cupric ions released from a copper pipe installed upstream of lead pipe, can directly deposit onto the lead surface, catalyzing corrosion of the underlying lead metal indefinitely. The general concept of deposition corrosion is well-established scientifically. The water industry also has documented occurrences of deposition corrosion where dissolved copper accelerated corrosion of iron piping (Hatch, 1955; Cruse, 1971; McNeill et. al., 2001).

Pitting of copper can also proceed by a type of galvanic action. Specifically, if particulates settle or deposit on the pipe wall, the area under the deposit is screened from the oxidant, giving rise to a difference in concentration. The oxidant-deficient area under the deposit can start a localized pitting attack, and once it is initiated in waters that sustain such reactions, the reaction can proceed until a leak forms.

Experimentally, galvanic corrosion reactions can be tracked by measuring the current that flows between the dissimilar pieces of metal. In the case of copper pitting, the dissimilarity arises from differences in chemical composition between otherwise identical pieces of metal.

#### ***4.1.3. Methods of tracking pits: Literature review***

The condensed version of the literature review presented in the paragraphs below establishes the motivation for a promising new method of monitoring pitting that will be tested during this work. The development of an accurate, inexpensive and rapid test of a waters' ability to support pitting (e.g., its pitting propensity) has been a "Holy Grail" of copper pitting research. Well over one half a century of research work has led to some partial successes (Table 4-3).

##### ***4.1.3.1. Macrocells with separate anode and cathode***

The very first attempts to monitor pitting used macrocells in which two different pieces of copper metal were physically separated from one another and connected via a wire (e.g. May, 1953; Mattson et al., 1968). Because all attempts to reproduce pitting in the laboratory as it occurred naturally had failed, it was necessary to artificially "start" the pitting reaction by 1) adding CuCl solid or other "initiator" to the water contacting the metal that was to become the anode, or 2) applying a continuous artificial electrical potential between the two wires that would force the anode to corrode. After placing a potable water of interest into contact with the cathode, the resulting pitting current that flowed between the anode or cathode could be measured. In waters that had a high pitting propensity, the pitting current would either increase or remain stable. In waters that had a low ability to support pitting or that were known to "kill" pits, the pitting current rapidly decreased between the anode and cathode. Mattson et al. (1968) demonstrated that in waters that "killed" pits, the tubercle forming over the copper anode was of very high resistance and low porosity, whereas in waters that supported pitting the tubercle was porous, consistent with the earlier discussion in Figure 4-1. The main drawback of the method is that the pitting process has to be started by adding CuCl solid or by application of the artificial potential. In many instances these "artificial" pits were

very dissimilar to those formed in practice, and the technique has given faulty guidance in some instances because of this deficiency.

#### 4.1.3.2. *Electrochemical rise*

The most widely applied (Edwards et al., 1993) and successful means of tracking pitting propensity relies on measurement of the electrical potential or  $E_{\text{corr}}$  (Table 4-2). This is a simple measurement obtained by measuring the voltage between metallic copper (e.g., copper pipe) and a reference electrode such as AgCl or a Calomel Electrode. Pourbaix (1969-1984) discovered that when new copper was placed into water,  $E_{\text{corr}}$  would typically rise to 0-100 mV after a few days and stabilize. But in waters that supported pitting, potentials would rise over a period of months to a critical value (Table 4-2), at which point pits had naturally initiated on the copper sample. This technique was recently used successfully to solve a pitting corrosion problem at Washington Suburban Sanitary Commission (WSSC). Multiple waters were screened using the test. The original water entering into the distribution system demonstrated  $E_{\text{corr}}$  rise, but the same water treated with orthophosphate did not (Marshall et al., 2004). The implication was that orthophosphate would act to stop pitting. After using orthophosphate, the frequency of pitting corrosion dropped dramatically in this system.

**Table 4-2.** Critical  $E_{\text{corr}}$  values from six sources.

Reference	Type of Pitting	$E_{\text{crit}}$ (vs Ag-AgCl)
Page, 1973	Soft-water	495
Al-Kharafi et al., 1989	Soft-water	49
Fujii et al., 1984	Hot-Water	195
Pourbaix, 1969	Cold-Water	215
Cornwell et al., 1973	Cold-Water	145-215
Lucey (unpublished)	Cold Water	105

The main drawback of this approach is that it is an indirect measure of pitting, and even experts do not understand exactly why the technique works. Even though it is the most widely utilized approach, there are also only a handful of documented cases in which the technique was successfully applied. The test can require a long duration before useful insights are obtained. For instance, in the study by Rushing et al. (2004) using synthesized WSSC water, one year of testing was required to unambiguously establish that the water would cause  $E_{\text{corr}}$  to rise.

#### *4.1.3.3. Electrochemical noise*

In the earliest investigations, in addition to  $E_{\text{corr}}$  rise, it was also noted that the  $E_{\text{corr}}$  value was highly variable in some waters in which pitting occurred. Some authors have correlated variability in  $E_{\text{corr}}$ , or the “electrochemical noise (ECN),” to pitting propensity of water. The potential of this method was demonstrated most convincingly by Smith and Francis in 1990. But Sandenbergh et al. (1996) did a follow-up study using electrochemical noise, and reported that the technique could sometimes give faulty insights into pitting. Specifically, he showed that electrochemical noise increased when copper corrosion rates were higher, and that the test was not always a direct predictor of pitting. He also demonstrated that the technique was extremely sensitive to the flow rate (1996), and that very low levels of noise were correlated to times when flow rate was low. The factors noted by Sandenbergh were confirmed by Rushing et al. (2002 and 2004), who demonstrated that large variations in  $E_{\text{corr}}$  were directly attributable to varying concentration of free chlorine in the water and flow rate. Large fluctuations were observed in  $E_{\text{corr}}$  even in waters that did not cause pitting. These factors could be a major interference to practical application of the electrochemical noise technique. Duranceau et al. (2004) felt that electrochemical noise was providing useful insights to pitting in a recent AWWARF project, but large pits were never formed in those short term tests. Thus, the overall usefulness of the approach as a tool to monitor pitting must still be established, and methods must be developed to overcome known interferences.

#### *4.1.3.4. Accelerated aging/cyclic voltametry*

This approach uses an electrochemical apparatus to artificially force copper to corrode at a high rate by applying a fixed potential such as +150 mV (Table 4-3) and a varying potential in the case of cyclic voltametry (e.g. Singh et al., 1992). In waters that support pitting, the measured current rises with time due to formation of an unprotective scale on the copper surface. The current decreases with time in a water that has low pitting propensity. In the cyclic voltametry approach, if a clockwise loop is formed, the water was deemed likely to cause pitting. Like most short term electrochemical tests, these approaches are very useful in classifying waters that can form protective high resistance tubercles over the anode versus those that do not. However, it does not tend to provide useful longer term insights to the cathodic reaction, which is also a critical factor. For instance, in the study by Marshall et al. (2005) that first reproduced pitting successfully, aluminum was shown to catalyze pitting by gradually stimulating the cathodic reaction rate over a period of months. The acceleration of the cathodic reaction is at least partly responsible for the characteristic  $E_{\text{corr}}$  rise observed in that water. The rate of pinhole growth is often thought to be limited by the cathodic reaction kinetics, rather than the anodic reaction. In summary, accelerated aging and other short-term tests such a cyclic voltametry typically provide only one half of the story in relation to reactions that are key for pitting.

#### *4.1.3.5. Electrochemical pitting test cell/multi-electrode arrays*

Goodman and Lucey (1984) developed a monitoring method in which the water of interest is passed very slowly through a macrocell consisting of a wire cathode and an anode comprised of twelve small copper wires. One of the wires was partly screened from solution. In a non-pitting water, the current passing through each of the 12 wires remain similar. This indicates that the water has a tendency to keep corrosion uniform, or preventing separation of anode and cathode. In water that supports pitting, the screened copper wire eventually begins to take a much greater percentage of the applied current than the other wires, thereby implying that corrosion has a tendency to localize. Ansuini (1991) refined Goodman and Lucey's apparatus by using voltage drops to quantify the inequality in currents between the different wires. As is the case with accelerated aging,



this approach only really provides useful insights to the anodic pitting reaction. Multi-electrode array are based on the same premise but use many more wires of smaller diameter.

