

**FORMATION OF ALUMINUM CONTAINING SOLIDS IN DRINKING WATER:
INFLUENCE ON Pb/Cu CORROSION,
Al SOLUBILITY AND ENHANCED SOFTENING**

Steven Joseph Kvech

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Marc Edwards, Chair
Andrea Dietrich
William Knocke

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ABSTRACT

Aluminum salts are used as the primary coagulants in the majority of United States drinking water treatment plants. Despite decades of practical experience, there are important knowledge gaps regarding the effects of residual Al on distribution system materials as well as specific types of solids formed. The first phase of this work examined the formation of aluminosilicate deposits in copper and lead pipes using water from Denver, Colorado. It was anticipated that these deposits could form barrier films on the pipe, protecting it from corrosion. However, the deposits had slightly detrimental effects on leaching of metal to water, and higher levels of aluminosilicates could further worsen corrosion by-product release.

The second phase of work attempted to extend understanding of aluminum solubility controls by accounting for effects of sulfate and formation of solids other than $\text{Al}(\text{OH})_3$ during water treatment. Sulfate was found to destabilize small $\text{Al}(\text{OH})_3$ colloids resulting in agglomeration into larger flocs from pH 5.0-6.2. At pH 9.0 and above, Al-Mg, Al-Mg-Si and Al-Si solids were discovered to control Al solubility, while also having significant impacts on the precipitation of calcite in the presence of silica and overall softening effectiveness. This could be of considerable importance to water treatment practice. These solids also had some potential for removal of arsenic, TOC and boron.

DEDICATION

This thesis is dedicated to my family for encouraging me to pursue graduate education. If it weren't for this time of discovery, I'd have never learned to juggle.

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AUTHOR'S PREFACE

This work follows the Virginia Tech manuscript format. Chapter I is a complete manuscript scheduled to be published in *Journal American Waterworks Association*, August of 2001. Chapter II will be submitted for publication to *Journal of Water Supply: Research & Technology-AQUA*.

Chapter I is a case study for Denver Water, addressing the formation of aluminosilicate solids in a water treatment distribution system and their possible reduction in corrosion by-product release of copper and lead plumbing materials. Chapter II is an investigation into the fundamental chemistry and formation of aluminum based solids in aqueous solutions relevant to drinking water systems.

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Role of Aluminosilicate Deposits in Lead and Copper Corrosion

Steve Kvech and Marc Edwards
Department of Civil Engineering, 418 Durham Hall
Virginia Tech
Blacksburg, VA 24061-0246

Abstract

Aluminosilicates frequently deposit onto plumbing materials in distribution systems. It was previously believed that these solids might provide some degree of corrosion protection to pipes, at expense of increased headloss, reduced flow and consumer complaints related to post-precipitation. However, this work demonstrates that new copper and lead pipe sections did not benefit from deposition of aluminosilicate solids. Under most circumstances, in fact, the presence of solids actually caused the release of more metal to drinking water when compared to solutions without solids. Final pH played a key role in determining the extent of copper corrosion, and the aluminum deposits prevented increases in pH during stagnation through a buffering action.

Introduction

Control of distribution system pipe corrosion has long been a challenge for the water treatment industry. With regulations mandating lower levels of metals such as lead and copper in water at the tap, innovative strategies that might prevent metal release merit additional research. Although dosing of corrosion inhibiting chemicals is commonplace it is not always effective. Other practical mitigation strategies could benefit the water industry, especially techniques that did not require purchase of chemicals.

Precipitation of silica with aluminum hydroxide is a common phenomenon in water treatment (Brace and Matijevic, 1977). Coagulants such as alum are typically the source for aluminum in these solids, whereas the silica is naturally present in waters at 5-50

mg/L as SiO₂. The dominant form of silica is thought to be monosilicic acid, although colloidal silica and biological silica are sometimes thought to be present (Baylis, 1937). Because the aluminosilicate solids precipitate slowly, soluble aluminum and silica can pass through a treatment plant and “post-precipitate” in the distribution system. Alternatively, colloidal aluminosilicates can directly pass through treatment processes such as filters.

It is well known that aluminosilicates and other aluminum solids can coat plumbing materials (Costello, 1984; Hudson, 1966). For example, analysis of a pipe incrustation within a rural German water supply (Schöler et. al., 1990) showed that aluminum was a major component. During a pipe cleaning test of two large water mains in Green Bay, WI, an aluminum silicate buildup was found on the pipe interior walls (Shea, 1993). Very similar uniform deposits were discovered in distribution systems of Lexington, KY (Public Works, 1985), Onondaga County, NY (Fitch and McCollum, 1986), and Rochester, NY (Kriewall et. al., 1996). Additionally, thick aluminum-polyphosphate precipitates have been documented in Chicago, IL (Goldsborough, 2000; Schock, 1999). Additionally, in one study of a desalination process (Butt et. al., 1995), prevention of scale formation on membrane units was investigated. An anti-scaling compound actually hastened the formation of amorphous aluminosilicate type sludge within these units. In general, these aluminum deposits have been x-ray amorphous.

In all of the above studies, aluminum film formation was viewed as an aesthetic and operational nuisance because it led to increased head loss and consumer complaints. It was only recently investigators hypothesized that the films might mitigate corrosion by acting as barriers to diffusion (Lauer et. al., 1992; AWWA , 1999). This hypothesis finds support in the materials protection literature since a Japanese company recently patented a specific aluminosilicate metal coating for corrosion inhibition (Sumitomo Metal Industries, 1982). Other spray-on corrosion resistant coatings composed of palygorskite clay solution (an aluminum silicate based clay) are also in use (Lavrentev et. al., 1990). Other researchers have investigated aluminum based film attachment to certain metal alloys at high temperatures (Sarioglu et. al., 2000).

If the aluminosilicate compounds formed naturally in water distribution systems were proven to protect plumbing, their benefits might outweigh the well documented drawbacks and explain some of the variations in corrosion observed from system to system. It might even provide an alternative means of controlling corrosion, and cause utilities to be cautious when making water quality changes that impact soluble aluminum in water. This work, using water from a system in which such deposits are suspected to be an active agent in corrosion prevention, was designed to test the idea that deposited aluminosilicates protect lead and copper pipes.

Materials and Methods

In late March 1999, 55 gallons (208 liters) of finished water from Denver's Moffat Treatment Plant were shipped to Virginia Tech in a plastic drum. Another 20 gallon (76 liter) shipment in late May 1999 followed. Samples of powdered lime, fluoride, and liquid alum samples were also shipped along with about 500 mL (0.13 gal) of material that had deposited onto distribution system pipe walls. The finished water was stored at 22°C before use, whereas all other samples were stored at 4°C.

Type M and Type L ¾ inch (19mm) inner diameter copper pipes were cut into 12-inch sections (305 mm), soaked in 1M sodium hydroxide (NaOH) for about an hour to remove organic deposits, and then rinsed three times with distilled deionized water. Rubber stoppers were used to cap pipe ends during experiments. Pure lead pipes, ¾ inch (19mm) inner diameter, were cut into 6-inch (152 mm) sections and prepared in similar fashion to copper pipes. All pipes were air dried and carefully weighed before experiments began.

Sample Handling and Analysis:

Before use in experiments, solutions were stirred with magnetic teflon coated stirbars. All pH measurements were made with a portable pH meter and combination electrode.

UV-254 absorbance was measured using a spectrophotometer^{*} and total organic carbon (TOC) was measured using a bench-top TOC analyzer[†] as per Standard Methods #5310c (APHA, 1998). Samples collected for metals analysis were acidified with 2% by volume concentrated nitric acid, heat digested at 60°C (140°F) for 3 hours, then quantified on an ICP-ES[‡] (Inductively Coupled Emission Spectrometer). Zeta potential of particles was determined using a Zeta-Meter[§].

The distribution system deposit sample was examined by x-ray diffraction^{**} (XRD). Semi-quantitative elemental analysis was carried out by SEM^{††} (scanning electron microscope) with EDS^{‡‡} (energy dispersive spectrometry), the ICP-ES method described above, and ICP-MS^{§§} (Inductively Coupled Mass Spectrometer). Small strips were cut from copper pipes after experiment termination and analyzed by SEM as well. The ICP-ES and ICP-MS analyses were conducted after digesting the deposit samples with 5% by volume nitric acid instead of the 2% for other samples. Macroscopic pictures of the deposits and pipes were made using a camera equipped with a macro lens. Moisture content was determined using Standard Method #2540B.

Preparation of Solutions for Corrosion Testing:

Four different types of solutions were prepared for use in experiments to illustrate impacts of the aluminosilicates on corrosion (Figure 1-1). Ambient water was used as collected, and filtered ambient water was created by passing this solution through a type SM 5.0 µm pore size membrane filter^{***} and then a type HA 0.45 µm pore size membrane filter^{†††} in sequence. The filtrate was then placed in a clean 5 gallon (18.9 liter) carboy. Subsequent experiments examined the role of pH and different levels of spiked solids in

* DU640 Spectrophotometer, Beckman Instruments, Inc., Fullerton, CA

† DC-80, Tekmar-Dohrmann, Cincinnati, OH

‡ SpectroFlame Modula Tabletop ICP FTMOA85, Spectro Instruments, Fitchburg, MA

§ Zeta Meter 3.0+, Zeta Meter Inc., Staunton, VA

** Series 2000 XRD, Scintag, Sunnyvale, CA

†† Series 2 SEM, CamScan, Cranberry Township, PA

‡‡ Quantum System 4000 EDS, American Nuclear Systems, Knoxville, TN

§§ ELAN 6000, Perkin Elmer, Toronto, Canada

*** Millipore Corporation, Bedford, MA

††† Millipore Corporation, Bedford, MA

copper and lead corrosion by-product release. “Spiked solids” samples were created by first dispersing distribution system deposits in a volume of reagent grade water, and then spiking the solids into filtered ambient water (Figure 1-1). pH was held constant in these samples as specified. Because a portion of these spiked solids might be expected to dissolved during holding, especially at lower pHs, a “dissolved solids” sample was produced by passing an aliquot of the “spiked solids” solution through a 0.45 μm pore size filter.

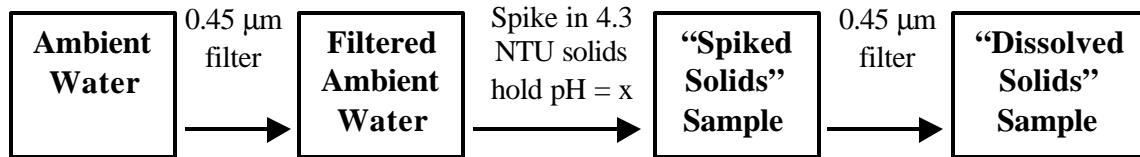


Figure 1-1) Preparation of solutions for testing

Pipe Exposure Protocols:

The first experiment was designed to compare copper and lead corrosion by-product release in ambient water and filtered ambient water. The general approach was to adjust 500 mL batches of each solution to pH 8.0 +/-0.05 with 0.5 M NaOH. After allowing the solution to stir for several minutes, the solution was poured into the lead and copper pipes closed on each end with a rubber stopper. Pipes rested lengthwise on the lab bench during stagnation and lab temperature was 23 +/-2°C (73 +/- 3.6°F). Pipes were emptied and then refilled with fresh solution every Monday, Wednesday and Friday, giving regular 2, 2 and 3 day weekly stagnation periods. At predetermined times, samples were collected from the pipes for metals analysis after a 48 hour (2 day) stagnation time. On occasion, the pH of the water was determined after stagnation.

The second experiment was designed to test the effects of differing concentrations of spiked solids at pH 8.0. A standard solution containing an equivalent 3.305 g/L dry solids of distribution system particles was obtained by diluting a small volume of deposited solids 1:100 with reagent grade water and mixing rapidly to suspend the

particles. This standard solution was then dosed to filtered Moffat water and turbidity was measured in NTU (nephelometric turbidity units) with a turbidimeter*. All solutions were carefully adjusted to pH 8.0 +/- 0.05. Thereafter, new copper and lead pipes were exposed and sampled as described in the first experiment.

