

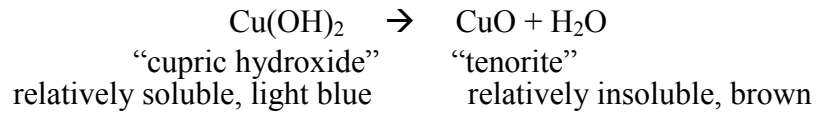
# CHAPTER I

## Introduction

Leaching of copper from home plumbing to drinking water is of interest due to environmental concerns and the United States Environmental Protection Agency (USEPA) Action Limit governing allowable levels of copper at the tap. In most circumstances the copper is released to drinking water from corroding pipe in a soluble form-- when water is allowed to sit stagnant in a copper pipe, the scale or rust layer on the pipe wall will slowly dissolve until the water is holding all the copper it can (Figure 1-1).

The identity of the scale (oxidized copper rust layer) that is on the pipe wall and in contact with the water is a key factor controlling the maximum soluble copper concentration in the water. Though it has been established that cupric hydroxide is the scale that controls solubility in new pipes,<sup>1-4</sup> at least 20 other different compounds of copper might form on the pipe as it ages under various circumstances, and each has its own color, rate of dissolution and maximum level of soluble copper. If more soluble solids on the pipe wall are replaced with less soluble solids, the concentration of soluble copper in drinking water will decrease.

Thankfully, it is a general rule of chemistry that solids are destined to change from more soluble to less soluble forms with time through this phenomenon which is termed "solids aging." Solids aging can be readily observed by placing fresh cupric hydroxide solids into a beaker and measuring soluble copper with time (Figure 1-2). Over a period of days in the laboratory,<sup>5</sup> the blue cupric hydroxide will gradually change to brown tenorite through a dehydration reaction:



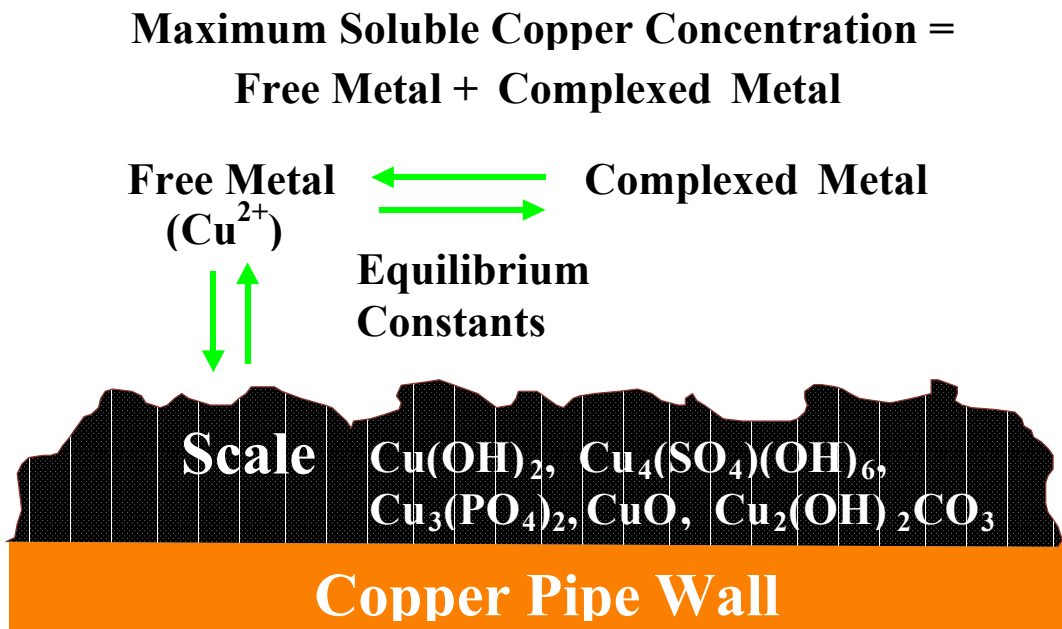
Transitions of this nature also occur with time in pipes, and as a result lower levels of copper are observed in old pipes than in new pipes. To illustrate, in a water at pH 6.6, alkalinity of 60 mg/L as CaCO<sub>3</sub> and 10° C, if a cupric hydroxide scale is on the pipe wall and controlling copper solubility, the predicted maximum soluble copper release to drinking water is 30 mg/L (Figure 1-3). In contrast, for an older pipe in which the cupric hydroxide scale has been replaced by a tenorite scale, the maximum soluble copper is only 0.8 mg/L in the same water. Thus, maximum levels of soluble copper that come from a pipe can be expected to decrease by factors of 10 or more as cupric hydroxide is replaced with tenorite (Figure 1-3). The transition to tenorite or other low solubility scales is often necessary before copper levels in drinking water will meet the EPA action limit of 1.3 mg/L copper.

The rate of the transition from cupric hydroxide to tenorite depends on the exposure conditions and the water quality. Whereas cupric hydroxide is completely converted to tenorite after just a few weeks in the laboratory at pH 7.0 at 23° C (i.e., Figure 1-1), lower temperatures, lower pH and natural organic matter (NOM) in water can maintain cupric hydroxide solids for months.<sup>5,6</sup> Drinking waters which are currently classified as “aggressive” in terms of copper corrosion by-product release, or which sustain high levels of copper release for years or decades, are believed to have constituents present that preserve cupric hydroxide solids on the pipe wall. Other than NOM, the identity of these constituents is unknown.<sup>6</sup>

The overall goal of this research is to examine some important fundamental and practical aspects of the cupric hydroxide transition to less soluble solids such as tenorite. Two phases of

research were conducted. The first phase examined the fundamental role of chlorine and silica--silica and chlorine commonly contact copper pipes in drinking water, and no information is available regarding their impact on the cupric hydroxide transition. Previous laboratory research has illustrated, however, that silica can interfere with aging of iron hydroxide solids.<sup>7</sup>

The final phase of research attempted to apply the newly generated fundamental understanding to greatly reduce, and ideally eliminate, rare problems associated with copper pipe in situations where soluble cupric hydroxide scale seems to persist for years or decades. The goal was to develop mild chemical treatments that could force the desirable transition to less soluble scale, such as tenorite, in a short time period. If successful, treatments could be applied by manufacturers to new pipe before installation, thereby preventing problems before they start. It is also conceivable that treatments could be applied after pipe installation if specific homes are experiencing higher than desired levels of copper at the tap.



**Figure 1-1. Scale attached to a copper pipe wall dissolves into solution, thereby introducing soluble copper to drinking water.**

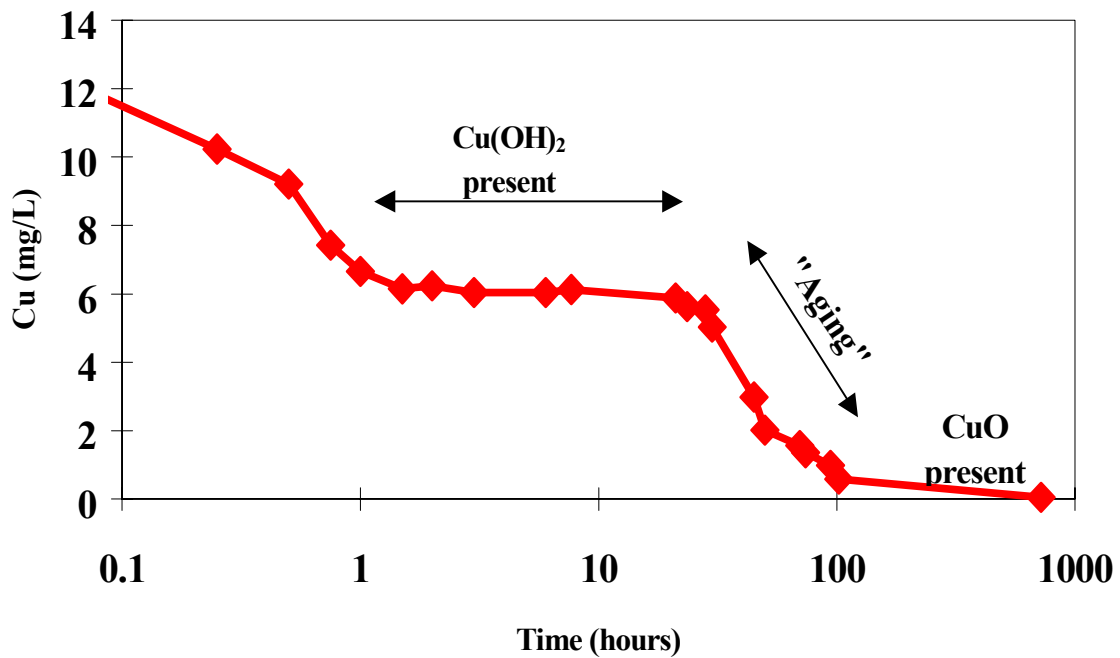


Figure 1-2. As cupric hydroxide ages to tenorite with time in a laboratory beaker, soluble copper in the water decreases from above 6 mg/L to well below 0.1 mg/L. The rate of aging is known to depend on pH and temperature (after Hidmi et al., 1999).

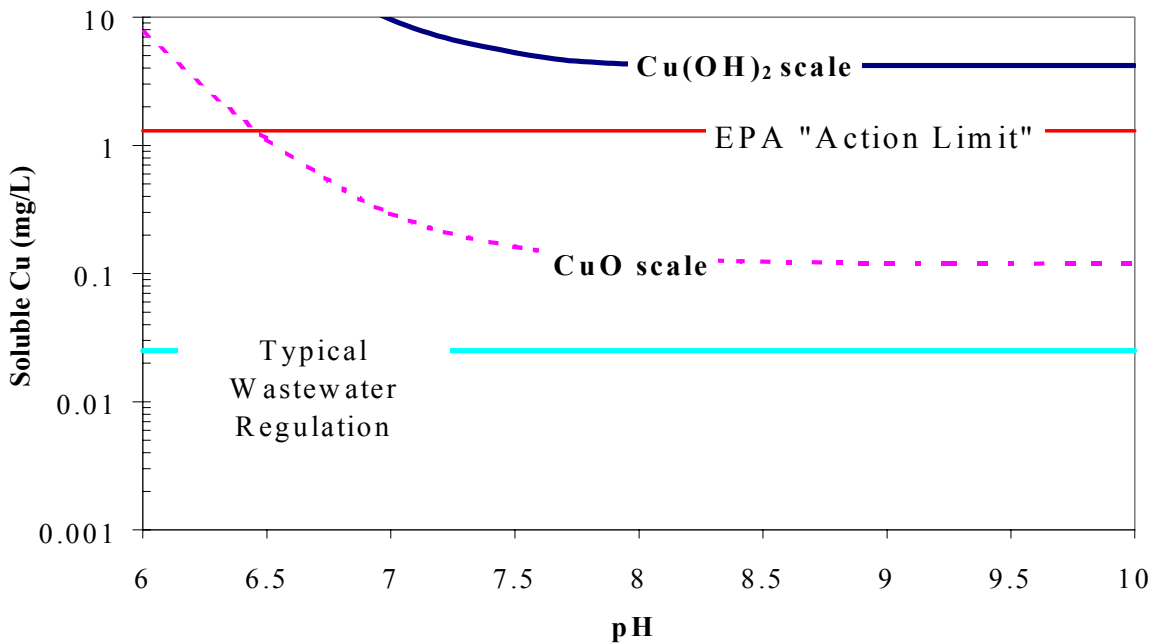


Figure 1-3. Predicted soluble copper as a function of pH in the presence of two solids typically found on pipe walls.  $\text{Cu(OH)}_2$  is found on new pipe, whereas  $\text{CuO}$  is commonly found on old pipe. Conditions: 10° C, alkalinity = 60 mg/L as  $\text{CaCO}_3$ .

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## CHAPTER II

### The Role of Pipe Aging in Copper Corrosion By-Product Release

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The presence of sulfate, bicarbonate and orthophosphate can change the type of solid present in systems containing cupric ion or cupric hydroxide solids. In some cases, a short term reduction in copper solubility is realized, but over longer periods of time formation of basic cupric sulfate (brochantite) and even cupric phosphate can ultimately prevent the formation of very insoluble tenorite or malachite phases. To the extent that this occurs, the presence of sulfate and phosphate in water can increase copper solubility over much longer time periods. The relative effect can depend on the anion concentration and the rate of solids precipitation. Low levels of sulfate tend to hasten the transition from cupric hydroxide to tenorite, whereas higher levels of sulfate can interfere with that transition. These possible effects should be considered when attempting to reduce copper corrosion by-product release from consumer plumbing, and similar transitions are likely important for other plumbing materials such as zinc, iron and lead.

#### KEYWORDS

Copper, Drinking Water, Cupric Hydroxide, Aging, Metastable Solids, Solubility, Internal Corrosion

#### Introduction

It is accepted that soluble copper concentrations within relatively new copper plumbing are controlled by cupric hydroxide equilibrium under at least some circumstances (Meyer et al, 1994; Schock et al., 1995; Werner et al., 1994; Edwards et al., 1996). Over the pH and temperature range most commonly encountered in drinking water distribution, equilibration with  $\text{Cu}(\text{OH})_2$  can lead to maximum soluble copper concentrations of about 2-10 mg/L. These levels are of regulatory concern, both from the perspective of the 1.3 mg/L EPA Action Limit for copper at the consumers' tap and very stringent wastewater discharge levels of 0.005-0.020 mg/L in many localities.

Recent work has highlighted the importance of solid identity and aging in control of cupric ion solubility (Hidmi and Edwards, 1999). When dilute nitrate solutions are supersaturated with cupric ion, basic cupric nitrate solids form first, followed by complete conversion to cupric hydroxide within a few hours. The subsequent transition from cupric hydroxide to tenorite invariably occurs within a few days over the pH range of 7-9 and water temperature of 4-25° C, thereby producing a concomitant 1-3 order of magnitude decrease in equilibrated levels of soluble copper (Edwards et al, 1994; Schock et al, 1994).

The laboratory trends in copper solubility with aging are perfectly consistent with observations of soluble copper release to drinking water from home plumbing; however, the desired transition in solubility control from cupric hydroxide to less soluble copper solids appears to be much slower. That is, relatively high levels of equilibrated soluble copper can persist for years in practice in home plumbing, as opposed to a few days for cupric hydroxide solids in the laboratory. Obviously, other constituents in natural water interfere with the expected transition of  $\text{Cu}(\text{OH})_2$  to less soluble copper solids.

Sulfate, bicarbonate, orthophosphate and NOM are among the common inorganic constituents in water that might interfere with such a transition, and indeed, their role in aluminum hydroxide solid transitions has been recognized for more than a decade (Violante et al, 1985). Sulfate is naturally present in water and is also indirectly added to drinking water through alum coagulation. Bicarbonate and NOM are both naturally occurring, whereas orthophosphate is commonly present naturally at  $\mu\text{g}/\text{L}$  levels or can be added at the  $\text{mg}/\text{L}$  level for corrosion control. This study will investigate the effect of these anions on the precipitation and aging of

copper solids formed in dilute nitrate solutions. It is anticipated that anions which accelerate transitions from  $\text{Cu}(\text{OH})_2$  to tenorite would be beneficial for copper release from home plumbing, whereas anions that hinder such transitions would be detrimental. Future research will have to address the validity of this hypothesis in pipes.