#### *4.1.3.6. Summary*

Overall, only limited data have been previously collected to document the usefulness of these tests. Only a few studies have been carried through to the point where large pits or fully penetrating pinholes formed on copper samples in the test water (e.g. Cornwell et al., 1973; Smith and Francis, 1990; Marshall et al., 2004; Fuji et al., 1984). Since the accuracy of a given electrochemical test must be judged by comparison to pits that form naturally on copper pipe in the same water, the lack of well-established pits in all other research is worrisome. Claims of strong correlation to presence of “micropits” visible under microscopy are particularly suspect. It is in the researchers’ experiences that micropits often die in waters before reaching a certain size, and the presence of micropits on copper pipe does not mean the water will cause copper tube failures. Any test that uses artificial currents, artificial potentials, or chemicals to initiate pits might not reproduce pits as they occur in practice, and therefore can provide faulty advice. The techniques that have the potential to track pitting without artificial currents, potentials or chemicals ( $E_{\text{corr}}$  rise and ECN) have provided useful insights, although they are indirect methods. It is not understood why they sometimes work. Data has also been collected proving these techniques in some cases can be subject to interference in the presence of free chlorine or chloramine disinfectant.

**Table 4-3.** Historical summary of pitting test in relation to proposed work.

<b>Pitting Test</b>	<b>Approach</b>	<b>Reference</b>	<b>Initiation/ Propagation</b>	<b>Comments</b>
Macrocell with physically separate copper anode and copper cathode	Measure current and potential difference between anode and cathode to track pit initiation and propagation.	Bengough and May, 1924; May 1953, Lucey , Sosa et al., 1999; Poubaix, 1971	Initiation and Propagation	A chemical difference that initiated pitting was imposed artificially by adding CuCl or by removing oxygen from the anode. The potential differences and currents that resulted in different waters were reasonably correlated to pitting tendencies.
Macrocell with pit wire anode and copper cathode	Artificially impose constant potential difference between anode and cathode, measure pitting current	Mattsson et al., 1968; Campbell, 1954	Propagation only.	Reasonable correlation of pitting currents with the water chemistries known to allow pits to propagate in hot water. Addresses both anodic and cathodic reactions.
Potential rise	Measure $E_{\text{corr}}$ for copper immersed in water	Pourbaix et al. 1971; Cornwell et al., 1973; Fuji et al, 1984; Rushing et al., 2002; Marshall et al., 2004	Initiation	In waters that support pitting, potential slowly rises to a critical value, at which point pitting begins. In waters that do not support pitting, this rise in potential does not occur. Good ability to distinguish between waters that cause pitting and those that do not in a given study.
Electrochemical noise	Two or three identical copper samples immersed in same pitting water, measure current between each.	Smith and Francis (1990); Sandenbergh et al., 1996; Kane et al, 2003; Rushing et al., 2004; Duranceau et al., 2004	Initiation	Results in Smith and Francis work and Duranceau et al. were considered promising. However, work by Sandenbergh et al. 1996 demonstrated that that the test actually detected uniform corrosion and not pitting tendencies. Rushing, Sandenbergh and Korshin both point out that much variation in $E_{\text{corr}}$ occurs during changes in flow due to different disinfection concentration.
Electrochemical Pitting Test Cell with Applied Potential	8 copper wires used as anodes at distances from 1 to 25 cm from the wire cathode. A 4 uA current is imposed.	Goodman et al., 1984;	Propagation	In waters that support pitting, the majority of the current is concentrated at the copper wire closest to the cathode. In waters that do not support pitting, the current gradually moves towards anodes located further from the cathode.
Accelerated aging	Platinum cathode and copper anode, imposed potential.	Shalaby et al., 1990; Edwards et al, 1993 and 1994; Singh et al, 1992	Propagation	In waters that support pitting, the anodic current rises with time of polarization. In waters that do not support pitting, current decreases with time.
Electrochemical Pitting Test Cell with Applied Current	12 copper wire tips used as potential anodes and a long exposed copper wire cathode. A 15 uA current is imposed.	Goodman et al., 1984; modification developed by Ansuini, 1991	Propagation	In waters that support pitting, the majority (often 100%) of the anodic current is carried by the single wire that is partly screened from the bulk water. In waters that do not support pitting, the current carried by this water is less than 20% of the total.
Proposed test: Separate anode and cathode	Wire anodes connected to large pipe cathode	This work	Initiation and Propagation	Pits formed naturally by differential flow, pit growth measured directly using ammeter.

Previous tests lacked realistic conditions. Ideally, a test could predict circumstances in which copper pipes would fail and separate the pitting anode from the cathode so that the corrosion current could be measured and used to estimate the time to fail. Despite the complexity and seeming variability of copper corrosion, this work strives to judge whether the occurrence of pitting is deterministic and predictable. If this was the case, then short tests can reliably determine what water qualities would be sure to cause pitting, and more importantly what conditions would stop pitting.

## **4.2 MATERIALS AND METHODS**

Knowledge gained in previous research was applied to how pits form naturally on copper pipe in practice. In the process of that evaluation, a method was developed that could track both pit initiation and propagation in the water industry.

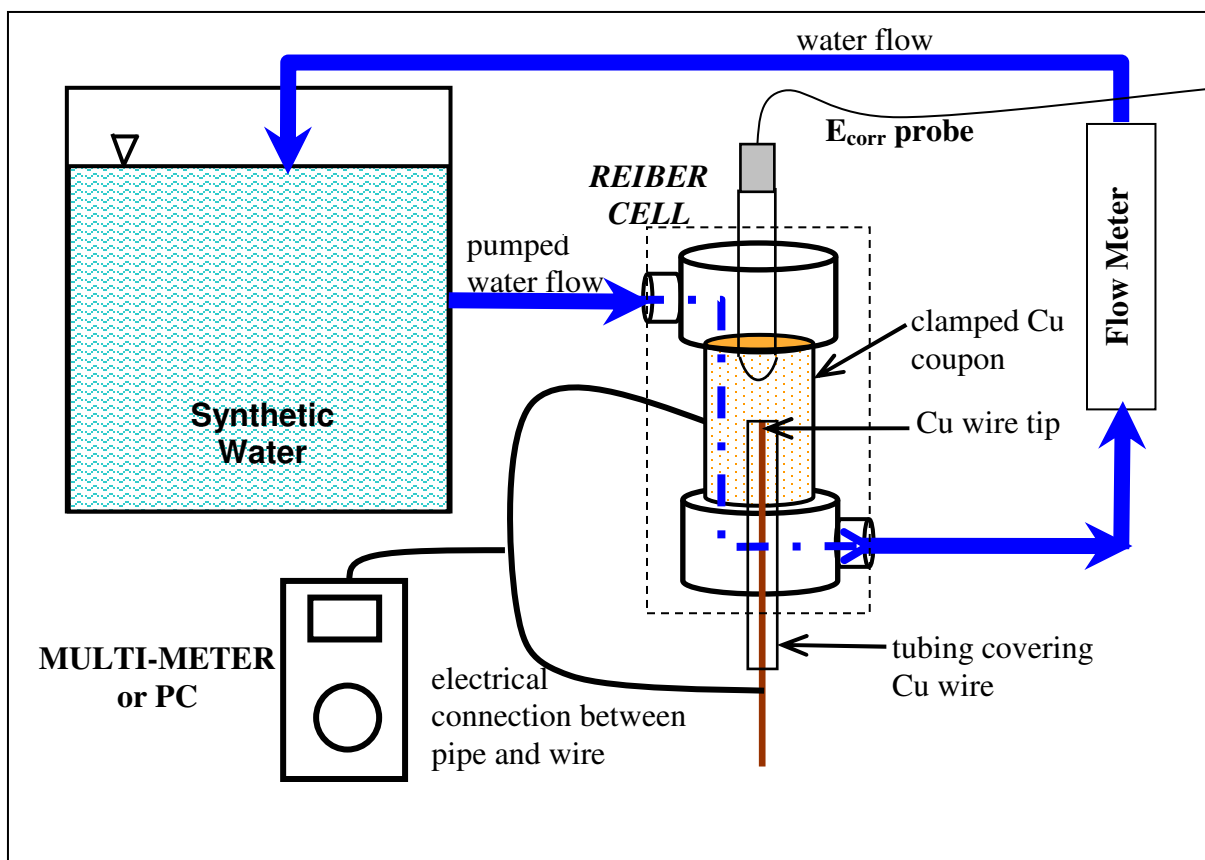
### ***4.2.1 Beaker setup to examine flowrate effect on $E_{corr}$***

Beaker tests investigating the effects of water velocity were performed using synthetic water prepared by adding 4.46 g  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 2.7 g of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and 6.14 g of  $\text{NaHCO}_3$  as reagent grade sodium or calcium salts to 108 L of filtered distilled and deionized water. At each water change,  $\text{Al}(\text{OH})_3$  solids were dosed into water at a level of 2 mg/L as Al. The  $\text{Al}(\text{OH})_3$  stock solution was created by raising the pH of 3,000 mg/L as  $\text{AlCl}_3$ –Al solution to 8.0 using NaOH, allowing the solids to settle, decanting the water until the conductivity of the suspension was less than that of the experimental water. The target free chlorine concentration was 4 mg/L as  $\text{Cl}_2$  from a bleach solution ( $\approx 6\%$  NaOCl). pH was targeted at pH 9.5 by adding 1 M HCl or NaOH, and no attempt was made to maintain alkalinity. The chlorine and pH levels were maintained at least once daily. Beakers were 4 1/2" in diameter (inner) and the stirbars used were 2" or 3" long.