The third and final experiment was designed to examine the interplay between pH, the spiked aluminosilicate solids, and copper corrosion by-product release. Three sets of solutions were tested, including all samples except for ambient water as described in Figure 1-1. The first solution sets were prepared from filtered ambient water, with adjustment to target pH values of 5.0, 6.0, 7.0, 8.0 or 9.0 with 1 M NaOH or HNO₃. A second set of samples were prepared by spiking the filtered ambient water with 15 mg/L distribution system solids (dry weight) to a final turbidity of 4.3 NTU, and then holding the pH at target values for 24 hours before use in experiments. This solution contains the constituents in the filtered ambient water, the spiked solids, plus the fraction of the solids that dissolved after pH adjustment and holding. The final set of “dissolved solids” solutions was prepared by filtering the “spiked solids” samples through a 0.45 µm pore size nylon disposable syringe filter†. In this manner, 15 samples were prepared for exposure to copper pipe as described previously (5 pH values x 3 sets of samples at each pH).

Results and Discussion

Initially, operating data from the Moffat Water Treatment Plant was reviewed and the composition of deposited solids from inside the distribution system was carefully determined. Thereafter, pipe experiments with finished water were executed to see the general effects of suspended particulate matter on copper and lead corrosion. In the final phase of work, the mechanistic impacts of aluminosilicate solids on corrosion were examined.

* 2100N turbidimeter, Hach Company, Loveland, CO

† Life Science Products Inc., Denver, CO

Background and Characteristics of the Solids:

Historical data, available as far back as 1994, was reviewed for key water quality constituents relevant to this study (Table 1-1). Effluent aluminum residuals have typically remained low at an average of 0.01 mg/L, but on occasion levels up to 20 times higher have been observed. The pH of the water is typically increased during treatment for corrosion control. Samples of fluoride and lime used at the plant were analyzed by ICP-ES and ICP-MS and found to contain negligible amounts of silica and aluminum. In addition, alum contained negligible values of silica. Thus, as expected, the most likely source of effluent aluminum is alum carryover and the silica that is naturally present in the raw water.

Table 1-1) Moffat plant raw and finished water characteristics from 1994 to 1999

measure	raw water temp degrees C	raw water pH	final pH	Alum dose mg/L as alum	total alkalinity mg/L as CaCO ₃	Al residual mg/L	effluent Mg mg/L	effluent SiO ₂ mg/L
average	11	7.53	7.85	31	24.9	0.01	2.37	7.2
maximum	17	8.08	9.20	42	37.0	0.23	4.20	9.3
minimum	0	6.80	7.29	18	5.0	0.00	1.10	5.9
std. deviation	3.30	0.19	0.13	5.67	6.48	0.02	0.78	1.31

Detailed analysis of deposited solids collected from inside a 96 inch (2.44 m) water main revealed important information about its physical and chemical properties. When wet, the sample had a uniform brown color, a paste-like consistency with some small gritty granules and a density of 1.22 g/cm³ (76.2 lb/ft³) (Figure 1-2). On average the sample contained 70% water by weight when dried at 104°C (219.2°F) for 24 hours, and 73% water by weight when dried at 220°C and 180°C for 1 or 24 hours. X-ray diffraction tests confirmed that the material was completely amorphous. This was not unexpected given the earlier literature review. SEM analysis (detecting elements of atomic number greater than sodium) semi-quantitatively illustrated that the elemental composition was mostly aluminum, followed by significant levels of silicon and a trace of calcium.



Figure 1-2) Sample of deposited solids from Denver distribution system

Combined quantitative data from ICP-ES, ICP-MS and TOC in digested samples allowed unambiguous identification of more than 82% of the solid weight (Figure 1-3). Using reasonable assumptions as to the compounds that are most likely present, approximately 96% of the deposit's weight would be accounted for (Figure 1-3). The high concentrations of aluminum hydroxide suggest that aluminum is precipitating in the distribution system with co-precipitation of silica. The presence of trace calcium in the deposits, somewhat unexpected in the soft water, probably resulted from colloidal solids produced when lime was added prior to filtration at the treatment plant.

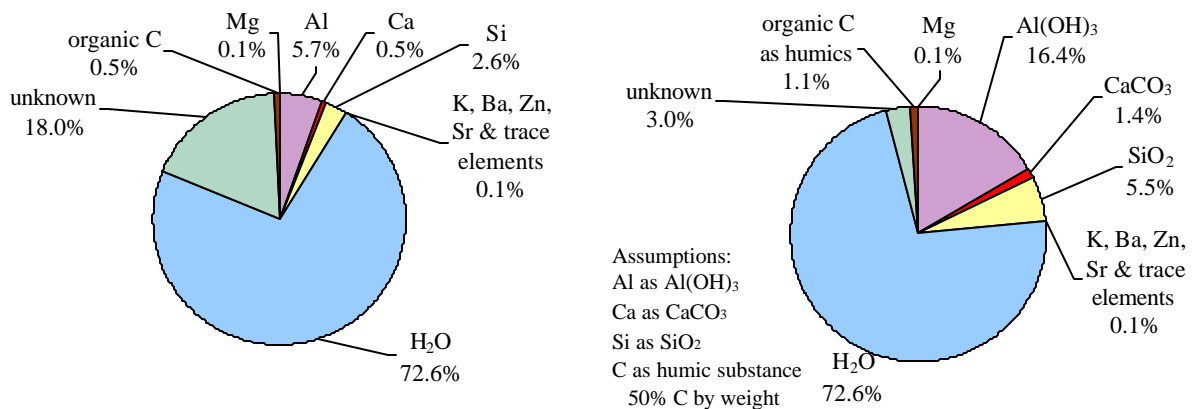


Figure 1-3) Solids composition determined by ICP-ES, ICP-MS and TOC analysis, original data (left) with compound assumptions (right).

Effects of Ambient Solids on Lead and Copper Corrosion:

The first 55 gallon (208 liter) shipment of unaltered Moffat finished water had a turbidity of about 0.15 NTU. After filtration the turbidity was reduced to 0.07 NTU. Though the differences in turbidity seem slight, a brown deposit was easily observed on the filters after passing only 2 liters of water (Figure 1-4). As the water aged during the experiment, it seemed that more of the particulate matter was removed by the 5.0 μm filter as would be the case if particles were gradually growing in size during storage. Analysis of the larger particles captured on the membrane filters by SEM suggested that they were similar to those collected from the distribution system pipe wall.

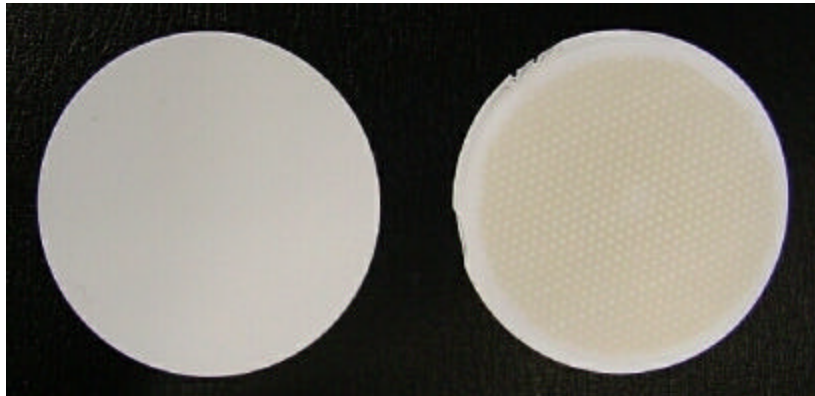


Figure 1-4) Unused filter (left), aluminosilicate solids (right)

Six lead and six copper pipes were exposed to ambient Moffat water (0.15 NTU) or filtered Moffat water (0.07 NTU) for 14 weeks. During the first week, release of corrosion by-products was very high from pure lead pipes as is expected (Figure 1-5). This continued through the second week, but by-product release eventually decreased to a relatively stable level. Copper release remained stable throughout the experiment. Ambient particles had a slight detrimental effect on release (85% confidence) as determined using a paired t-test on the data set. There was no significant difference in lead release (Figure 1-5). It is clear that the aluminosilicate solids did not aid in reducing levels of corrosion by-products over the short term (14 weeks), and could be detrimental. One caveat to this conclusion is that aluminum levels in both unfiltered and filtered

Moffat water were fairly low (< 0.01 mg/L). At these levels, deposits that could provide a significant barrier to corrosion might take a long time to accumulate. Consequently, a new phase of experiments with higher levels of solids was initiated.

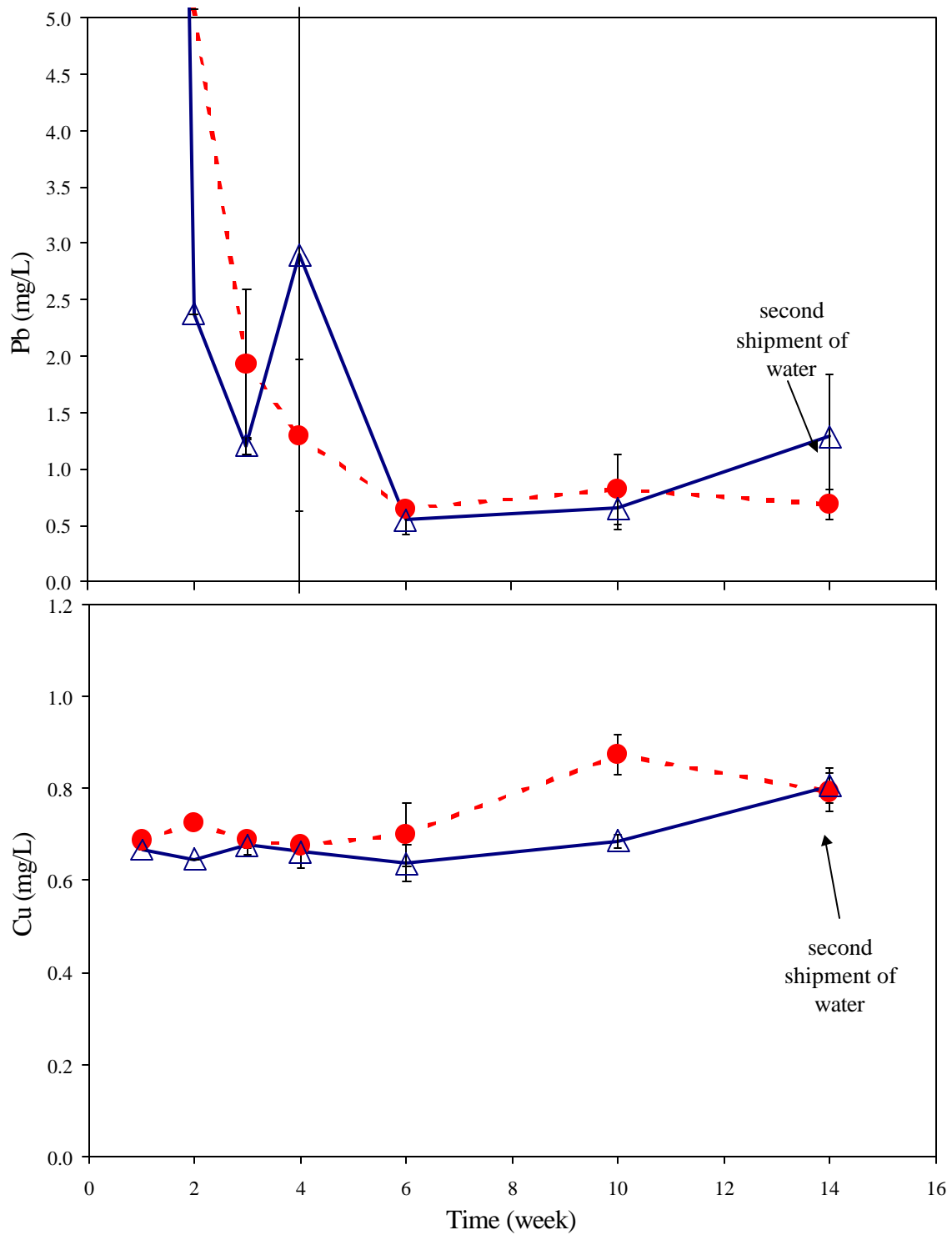


Figure 1-5) Experiment 1 lead and copper release over time. Initial pH = 8.0. Error bars indicate 95% confidence interval.