## **Materials and Methods**

The role of anions in copper solubility and aging was assessed experimentally by techniques described in Hidmi and Edwards (1999). Initially, a one liter solution containing 1 mM  $\text{NaNO}_3$  and 0.5 mM cupric nitrate was constituted from reagent grade water. In order to examine the role of chemical addition in copper solubility, three types of experiments were conducted. In the first, cupric nitrate addition was immediately followed by addition of 0.5 mM of either  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{SO}_4$ , or  $\text{Na}_3\text{PO}_4$  as desired in specific experiments. Thereafter, the experiment was initiated by dropwise addition of 1 M  $\text{NaOH}$  over a 15 minute period until pH 7.0 was achieved. As the experiment progressed, acid or base additions were made as necessary to maintain pH 7.0 and concentrations of soluble copper were determined after filtration through a 0.45  $\mu\text{m}$  pore size filter. Solutions were mixed throughout the experiment with a 5.0 cm magnetic stirrer at 200 rpm.

In the second type of experiment, the solution containing cupric nitrate and sodium nitrate was first titrated with  $\text{NaOH}$  to pH 7.0 and allowed to age for 2 hours. This procedure was previously demonstrated to produce cupric hydroxide (Hidmi and Edwards, 1999). Thereafter, 0.5 mM of the anion of interest was added to the solution now containing  $\text{Cu}(\text{OH})_2$  solid and the remainder of the experiment was conducted as before. Both types of experiments



might be relevant to control of copper release from pipes in potable water. For example, the first experiment assesses whether a solid other than  $\text{Cu}(\text{OH})_2$  might form initially on a pipe surface if a particular anion is present, whereas the second examines effects of each anion on the possible transformation of cupric hydroxide to less soluble copper solids with age.

The third type of experiment was initially designed to be similar to the first, but three changes were made which somehow influenced experimental results. In the first two experiments, the temperature was at  $23 \pm 1.5^\circ \text{C}$ , whereas a constant temperature room at  $20 \pm 0.1^\circ \text{C}$  was used in the third experiment. Moreover, instead of adding base dropwise and raising pH to 7.0 in the first 15 minutes, 1 M NaOH was added in 50  $\mu\text{L}$  increments every 5 minutes until pH 7.0 was achieved, typically in 45 minutes. Finally, to maintain equivalent charge in solutions to the extent possible, as target anion concentrations were increased, the initial sodium nitrate concentration was decreased on an equivalents basis. No other changes in experimental protocol were made.

Copper and phosphorus were determined using Inductive Coupled Plasma - Emission Spectroscopy (ICP-ES) with a detection limit of 0.001 mg/L copper and 0.01 mg/L phosphate. Sulfate concentrations were measured using a Hach spectrophotometer DR 2000 in experiments #1 and #2, and bicarbonate was calculated from measurements of alkalinity and pH. Sulfate was determined directly using an (ICP-ES) in experiment #3. Turbidity was monitored with a HACH DR 2000.

## Results and Discussion

The type and order of anion addition controlled the identity of solid formed and copper solubility with age. The first set of experiments examined the identity of solids formed when cupric was precipitated in the presence of the indicated anions, whereas the second and third examines effects of anions added to pre-formed  $\text{Cu}(\text{OH})_2$ .

### Cupric ion precipitation in the presence of target anions

When sulfate, bicarbonate or phosphate anions were present prior to base addition, the solids that were formed did not contain appreciable concentrations of nitrate. Moreover, the crystalline identity of the dried precipitated solids did not change as determined by XRD at experimental times of 5, 96 hours and one month (Table 2-1). In the presence of bicarbonate, the wet chemical analysis of bicarbonate and  $\text{OH}^-$  consumption per mole copper precipitated was completely consistent with malachite formation-- this was also the only solid phase detected by XRD. Likewise, in the presence of sulfate the wet chemical analysis and XRD were completely consistent with the exclusive formation of brochantite.

Copper solids precipitated with orthophosphate were completely x-ray amorphous at all times tested. To better characterize these solids, samples of the precipitate collected after 96 hours and one month of aging were dissolved in nitric acid at pH 2.0. The molar ratio of Cu:P in the solid was  $1.5 \pm 0.06$ , consistent with the formation of  $\text{Cu}_3(\text{PO}_4)_2$ .

During the initial precipitation phase, the rate of decrease in soluble copper concentrations depended on the type of anion tested (Figure 2-1). For example, in the presence

of sulfate soluble copper concentrations were relatively stable within 3 minutes of precipitation and did not change during one month of aging. In contrast, it took more than 96 hours to achieve stable copper levels when orthophosphate or bicarbonate ions were present (Figure 2-1).

**Table 2-1. Characteristics of solids formed when cupric ion was precipitated in the presence of 0.5 meq of each anion.**

Anions Added	Chemical Composition of		Calculated $K_{sp}$ @ 720 hours	Reported $K_{sp}$
	XRD	Stoichiometry#		
SO <sub>4</sub>	brochantite	Cu <sub>3.8</sub> (OH) <sub>5.4</sub> SO <sub>4</sub>	-17.32	-15.38
H CO <sub>3</sub>	malachite	Cu <sub>4.1</sub> (OH) <sub>5.6</sub> CO <sub>3</sub>	6.24	5.48
PO <sub>4</sub>	amorphous	Cu <sub>3.1</sub> (PO <sub>4</sub> ) <sub>2</sub>	30.23	36.86

\*As reviewed by Schock (1996) based on data from Linsay (1979), Smith and Martell (1976)

# based on wet chemical analysis

The observed decrease in soluble copper concentrations with time might be due to formation of lower surface area solids as solids age. Alternatively, a slow approach to equilibrium for a given solid phase could cause the same effect, with supersaturated solutions gradually approaching equilibrium. To discern between these two possibilities, precipitated solids were collected in the above experiments after 1 and 5 hours of aging. Thereafter, these solids were resuspended in a fresh solution containing the same final concentration of the relevant anions, ionic strength and pH, but without the soluble copper.

In all instances, after 1 hour the soluble copper was virtually identical to that obtained during the precipitation experiment at the same time period. This strongly indicates that cupric ion in the water was equilibrated with the solid, and that the decreasing soluble copper with time is due to production of solid with lower intrinsic solubility. Other observations are also consistent with this hypothesis. For example, increases in turbidity went far beyond that expected based on the slightly higher mass of particles formed during aging, suggesting a shift to increasing particle size.

From a practical perspective, the results illustrate the dichotomy of aging effects on copper solubility. For instance, precipitation of basic copper sulfate (brochantite) leads to lower initial levels of soluble copper than in its absence; however, after 2 hours the relative solubility was reversed. A similar effect was observed for orthophosphate, in that short term decreases in soluble copper were observed relative to the control, but longer term solubility was actually higher. For orthophosphate, however, the long term increase in solubility was not as dramatic as for sulfate.

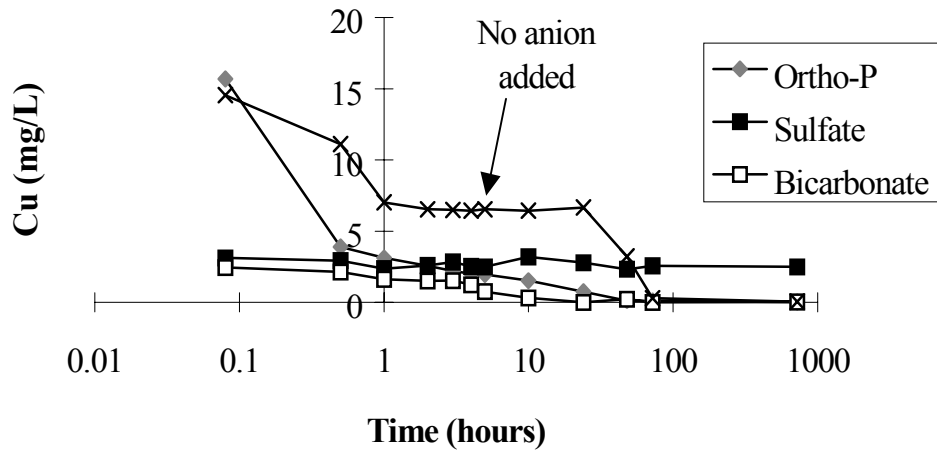
### **Impacts of added anions on preformed $\text{Cu}(\text{OH})_2$**

The addition of sulfate or bicarbonate anions to cupric hydroxide aged for 2 hours produced a drop in soluble copper concentrations within 3 minutes (Figure 2-2). This suggests a possible shift in control of solubility from cupric hydroxide to brochantite or malachite. XRD analysis on solids collected after 1 hour and one month of aging illustrated that these transformations were complete for sulfate, since no cupric hydroxide could be identified. The

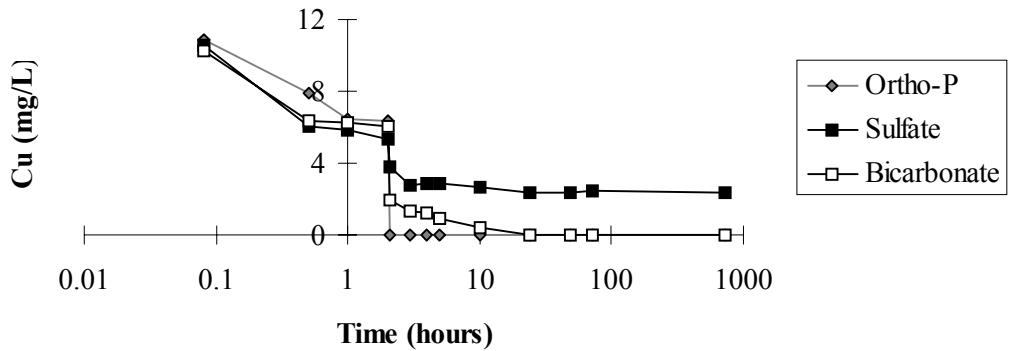
complete absence of cupric hydroxide from the sample after one hour of aging indicates the rapid nature of this transformation.

In contrast, when bicarbonate was added to previously formed cupric hydroxide, a mixture of malachite and cupric hydroxide were present in the first hour, gradually changing to a combination of malachite and tenorite after one month of aging. Phosphate addition markedly reduced copper levels, but formed an amorphous structure that could not be identified using XRD analysis. Wet chemical analysis proved that the transformation was not completely consistent with  $\text{Cu}_3(\text{PO}_4)_2$  formation, so it is likely that some  $\text{Cu}(\text{OH})_2$  was also present underneath a cupric phosphate or sorbed phosphate coating.

Once again, from a practical perspective, the presence of sulfate caused a short-term decrease in soluble copper concentrations, but over a longer period hindered the formation of less soluble copper phases. Similarly, although the trends are not visually apparent in Figure 2-2, addition of orthophosphate caused lower soluble copper levels short-term, but longer term actually led to somewhat higher copper solubility when compared to systems without orthophosphate addition.



**Figure 2-1. Soluble copper in the presence of the indicated anion after during base-induced precipitation at pH 7.0 and 23° C (above). Representative turbidity of solution with bicarbonate as a function of experimental time (below).**



**Figure 2-2. Soluble copper concentration after the addition of 1.0 mM of the tested anions to a solution initially containing  $\text{Cu}(\text{OH})_2$ .**

## **In-depth Examination of Sulfate Effects**

Concentration dependency of sulfate effects was examined using experiments with 9 levels of sulfate between 0 and 5 mM. Over the sulfate range of 0-0.5 mM, total equivalents of charge in solution were normalized at 2 meq/L by reducing the NaNO<sub>3</sub> addition in proportion to the sulfate addition (Table 2-2). At sulfate concentrations above 0.5 mM, however, ionic strength increased progressively and nitrate levels were constant at 1 mM.

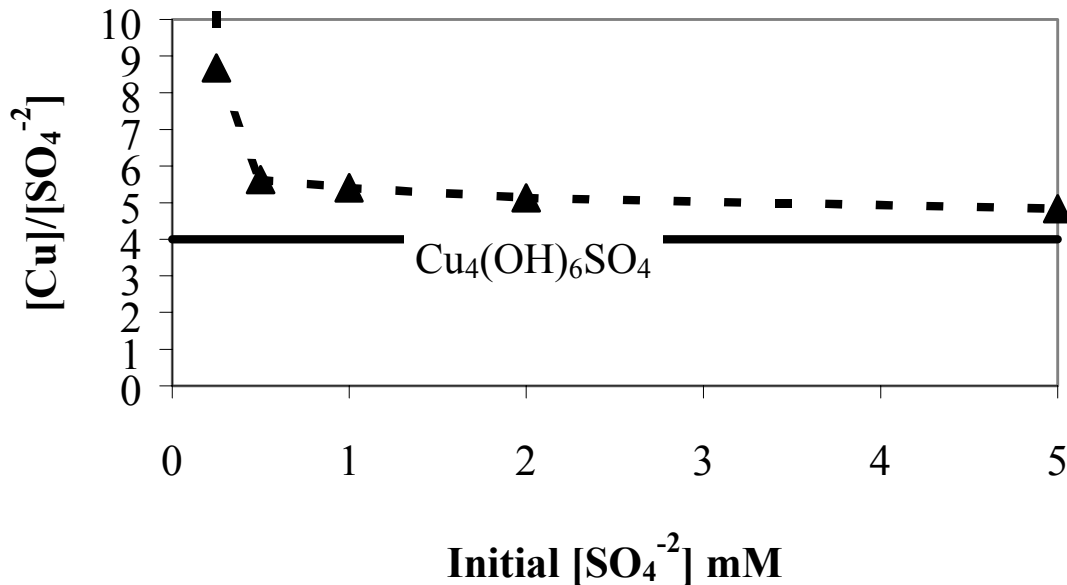
The concentration of sulfate in the solid progressively increased with initial sulfate in solution, approaching but not meeting the expected ratio of 4 Cu:1 SO<sub>4</sub><sup>-2</sup> expected in bronchantite (Figure 2-3). After 2 hours, 24 hours and 50 days, data on soluble copper was noteworthy from many perspectives (Figure 2-4). First, levels of copper in the absence of sulfate remained at the 0.5 mg/L level, which is much different than the 0.01-0.05 µg/L levels in earlier experiments. The most likely explanation for this is the slightly altered rate of base addition and lower experimental temperature. We are currently investigating this issue with additional experiments.

At most time periods, even 0.05, 0.1 or 0.25 mM of initial sulfate decreased copper solubility compared to the control at 2 and 24 hours. Since the concentration of sulfate in the solid was less than 1 for every 8 copper ions, this is not attributable to bronchantite formation. Instead, it is consistent with sulfate catalysis of Cu(OH)<sub>2</sub> aging. The copper minimum solubility consistently occurred at 0.5 or 1 mM of sulfate. At higher levels of sulfate, solubility increased with > 95% confidence. Experiments with a cupric ion specific electrode confirmed that copper was not being significantly complexed at these levels of sulfate. Instead, the increased copper

concentration is close to that expected based on the higher ionic strengths with higher initial sulfate levels (see trend line in Figure 2-4 and ionic strength in Table 2-2). In other words, above 0.5 mM initial sulfate, the same solid appears to be controlling solubility.