#### ***4.2.2 Cell setup for investigation of chloride, pH, NOM, & P***

The basic experimental synthetic water, which was previously shown to promote copper pitting, was prepared by adding 4.46 g  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 2.7 g of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , and 6.14 g of  $\text{NaHCO}_3$  as reagent grade sodium or calcium salts into 108 L of filtered distilled and deionized water at pH 9.5. Free chlorine (4 mg/L  $\text{Cl}_2$ ) and 2 mg/L Al solids were added at the start of the experiment and at each weekly water change, but only free chlorine and pH were replenished daily. This described recipe is referenced in experiments as the “original water.” 3/4” type M copper couplings were purchased from a local hardware store, polished, and placed in flow-through polarization cells. The wire serving as the anodic copper piece in the experiment was Hillman 18 gauge copper wire with a clear coating on the exterior of the wire that is a product of the manufacturing process. The end inserted into the water was sanded with 250 grit and then 600 grit sandpaper so that the wire tip would be flush with the Teflon tubing that surrounded the wire. In addition, the contact points between the wire and the electrodes, which also connected to the computer, were sanded to ensure an electrical connection by removing the clear finish. The diameter of the copper wire is the approximate size of the hole of some pits formed in a copper pipe.

Thirty-two liters of simulated drinking water was circulated through the cells at a flowrate of 1.5 gpm (1 ft/s) through each cell. In all experiments, free chlorine was measured using the DPD colorimetric test per standard method 4500-Cl G. Current measurements were collected hourly using a multiplexer connected to a personal computer where a program maintained zero voltage difference between the pipe and the wire. Corrosion potential ( $E_{\text{corr}}$ ) was measured with a multimeter throughout the experiment. A diagram of the experimental setup is in Figure 4-2. Eight tests were conducted at once using a Gamry electrochemical data analysis system. Based upon the conventional setup of the Gamry collection system, a negative current would be indicative of anodic pitting at the copper wire. A positive current indicates that the wire was cathodic relative to the pipe.



**Figure 4-2.** Electrochemical testing setup to measure Cu corrosion in flow-through cells.

Over 66 days the previously described synthetic pitting water was circulated through the cells, after which time the eight cells were separated into two groups for short-term experiments. Each group contained a cell that exhibited positive current densities and another with high negative currents in order to observe a range of responses. In the first group, the pH for the four cells was incrementally decreased following a water change to pH 8.2, 7.2, and 6.2 using 1 N HCl. The second group was subjected to increasing amounts of chloride by 300%, 1000%, and 3000% in  $\text{Cl}^-$  concentration compared to the initial concentration of 26 mg/L  $\text{Cl}^-$ , by dosing  $\text{CaCl}_2$  into the synthetic water. Each pH or chloride level condition was sustained for 24 hours, and the current and  $E_{\text{corr}}$  measurements were collected. After that, the original water condition was restored and sustained for 11 days to allow the cells to equilibrate. Then the effects of natural organic matter (NOM) and phosphate were investigated, with the conditions lasting for 3 to 4 days at each level. NOM was added from a stock of Aldrich humic acid, and phosphate was added as  $\text{NaH}_2\text{PO}_4$ . This experiment examined and determined whether the pitting

rate declined with decreasing pH and increasing  $\text{Cl}^-$ , NOM, or P, which is expected based on previous studies. If the conditions affected the testing cells as the established corrosion beliefs, then the setup likely yielded reliable results.

### 4.3 RESULTS AND DISCUSSION

Beaker tests were unsuccessful in deterministically forming pits on wires. After establishing that increased flowrate in the beaker tests increased corrosion potential, the effects of varying water quality were investigated in an electrochemical test in cells, which could accommodate faster flowrates. In the first stage, the effect of increased chloride concentration and decreased pH were investigated. After 3 days at the varied chloride and pH conditions, the water was returned to the original conditions for another week so that the cells could restabilize. After the restabilization period of 11 days, the effects of increased phosphate and natural organic matter (NOM) were determined. First, low levels of P or NOM were dosed into the waters. After 3 days a larger amount was dosed, and results were observed for 4 days before the original water condition was restored.

As a reference for determining whether copper is in pitting or non-pitting potentials, Oliphant stated that above +100 mV vs. SCE (standard calomel electrode) is Cu pitting (2000). Oliphant also noted that for every ten-fold increase in cupric ion ( $\text{Cu}^{2+}$ ) concentration, released as a copper corrosion by-product, the potential of the copper metal increases 30 mV. Knowing the  $E_{\text{corr}}$  at a given pH, the region on the pE-pH diagram can be determined, indicating whether the metal is immune, passive, or corroding.

$E_{\text{corr}}$  and current density are both used as measures of corrosion intensity. The  $E_{\text{corr}}$  data presented in the following sections are the corrosion potentials for the pipe-wire system. Because the pipe has a much larger surface area, the  $E_{\text{corr}}$  is representative of that of the pipe surface potential. For the most part, cells with higher system  $E_{\text{corr}}$  also had the greatest voltage difference between the pipe and the wire as well as high pitting currents.

This further demonstrates the importance of the cathode in driving pitting. corrosion rates.

The corrosion current and potential measurements presented from the test cells served to compare current concepts with the results found from the tests. However, as the results are presented, interpretations of these results are made.