Effects of Solids Concentration on Lead and Copper Corrosion:

To test whether the previous results arose from inadequate film formation, a 1:100 dilution of the solid pipe deposits were spiked to the filtered Moffat water at varied levels to give a range of solids concentrations. The resulting solutions had turbidities of 0.04, 0.1, 0.2, 0.5, 1.5 and 5.0 NTU. The experiment was conducted with one lead and one copper pipe at each condition. Experimental data from weeks 2 through 14 were compared using a paired two sample t-test for means as well as conventional confidence intervals for replicate samples.

As before, the added solids did not benefit either lead or copper corrosion. In fact, above about 1.5 NTU, the solids caused higher metal release (99% confidence) for both copper and lead when compared to the lowest levels of solids using a t-test (Figure 1-6). There is also a linear relationship between released lead and copper versus spiked turbidity. For each additional 1 NTU of turbidity due to solids, lead and copper release increased 0.34 and 0.27 mg/L respectively (Figure 1-6).

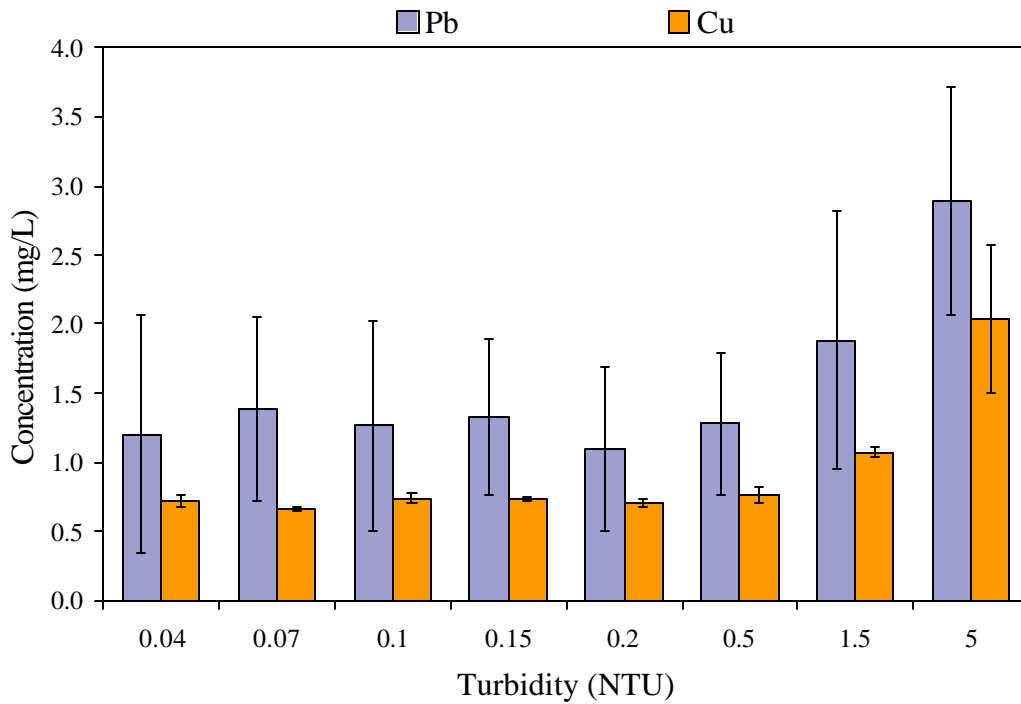
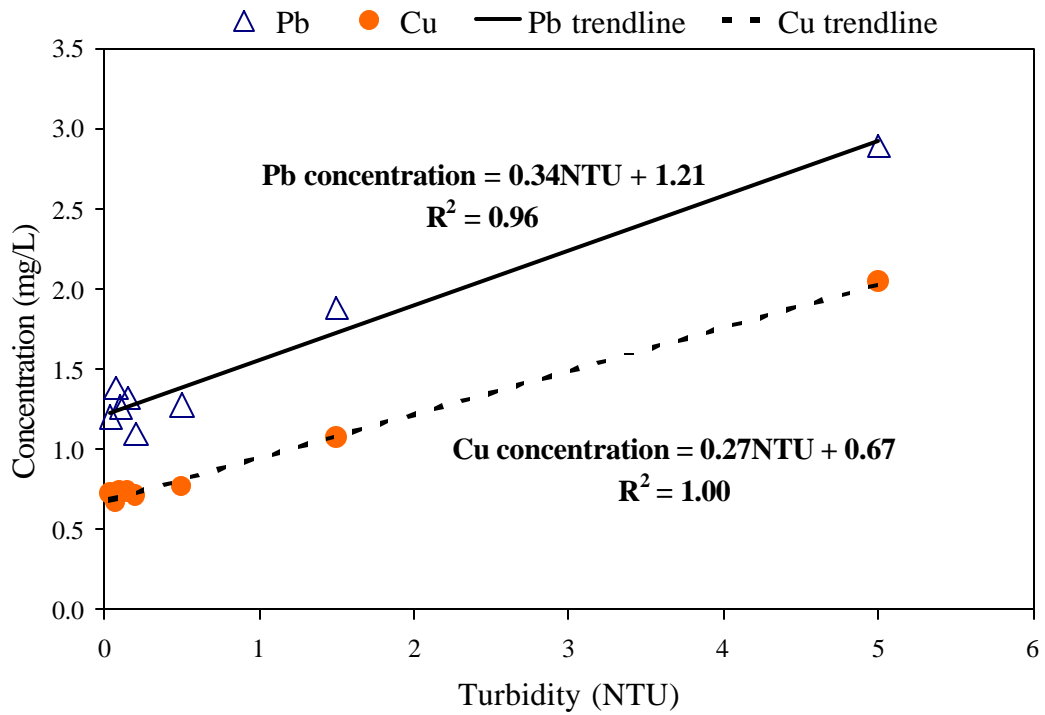


Figure 1-6) Effect of solids level on lead and copper corrosion by-product release weeks 2-14. Initial pH = 8.0. Error bars indicate 95% confidence interval.

Aluminum sorption from the water to the pipes was similar for both lead and copper (Figure 1-7); however the lead pipes sorbed significantly more silicon than their copper counterparts. This trend was also observed in the first experiment. It also seems consistent with other experiments in the literature where naturally occurring silica at 20 mg/L SiO₂, pH 8.2 and low alkalinity slowly sorbed to lead pipes, but in that case the silicon actually reduced lead corrosion over 8 to 9 months (Sorg and Bell, 1986).

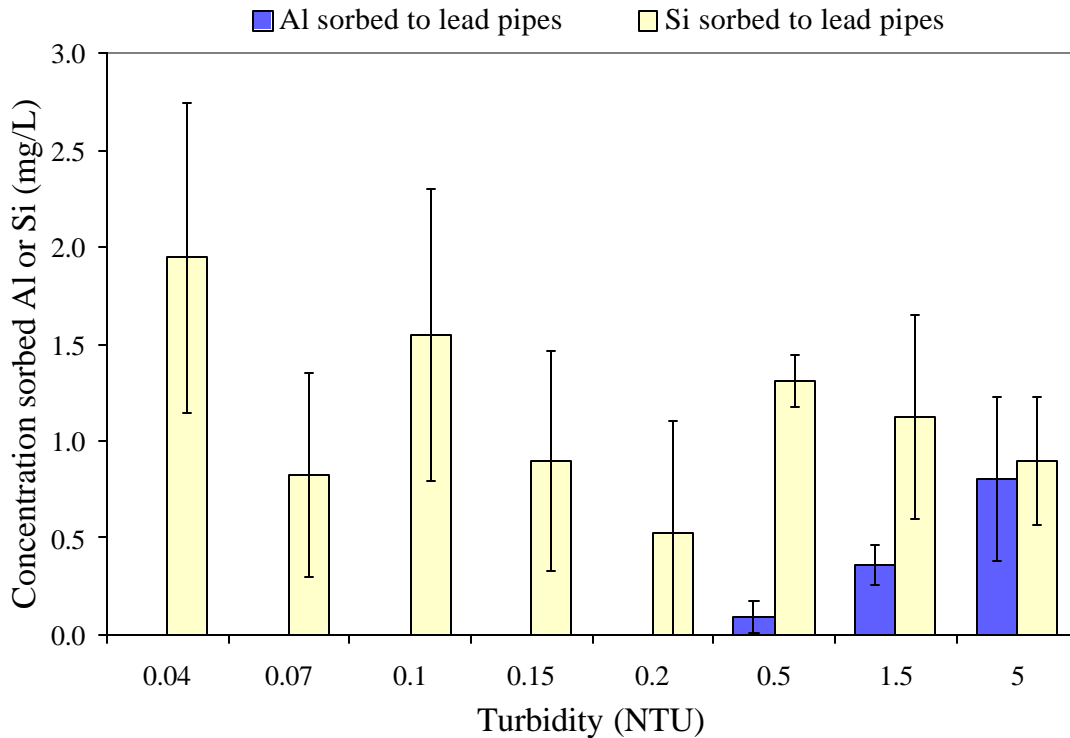


Figure 1-7) Al & Si sorbed in lead pipes based on solids in water weeks 2-14. Al results were similar for copper pipes. Error bars indicate 95% confidence interval.

Of particular interest is that the added solids seemed to have similar effects as the ambient solids in the earlier experiments. At the end of the study, all pipes were cut open and examined visually. Copper pipes exposed to higher concentrations of spiked solids had developed a blue-green scale layer (Figure 1-8 and Appendix A). Subsequent analysis of the surface film with SEM/EDS demonstrated that the outer film was more than 70% aluminum and silica in spots (for elements with atomic weight above 23), although small areas of the pipe without this coating could also be detected. Even though

a thin layer of deposit had built up on the pipe surface, lead pipes showed no visually detectable differences in scale layer morphology at different solids concentrations. Changes in pipe weights due to scale buildup and corrosion were negligible during the few months of the experiment.

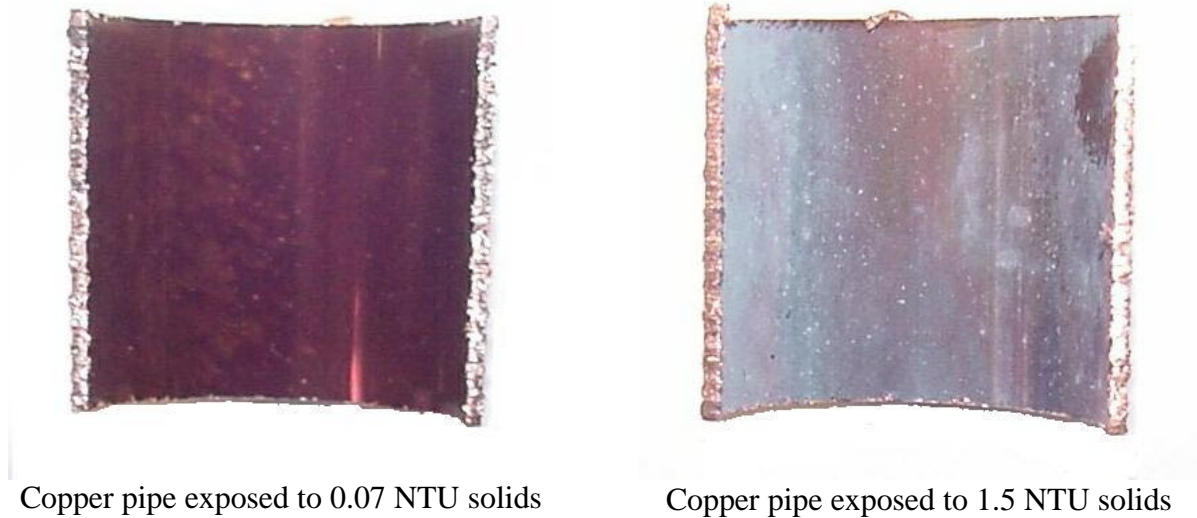


Figure 1-8) Visual effect of high solids on copper pipe scale after 14 weeks of exposure

Mechanistic Effect of Particulate and Soluble Material on Corrosion:

Several questions remained. First and foremost, would the observed detriments occur only at pH 8.0, or would expected benefits be obtained if the solids were spiked to the water at lower pH? Are the significant effects due to the added particulate matter, or is a portion of the added solids dissolving and impacting corrosion? Finally, what physical and chemical properties, if any, seem to be driving the interaction of aluminum silicon solids with copper piping? The final experiment was designed to answer these questions.