**Table 2-2. Summary of experimental results in experiment with variable initial sulfate.**

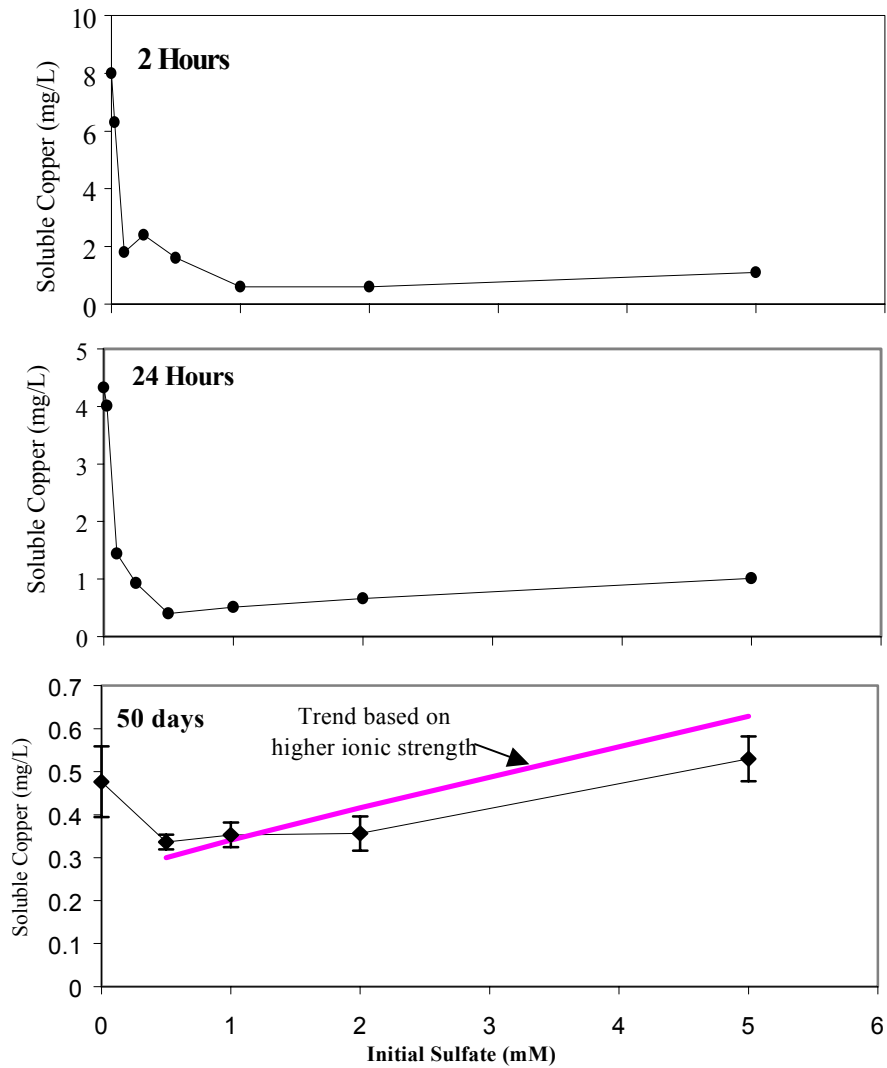
Initial Sulfate	Solid Color @ 8 hrs.	Solid Color @ 1200 hrs.	[Soluble @ 8 hours	[Soluble Cu] @ 1200	[NO3] mM	Final Charge (meq/L)	Ionic Strength (mM)
0	blue	brown	4.8	0.53	2	2	2
0.025	blue	brown	4.5	0.26	1.95	2	2.025
0.1	blue	brown	1.87	0.18	1.8	2	2.1
0.25	blue	blue	1.28	0.37	1.5	2	2.25
0.5	blue	blue	0.81	0.3	1	2	2.5
1	blue	blue	0.44	0.29	1	3	4
2	blue	blue	0.86	0.29	1	5	7
5	blue	blue	1.23	0.53	1	11	16



**Figure 2-3. Incorporation of sulfate into the solid formed increased with higher initial sulfate in the water.**



Figure 2-4. Effect of initial sulfate on soluble copper levels at 2 hours, 24 hours and 50 days of aging.



## General Conceptualization for Copper Corrosion By-Product Release

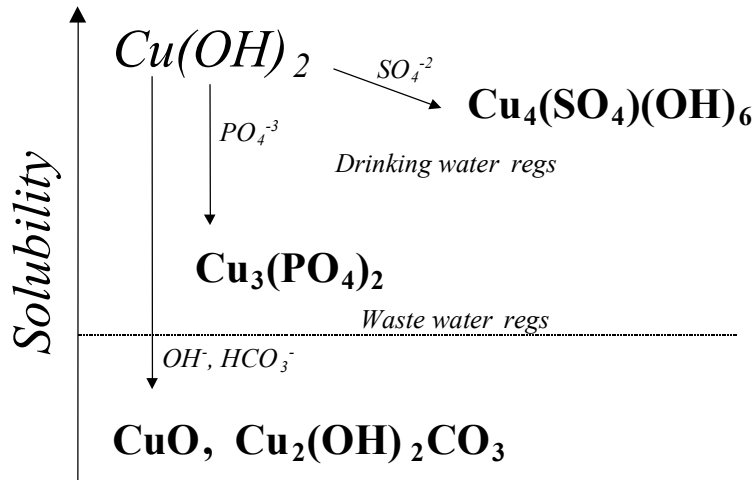
The trends noted in the above experiments provide unambiguous insight to certain factors that might influence soluble copper release from copper plumbing. The simplistic conceptualization starts with the assumption that, for a given pipe at a given age, there is a solid scale on the pipe wall that controls the concentration of free copper equilibrated with the water (Schock et al., 1994). As a general rule, free copper concentrations depend on the type of scale that is present, leading to decreased solubility in the order:  $\text{Cu}(\text{OH})_2 > \text{Cu}_4(\text{SO}_4)(\text{OH})_6 \gg \text{Cu}_3(\text{PO}_4)_2 > \text{CuO}$  and  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ . As a result, when comparing soluble corrosion by-product release from pipes with a similar controlling solid phase, such as for relatively new copper pipes in which  $\text{Cu}(\text{OH})_2$  solid is thought to dominate, soluble corrosion by-product release will tend to increase with lower pH, higher alkalinity, higher NOM and lower temperature. This is consistent with recent observations for certain trends in utility compliance and by-product release at consumer taps (Edwards et al., 1996).

However, longer term, changes in the type of solid that are present can play increasingly important roles (Figure 2-5). In waters with high sulfate, for example,  $\text{Cu}(\text{OH})_2$  might be converted to brochantite solid, the formation of which can hinder formation of either malachite or tenorite for an indefinite time period. In such cases, relatively high rates of soluble copper corrosion by-product release will be sustained until lower solubility solids such as malachite or tenorite form, if ever. Similarly, the addition of orthophosphate seems to produce a fairly rapid change in solubility control from cupric hydroxide to cupric phosphate, which in turn produces a substantial short term beneficial reduction in soluble copper release. However, longer term, it

seems to prevent formation of the lower solubility tenorite or malachite solids, and also necessitates continuous dosing of orthophosphate to maintain advantages relative to cupric hydroxide. This explains why orthophosphate inhibitor dosing can lead to short-term benefits and slight long term detriments for copper corrosion by-product release.

Obviously, other factors such as temperature, cationic constituents and dual ion interactions could play important roles. For example, in the type of experiment outlined in Figure 2-2, what relative levels of sulfate to bicarbonate would shift the  $\text{Cu}(\text{OH})_2$  transformation from malachite to brochantite? This critical level would control whether a long term benefit or detriment would result. The rates of solid precipitation, as controlled by the rate of  $\text{OH}^-$  addition in experiments, was also important. Does this mean that the rate of copper corrosion and cupric ion release within pipes is also an important factor in determining the type of solid phase formed? Finally, more information is needed on the concentration dependency of effects for key anions such as sulfate. As noted in the final experiment, sometimes low levels of an anion greatly reduce solubility by enhancement of aging, whereas higher levels can cause higher solubility due to formation of a relatively stable, higher solubility phase.

In summary, much additional work is necessary to better understand the intricacies of copper corrosion by-product release; however, simple experiments like those executed for this work can be useful in providing important trends to be examined in monitoring data.



**Figure 2-5. Simplistic model of equilibrated soluble copper in the presence of various scales.**

### Conclusions

The presence of sulfate, bicarbonate and orthophosphate can produce immediate changes in the type of solid present in systems containing cupric ion or cupric hydroxide solids. These changes, in turn, lead to short term reductions in copper solubility. However, over longer time periods, formation of basic cupric sulfate (brochantite) and even cupric phosphate can ultimately prevent the formation of very insoluble tenorite or malachite phases. To the extent that this occurs, the presence of sulfate and phosphate in water can increase copper solubility over much longer time periods.

For a given anion, the relative effect can be expected to depend on its concentration and rate of solid precipitation, as well as other factors. Low levels of sulfate tend to hasten the transition from cupric hydroxide to tenorite, whereas higher levels of sulfate interfere with that transition. These possible effects should be considered when attempting to reduce copper

corrosion by-product release from consumer plumbing, and similar transitions are likely important for other plumbing materials such as zinc, iron and lead.

### **Acknowledgements**

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## Chapter III:

### The Role of Silica and Chlorine in Cupric Hydroxide Aging

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Experiments were conducted to investigate the fundamental reactions between dimeric silica and cupric hydroxide at pH 7-10.5 and silica concentrations between 0-30 mg/L. The sorption density ranged from 0-0.77 M Si/ M Cu depending on aged solids and initial silica concentration, but was not a strong function of pH if the silica was present in excess. At all pHs studied, sorption of silica to  $\text{Cu}(\text{OH})_2$  slowed the aging of the blue cupric hydroxide solids as noted by color changes and surface chemistry. On the other hand, chlorine concentrations between 5-65 mg/L hastened cupric solid aging at pH 6 and pH 7, and cupric species caused loss of free chlorine.

#### Introduction

Cupric hydroxide solubility can control copper removal from industrial wastewaters and release of copper to drinking water from home plumbing. Previous research has demonstrated that several factors influence cupric hydroxide solubility including pH and temperature.<sup>1,2</sup> In addition, the transition of relatively soluble cupric hydroxide [ $\text{Cu}(\text{OH})_2$ ] to less soluble tenorite [ $\text{CuO}$ ] as pipes age is one reason why plumbing in older homes is often less problematic from the perspective of environmental loading and United States Environmental Protection Agency (USEPA) action limit (AL) regulating copper release at the consumer's tap.

The transition rate of cupric hydroxide to tenorite is decreased at lower pH, lower temperature, and in the presence of natural organic matter (NOM).<sup>1,2</sup> Other constituents present in water are believed to influence the rate of this transition in home plumbing, since high levels of copper release are sustained for decades in some waters (consistent with persistent cupric

hydroxide scale), while insignificant levels of copper consistent with tenorite solubility are observed a few days after installation in waters with similar alkalinity, temperature and pH.

Silica and chlorine are two important constituents in water that commonly contact copper pipe, and their impact on the cupric hydroxide to tenorite transition has not been previously studied. Silica sorbs to iron and aluminum hydroxides<sup>3,4</sup> and interferes with their aging,<sup>5</sup> so it is logical to expect that similar reaction 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 rates, some previous research demonstrated that dosing of free chlorine lead to marked reductions in copper release to drinking water under some circumstances.<sup>6</sup> While these observed benefits are commonly attributed to control of microbes that accelerate corrosion, it was deemed advisable to confirm the assumption that chlorine does not influence the chemistry of inorganic cupric species.

## **Materials and Methods**

**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, 1 M sodium hydroxide base was added to 0.5 mM cupric nitrate and 1 mM sodium nitrate at three different rates and dosages. Rates of addition tested included 1) adding 815 uL of NaOH in a single step, 2) dosing 50 uL every five minutes for forty-five minutes, and 3) addition of 400 uL 0.1 M NaOH every 20 minutes for four hours, with two final doses of 600 uL 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  $[\text{OH}]/[\text{Cu}]$  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 a titration time of 45 minutes.

**Sorption of Silica to Copper.** The role of silica (0-30 mg/L) and pH in copper solubility and aging at 20 ° C was assessed experimentally by using techniques described by Hidmi and Edwards<sup>1</sup> and Edwards et al.<sup>2</sup> To eliminate concerns of silica leaching from glassware, plastic Nalgene bottles were used for reactors and all reagent grade stock solutions. pH measurements were made by using a pH meter and a combination electrode using Standard Method 4500-H<sup>+</sup> B.

Cupric hydroxide solids were preformed by dosing 350 uL 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 was  $\text{Cu}(\text{OH})_2$  consistent with results of Hidmi et al.<sup>1</sup> (Table 3-1).



**Table 3-1: Solids identified 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	not 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	not Cu(OH) <sub>2</sub> , unidentified peaks
30 mg/L as SiO <sub>2</sub> , pH 9.2, aged 8 hrs	blue	not 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

Thereafter, aliquots of this suspension were taken from a well stirred suspension, and a desired level of silica was dosed from a 8 g/L stock solution of SiO<sub>2</sub> along with a predetermined dose of 1 M HCl to maintain constant pH 7 ± 0.1. 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 +/- 0.20 units of the target during the first eight hours and +/- 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.

**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 acidified in 2% HNO<sub>3</sub>. 50 mL of sample water was also passed through a 0.45 µm Millipore nitrocellulose filter. The filtrate was collected and analyzed for soluble species, and the filter with the solids was then acidified 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) according to Standard Method 3120 B.

**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.

## Results and Discussion

### Reaction of Silica with Cupric Hydroxide.

**Sorption Density.** It was initially considered possible that the silica was reacting with cupric hydroxide by a precipitation reaction such as:



The molar ratios of copper to silica 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, it did not form exclusively, although both cupric hydroxide and  $\text{CuH}_2\text{SiO}_4$  might both be present. Considering the Si: Cu ratios and assuming that only cupric hydroxide and diopside were present, the concentration of diopside could be as much as 2-29 % of the total copper. The solids were also analyzed by using 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 3-1). Because the solids were initially cupric hydroxide, the solubility of diopside was never exceeded at pH 7.0, and no CuSi solids were identified by x-ray diffraction, all further discussion assumes the solids are cupric hydroxide with silica sorbed to the surface in a monomeric or polymeric form.

The sorption density of silica 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. Therefore, 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.

The sorption of silica to iron is now relatively well understood.<sup>5</sup> Likewise, earlier studies with aluminum hydroxides found that silica first sorbed in a monolayer, followed by a slower forming multilayers.<sup>4</sup> However, there is not extensive fundamental information on silica reactions with cupric hydroxide.<sup>7</sup> The silica sorbed very strongly to the surface of cupric hydroxide (Figure 3-1). 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 SiO<sub>2</sub>, and unlike prior reports for iron and aluminum, the sorption density is a relatively weak function of pH (Figure 3-1). 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.

**Sorption and Zeta Potential.** In the sorption experiments, zeta potential varied from +45 to -30 millivolts depending on the pH and silica concentration, and as pH and silica concentration increased the zeta potential decreased (Figure 3-2). Thus, silica sorption converts positively charged sites on the cupric hydroxide surfaces to neutral and negative 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 the added silica.