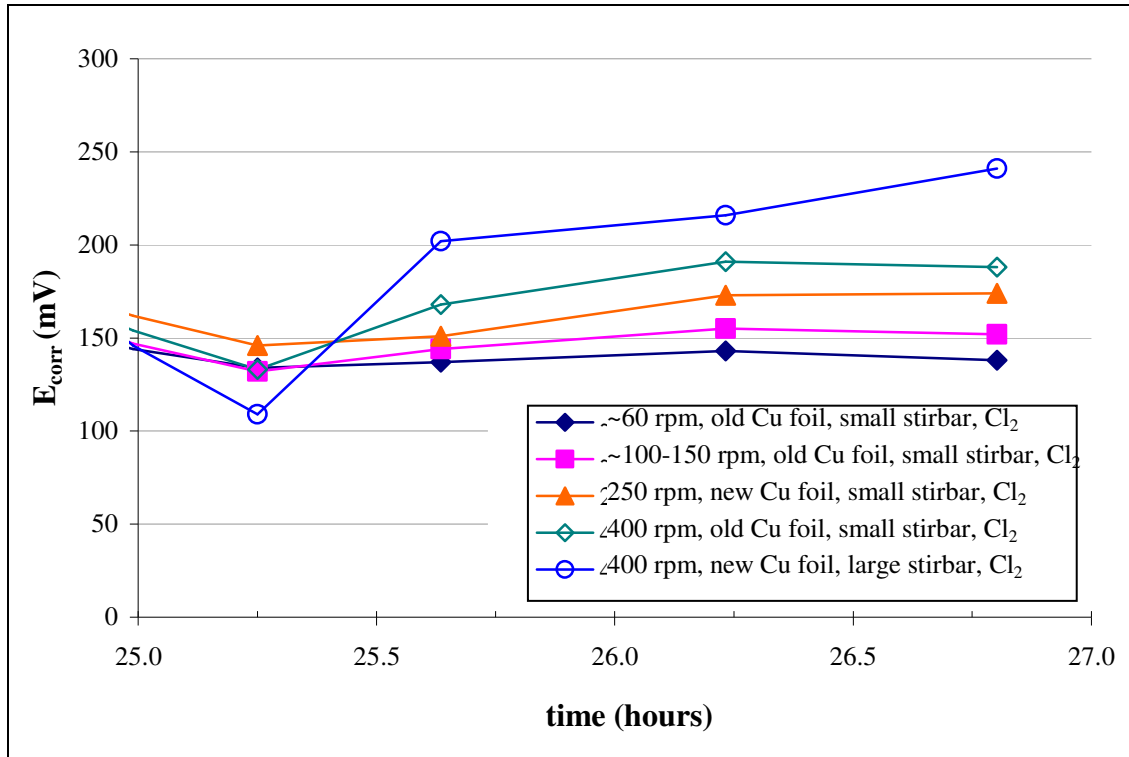
#### ***4.3.1 Initial attempts***

The first stage of the experiment served to develop a new testing protocol, to see where deposits form, to monitor currents that drove pitting, and to vary the relative anode to cathode areas. In the beaker test using two copper electrodes, connected in zero resistance ammeter mode, the role of the anode and cathode were examined during a corrosion reaction (Appendix, Figure A-4). Prior to the start of the test, one of the two electrodes was soaked for at least a day in a solution containing 3,000 mg/L aluminum solids as Al to initiate attachment of the positively charged aluminum hydroxide. The potentiostat measured the current between the two electrodes, which is proportional to the extent of reaction between the separated anodic and cathodic areas. Theoretically, by changing the dimensions of the two wires, we could directly examine the role of cathode to anode area. However, after some time,  $E_{\text{corr}}$  and current did not increase to significant pitting rates, and it was discovered that increased water velocity could greatly increase the pitting rates measured. Thus, flow-through cells were used instead of beakers because the flowrate could be increased high enough without risking the introduction of excessive bubbles in the system as would be seen in the beakers.

#### ***4.3.2 Effect of flowrate in beakers***

The greatest  $E_{\text{corr}}$  values occurred in conditions of higher water velocities, approaching turbulent conditions (Figure 4-3). Lower velocities yielded significantly lower corrosion potential values. Copper foil with free chlorine ( $\text{Cl}_2$ ,  $\text{OCl}^-$ ,  $\text{HOCl}$ ) and a low water velocity of 60 rpm had an  $E_{\text{corr}}$  of 130 mV vs. Ag-AgCl, whereas the 400 rpm stir rate

reached potentials of 190 mV. With a 2-3 inch stirbar and a mixing intensity,  $E_{\text{corr}}$  reached 240 mV.



**Figure 4-3.** Corrosion potential ( $E_{\text{corr}}$ ) increases with increased water flow velocity. A consistent example of the results from the beaker test is displayed here.

#### 4.3.3 Deterministic pitting

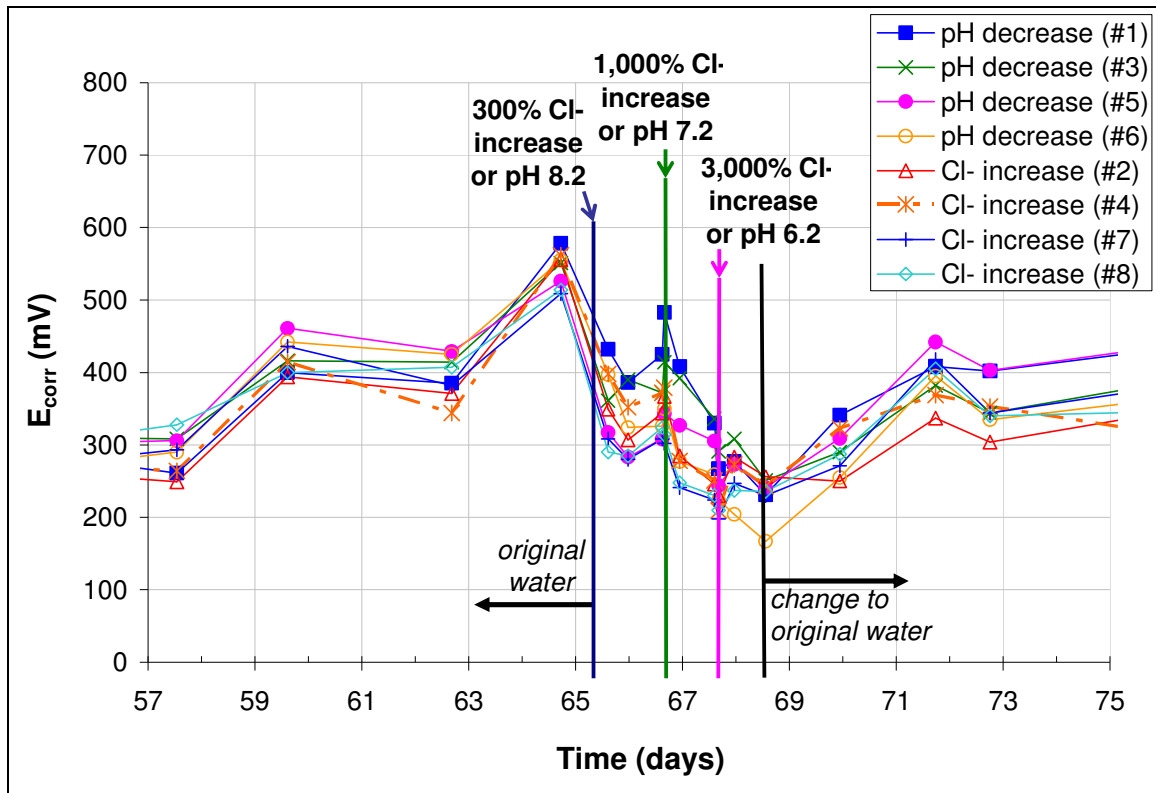
A negative current density indicates that the electron flow proceeds from the wire to the pipe, and that the wire is the anode. Conversely, if the current instead was positive, the pipe would be anodic and thus releasing ions and electrons while the wire consumed electrons. A current density or pitting rate of  $1 \mu\text{A}/\text{cm}^2$  creates a pit in a Type M copper pipe in 61 years ( $\text{ATF} = 61 \text{ years}$ ), which is calculated from the equation,  $r = 0.129 \cdot ia / (nD)$  where  $r$  is the corrosion rate (milli-inches/year),  $i$  is current density ( $\mu\text{A}/\text{cm}^2$ ),  $n$  is # electrons transferred for each atomic weight reacted,  $a$  is atomic weight, and  $D$  is density of alloy ( $\text{g}/\text{cm}^3$ ).



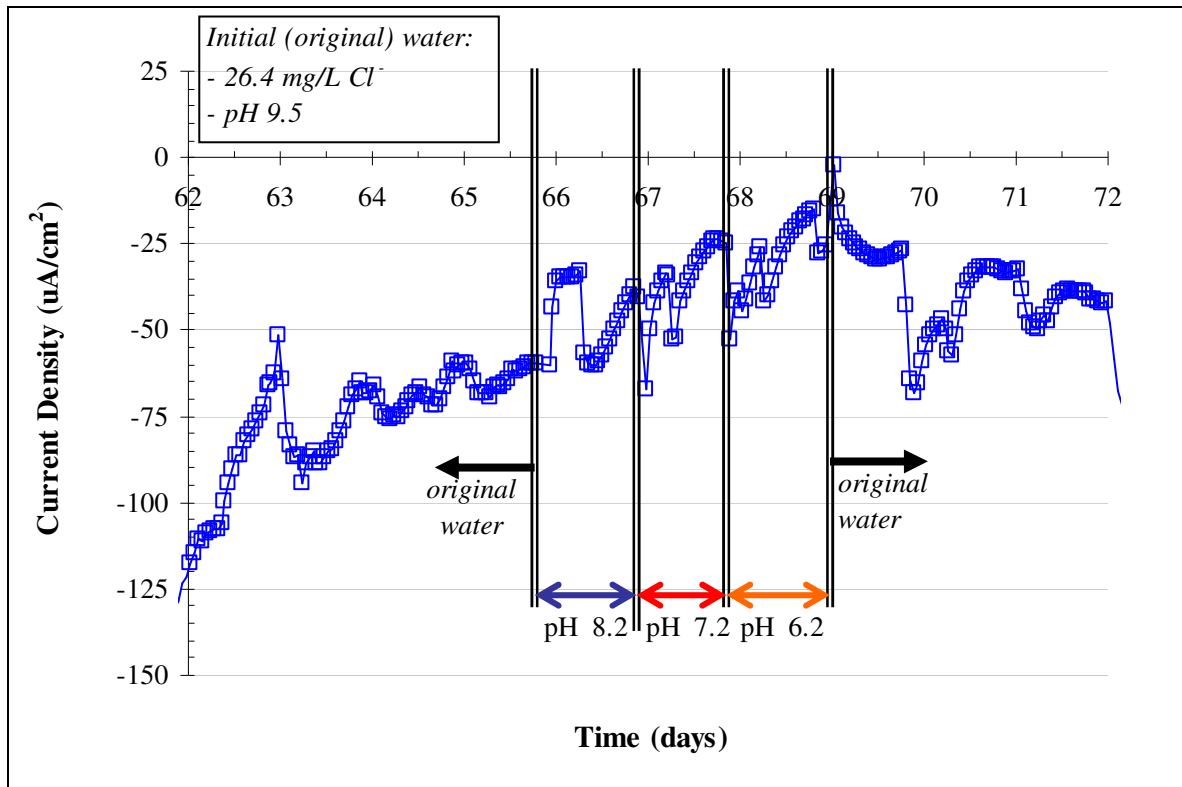
In this experiment, we were able to initiate pitting deterministically on wires by varying the water quality. In addition, running the previously specified water condition for 2 months, all cells developed at some point a current magnitude of  $10 \mu\text{A}/\text{cm}^2$ , which equates to an approximate time-to-failure (ATF) of 6 years. Even stronger anodes were measured in 3 out of the 8 cells, reaching current densities of  $-100 \mu\text{A}/\text{cm}^2$  or an ATF of 7.3 months.