Only copper pipes were used in this study because of the number of pipes involved, and the similarities observed between copper and lead in the preceding experiments. As described in the methods section, three water samples were tested including: filtered

water, filtered water spiked with solids, and a dissolved solids sample (Figure 1-1). Five levels of pH from 5-9 were tested as influent to the pipes.

As might be expected, the three prepared sets of solutions differed considerably with respect to particle surface charge, dissolved natural organic matter and levels of soluble silicon and aluminum (Figure 1-9). All of these factors might have an impact on copper corrosion (Rehring and Edwards, 1996). The major difference was that the sample with spiked solids had higher concentrations of aluminum and silica than the filtered sample or the dissolved solids sample, consistent with high concentrations of particulate aluminum and silica. Moreover, at low pH, the dissolved solids sample had more soluble aluminum and soluble silica than did the filtered sample. Naturally, zeta potential could only be determined for the solution with the solids spike present. The solids had a point of zero charge near pH 6.0.

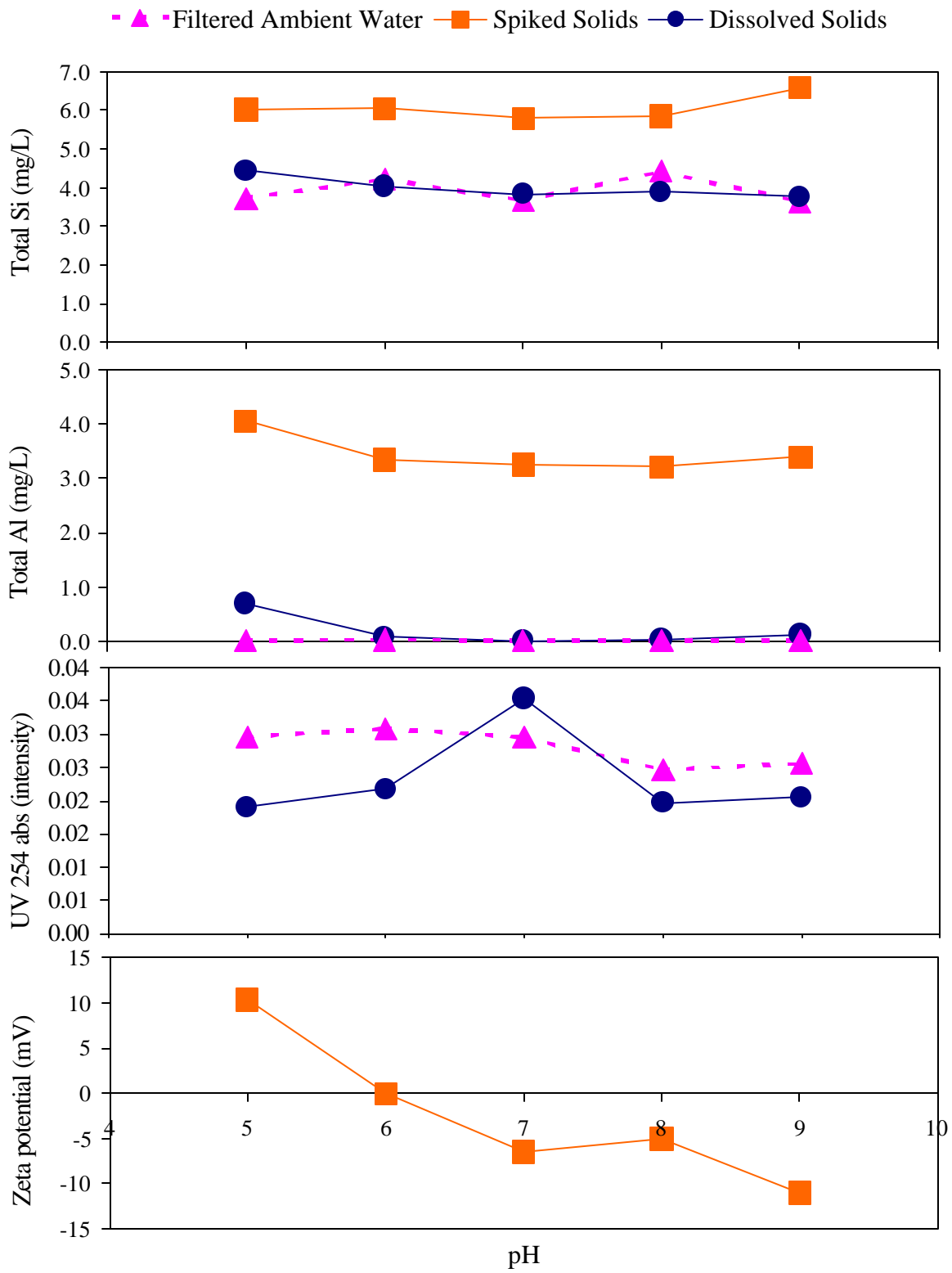


Figure 1-9) Initial characteristics of Experiment 3 solutions

When these waters were placed into copper pipes, similar patterns of copper release occurred in the sample with spiked solids and dissolved solids below neutral pH (Figure 1-10). Overall, the solutions with spiked solids and dissolved solids increased copper release at pH 5 and 6, but significantly decreased release at pH 7.0. At pH 8 and 9, however, the dissolved solids and filtered water sample behaved similarly. These trends indicate that the portion of the spiked solids that dissolved in the water worsened copper corrosion at pH less than 7.0, while at pH 8 and 9 the added particulate matter was the cause of higher copper release.

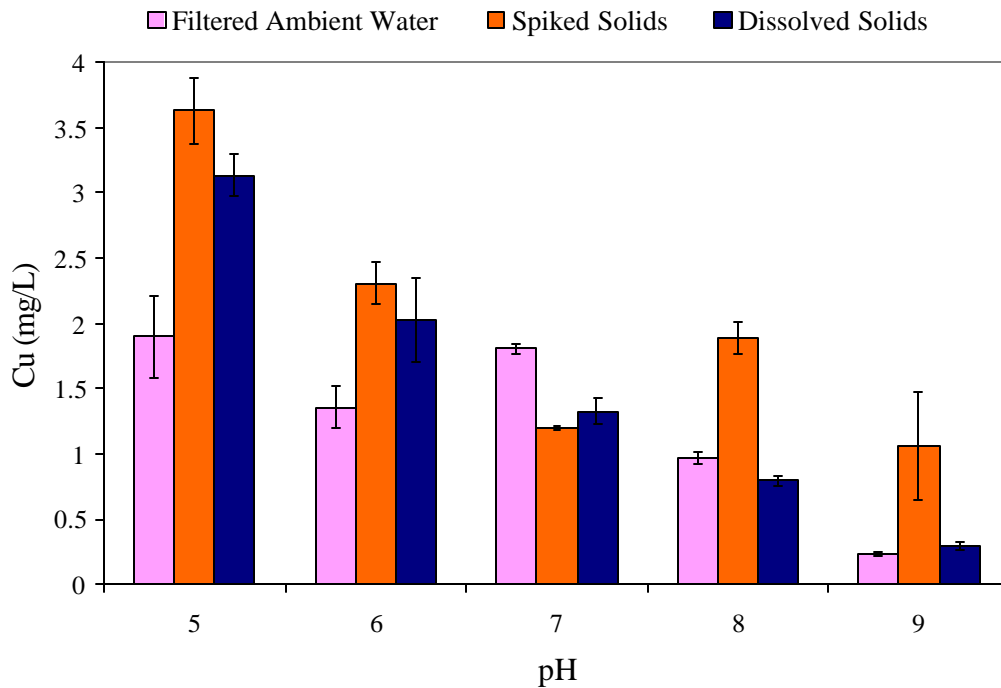


Figure 1-10) Week 13 comparison of solids versus soluble fraction.

What fraction of the dissolved solids might be causing detrimental effects at pH below 7.0? One possibility is differences in dissolved organic carbon (DOC). As indicated by differences in UV-254, 20-30% of the organic matter was removed from solution by spiking the solids. If organic matter was detrimental, as is currently believed for most cases of copper corrosion by-product release it would be expected that copper release

should decrease compared to the ambient filtered water (Edwards et al., 1999). This did not occur, so it seems likely that the differences in NOM were not responsible. More important, perhaps, is the impact of spiked solids on the final pH after stagnation in the pipes. That is, even though the waters had the same pH when put into the pipe, measurements of pH after stagnation revealed that solutions spiked with solids were consistently 0.5 pH units lower than in samples without spiked solids. A plot of copper release versus final pH in the pipes suggests that this effect is probably dominant (Figure 1-11). It is uncertain why this occurs, but it is clear that the dissolved fraction of the spiked solids was preventing beneficial increases in pH within the pipe during stagnation. There were interesting visual differences in pipe scale at each condition which also illustrate the significance of aluminosilicates (Appendix B).

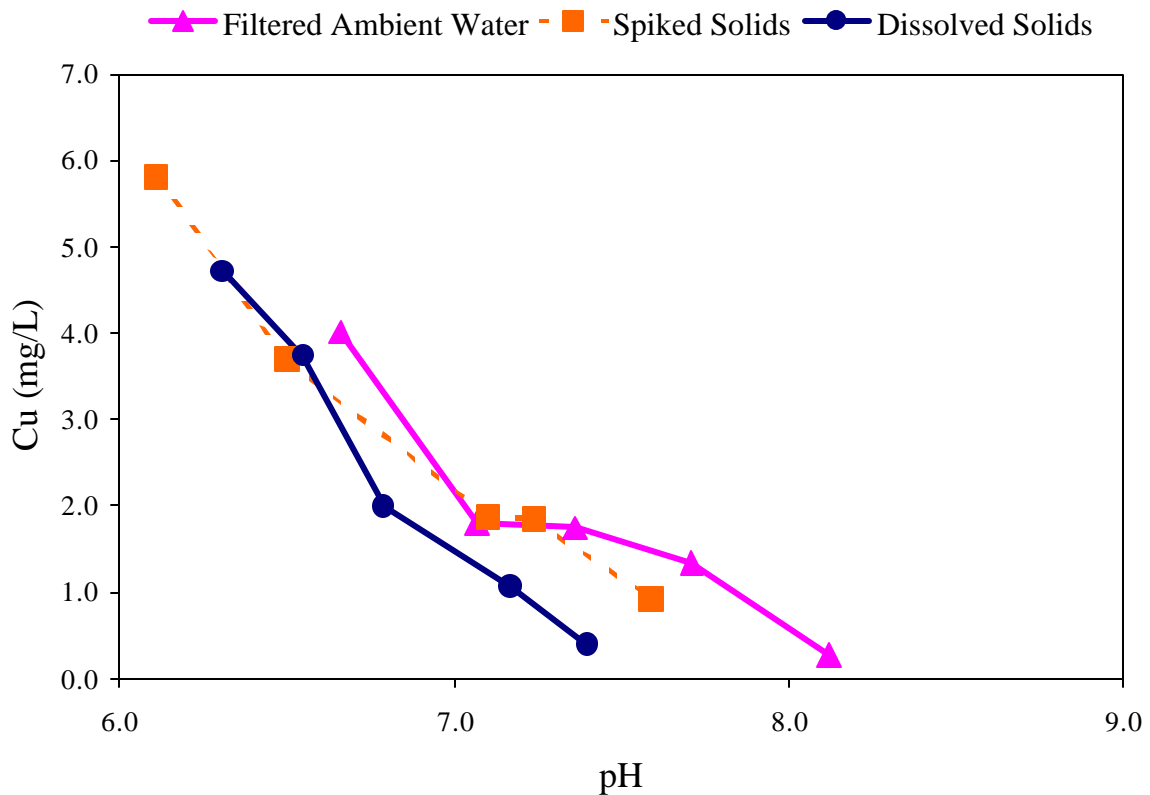


Figure 1-11) Copper release versus final stagnation pH. Week 8 data.