**Transition Time of  $\text{Cu}(\text{OH})_2$  to  $\text{CuO}$ .** For iron 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.<sup>8</sup> Observations of color changes in 32 experiments for this work demonstrated that silica played a similar role in the transition from cupric hydroxide to tenorite. That is, when cupric hydroxide ages in the laboratory at 20 degrees C, it changes color from the more soluble blue cupric hydroxide to the less soluble brown tenorite. This transition occurs in a few hours at pH 9, but requires a few days at pH 7. 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 3-3 and Figure 3-4), the cupric solids never changed color to brown. Even when the pH is raised to 10, the cupric hydroxide solids remained blue for over one month when 30 mg/L silica was present (Figure 3-3), whereas the

transition to tenorite was complete in a few hours when silica was absent. At a fixed pH of 9.2, solutions containing zero silica change brown immediately, but solutions with 7.5 mg/L as SiO<sub>2</sub> took 600 hours to change and solutions containing greater than or equal to 10mg/L as SiO<sub>2</sub> did not do so after 2100 hours (Figure 3-3). Analysis of XRD patterns of representative solids confirmed that the transition of blue to brown in the experiments without silica corresponded with disappearance of cupric hydroxide, Cu(OH)<sub>2</sub>, and the appearance of tenorite, CuO (Table 3-1). If silica was present, only weak peaks were observed, with no strong signal of Cu(OH)<sub>2</sub> or CuO.

**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 SiO<sub>2</sub> when compared to 0-5 mg/L SiO<sub>2</sub>, resulting in longer required time periods for soluble copper to drop below the 1.3 mg/L Action Limit for copper (Figure 3-7). 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 change the concentration of free copper in a standard solution—thus, the evidence suggests that silica was causing higher solubility 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 cupric hydroxide was maintained for long time periods. This is surprising and deserves future study.

Particle size, unlike copper solubility, was greatly influenced by the concentration of silica at pH 9.2. Although the size of all particles was above the Malvern's detection limit of 3 microns, the general trend was that the higher the silica concentration, the larger the particles.

Moreover, the solids in systems with silica are less dense and tended to remain suspended much longer than in the system with tenorite.

### **Reaction of Chlorine with Cupric Hydroxide.**

The initial assumption was that free chlorine would not react with cupric hydroxide, but testing of this possibility indicated that the chlorine reacted with cupric ion, and vice versa. In the absence of copper, chlorine decays slowly in solution, although it is known that factors such as light and heat can accelerate decomposition.<sup>9</sup> The previous literature suggests that copper has only a slight positive influence on standard DPD tests that test for chlorine (Standard Method 4500 CLG) used in this experiment,<sup>10</sup> and our own QA/QC tests confirmed that the presence of cupric ion did not interfere directly with the measurement of free chlorine.

If cupric species are present, however, the chlorine decays 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 3-8). Moreover, in the presence of 5-65 mg/L chlorine, the blue cupric hydroxide solid color changes immediately (< 10 minutes) to brown at pH 7, although soluble copper did not decrease to levels consistent with tenorite solubility (Figure 3-9) and free copper was not impacted as determined by the ion specific electrode. Silica seems to decrease the decay of free chlorine in the presence of copper (Figure 3-8), and slow the effects of free chlorine on changes in solid color (Figure 3-4,3-5,3-6).

**Table 3-2: Percent chlorine or Cu(OH)<sub>2</sub> solid loss that can be accounted for by the indicated reaction.**

Reaction	Cl <sub>2</sub> decay?		Explain Cu loss and color?	
	5 mg/L Cl <sub>2</sub>	65 mg/L Cl <sub>2</sub>	5 mg/L Cl <sub>2</sub>	65 mg/L Cl <sub>2</sub>
$\text{Cu}^{+2} + 2\text{OCl}^- \rightarrow \text{Cu}(\text{OCl})_2(\text{s})$	Yes	Yes	No	Yes
$\text{H}_2\text{O} + 2\text{Cu}(\text{OH})_2 + \text{OCl}^- \rightarrow 2\text{Cu}(\text{OH})_3 + \text{Cl}^-$	Yes	No	No	Yes
$2\text{HOCl} \xrightarrow{\text{Cu}^*} 2\text{H}^+ + 2\text{Cl}^- + \text{O}_2$	Yes	Yes	No	No
$\text{Cu}(\text{OH})_2 \xrightarrow{\text{Chlorine}} \text{CuO}$	No	No	Yes	Yes

\*Catalyzed by copper plumbing

Aside from the obvious impact of chlorine on Cu(OH)<sub>2</sub>, we initially presumed that the observed chlorine decay was an artifact. However, the literature suggested at least four possible reactions that might be operative (Table 3-2). For instance, soluble cupric ion could react with free chlorine to form a copper hypochlorite solid.<sup>11</sup> While the solubility of this solid is unknown, if it formed, it could explain loss of 100 % of the chlorine observed in the two experiments, but the stoichiometry suggests that it could not have quantitatively converted all Cu(OH)<sub>2</sub> to Cu(OCl)<sub>2</sub>. The second possible reaction is that chlorine is an oxidant for the conversion of copper (II) to a hypothesized less soluble copper (III) species;<sup>12</sup> however, this reaction could convert only 28% of the cupric solid at the lower chlorine dose, and cause loss of only 27% of 65 mg/L free chlorine at 65 mg/L.

The final possibilities are that copper is a catalyst for a reaction in which hypochlorous acid is converted to oxygen, or that chlorine is a catalyst for copper aging.<sup>13</sup> However, given that both proposed catalysts were changed, both reactions had to occur simultaneously. There is no obvious explanation for the observed reactions, and it is certainly important enough to deserve additional research.

## Acknowledgements

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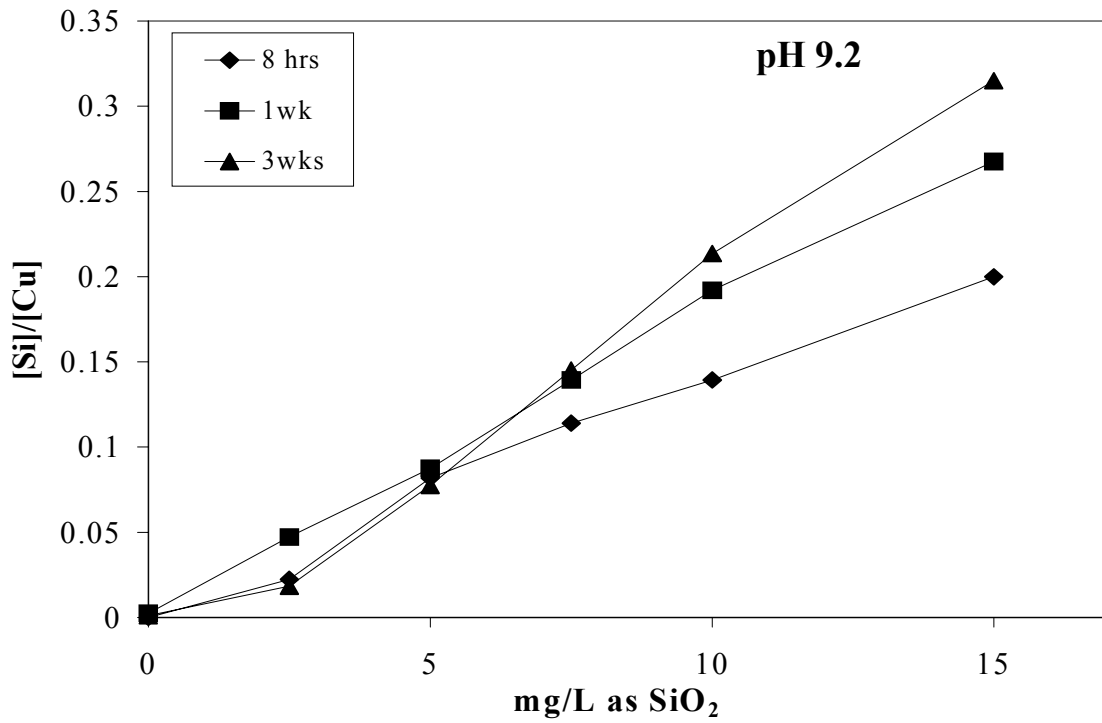
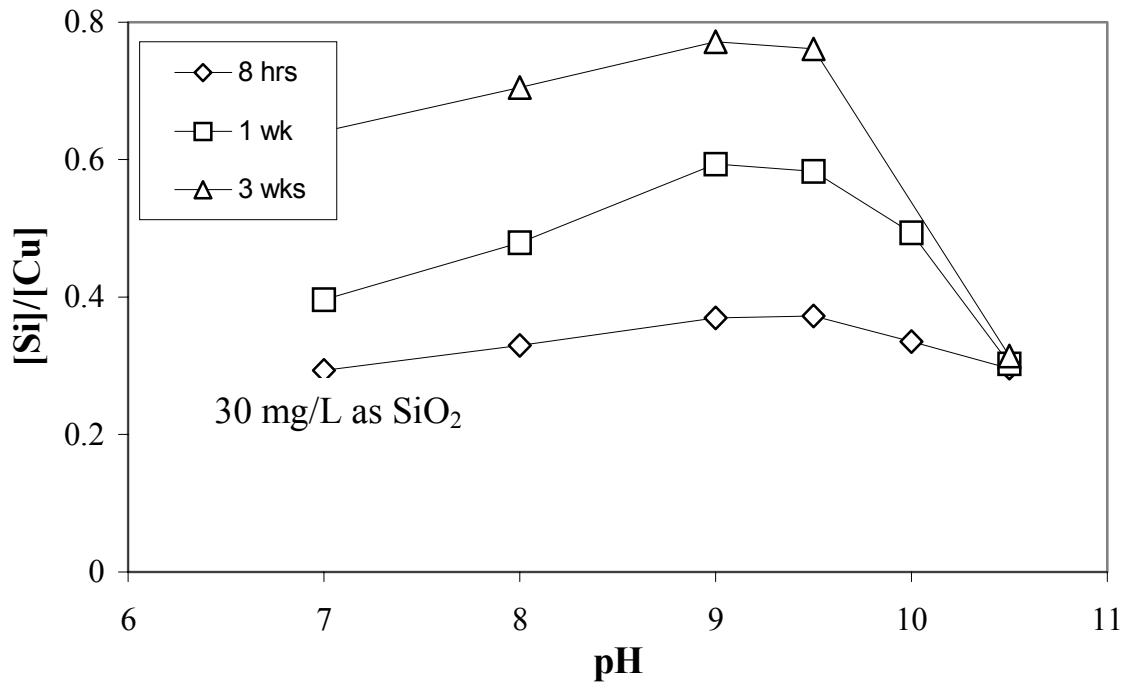
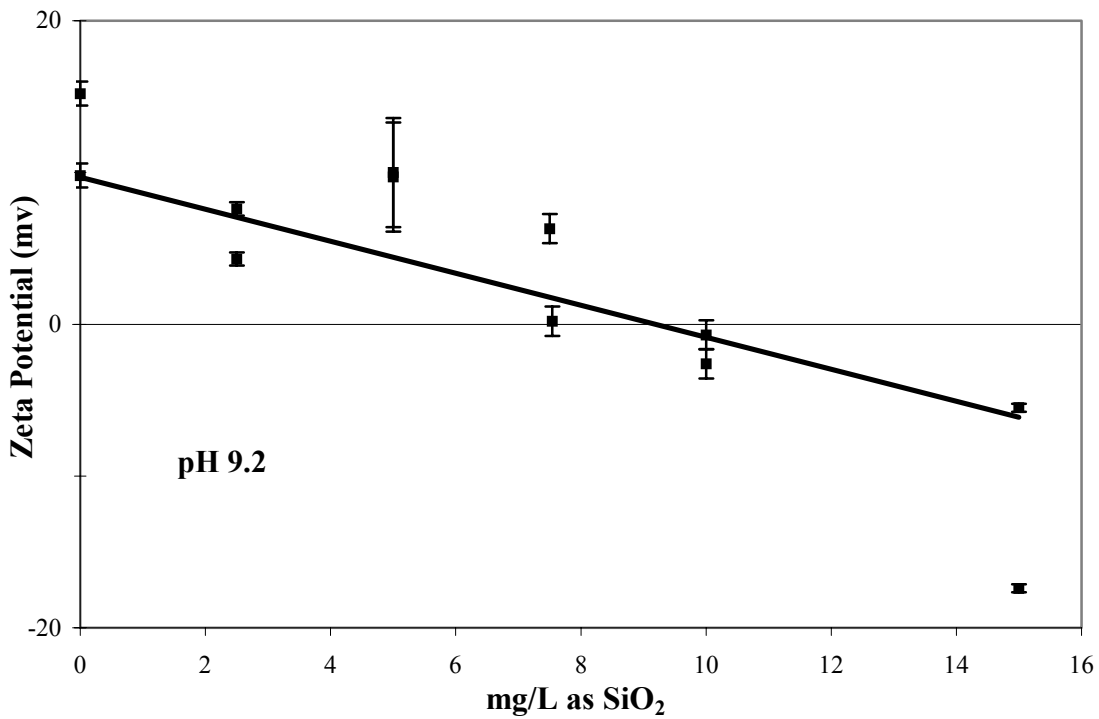
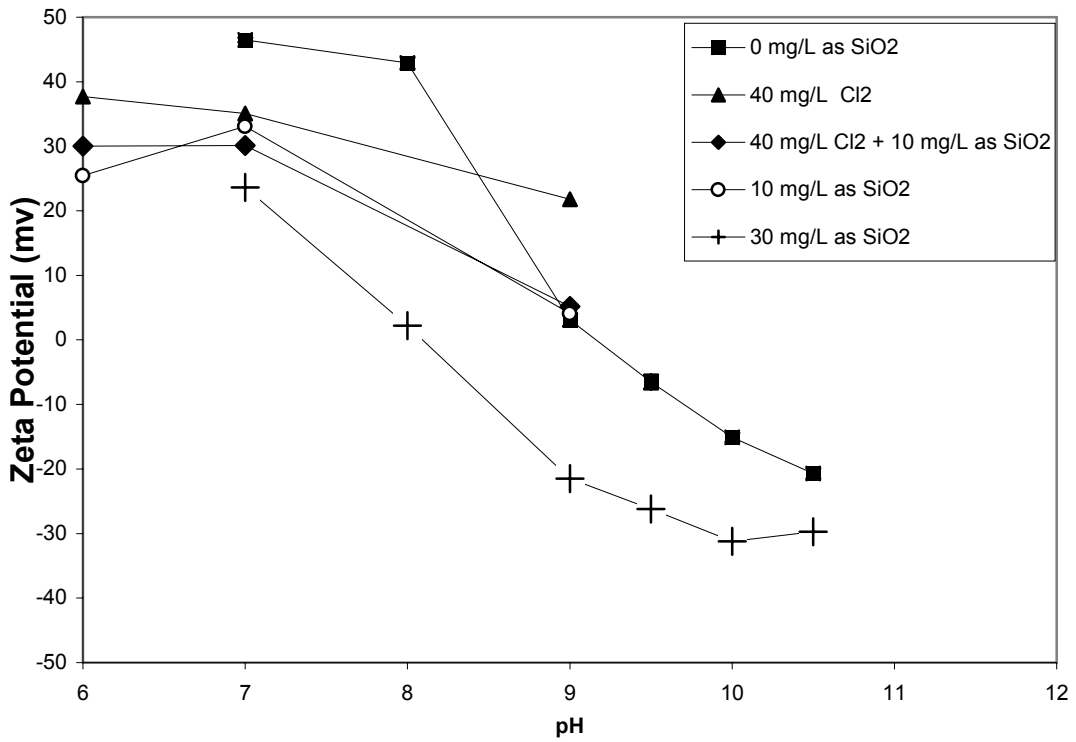
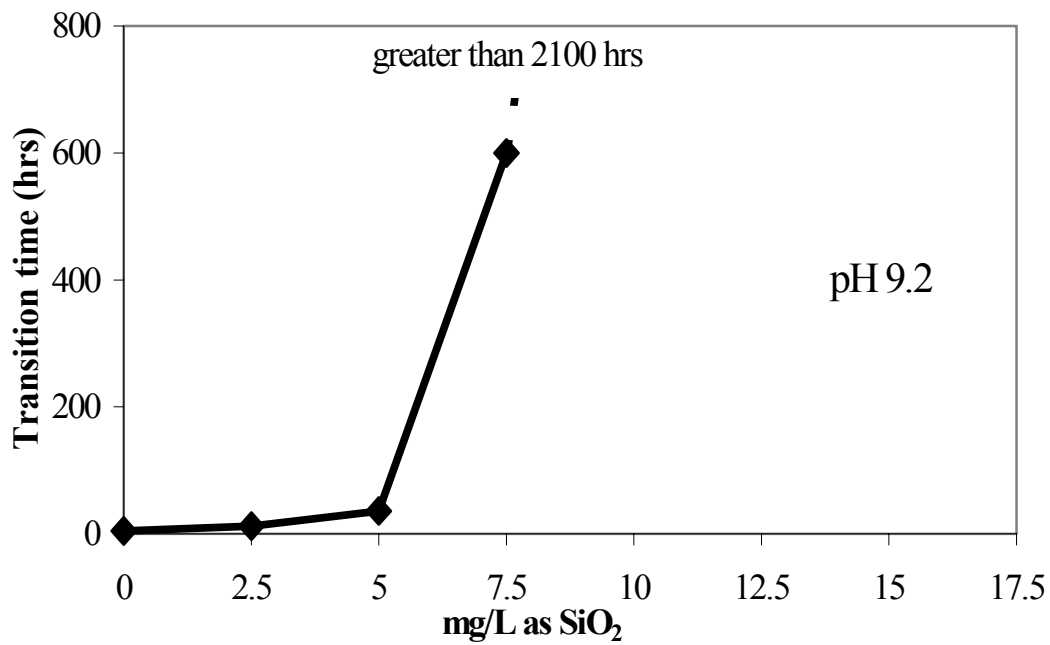
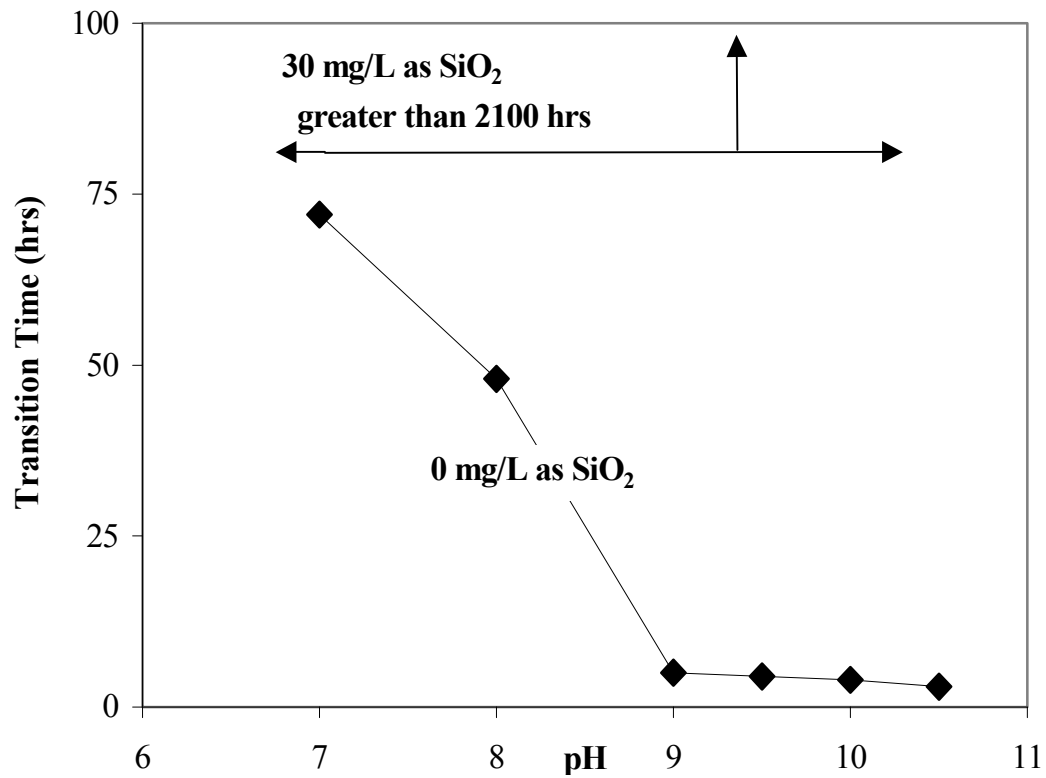