#### **4.3.4 pH effects**

By decreasing the pH from 9.5 to 8.2, 7.2, and 6.2,  $E_{\text{corr}}$  gradually declined by about 150 mV (Figure 4-4). The current density also slowly decreased in magnitude to an ATF of 2.4 years, although the pitting rate initially was approximately 1 year until failure (Figure 4-5). Following the water change back to the original water conditions, both  $E_{\text{corr}}$  and current density appeared reversible, restoring to the values observed prior to the pH decrease. This trend supports the observations of Rushing et al. and Marshall et al. who saw pitting to be greatest at pHs greater than 8.0 (Rushing, 2004; Marshall, 2004). The variations or “noise” of the current measured are a result of chlorine addition and decay because chlorine increases  $E_{\text{corr}}$  and current becomes more negative. The original water was the water recipe containing 41.3 mg/L  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 25 mg/L of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , and 0.057 mg/L of  $\text{NaHCO}_3$  as reagent grade sodium or calcium salts in filtered distilled and deionized water at pH 9.5 with 4 mg/L free chlorine as  $\text{Cl}_2$  and 2 mg/L Al solids.



**Figure 4-4.** The corrosion potential ( $E_{\text{corr}}$ ) decreased for pH decrease and chloride addition. Greater  $E_{\text{corr}}$  is an indication of pitting propensity.

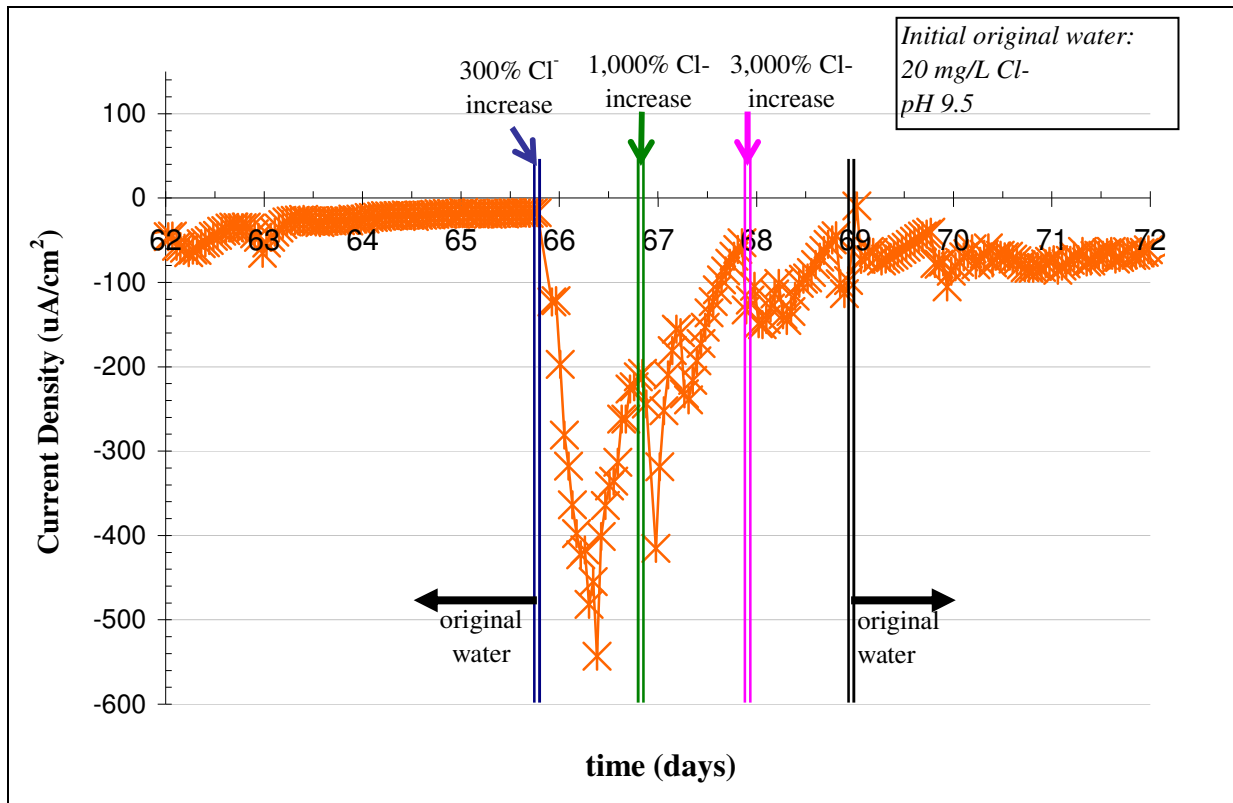


**Figure 4-5.** Corrosion rate decreased in magnitude with pH decrease. The current density is a direct proportion of the corrosion rate.

#### 4.3.5 Chloride effects

When the chloride concentration was increased 300%, 1000%, and 3000% of the original value of 26 mg/L  $\text{Cl}^-$ ,  $E_{\text{corr}}$  gradually declined by about 150 mV (Figure 4-4).

Immediately after the change in water condition (i.e. addition of chloride), the corrosion current appeared to increase to an ATF of 1.3 months before decreasing after approximately 12 hours. The effects appeared to be reversible following the change back to the original water recipe (Figure 4-6). The fluctuations in the current was a result of replenishing free chlorine and pH level to the targeted 4 mg/L  $\text{Cl}_2$  and pH 9.5 twice daily. These results support previous suspicions that an increased chloride concentration in copper pipes decreases the pitting rate (Marshall, 2004).

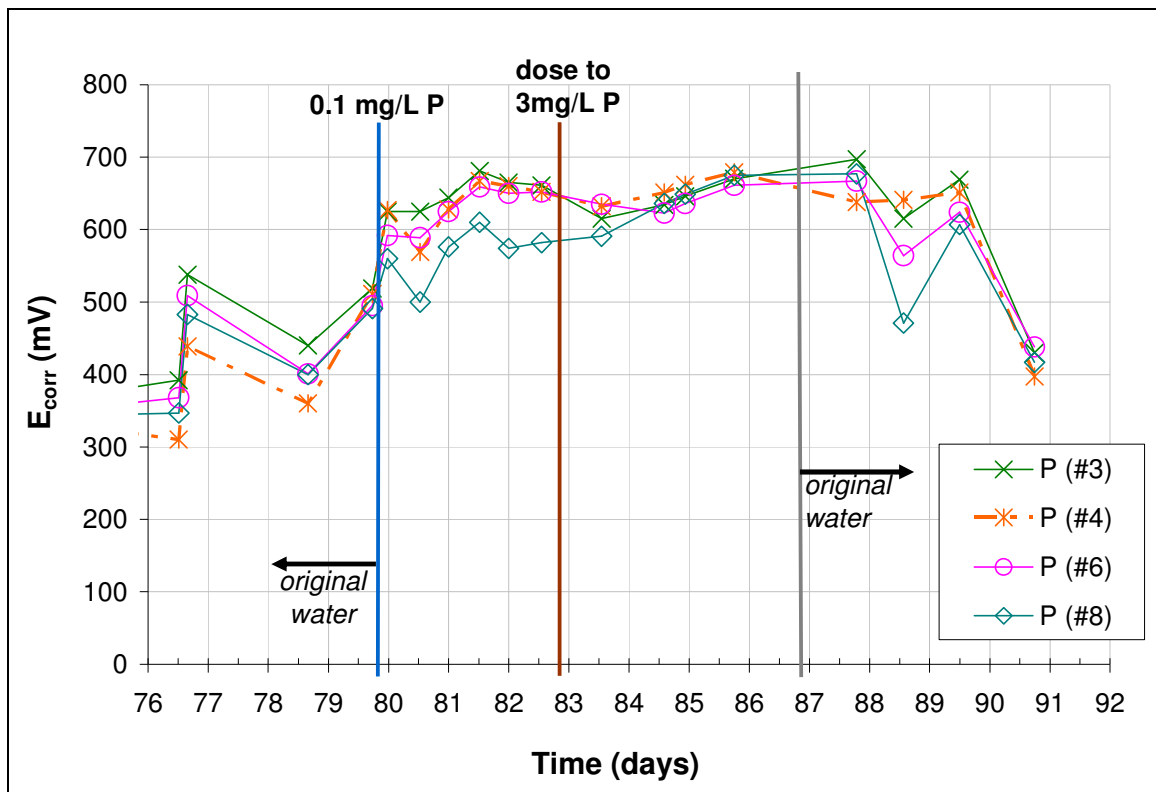


**Figure 4-6.** Overall, the corrosion current density decreased in magnitude with an increasing chloride concentration. Directly following the chloride addition, chlorine replenishment, and pH adjustment, the corrosion current would worsen, but over time decline.