The Literature Revisited:

In general, only adverse effects could be attributed to aluminosilicate solids for lead and copper corrosion by-product release. The only exception was at pH 7.0, where spiked solids significantly improved copper corrosion by-product release. Thus, the expectation that these solids would only benefit corrosion was not realized.

Some caveats to this conclusion are necessary. First, as noted earlier, the experiments were relatively short term, and it is possible that thicker deposits would prove beneficial. Moreover, even though the Denver water tested was a basis for the hypothesis that aluminosilicate deposits were beneficial (Lauer et. al., 1992) it is possible that “good” deposits might form under other circumstances, whereas “bad” deposits formed in the laboratory study for reasons unbeknownst to us at this time.

However, a re-examination of the literature is instructive. The previous study of the Denver system, which strongly suggested that aluminosilicate deposits were beneficial, started with the assumption that the water should be highly corrosive given its low hardness and resulting negative Langelier index (Lauer et. al., 1992). Because the water did not cause anticipated problems with lead and copper release, a search was made for possible explanations, and the deposited aluminosilicates emerged as a likely explanation. Since the time of that study, however, the “Langelier index” approach has been proven invalid for predicting the corrosivity of a water in relation to lead and copper corrosion (Edwards et. al., 1996; AWWA, 1996). Thus, the question arises as to whether this water was unusually non-corrosive, or whether it is just typical of waters with similar pH and alkalinity.

Our analysis suggests that it is just typical. For instance, the average reported 90th percentile copper value was 0.36 mg/L and that for lead was 0.012 mg/L in the Denver system. A 1995 survey (Dodrill, 1995) demonstrates that for similar systems producing water with a pH range of 7.81-8.40 and alkalinity between 0-29 mg/L as CaCO₃, the median level of 90th percentile copper was 0.21 mg/L and the median level of 90th percentile lead was 0.013 mg/L. Thus, the observed levels of copper and lead are not

unusually low at Denver compared to other utilities, and given the benefits of 20:20 hindsight there are no unusual benefits to attribute to deposited aluminosilicate solids. In summation, while the basic hypothesis remains sound, there is not strong evidence in the literature that clearly shows benefits from the particles. In fact, most recent work demonstrates that particulates in water cause increased Pb and Cu release, as was observed herein (Boulay and Edwards, 2000; DeMora et. al., 1987; Hulsmann, 1990). On the other hand, the results obtained at pH 7.0 for copper in this work suggest that benefits might be obtained under at least some circumstances.

Conclusions

Contrary to expectations, aluminosilicate solids did not always protect copper and lead plumbing materials. Indeed, most observed impacts were detrimental, and minor benefits were only noted at neutral pH for copper pipe. The solids did buffer against pH changes, but in waters initially at low pH this effect was also detrimental. At high pH, the particulate matter caused higher levels of copper and lead release, although the detriments are not significant at typical levels of turbidity commonly encountered in water distribution systems.

Acknowledgement

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CHAPTER II

Formation of Al-Mg Containing Solids in Water Treatment: Implications for Control of Effluent Al, Removal of Contaminants and Enhanced Softening

Steve Kvech

Marc Edwards

Department of Civil/Environmental Engineering,
418 Durham Hall
Virginia Tech
Blacksburg, VA 24061-0246

Abstract

Potential control of aluminum solubility in water by solids other than $\text{Al}(\text{OH})_3$ was examined at pH values below 6.0 and above 8.5. At pH below 6.0 the presence of sulfate increased the size of $\text{Al}(\text{OH})_3$ colloids; however, $\text{Al}(\text{OH})_3$ solids were still dominant in the presence of sulfate, silica or potassium. At higher pH values, aluminum and magnesium were discovered to form a new solid phase with the approximate formula $\text{Al}_2\text{Mg}(\text{OH})_7$. When silica was also present in these systems, data suggest different solids formed with the approximate formulas $\text{Al}_2\text{MgSiO}_2(\text{OH})_7$ or $\text{Al}(\text{SiO}_2)_2(\text{OH})_3$. Silica interfered with calcium removal by softening, and added Al reduced this interference. It is possible that Al added during softening can enhance removal of other contaminants by removing silica or by forming new sorbents in-situ.

Introduction

Aluminum coagulants have come under scrutiny in recent years due to concerns about metal residuals in the public water supply. In response, the USEPA has established a secondary drinking water regulation (SDWR) of 0.05-0.2 mg/L aluminum for aesthetic reasons. Canada has introduced operational guidance values from 0.1 to 0.2 mg/L

aluminum (Health Canada 1999), the World Health Organization suggests 0.2 mg/L maximum Al (World Health Organization 1998), and California currently has a state maximum contaminant level (MCL) of 1.0 mg/L (California DHS 2000). There are also lingering concerns about conditions such as Alzheimer’s disease, which may be linked to aluminum ingestion, although recent reviews suggest this is unfounded (Reiber et. al. 1995).

It is generally accepted that Al(OH)₃ solids control the concentration of soluble aluminum in drinking water (Jekel 1989). However, a review of the literature suggests that other solids might be important (Table 2-1). With the introduction of enhanced coagulation to increase disinfectant by-product (DBP) precursor removal from raw water, more coagulant is now being added to water and at lower pH values. Additionally, some plants are considering alum addition as a coagulant aid in softening processes to improve settling, reduce effluent turbidity and enhance DBP precursor removal (Shorney et. al.1999). Assumption of Al(OH)₃ solubility control predicts that aluminum would be completely soluble during softening above pH 9.0, although this is obviously not true in practice. In addition, some researchers have noted increased magnesium precipitation when supplemental Al coagulants are used even though the pH is shifted below that necessary to form Mg(OH)₂ solubility control (Shorney et. al. 1999; Baylis 1937). To better understand these issues, this work explicitly examined potential formation of Al containing solids other than Al(OH)₃ in laboratory scale experiments.

Table 2-1) Al and Mg containing solids which could be important in water treatment

Candidate solid	Formula	Predicted pH range	Reference
alumino-silicate	Al _x Si _y (OH) _z	< 6.0, > 9.0	(Brace & Matijevic 1977)
alunite	KAl ₃ (SO ₄) ₂ (OH) ₆	< 6.0	(Nordstrom 1981)
basaluminat	Al ₄ (OH) ₁₀ SO ₄ * 5H ₂ O	< 6.0	(Nordstrom 1981)
amorphous aluminum hydroxide	Al(OH) ₃	< 5.8	(Letterman & Vanderbrook 1983)
palygorskite/sepiolite	(Mg,Al) ₂ Si ₄ O ₁₀ (OH) _x * 4H ₂ O	?	(Nickel & Nichols 1991)
magnesium silicate	Mg _x -Si _y -(OH) _z	> 9.0	-

Two groups of experiments were conducted based on the pH range where solids are likely to form. The low pH (4.7-6.2) experiments examined the impact of sulfate, silica and potassium on aluminum solubility. High pH (9.0 and above) experiments mainly investigated potential formation of solids containing aluminum, magnesium and silica. To the extent that new solids were identified, the work also conducted a preliminary assessment of their ability to remove contaminants and otherwise improve treatment.

Materials and Methods

Unless otherwise stated, fresh solutions of 0.01 M NaNO₃ were prepared using distilled-deionized water exceeding 18 MΩ resistivity in 500 mL plastic (high-density polyethylene) bottles. Stock solutions of various ions were prepared from reagent grade chemicals as either Na⁺ or NO₃⁻ salts. The stock solutions or salts were spiked to solutions along with a predetermined dose of 1M HNO₃ or 1M NaOH to achieve a targeted initial pH for reactions. The pH was maintained to +/- 0.1 units unless stated otherwise through the addition of HNO₃ and/or NaOH. The headspace above the solution was purged with nitrogen gas. Bottles were placed on a shaker table at roughly 100 rpm. All experiments were conducted at room temperature, (20°C +/- 3°C). Some experiments were also conducted in a jar test apparatus*. In experiments with sulfate at low pH, solutions were mixed at 100 rpm for 1 minute followed by a 20 rpm mix for 30 minutes. In softening jar tests, solutions were mixed at 100 rpm for 3 minutes followed by a 20 rpm mix for 3 hours.

Sampling and Analysis:

All soluble metals samples were filtered through 0.45 μm pore size nylon syringe filters[†]. Additionally, for quantification of small colloids, experiments with sulfate at low pH were filtered through a 0.025 μm pore size membrane filter[‡]. These samples were

* PB-700 Jartester, Phipps and Bird, Richmond, VA

† #8054-NS, Life Science Products Inc., Denver, CO

‡ VSWP 025 00, Millipore Corporation, Bedford, MA

acidified to 2% by volume using concentrated nitric acid prior to quantitative analysis using an inductively coupled plasma emission spectrometer^{*} (ICP-ES). A concomitant metals analyzer[†] (CMA) was used to improve arsenic sensitivity via hydride generation when required. Total organic carbon (TOC) samples were pretreated by acidification with phosphoric acid to below pH 4 and bubbled with nitrogen gas for five minutes to strip carbon dioxide. TOC was measured using a portable TOC analyzer[‡]. Zeta potential was measured using a Malvern Zetasizer 3000 HS[§] or, in some softening jar tests a Zeta Meter 3.0+^{**}. Turbidity, in NTU, was measured using a turbidimeter^{††, ‡‡}. Some solids generated in sufficient quantity were centrifuged, dried in a dessicator, crushed and analyzed using x-ray diffraction (XRD)^{§§}.

Results and Discussion

Experimental results are presented in four sections including: 1) low pH solids, 2) high pH solids, 3) a practical examination of solids formed at high pH in relation to contaminant removal and 4) the effects of Al addition on calcium precipitation and softening.

Low pH Solids:

The solubility of amorphous aluminum hydroxide limits the lower pH at which aluminum coagulants can be used to about pH 5.5-5.8 depending on temperature (Morris & Knocke 1984; Jekel & Heinzmann 1989; Van Benschoten et. al. 1992). However, it has long been known that anions, such as sulfate, can alter the pH range of optimal coagulation (Miller 1925; Peterson & Bartow 1928; Mattson 1930; Black et. al. 1933; Marion & Thomas 1946; Hanna & Rubin 1970; Letterman & Vanderbrook 1983). More recently,

* JY Ultima ICP-ES, JY Emission, France

† CMA Hydride Generator, JY Emission, France

‡ 800 Portable TOC analyzer, Sievers, Boulder, CO

§ Zetasizer 3000HS, Malvern Instruments, Worcestershire, United Kingdom

** Zeta Meter 3.0+, Zeta Meter Inc., Staunton, VA

†† 2100N Turbidimeter, Hach Company, Loveland, CO

‡‡ Digital Direct-Reading Turbidimeter, Orbeco-Hellige, Farmingdale, NY

§§ Series 2000 XRD, Scintag, Sunnyvale, CA

other constituents in the water have been suggested to accelerate the aging of amorphous $\text{Al}(\text{OH})_3$ to more crystalline phases that would be much less soluble (Violante & Huang 1985). Other evidence supports the formation of different solids in the low pH range such as basaluminate, aluminosilicate and alunite (Table 2-1).

Experiments were designed to determine if SiO_2 , K^+ and SO_4^{-2} decreased Al solubility at low pH, and if so, whether the mechanism was accelerated aging of $\text{Al}(\text{OH})_3$ formation of solids other than aluminum oxyhydroxides or colloid destabilization. Initial experiments focused on the role of sulfate. The basic experimental approach was to prepare a solution with a target level of sulfate, dose it with aluminum nitrate to a final concentration of about 5 mg/L Al, and then immediately raising pH to the desired value using NaOH. A jar tester was used with a 1 minute 100 rpm rapid mix and 30 minute 20 rpm flocculation cycle.