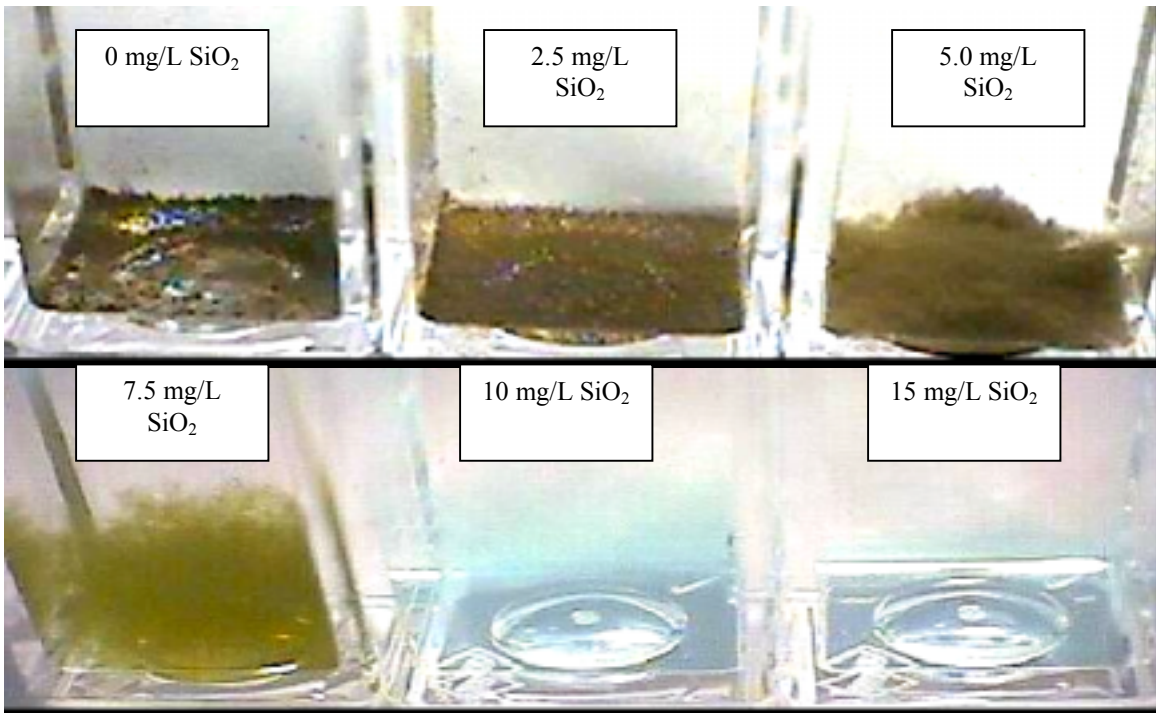
Figure 3-1: Sorption density of cupric hydroxide waters with varying silica concentration (above) and pH (below).



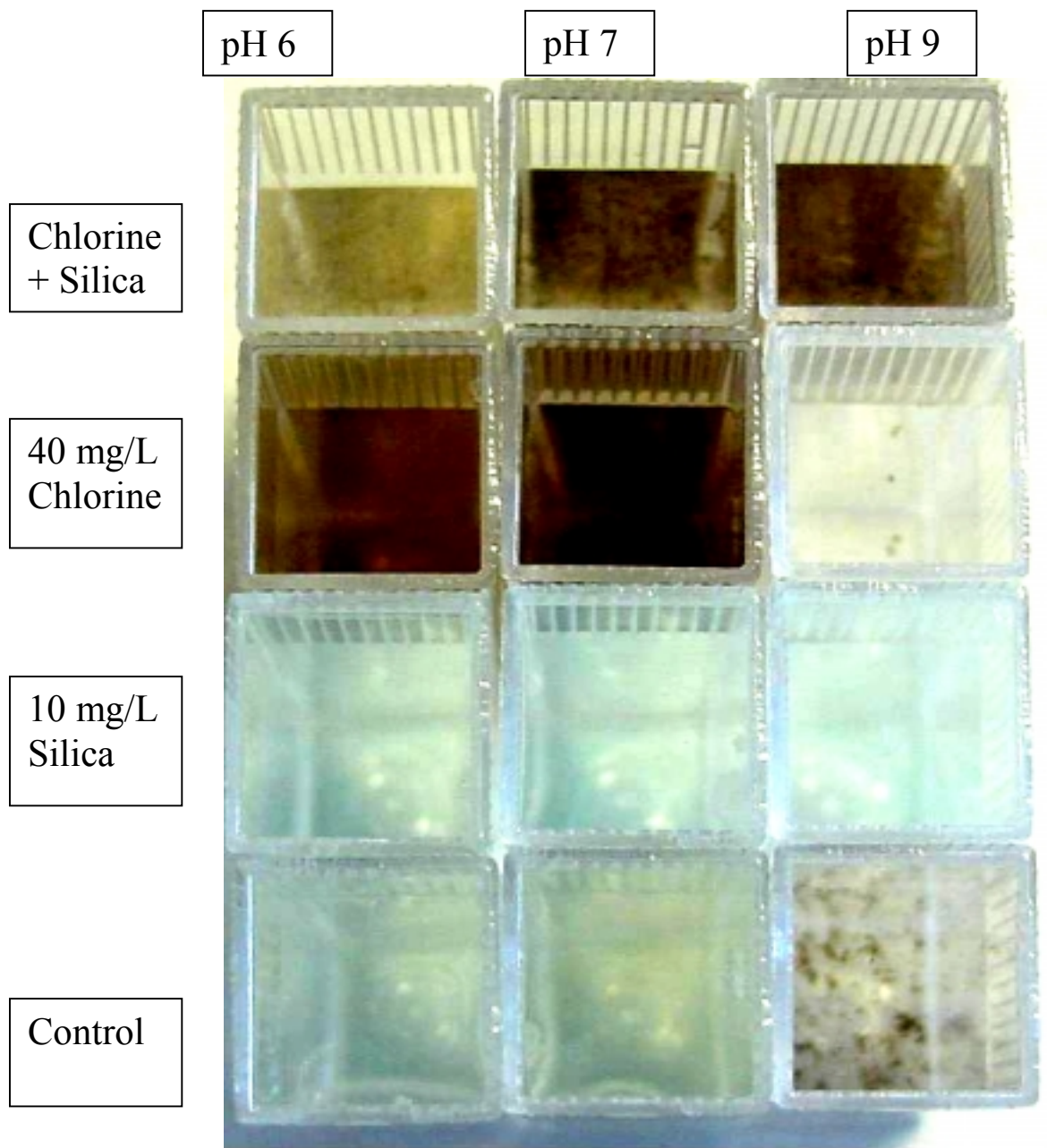
**Figure 3-2: Zeta potential versus pH for waters initially containing cupric hydroxide at pH 7, with a dose of chlorine and/or silica, before final pH adjustments.**



**Figure 3-3: Transition time from the blue to brown solid is plotted for varying pH (above) and silica concentrations (below).**

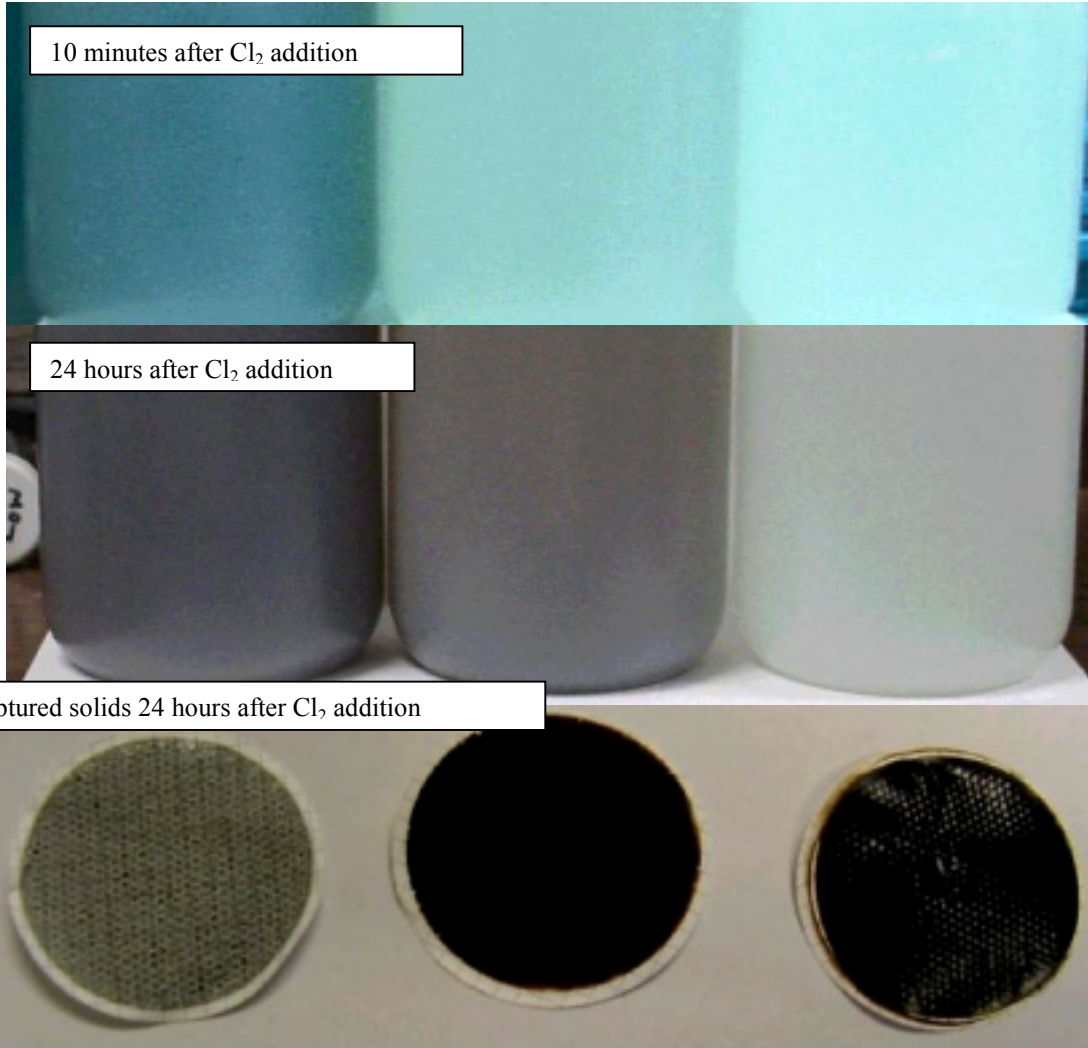


**Figure 3-4. Solids present after preformed, blue  $\text{Cu}(\text{OH})_2$  was dosed with the indicated concentration of  $\text{SiO}_2$  concentration, and then aged 24 hours at pH 9.2.**



**Figure 3-5: Photograph after 24 hrs for twelve different conditions. All waters initially contained cupric hydroxide aged 2 hours at pH 7.**

65 mg/L Cl<sub>2</sub>, No SiO<sub>2</sub>      65 mg/L Cl<sub>2</sub>, 10 mg/L SiO<sub>2</sub>      No Cl<sub>2</sub>, No SiO<sub>2</sub>



**Figure 3-6:** At pH 7, if no silica or Cl<sub>2</sub> is present, blue Cu(OH)<sub>2</sub> solids gradually change to brown CuO in about 24 hours (right). If chlorine is added, the blue solids immediately (< 10 min.) turn light brown (left), but if both silica and Cl<sub>2</sub> are added (middle), the rate of transition to brown colored solids is between these extremes (middle).