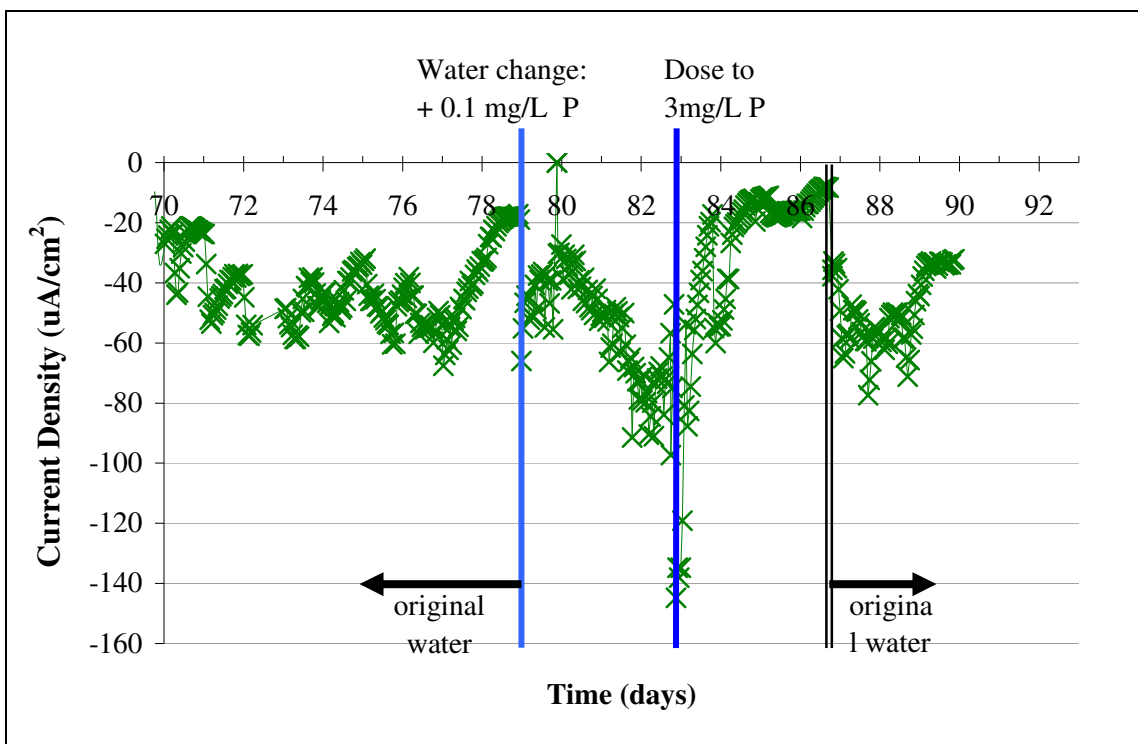
#### 4.3.6 Phosphate effects

$E_{\text{corr}}$  was not largely affected by phosphorus (P) addition (Figure 4-7). However, the phosphorus amount initially caused a current density increase to  $-145 \mu\text{A}/\text{cm}^2$  or an ATF as quickly as 5 months after the dose of 3 mg/L P, and then the current flow dropped to around  $-13 \mu\text{A}/\text{cm}^2$  or an ATF of 4.7 years (Figure 4-8). After restoring the initial water conditions that did not contain P, the electron flow increased again for some of the cells to approximately  $-88 \mu\text{A}/\text{cm}^2$  or ATF of 8 months.

The results seen here demonstrate how variable the effect of phosphate can be. In the field, utilities experiencing pitting problems often attempt to dose phosphate in the drinking water, and no improvements are seen. Furthermore, most utilities use phosphate as a corrosion inhibitor and observe no pitting outbreaks.



**Figure 4-7.** The corrosion potential ( $E_{\text{corr}}$ ) did not appear to increase when 0.1 mg/L P and 3 mg/L P was added to the water. Based on  $E_{\text{corr}}$  values, the corrosion potential of the wire-pipe system decreased after removing phosphate from the water.

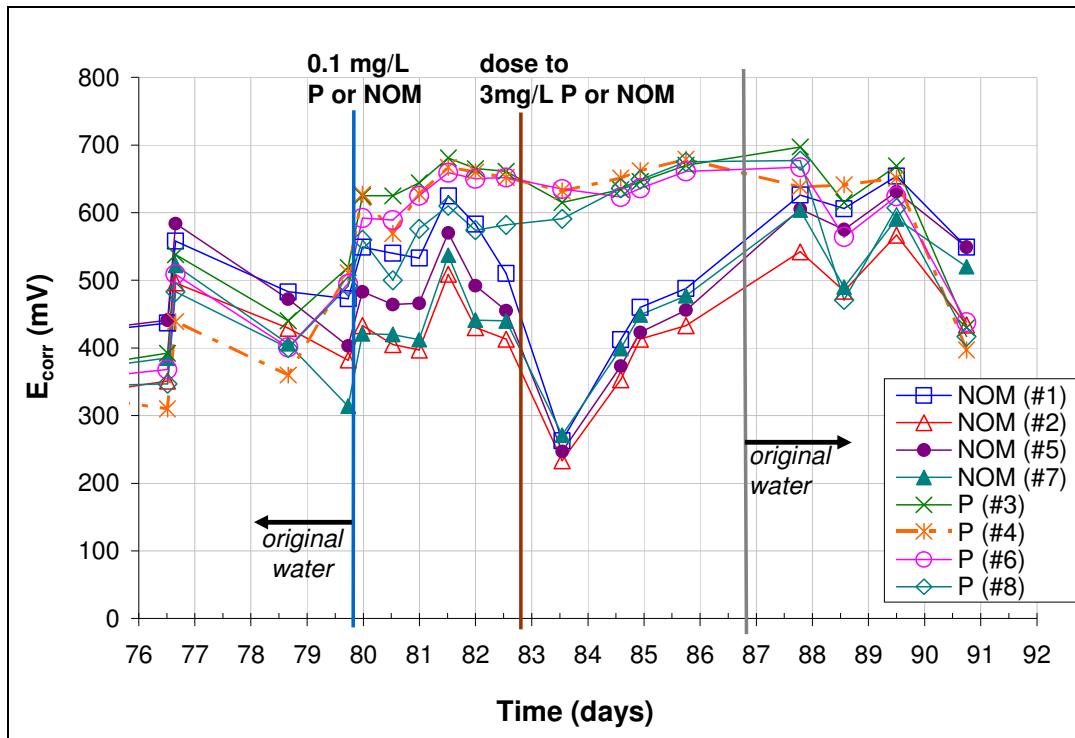


**Figure 4-8.** The corrosion rate did not decrease with a low amount of phosphate (0.1 mg/L P), and in fact appeared to increase after 2 days. However, after 3 mg/L P was added to the water, the current density did increase but then declined to under -20 uA/cm<sup>2</sup>.