After 30 minutes at the desired pH, sulfate of 30 mg/L drastically reduced aluminum solubility based on filtration with a 0.45 μm pore size filter compared to water with 0 or 3 mg/L sulfate (Figure 2-1). This is perfectly consistent with the hypothesis of Letterman & Vanderbrook (1983). At pH 5.0 however, filtration through a 0.025 μm pore size filter removed as much as 80% of the Al passing a 0.45 μm pore size filter proving that a significant fraction of aluminum in these solutions is colloidal. At 30 mg/L sulfate and above there is very little colloidal aluminum in all cases. This suggests that sulfate is actually destabilizing colloidal $\text{Al}(\text{OH})_3$ and causing agglomeration into larger “floc” particles. The importance of colloidal aluminum rules possible aging of $\text{Al}(\text{OH})_3$ as a mechanism of solubility control by SO_4^{-2} .

The molar ratio of Al:S varied between 2.5 to 6.5 in the solid collected on filters. When these ratios were compared to the ratio in the candidate solids (Table 2-1), it was clear that none of the alternative solids were forming exclusively. Moreover, if Al- SO_4 solids were forming, true soluble aluminum should decrease at higher sulfate concentrations, but this did not occur. For example, at pH 5.3 the same concentration of aluminum passed through a 0.025 μm pore size filter at 30 or 200 mg/L sulfate.

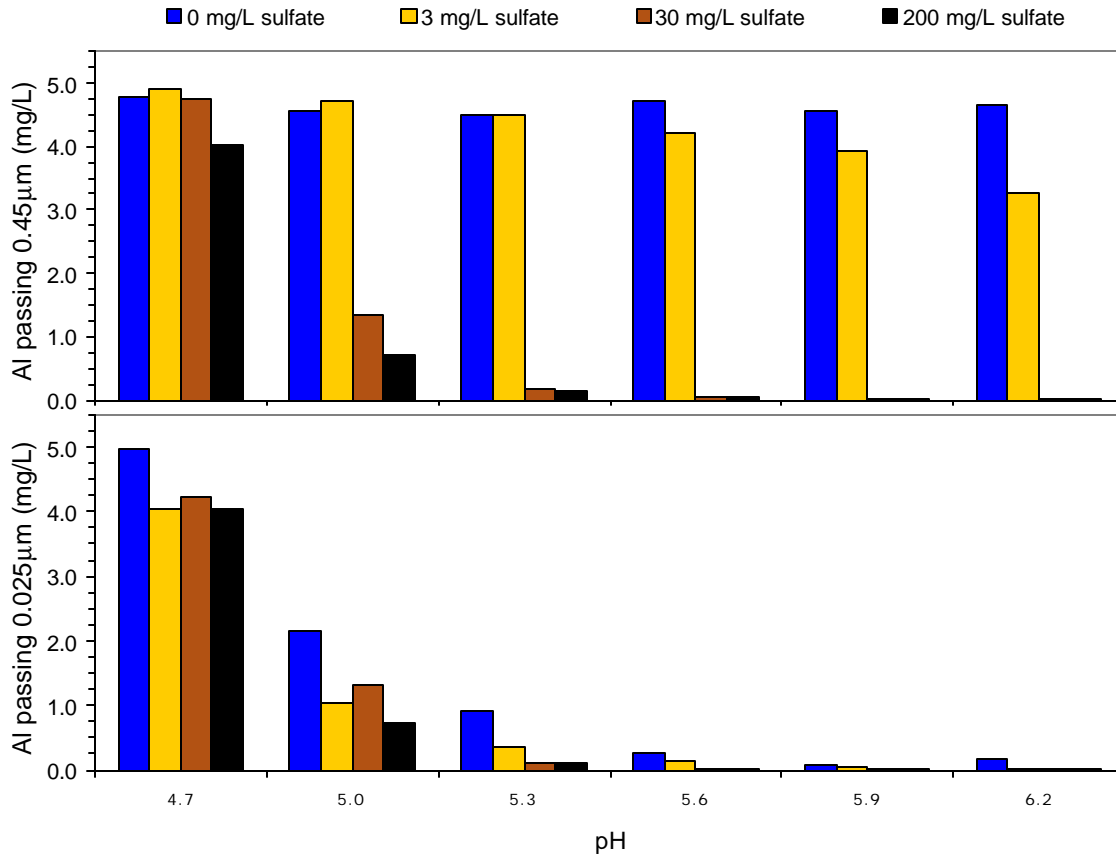


Figure 2-1) Effect of sulfate of Al solubility after 30 minutes, 5 mg/L total Al dose

Further evidence that sulfate was sorbing to the $\text{Al}(\text{OH})_3$ floc surface and increasing colloid size, rather than forming a new solid phase or accelerating aging, was obtained using the sulfate surface complexation model of Chen (2001). Actual sulfate removals observed in this work correlate well with model predictions based on this author's work with preformed amorphous $\text{Al}(\text{OH})_3$ solids (Figure 2-2).

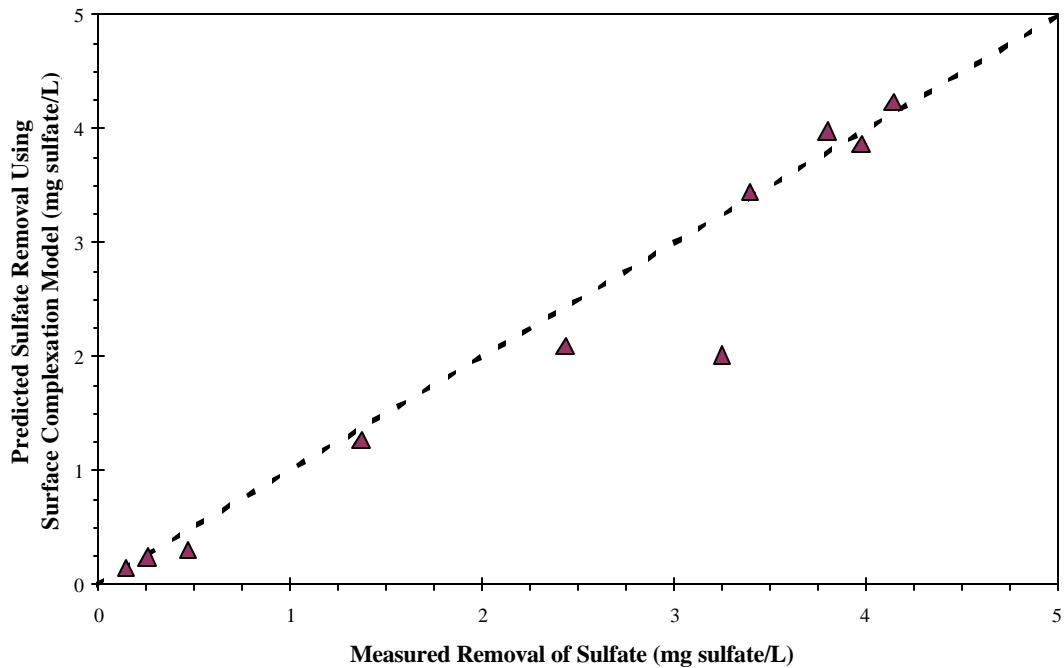


Figure 2-2) Sulfate removal in these experiments compared to surface complexation model predictions for SO_4^{-2} sorption onto $\text{Al}(\text{OH})_3$ (Chen 2001)

A range of experiments was conducted with silica and potassium following the same general protocol as for sulfate. In solutions stirred for 24 hours containing 30-40 mg/L SiO_2 and 5 mg/L Al, sampling revealed a 10-12% decrease in soluble Al and a 3-4% decrease in soluble Si at pH 5.0. Particles were not visible with the naked eye in these systems, which would suggest poor settling properties. Experiments with potassium used a 7 mg/L K concentration, 5 mg/L Al and variable sulfate. pH values of 4.7 and 5.6 were targeted at sulfate levels of 3, 30, and 300 mg/L SO_4^{-2} as well as one test at pH 5.0 and 30 mg/L SO_4^{-2} . Potassium remained completely soluble in these tests. Consequently, formation of lower solubility potassium or silica containing solids during water treatment at this lower pH range was deemed unlikely.

High pH Solids:

Control of Al solubility by amorphous $\text{Al}(\text{OH})_3$ formation or even gibbsite would limit Al-salts to coagulation processes below pH 9.0 if it was desired to maintain soluble Al less than the SDWR of 0.05-0.2 mg/L (Figure 2-3). However, it has become common practice to add aluminum based coagulants during softening at higher pH without noteworthy problems in controlling residual Al (Shorney et. al. 1999). Current theory and practical results are in obvious conflict regarding Al solubility at high pH.

The experimental plan sequentially examined: 1) formation of $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ solids alone, 2) possible formation of $\text{Al}_x\text{Mg}_y(\text{OH})_z$ solids and 3) possible formation of $\text{Al}_v\text{Mg}_x(\text{Si}(\text{OH})_4)_y(\text{OH})_z$ solids. Theoretical curves generated using the computer program MINEQL for brucite ($\text{Mg}(\text{OH})_2$), fresh $\text{Mg}(\text{OH})_2$, gibbsite ($\text{Al}(\text{OH})_3$ crystal), diaspore (AlOOH crystal) and amorphous $\text{Al}(\text{OH})_3$ were plotted for comparison to experimental data (Table 2-2 and Figure 2-3). As expected the solubility of Mg^{+2} was roughly consistent with $\text{Mg}(\text{OH})_2$ precipitation above 10.5. Likewise, the measured solubility in the system with aluminum alone after 24 hours was between that predicted by amorphous $\text{Al}(\text{OH})_3$ and more crystalline gibbsite, and 100% of the 5 mg/L Al was soluble above pH about 9.7.

When both Mg^{+2} and Al^{+3} were present, solubility of both Mg^{+2} and Al^{+3} was markedly decreased between pH 9.2-10.5 compared to each cation alone. This suggests formation of a $\text{Mg}_x\text{Al}_y(\text{OH})_z$ containing solid. Note that above pH 10.5 soluble aluminum remains very low, even compared to highly crystalline aluminum oxyhydroxide phases such as gibbsite and diaspore. This further supports the notion that a Mg-Al containing solid is forming directly. Finally, x-ray diffraction tests indicated that the Mg-Al solid was amorphous in nature.