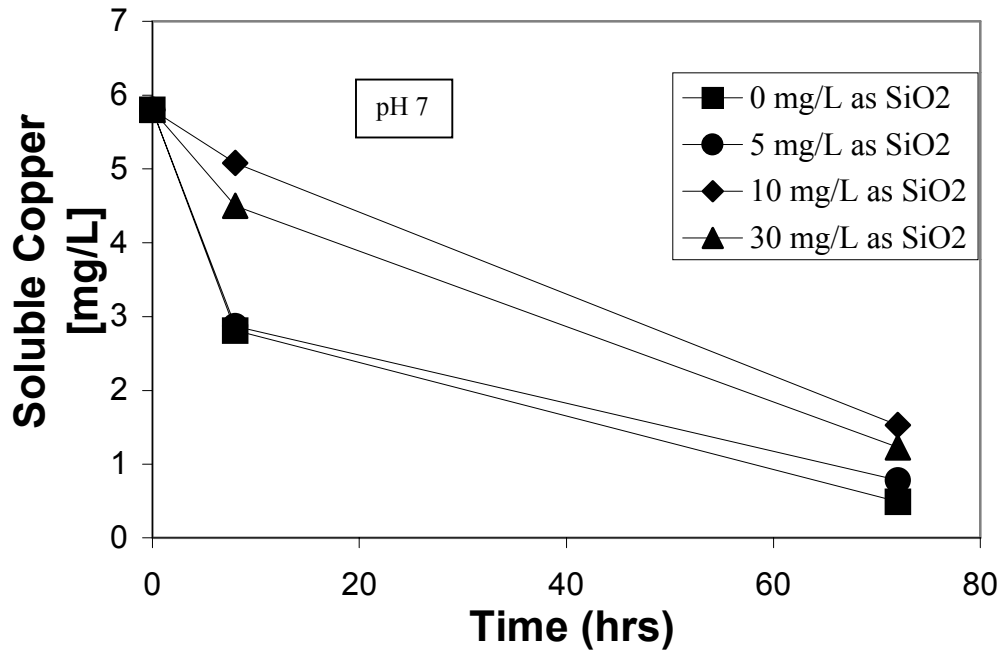
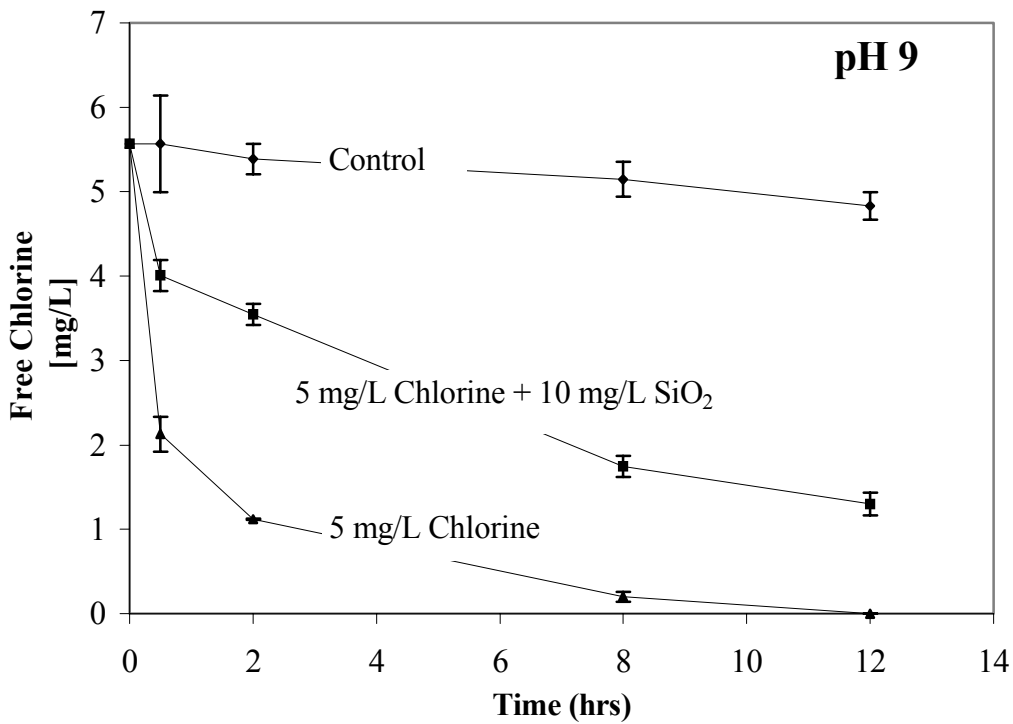
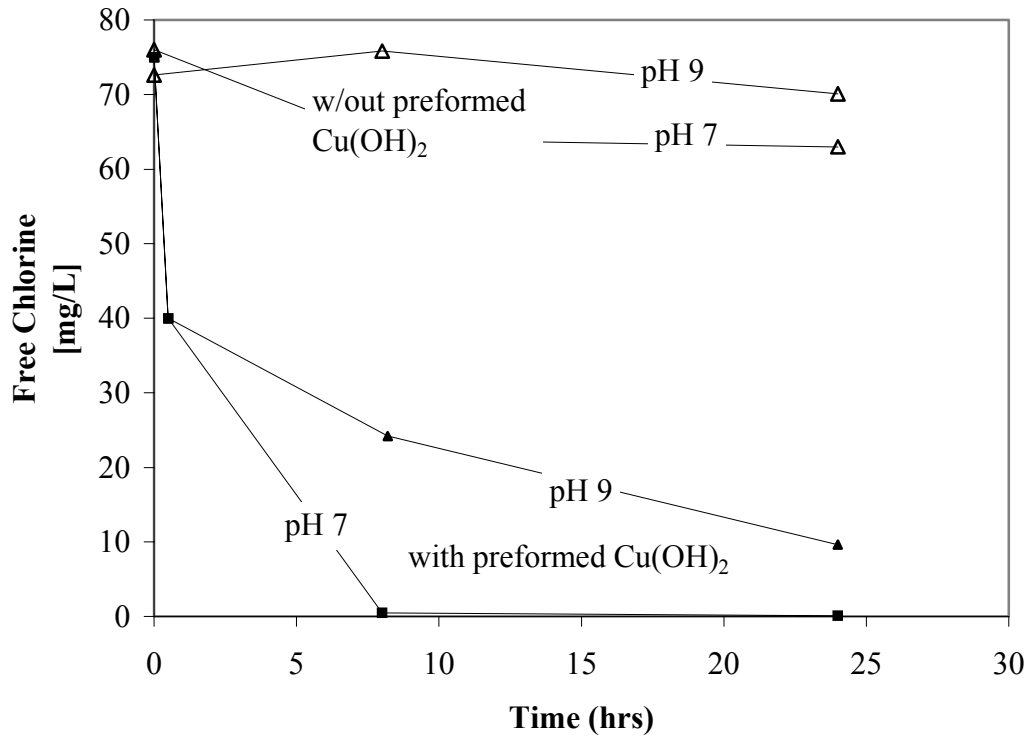
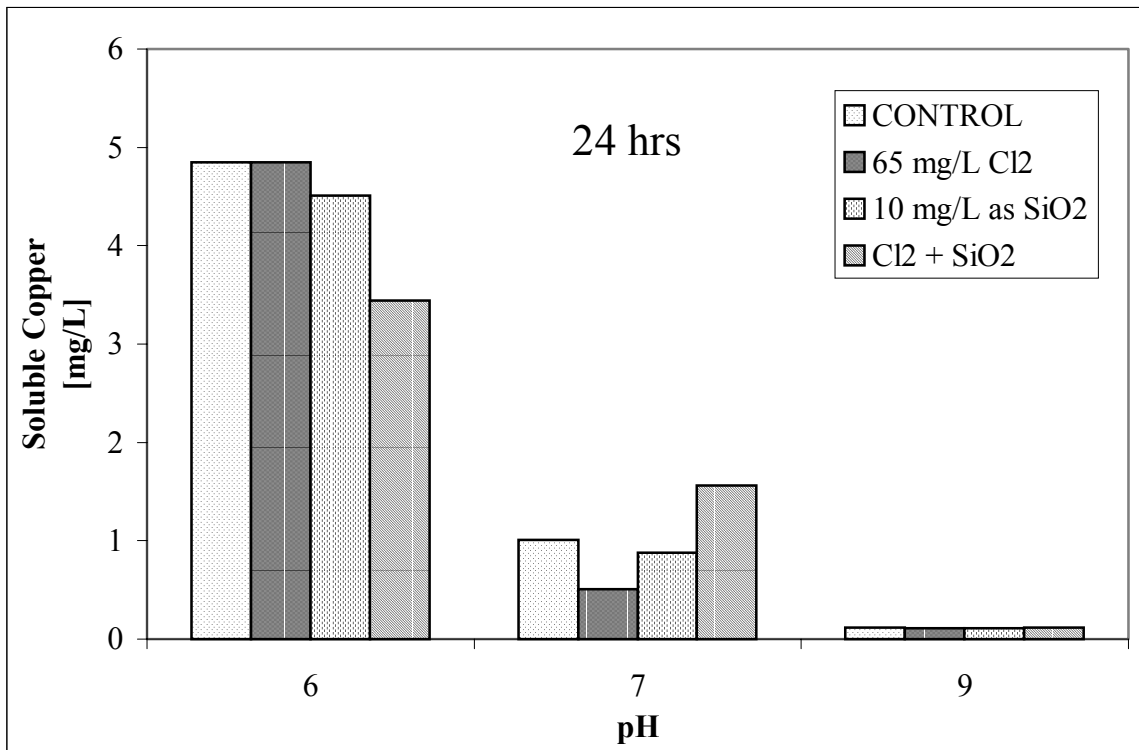
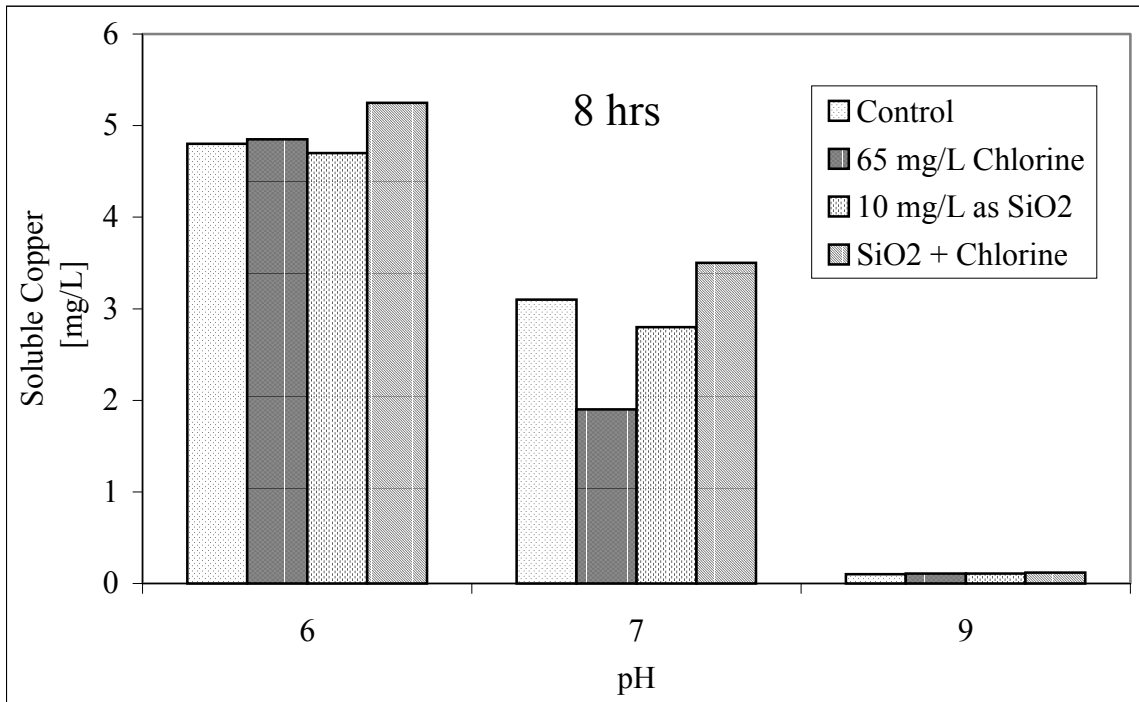


Figure 3-7: Soluble copper at pH 7 for solutions initially containing cupric hydroxide.



**Figure 3-8: 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 3-9: Soluble copper versus pH at 8 and 24 hrs for solutions with silica and/or chlorine.**

## CHAPTER IV

### Accelerating the Aging of Copper Pipe

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Experiments were conducted to investigate whether chemical treatments can reduce copper release from new pipes. Lime, caustic, sodium bicarbonate, and chlorine treatments reduced copper by product release at greater than 95 % confidence, whether the treatment was applied to a new pipe or a pipe that was previously exposed to water for one week. Pre-treatments did not make new pipes resistant to continuous sulfide attack.

#### Introduction

It is well known that copper release from home plumbing gradually decreases with time through a process termed pipe aging. Among the factors contributing to this phenomenon, gradual replacement of more soluble solids with less soluble solids in scale of the pipe wall is thought to be key in many circumstances. In some waters, the transition from soluble scale compounds like cupric hydroxide  $[\text{Cu}(\text{OH})_2]$  to less soluble compounds like tenorite  $[\text{CuO}]$  occurs within a few hours or days, yet in other waters the transition does not seem to occur at all. In a few localities facing especially stringent environmental regulation of copper in wastewater treatment plant effluent, this has caused scrutiny of new copper pipe installation, and in some cases a ban on new copper in home plumbing has been discussed.

Given that copper has many unique and desirable characteristics as a home plumbing material including service as a ground, relative ease in preventing bursting due to freezing, low cost, proven performance and bactericidal action, it is desirable to consider approaches that

would overcome problems with slow aging. For instance, since it has been proven that natural organic matter (NOM) in water is one factor that can slow aging, completely removing NOM at the water treatment plant would probably allow aging to occur quickly in many waters.

Unfortunately, due to the fact that corrosion of iron, concrete, plastic, and brass plumbing materials is also of concern, and the high costs of NOM removal, utilities cannot always make such changes specifically to prevent copper release from newly installed pipes.