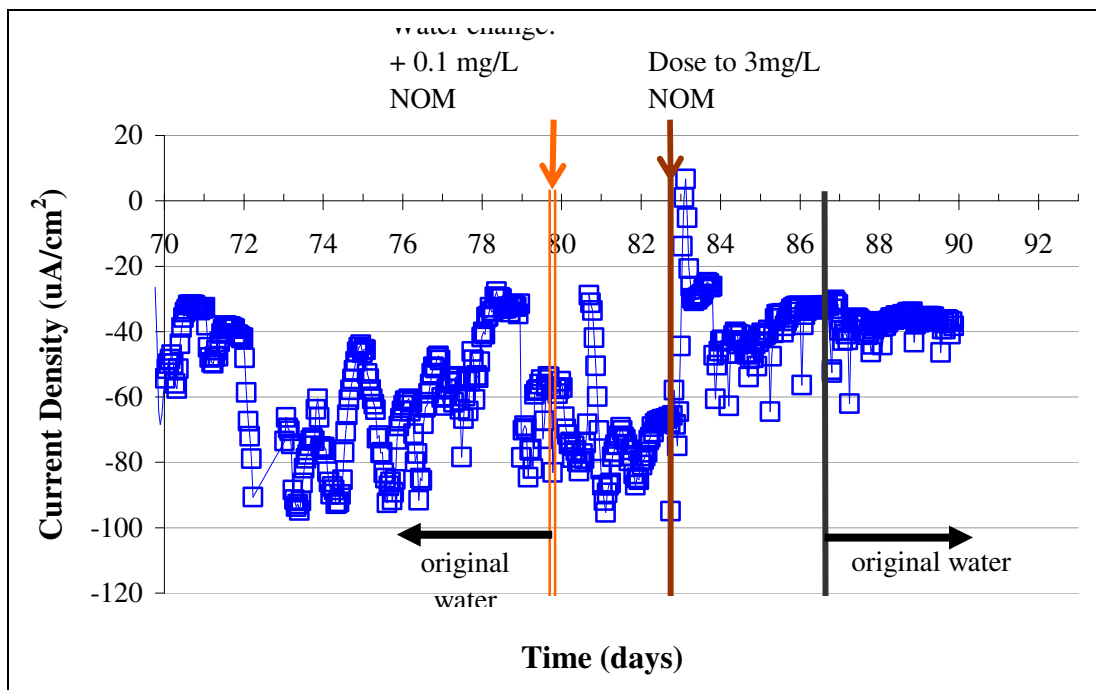
#### 4.3.7 NOM effects

$E_{\text{corr}}$  values dropped with natural organic matter (NOM) addition (Figure 4-9). A greater  $E_{\text{corr}}$  drop was measured after the dose of 3 mg/L NOM as total organic carbon (TOC). Even after restoring the initial water conditions sans NOM, the current density did not continue to develop (ATF 18 months) and instead stayed at a lower magnitude indicating that corrosion was slowed (Figure 4-10). This drop could be a result of the oxidant reacting with the NOM.

The amount of NOM allowed in drinking water has dramatically reduced following concerns of disinfection by-products such as halo-acetic acids (HAA5). This is important because the EPA is more concerned with the potential formation of carcinogens that could affect people after prolonged exposure rather than the more immediate effects of copper pitting.



**Figure 4-9.** Based on  $E_{\text{corr}}$ , NOM addition created the greatest drop in corrosion potential while phosphorus addition had a nearly constant potential throughout.



**Figure 4-10.** The corrosion current density did not change much with a low amount of NOM added to the water; however, dosing 3 mg/L NOM into the water decreased the average corrosion current compared to when no NOM was in the water (Days 70-80).

#### **4.4 CONCLUSIONS**

From this work, three main conclusions were established:

- Increased water velocity was important in pit initiation.
- By changing water quality and conditions, pitting could ensue or lessen deterministically. To lessen the pitting rate, the pH was decreased or the levels of chloride, P, NOM were increased.
- A large step in this setup was the ability to track pitting currents real-time.

For future work, water conditions should be tested for longer periods of time instead of only a few days so that the copper and scaling could stabilize. Also, it would be important to test the application in the field and in a larger scale, and this technique could eventually optimize the corrosion inhibitor dose that would “kill” pits. This method would be a leap forward for water utilities dealing with pitting, even if it would only work in ½ of all cases. As an added benefit, the construction costs and required skill level are both low with this apparatus and are completely within the grasp of normal water quality personnel at utilities.

#### **4.5 ACKNOWLEDGEMENTS**

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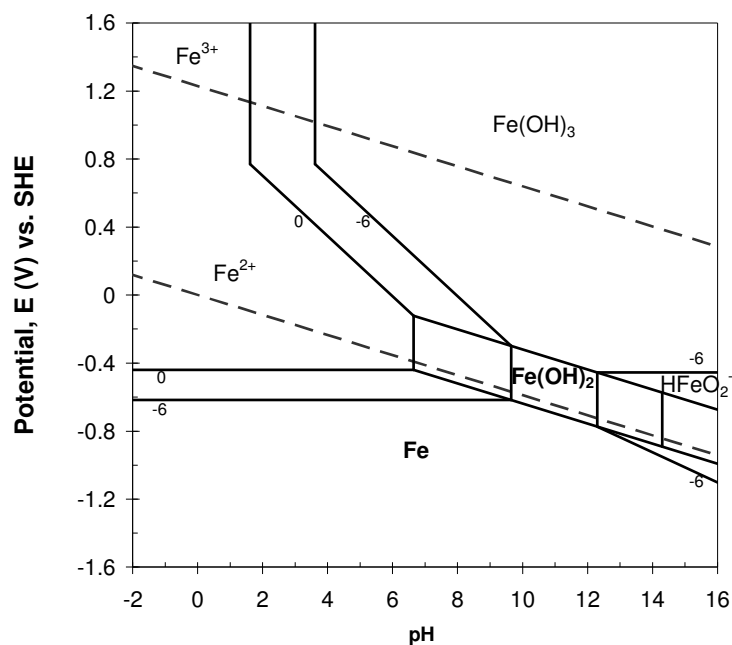
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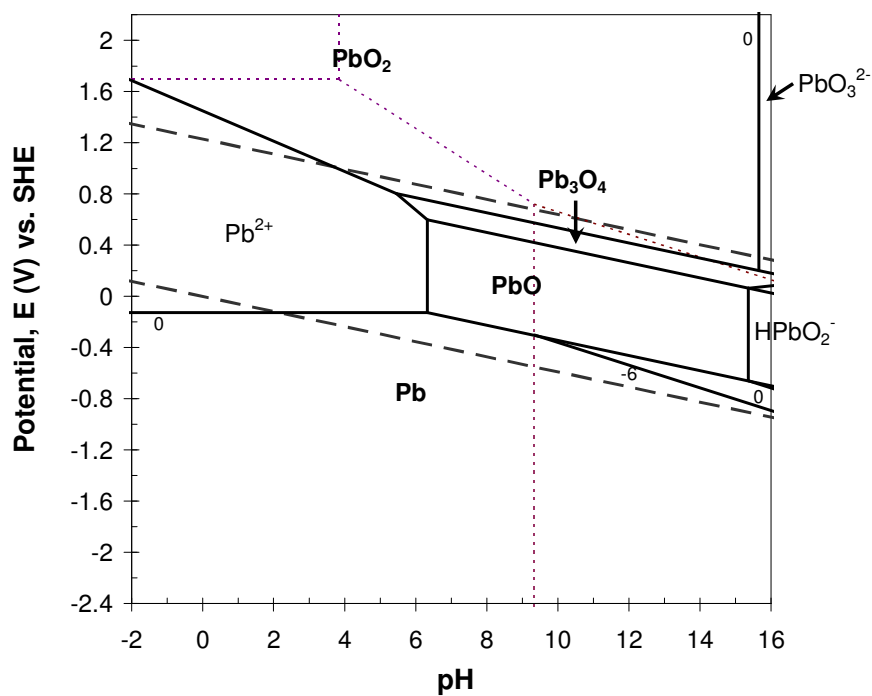
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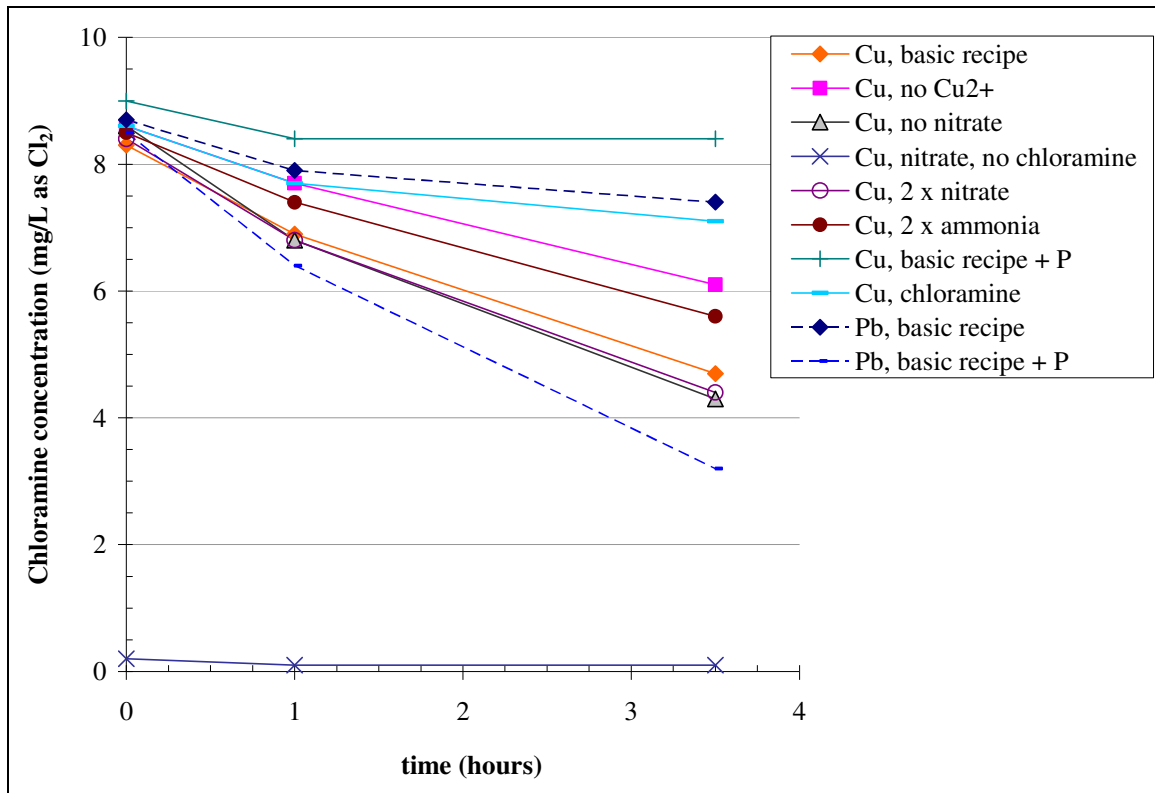
## 5.1 Appendix