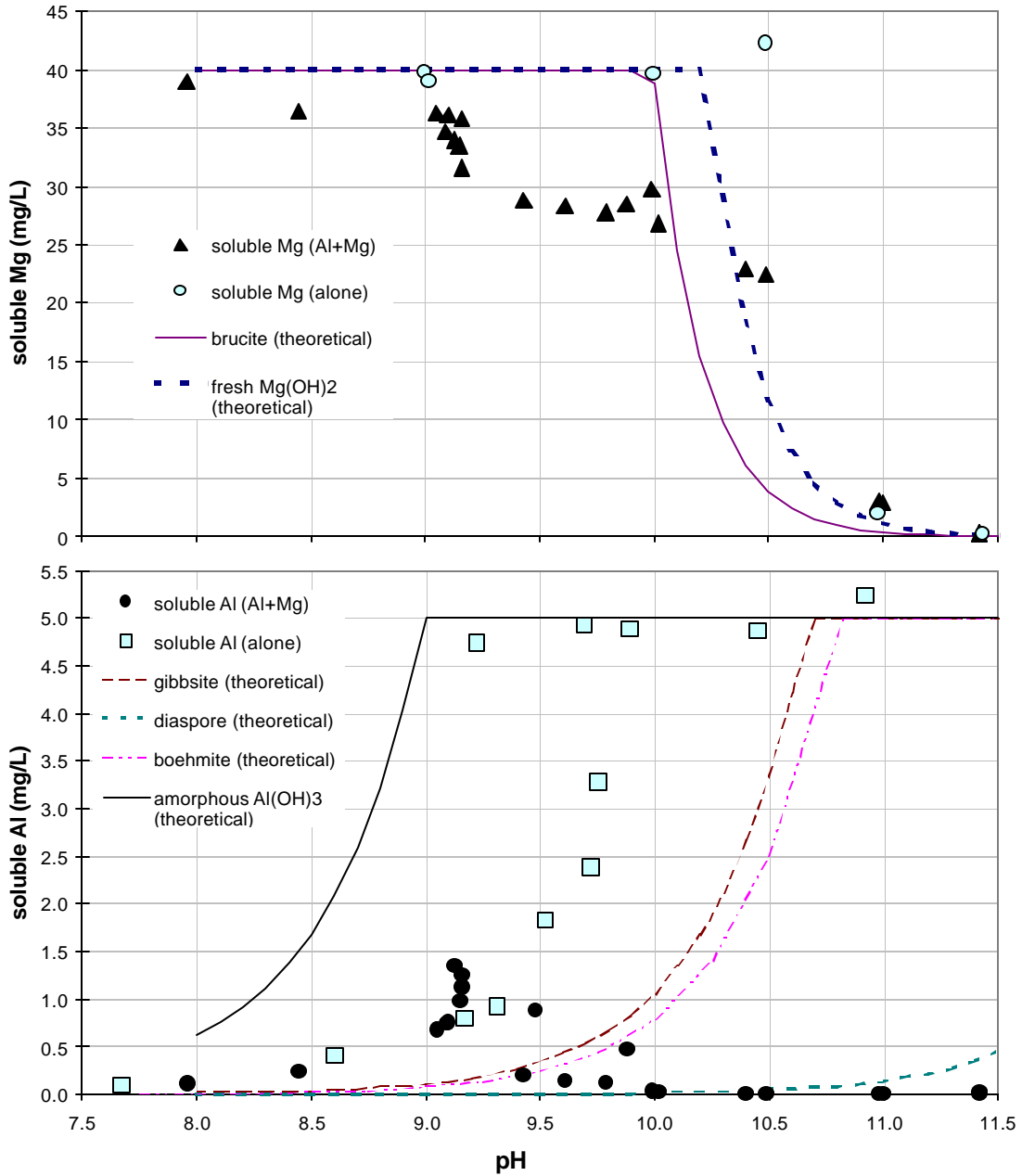


Figure 2-3) Solubility of Mg⁺² and Al⁺³ by themselves, and combined at pH 7.5-11.5. Theoretical curves calculated using MINEQL

Spinel (Al₂MgO₄) was the only aluminum magnesium oxide solid cited in the literature, although based on reported log K_{sp}= -75.67 the solid is not predicted to form in this system. Furthermore, the solid formed in this study had an average Al:Mg stoichiometric ratio of 1:2 +/- 0.6, inconsistent with spinel. Based on the formula of AlMg₂(OH)₇ and

the dissolution reaction as written in Table 2-2, the conditional average conditional log $K_{sp} = -57.6$.

Table 2-2) Formation/Dissolution reactions with K_{sp} . Conditional K_{sp} for the last 3 solids estimated based on data collected in this study.

Solid Formation/Dissolution Reaction	Solid Name	Characteristics	log K_{sp} 20° C
$Al(OH)_3(s), \text{amorphous} \leftrightarrow Al^{+3} + 3OH^-$	amorphous aluminum hydroxide	opalescent	-31.28
$Al(OH)_3(s), \text{gibbsite} \leftrightarrow Al^{+3} + 3OH^-$	gibbsite	crystalline	-32.94
$AlOOH(s), \text{diaspore} + H_2O \leftrightarrow Al^{+3} + 3OH^-$	diaspore	crystalline mineral	-34.82
$Mg(OH)_2(s), \text{fresh} \leftrightarrow Mg^{+2} + 2OH^-$	fresh magnesium hydroxide	opalescent/whitish	-10.32
$Mg(OH)_2(s), \text{brucite} \leftrightarrow Mg^{+2} + 2OH^-$	brucite	crystalline	-10.88
$Al_2MgO_4(s), \text{spinel} + 4H_2O \leftrightarrow 2Al^{+3} + Mg^{+2} + 8OH^-$	spinel	crystalline	-74.55
$AlMg_2(OH)_7(s) \leftrightarrow Al^{+3} + 2Mg^{+2} + 7OH^-$	Al-Mg solid (this study)	opalescent small particles, very poor settling properties	~ -57.6
$AlMg_2(Si(OH)_4)(OH)_7(s) \leftrightarrow Al^{+3} + 2Mg^{+2} + Si(OH)_4 + 7OH^-$	Al-Mg-Si solid (this study)	opalescent, floc forming, settles well	~ -61.1
$Al(Si(OH)_4)_{1.8}(OH)_3(s) \leftrightarrow Al^{+3} + 1.8Si(OH)_4 + 3OH^-$	Al-Si solid (this study)	clear/opalescent, forms after Al-Mg-Si solid forms. Si range 1.8 +/- 0.2	~ -41.1

The next set of experiments was conducted in waters that also contained silica. Silica has long been known to have considerable importance in coagulation processes (Baylis 1937) and is commonly present in natural waters at concentrations up to 50 mg/L as SiO_2 , but rarely below 5 mg/L as SiO_2 . Silica levels in our tests were selected to represent a range

commonly encountered in natural water, while magnesium was maintained at 40 mg/L and aluminum was dosed at 5 mg/L. Specifically, SiO₂ levels of 0, 8, 15, 25 and 50 mg/L were tested. A survey of surface waters (Davies & DeWiest 1966) indicated that these levels correspond to 0, 10, 50, 75 and 99th percentiles of SiO₂ occurrence in US surface water. Likewise, 40 mg/L Mg⁺² corresponds to the 90th percentile of Mg occurrence.

Qualitatively, the presence of silica caused a fundamental change in the kinetics of aluminum precipitation (Figure 2-4). Soluble aluminum decreased much more rapidly in the first few hours when silica was present compared to when it was absent, which is particularly relevant to the ~1-8 hour detention times common in water treatment practice (Figure 2-4). Excluding the long term result with no silica there is also a direct reduction in soluble aluminum at higher silica concentration.

At much longer time periods the systems without silica eventually had non-detectable levels of soluble Al, whereas the solutions with silica achieve relatively stable values of soluble Al (Figure 2-4). This suggests that the pure AlMg₂(OH)₇ solid is not forming when silica is present in solution, even though it has lower Al solubility. Moreover, since the K_{sp} of the AlMg₂(OH)₇ solid is exceeded even when low levels of SiO₂ are present, it is clear that this solid is not controlling Al solubility in any of the systems with silica. The authors speculate that silica poisons formation of this solid phase. Soluble Al in the solution without silica was found to increase from 24 to 100 hours before falling to near undetectable levels. This trend was duplicated in repeat tests, however it is not clear why the fluctuations occurred.

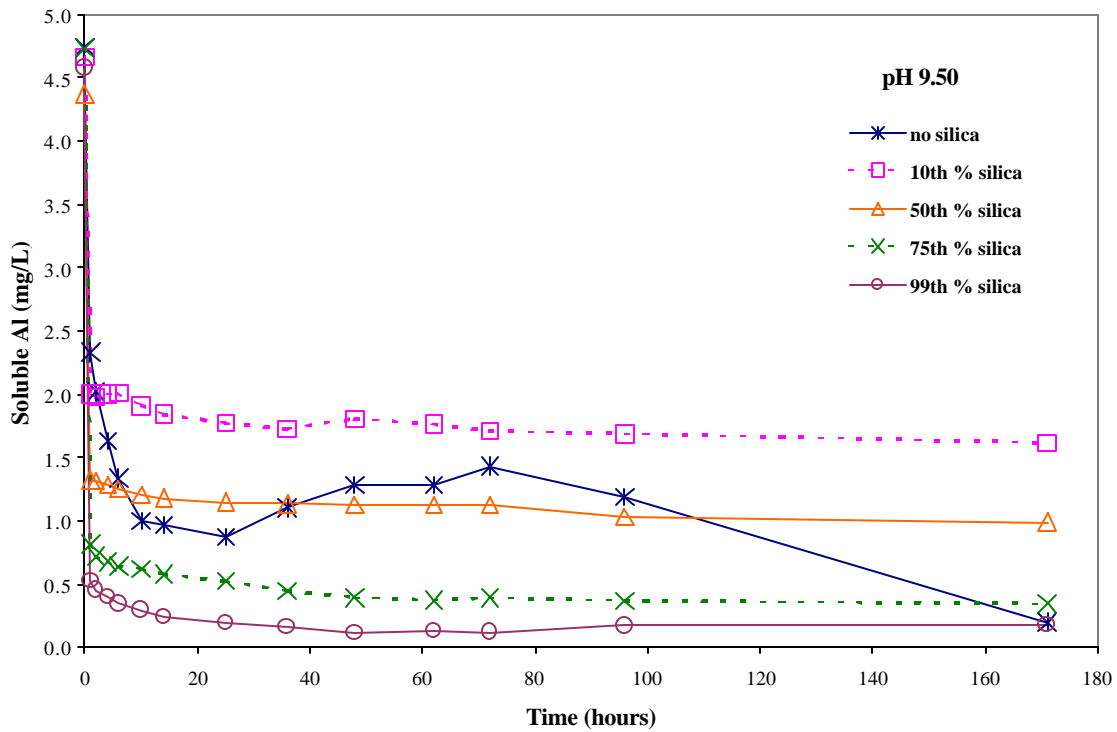


Figure 2-4) Aluminum solubility over time, 5 mg/L Al, 40 mg/L Mg, variable SiO₂

The behavior of magnesium in the system with Al, Mg and Si is also of interest.

Whereas the soluble concentration of Al and Si decreased smoothly with time, the soluble concentration of Mg⁺² reached a minimum at about 4-10 hrs and then increased thereafter (Figure 2-5). This type of behavior is most consistent formation of an Al-Mg-Si solid first, followed by conversion to a less soluble Al-Si solid phase.

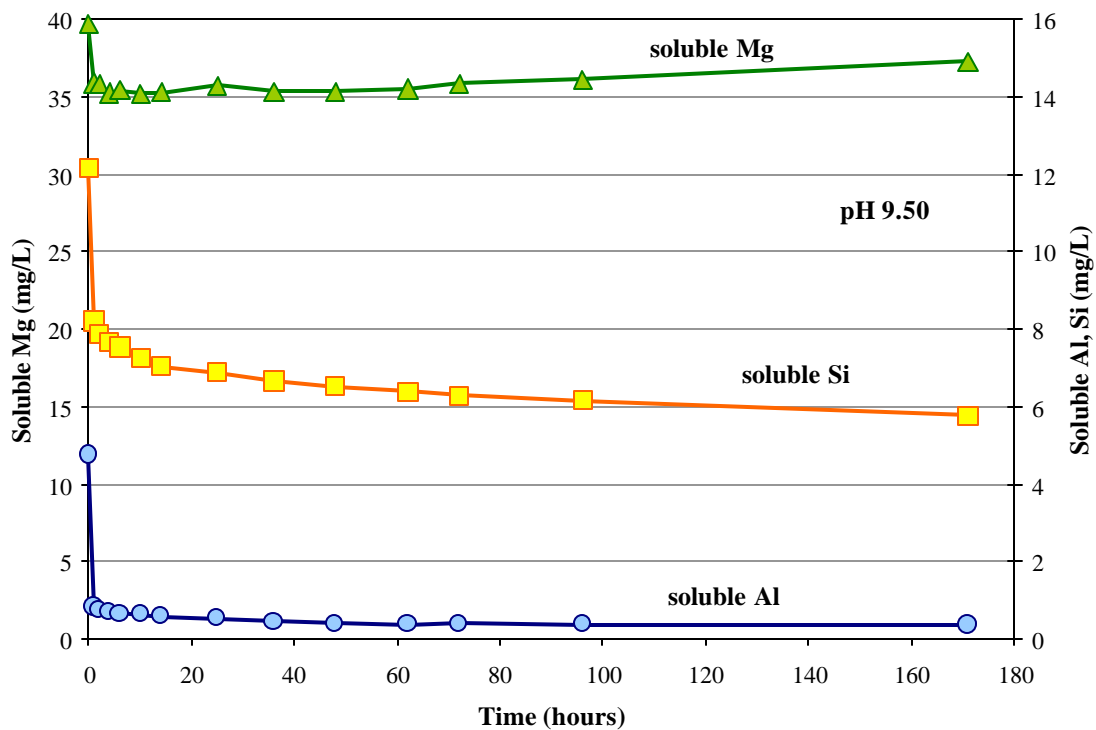
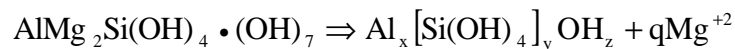


Figure 2-5) Typical soluble species profile over time, 75th percentile silica level shown

The solid forming from 0-10 hours had the approximate composition $\text{AlMg}_2\text{Si}(\text{OH})_4\text{-(OH)}_7$. It is assumed that this solid is present in all systems with silica, even at longer reaction time periods. Based on the measured decrease in Al and Si with time, and increased Mg^{+2} , the stoichiometry of the assumed Al-Si solid can be estimated:



The average calculated stoichiometric ratio Al:Si in the solid was 1:1.8 +/- 0.2.