The problem might also be solved by employing simple chemical treatments to chemically accelerate the aging (passivation) process; if successful, pipes might be easily treated (aged) by manufacturers before sale, by utilities before routine use, or by plumbers after installation. This basic idea is not new. For example, recent work on copper roofing materials has highlighted the need to form artificial patinas on copper which are beautiful, but which also have reduced environmental impacts in terms of copper leaching and improved resistance to air pollution.<sup>1</sup> Likewise, manufacturers of brass faucets have supported research into chemical pretreatments that can be conducted before fixture sale, and which reduce lead leaching to drinking water, with some very impressive results.<sup>2</sup>

The primary goal of this work is to examine mild chemical treatments that can greatly reduce, and ideally eliminate, high levels of copper release associated with installation of new copper plumbing. A secondary goal was to determine if the chemical pretreatments might also impart resistance to sulfide-induced copper corrosion, which arises in rare circumstances from formation of a deleterious copper sulfide scale after installation that can catalyze copper

corrosion. Sulfide induced corrosion can lead to premature pipe failures, as well as darkened water attributed to release of copper sulfide particulates.<sup>3</sup>

## Materials and Methods

Two phases of experiments were conducted to determine the effect of pre-treatments on copper corrosion. The first examined the effect of chemically accelerated aging on copper release from pipe. The second examined the effects of pre-treatment and silica on sulfide induced copper corrosion. Copper pipes (3/4" Type M) were purchased at a local hardware supply store, cut into 1-foot sections, and then weighed to determine the initial mass. A low pH, high alkalinity drinking water (Table 1) was synthesized that is typical of ground-waters which tend to support high levels of copper release for a month or so before copper aging occurs.<sup>4</sup> Likewise, a high pH, low alkalinity water, typical of those in which severe sulfide corrosion is reported, was also synthesized.

**Table 4-1 – Drinking Water Synthesized for Use in Research**

<b>Salts in the Base Solution</b>	<b>Low pH, high alkalinity water</b>	<b>High pH, low alkalinity water</b>
<b>NaCl</b>	0.4 mM	0.4 mM
<b>Na<sub>2</sub>SO<sub>4</sub></b>	0.25 mM	0.25 mM
<b>NaHCO<sub>3</sub></b>	6 mM	0.3 mM
<b>Na<sub>2</sub>SiO<sub>3</sub></b>	15 mg/L as SiO <sub>2</sub>	15 mg/L as SiO <sub>2</sub>
<b>pH</b>	6.3	9.2

### **Phase 1. Mild Treatments to Accelerate Pipe Aging**

Four mild chemical solutions which were deemed likely to accelerate aging included 1) lime solution of pH 12, 2) caustic solution of pH 12, 3) CO<sub>2</sub>/NaHCO<sub>3</sub> solution of 0.1 M and 4) solution containing 5 mg/L free chlorine. Solution 1 and 2 were considered likely to form a tenorite scale on the pipe surface, whereas solution 3 was targeting malachite scale, and solution 4 tested impacts of chlorine dosing which is often employed before pipes are brought into service. As noted in the earlier chapter, chlorine had obvious visual impacts on cupric hydroxide solids, even though the specific reactions involved are not understood.

Pre-treatments involved filling pipe sections with a single batch of the indicated solution, allowing 48 hours to react, and then rinsing the pipes with the synthetic water 3 times before use in experiments. Control pipes were used without any pretreatment, making 5 conditions total, and 5 pipes were generated at each condition to support statistical analysis and confidence testing.

The above exposure protocol is representative of treatments that might be performed after manufacture or just before installation (pre-treatment). It is also advantageous to test the effectiveness of treatments that might be applied after the pipe is installed (i.e. post installation treatment or post-treatment), since this may be useful in many circumstances. For these tests, 5 pipes were treated using each condition as before; however, the pipes were previously exposed to the aggressive water for one week. In other words, in this set of experiments, a characteristic scale was allowed to form first, and the goal was to convert it to a passive scale afterwards.

Water was changed in the pipes every Monday, Wednesday, and Friday, and pipes were closed on each end with rubber stoppers and allowed to sit stagnant horizontally between changes. After one week and one month exposure, the concentration of copper corrosion by-products in water from each pipe was determined by Inductively Coupled Plasma Emission Spectrophotometer (ICP-ES) according to Standard Method # 3120 B.

## **Phase 2. Resistance of Pre-Passivated Pipe to Sulfide Attack**

This experiment was designed to determine if pretreated pipe would be more resistant to sulfide induced copper corrosion—previous research conducted for CDA suggested that at least some resistance to sulfide attack occurred for pipe with naturally passivated surfaces. Pipes were pretreated with either the lime solution at pH 12 or the  $\text{CO}_2/\text{NaHCO}_3$  solution of 0.1 M at pH 6.0 for the test. Thereafter, some of the pipes were exposed to the synthetic waters listed in Table 4-1, and others were exposed to the same water but with 10 ppm sulfides for one month at pH 6.3 and pH 9.2. There were also pipes serving as the control at each pH without any pre-treatment, making 3 conditions, and 30 pipes total considering there are five pipes at each condition with sulfides. Corrosion by-product release was monitored at one week and one month.

Finally, the role of silica in modifying sulfide attack was explicitly examined at pH 9.2 in pipes containing 0, 15, and 50 mg/L as  $\text{SiO}_2$ . Three pipes were tested at each level of silica in water with and without sulfides.

## **Statistical Testing**

A standard deviation on the population mean was used to determine 95 % confidence

intervals for statistical tests and graphical presentation of data. In addition, a statistical package (NCSS 97) was used to check 95 % confidence intervals using an analysis of variance approach. Conclusions drawn from NCSS were in agreement with the standard confidence intervals generated in Excel.

## **Results and Discussion**

Experimental results are organized into two sections according to the two phases of experiments conducted.

### **Mild Treatments Accelerated Pipe Aging.**

One concern was that the mild pre-treatments themselves might cause release of an excessive amount of copper from the pipe. To examine this, solutions emerging from the pipes after the treatments were conducted were examined for copper concentration. Copper in the treatment solutions ranged from only 0.2 to 4.2 mg/L, and therefore, copper leaching was not a significant concern (Figure 4-1).

Upon subsequent exposure to the low pH high alkalinity drinking water, pre-treatments proved to be effective at reducing copper release from pipes after one week and one month exposure to the aggressive waters at pH 6.3. The percentage reduction ranged from 55 to 82 % at one week, and all four pre-treatments reduced copper release at greater than 95% confidence compare to pipes with no pre-treatment. After one month, the control pipe still released an average copper level greater than the Action Limit for copper of 1.3 mg/L, while pipes that were pre-treated released less than this limit. Lime and caustic were the most effective pre-treatments after one week and one month exposure to the pH 6.3 waters (Figure 4-2).

The above results are for treatments that might be applied after manufacture or just before installation. Another question of interest was "Is it better to apply the treatment before (pre) or after (post) installation?" To answer this, percent decrease in copper pipes treated after installation (post) versus before installation (pre) was calculated by the following equation:

$$\% \text{ Reduction} = 100 * ([\text{Pre-treatment Total Cu}] - [\text{Post-treatment Total Cu}]) / [\text{Pre-treatment Total Cu}]$$

If this is negative, pre-treatment is better than post-treatment, whereas if it is positive, post-treatment is better. For instance, with caustic and sodium bicarbonate, pre-treatments were more effective than post-treatments after one week. On the other hand, lime and chlorine performed best as a post-treatment. Interestingly, the highest percent decrease in total copper was in pipes exposed to chlorine after initial exposure to water (Figure 4-3).

## **Phase II Results**

Comparing control pipes with and without sulfides, copper release was 2.4 times higher at pH 6.3 and 481 times higher at pH 9.2 after one month exposure (Figure 4-4). Copper release did not significantly decrease with time if sulfides were present, consistent with sulfide induced copper corrosion as noted elsewhere.

Did pre-treatments improve resistance to sulfide attack? The lime pre-treatment did decrease copper release compared to the control after one week exposure to the drinking water with added sulfide at pH 6.3 or pH 9.2, but the decrease was only significant at 95% confidence at pH 6.3 (Figure 4-5). The protection imparted by pre-treatments were not sustained for one month of sulfide exposure; for example, copper release increased 800 % for the pipes pretreated



with lime after one month compared to one week. Sodium bicarbonate pre-treatment did not significantly alter copper release compared to the control in the presence of sulfides.

Other work attempted to determine the effects of silica on sulfide induced corrosion of copper. At pH 9.2 without sulfides, silica did not significantly impact copper release. However, after one week and one month, 15 and 50 mg/L silica increased copper release in waters with sulfides, when compared to the same water with no sulfides (Figure 4-4).

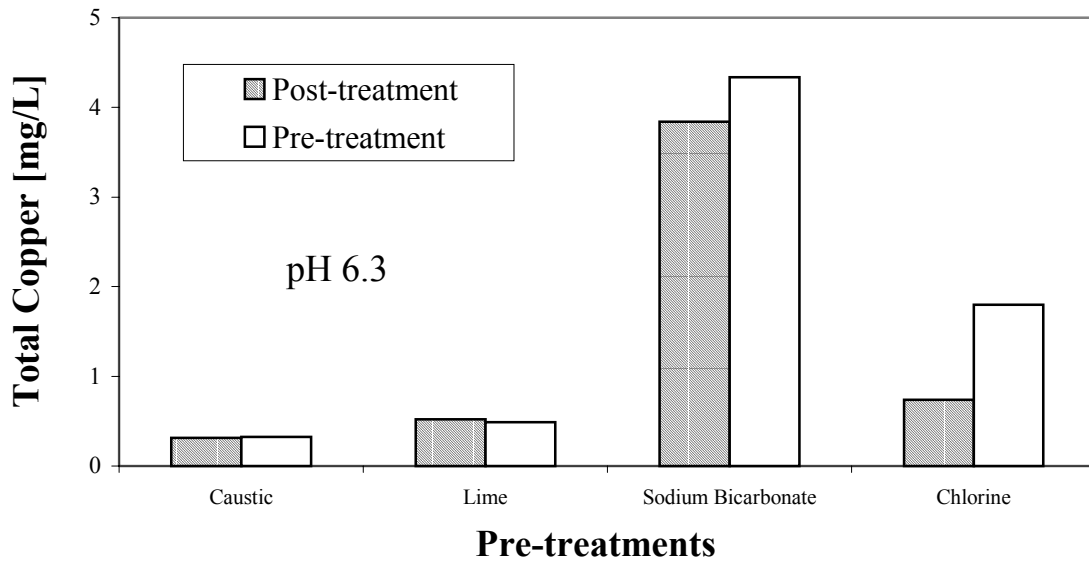
More than 87% of the copper by product release after one week was soluble. After one month, greater than 89% of the copper was soluble. However, after one month in the presence of sulfides, high concentrations of particulate copper were observed (Figure 4-6). This result might be why chemical pre-treatments did not help matters after prolonged sulfide attack. Even if soluble release was decreased, which is the goal of the pre-treatments, the problem is with the high concentrations of particulate copper.

## Acknowledgements

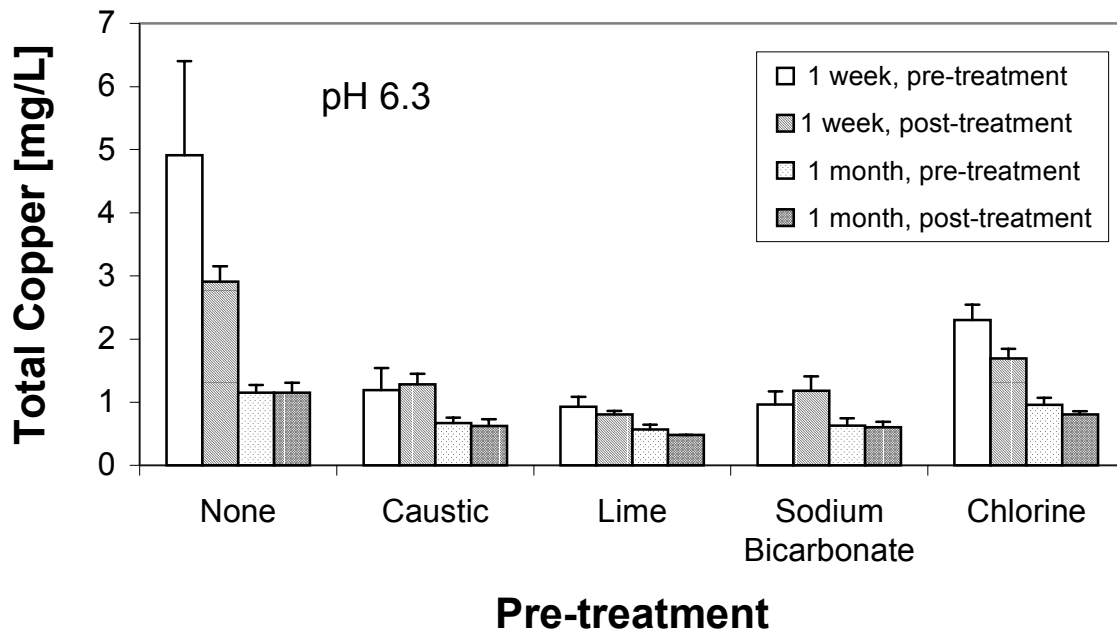
This work was funded by the Copper Development Association. The opinions, findings, and conclusions or recommendations are those of the authors and do not necessarily reflect the views of the Copper Development Association.