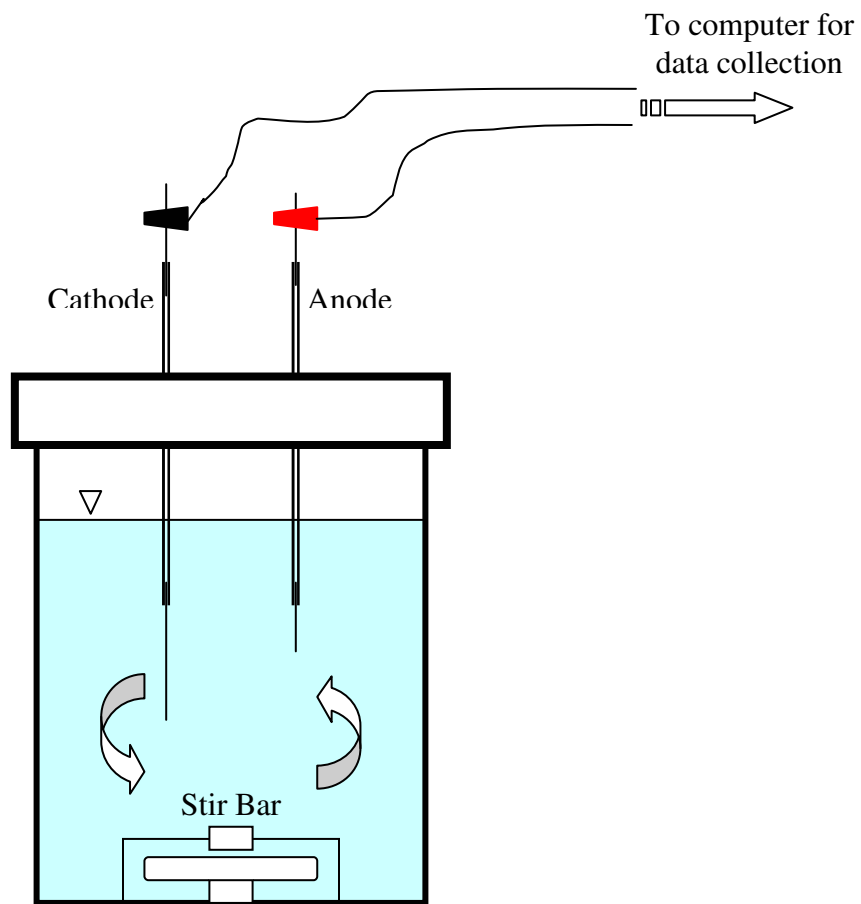
**Figure A-1.** Potential-pH diagram for iron-water system at 25°C.



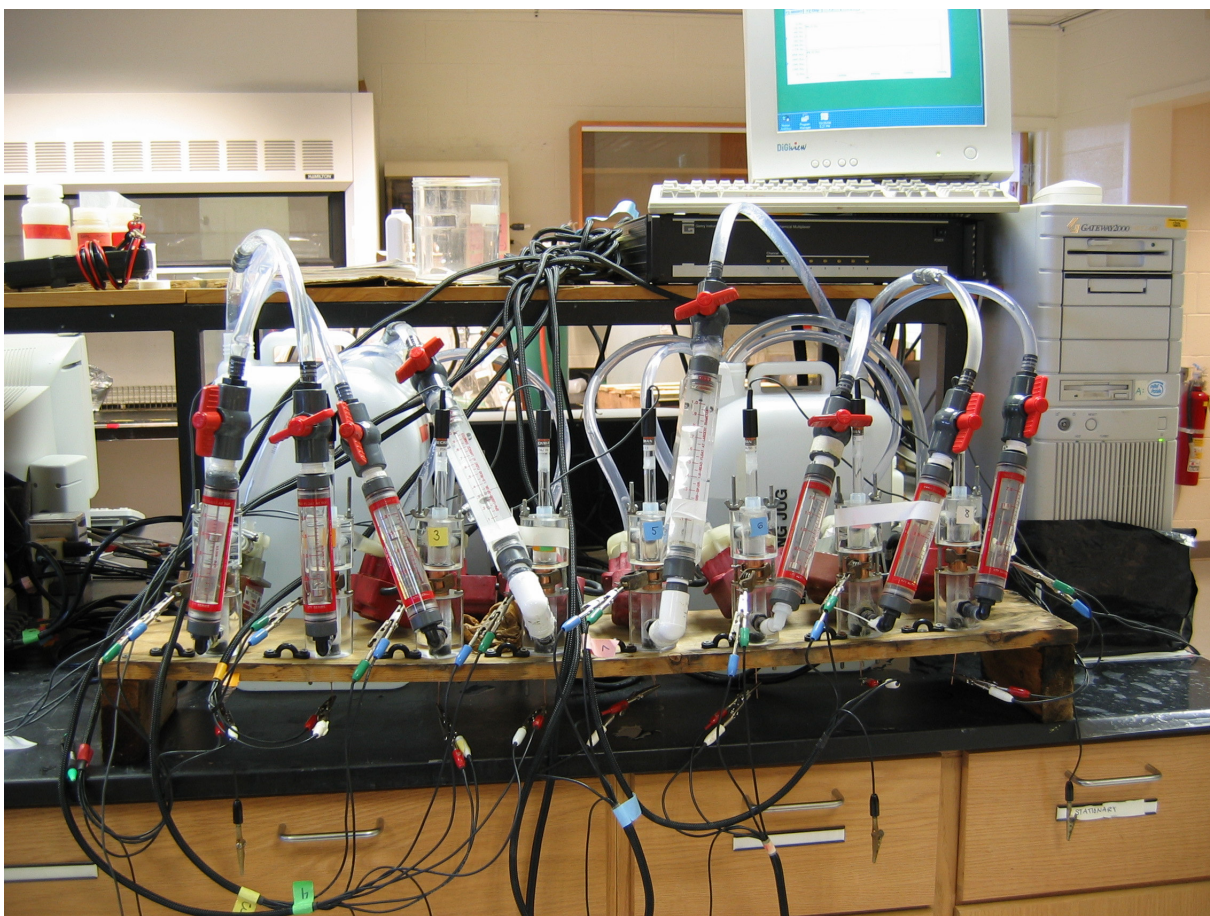
**Figure A-2.** Potential-pH diagram for lead-water system at 25°C.



**Figure A-3.** Chloramine decay over 4 hours for 0.2 g copper or lead granule metal in a well-mixed condition.



**Figure A- 4.** Experimental electrochemical cell setup.



**Figure A- 5.** Photo of flow-through cell experiment in progress.