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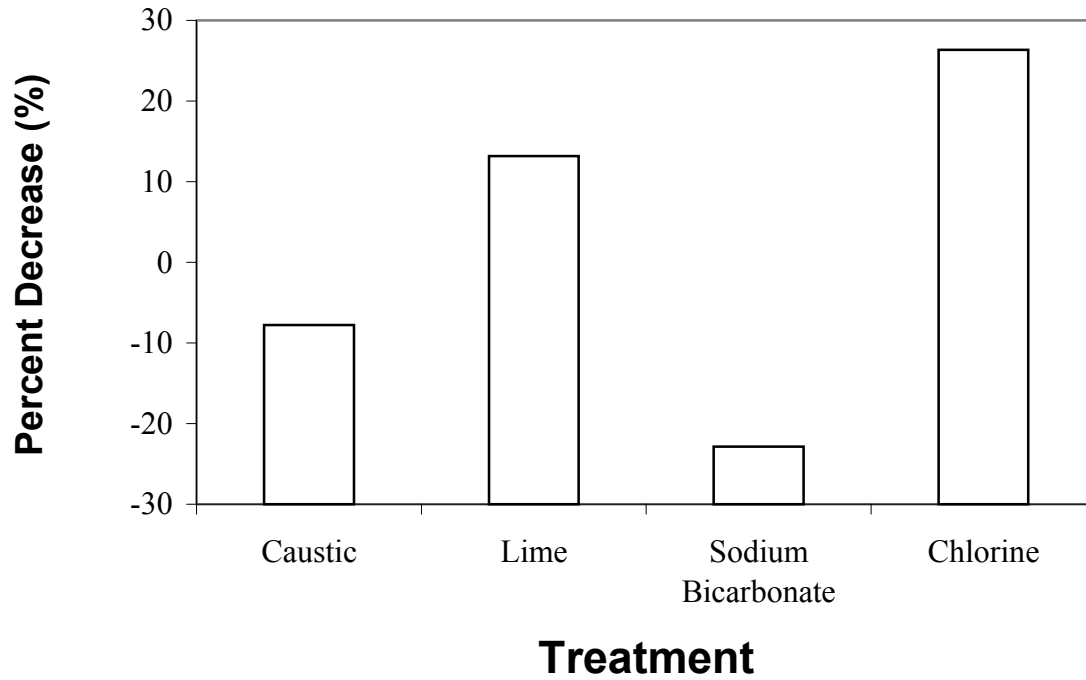
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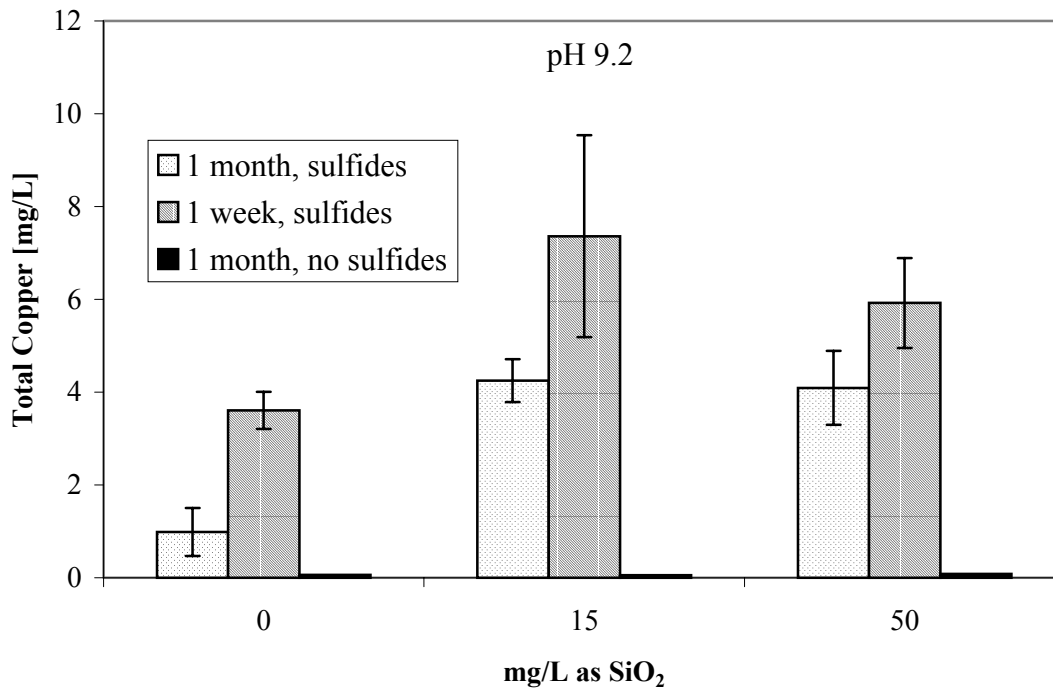
**Figure 4-1: Total copper concentration in waters produced during pipe treatment using mild chemical solutions.**



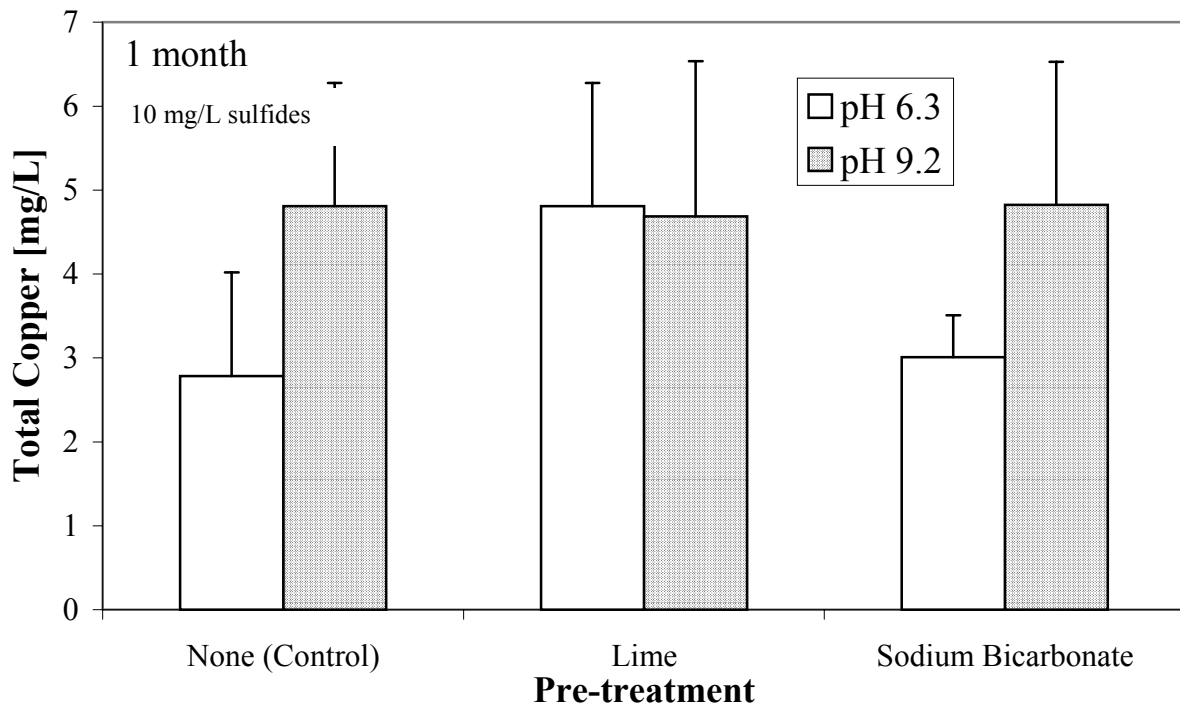
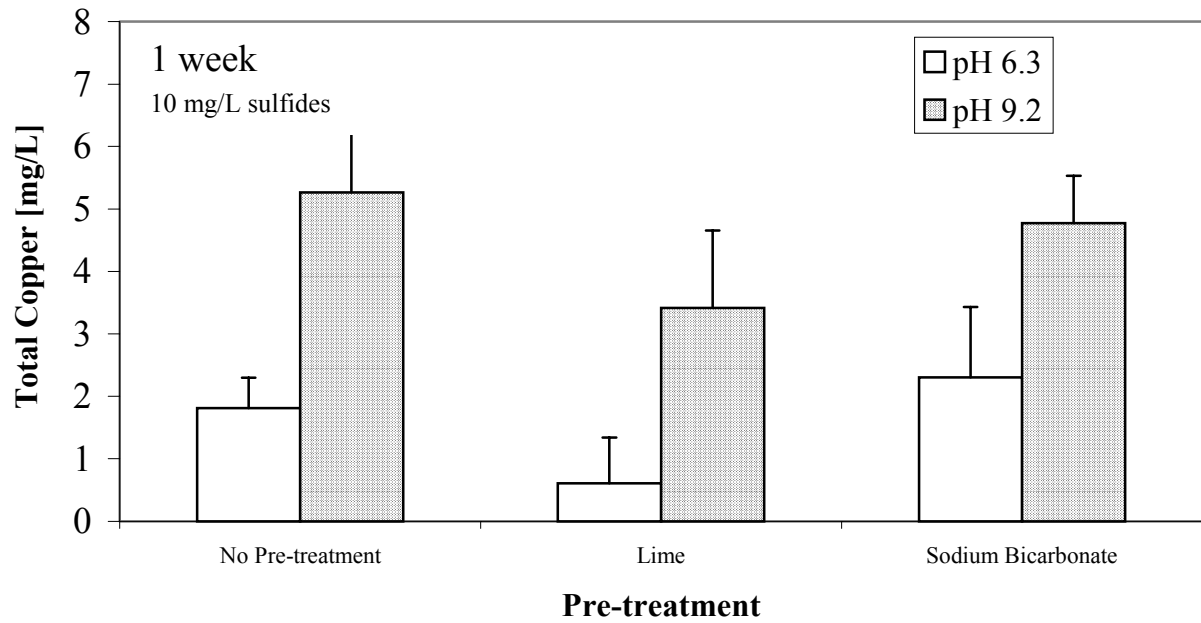
**Figure 4-2: Total copper release is plotted for different conditions when pipe is untreated (none), treated before exposure (pre-treatment), and after exposure (post-treatment). Error bars indicate 95% confidence on five replicate pipes.**



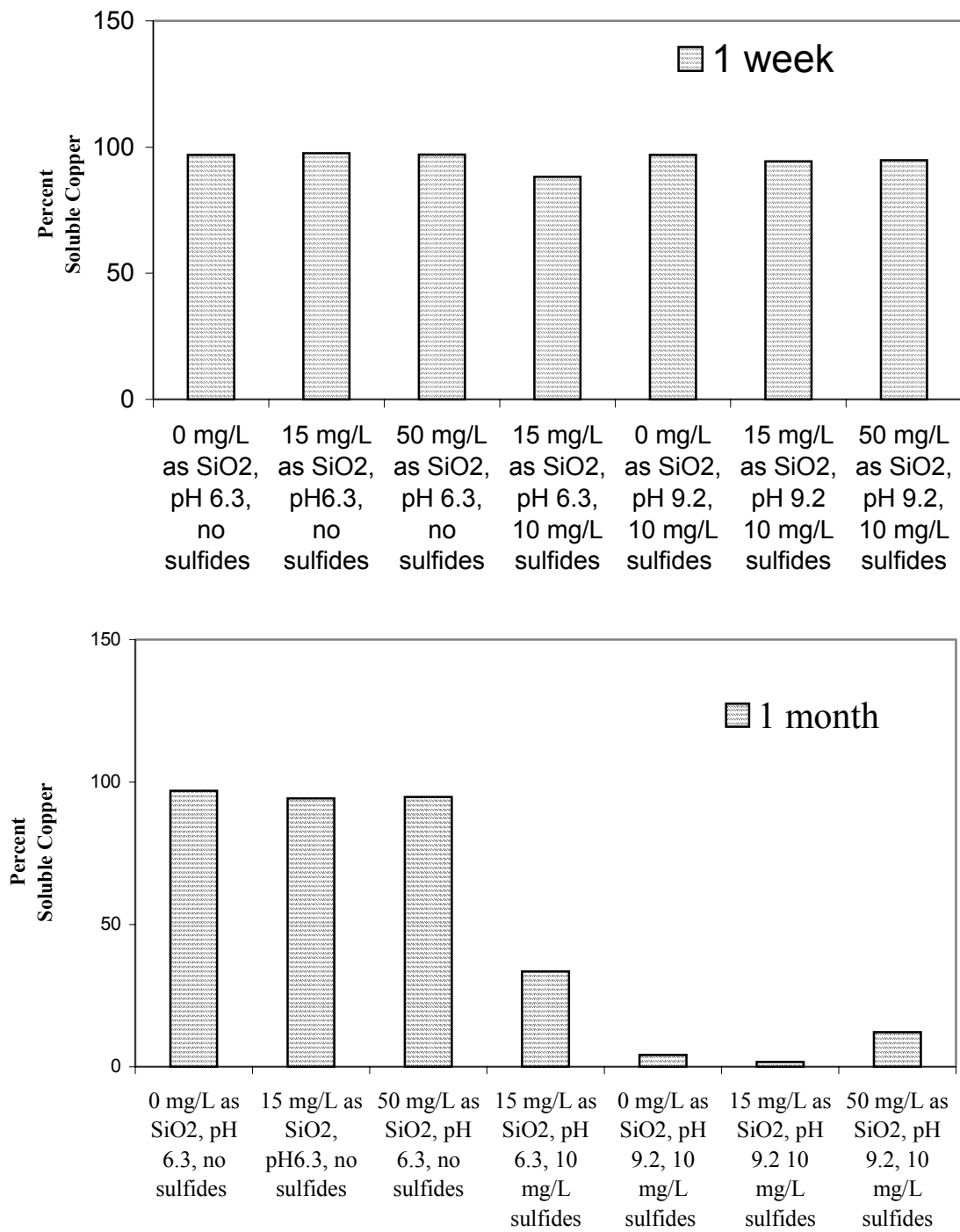
**Figure 4-3: Percent decrease in total copper release at pH 6.3 when pipes are treated after installation (post) versus before installation (pre).**



**Figure 4-4: Effects of silica on total copper release after one week and one month exposure to waters at pH 9.2, with and without sulfides**



**Figure 4-5: Pre-treatment versus total copper concentration after one week (above) and one month (below) in pipes containing 10 mg/L sulfides at pH 6.3 and pH 9.2.**



**Figure 4-6: Percent soluble copper after one week (above) and one month (below) of exposure to different waters containing varying concentrations of silica both with and without sulfides at pH 6.3 and pH 9.2.**



## KIMBERLY ALICE POWERS

### OBJECTIVE

*To contribute to society by planning and implementing solutions for an array of circumstances encountered in the management of our water resources.*

### EDUCATION

**Virginia Tech:** Masters in Environmental Engineering

graduated 12/2000 Cumulative *G.P.A.* 3.39

**University of Georgia:** Honors Program, Bachelor of Science in Environmental Health, graduated 6/1998 - Cumulative *G.P.A.* 3.86

### EXPERIENCE

**Research Assistant--Department of Civil Engineering, Virginia Tech, 5/1999-Present**

- ◆ Operation & Maintenance of the Malvern, Zeta Meter, Cupric electrode, pH probes
- ◆ Development of method for measuring copper, sulfate, phosphate, silica, and calcium on the Induced Coupled Plasma (ICP) and method for measuring chloride and nitrate on the Ion Chromatograph (IC)
- ◆ Responsible for the updated web page of Marc Edward's research group

**Teaching Assistant--Department of Civil Engineering, Virginia Tech, 8/1998-5/1999**

- ◆ Graded and tutored students in an Environmental Engineering course

**Biological Science Aide--Conservation Research Center, USDA, 6/1997-8/1997**

- ◆ Measured groundwater with a Time Domain Reflectometer (TDR)

**Intern--Department of Natural Resources, EPD NE Region GA, 4/1997-6/1997**

- ◆ Created risk assessment of compounds in river bodies of Georgia

**Whitewater Rafting Guide--Wildwater Ltd., Ocoee & Chattooga Rivers, 6/1994-6/1996**

- ◆ Navigated Class V whitewater and reacted quickly under pressure

### COMPUTER SKILLS

Software: Windows 98/00, Microsoft Excel, Word, Power Point, Mineql<sup>+</sup>, Geographic Information Systems (GIS)- ARC/INFO, ARCVIEW; Hardware: Global Positioning System (GPS), Scanner, Digitizer

## **HONORS**

**William R. Walker Graduate Research Fellow Award: Virginia Water Research Center for an exceptionally outstanding graduate student in water resources.** presented at the Virginia Water Research Symposium, 1/9/2001, Hotel Roanoke

Sussman Fellowship, 5/2000-9/2000

Representative for Civil Engineering in the Graduate Student Assembly, 9/1999-9/2000

Member of American Water Works Association, 8/1998-Present

Pratt Research Fellowship: Virginia Tech, 1998-1999

John J. Sheuring Scholarship: Georgia Environmental Health Association, 4/1998

Hope Scholarship: Georgia, 1996-1998

President of local chapter of National Honorary Society, 1997-1998

## **HOBBIES**

### **Whitewater Kayaker**

-1<sup>st</sup> Place, New River, April 2000, American Whitewater Association

-1<sup>st</sup> Place, Potomoc River, June 2000, National Organization of Whitewater Rodeos