Data collected from 4-14 hours determined the average conditional $\log K_{sp}$ of $\text{Al-Mg}_2\text{-Si}(\text{OH})_4\text{-(OH)}_7$ to be about -61.1. Similarly, data from 72-96 hours determined the average conditional $\log K_{sp}$ of $\text{Al-(Si}(\text{OH})_4\text{)}_{1.8}\text{-(OH)}_3$ to be about -41.1. The usefulness of these K_{sp} values, based on an ability to predict soluble aluminum in comparison to measured values, is quite good (Figure 2-6).

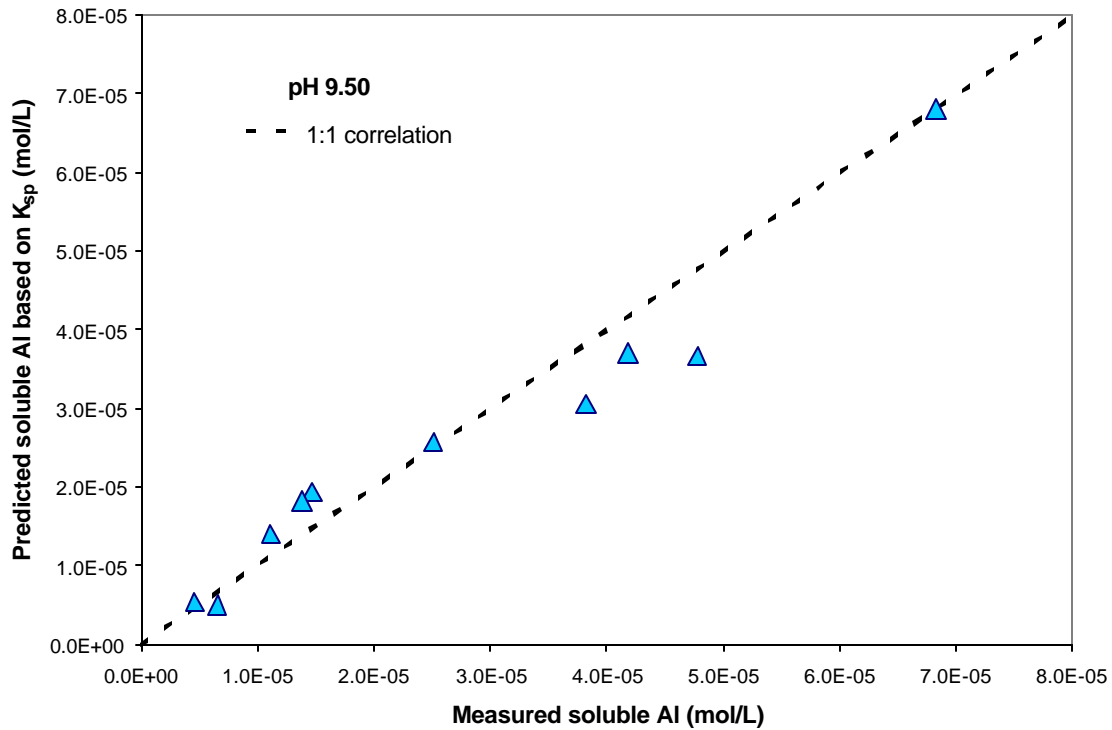


Figure 2-6) K_{sp} based soluble Al prediction compared to observed soluble Al data at 24 hours

Screening experiments with other ions (70 mg/L Ca^{+2} , 200 mg/L SO_4^{-2} , 0.3 mM CO_3^{-2} , 7 mg/L K^+) at pH 9.3 showed no evidence that these ions hindered formation of Al-Mg-Si-OH or Al-Mg-OH solids or led to formation of different solids. Finally, X-ray diffraction revealed that Al-Mg-Si-OH and Al-Si-OH had distinctive patterns although no definitive match was possible with known solids (JCPDS 1997).

Physical Properties of High pH Solids and Contaminant Removal:

The preceding section tentatively identified three new Al solid phases of interest at higher pH including $AlMg_2(OH)_7$, $Al-Mg_2-Si(OH)_4-(OH)_7$ and $Al-(Si(OH)_4)_{1.8}-(OH)_3$.

Additional experiments were conducted to examine their influence on settling properties, final turbidity, floc formation time, zeta potential and contaminant removal.

The difference in visual and settling characteristics of the Al-Mg solids with and without Si further distinguished Al-Mg-OH from Al-Mg-Si-OH based solids. In the system forming Al-Mg-Si-OH solids, visible flocs appeared within seconds, whereas Al-Mg solids were not visible to naked eye until after at least 30 minutes of mixing. Even after 30 minutes, solutions with Al-Mg solids alone remained hazy, without distinct flocs (Appendix C shows a comparison at much higher solids concentration).

To examine this phenomenon in more detail, a jar test experiment was conducted using 40 mg/L Mg, 5 mg/L Al and a variable silica concentration from 0-50 mg/L SiO₂. Turbidity, zeta potential and floc formation were tracked after rapid-mix at 100 rpm for 2 minutes, followed by a 5 hour slow-mix period at 30 rpm. A 1 hour settling period concluded the test (Table 2-3).

Table 2-3) Turbidity and zeta potential data at pH 9.5

Solution name	Turbidity at end of flocculation	Settled water turbidity	Zeta potential
silica %ile	NTU	NTU	mV
no silica	1.87	1.68	+18.6 +/- 4.6
10 th %	1.42	0.04	-6.0 +/- 3.3
50 th %	1.73	0.03	-13.7 +/- 6.0
75 th %	2.00	0.07	-10.1 +/- 9.3
100 th %	2.85	0.15	-12.9 +/- 4.9

Turbidity after flocculation increased at higher silica concentration and settling was markedly improved (Table 2-3). The presence of silica shifted zeta-potential from distinctly positive to negative. A study on Al-Mg hydroxide sols (Han et. al. 1998) formed at high temperatures also found highly positive zeta potentials and poor floc settling characteristics which were desirable when applied to oilfield drilling situations.

Another set of experiments sought to address the ability of the new solids to remove contaminants from water, specifically arsenic, TOC and boron. This was tested by

spiking each contaminant individually to a solution of 40 mg/L Mg, 40 mg/L SiO₂, forming the new solids in-situ with a 5 mg/L Al dose, and later sampling for total and soluble fractions of each contaminant. Approximately 5 mg/L TOC was added using a concentrated soluble natural organic matter solution. Arsenic was dosed at 80 µg/L and boron at 900 µg/L from concentrated stock solutions. For the cases with arsenic and TOC, a jar test experiment was conducted at pH 9.5 with the following treatment sequence: 2 minute rapid mix at 100 rpm, 2 hour 30 rpm mix, 1 hour 20 rpm mix, and 1 hour settling. Al-Mg-Si-OH solids removed roughly 12% of the total arsenic present and around 40% of the TOC.

Boron is a contaminant that is very difficult to remove from water, but may be regulated by EPA in the near future. Two bottled solutions containing 900 µg/L boron were prepared and dosed with chemicals to form either Al-Mg-OH or Al-Mg-Si-OH solids. These bottles were placed on the shaker table and sampled several times over 24 hours for total and soluble B. After 2 hours of mixing, boron removal seemed to plateau in both solutions. The Al-Mg-OH solid was capable of removing about 20% of the total B, whereas the Al-Mg-Si-OH solids achieved a 9% removal. Given the difficulties in removing boron, these results deserve follow up study.

Effect of High pH Solids on Calcium Precipitation and Enhanced Softening:

Some unanswered questions regarding use of aluminum salts as softening aids still remain. Do these new solubility controls explain why aluminum dosing is possible in practice? Two jar test experiments were carried out at pH 9.5 to determine if Al-Mg-OH or Al-Mg-Si-OH solids could influence calcium removal, improve softening or control residual Al. These waters had roughly 100 mg/L calcium, 150 mg/L bicarbonate and 7.0×10^{-3} M NaNO₃ in addition to aluminum from 0-2.0 mg/L, 0 or 40 mg/L SiO₂ and 0 or 40 mg/L Mg⁺² (Figure 2-7). More jar tests were run at pH 10.0 and 10.5 with the same makeup as above, but varied levels of SiO₂ and Mg⁺². The order of chemical addition in these tests was as follows: NaNO₃ → Na₂OSiO₂ + HNO₃ to ~ pH 8.0 →

$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{NaHCO}_3 \rightarrow$ (begin rapid mix) $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
+ NaOH to desired pH.

Jars were rapid mixed at 100 rpm for 3 minutes, slow mixed at 20 rpm for 3 hours and settled for 1 hour. After the first settling period the samples were stirred again at 20 rpm until the 24 hour mark when the suspensions were allowed to settle again for 1 hour. Turbidity was recorded during flocculation and after settling (Figure 2-7 & Appendix D-E). In the first jar test, pH was adjusted immediately to 9.5 during rapid mix, early in flocculation and then allowed to drift downwards to pH 8.4-8.7. In a second jar test, pH was held constant at 9.5 +/- 0.1. Samples for total metals were taken at the onset of slow mixing and soluble species samples were drawn after 3 and 24 hours of slow mixing (Figure 2-7 & Appendix E). Solutions at pH 10.0 and 10.5 were only mixed for 3 hours at constant pH and sampled only for total and soluble metals.

At pH 9.5, physical differences in visible flocs were immediately apparent (Table 2-4, Figure 2-7 & Appendix E). These visual effects agreed in most respects with what was seen in earlier tests without calcium. Addition of aluminum dramatically increased floc size and reduced visible floc formation time as compared to calcite alone at pH 9.5. In solutions containing Al, Mg and Si, larger particles develop, whereas in the absence of Si the suspension is a milky dispersion. The formation of dense settling flocs and soluble Al less than 0.5 mg/L in the solution without Mg was unexpected since an Al-Si solid did not form in previous experiments unless an Al-Mg-Si solid formed first. Apparently the calcite in this test might also serve to nucleate this solid phase or perhaps the Al is co-precipitated with calcite.

Table 2-4) Qualitative observations, second softening jar test (pH held at 9.5)

Test Solution *	flocculation time and observation	
	20 minutes	70 minutes and beyond
0 mg/L Al	no visible particles	small particles, some settled
0.5 mg/L Al	some medium flocs	some huge compact flocs
1.0 mg/L Al	some large flocs	many huge compact flocs
2.0 mg/L Al	many large flocs	many huge compact flocs (less white)
1.0 mg/L Al, no SiO ₂	many small flocs	many small flocs
1.0 mg/L Al, no Mg	some large flocs	many large dense/settling flocs, some small particles

* all contain 100 mg/L Ca⁺², 150 mg/L HCO₃⁻, 40 mg/L SiO₂, 7x10⁻³ M NaNO₃ unless indicated otherwise

Visual observations at pH 10.0 and 10.5 with 1.0 mg/L Al were similar. In general, as Mg concentration was increased from 0 to 10 mg/L, flocs appeared larger and more numerous regardless of SiO₂ concentration. As SiO₂ concentration increased from 0 to 20 mg/L for a given Mg, there was little change in floc appearance except in the case at 5 mg/L Mg when flocs did get larger. In nearly all of the tests, flocs settled rapidly and in many cases larger particles settled in the jars during flocculation. Turbidity measurements were not taken for jar tests at pH 10.0 and 10.5.

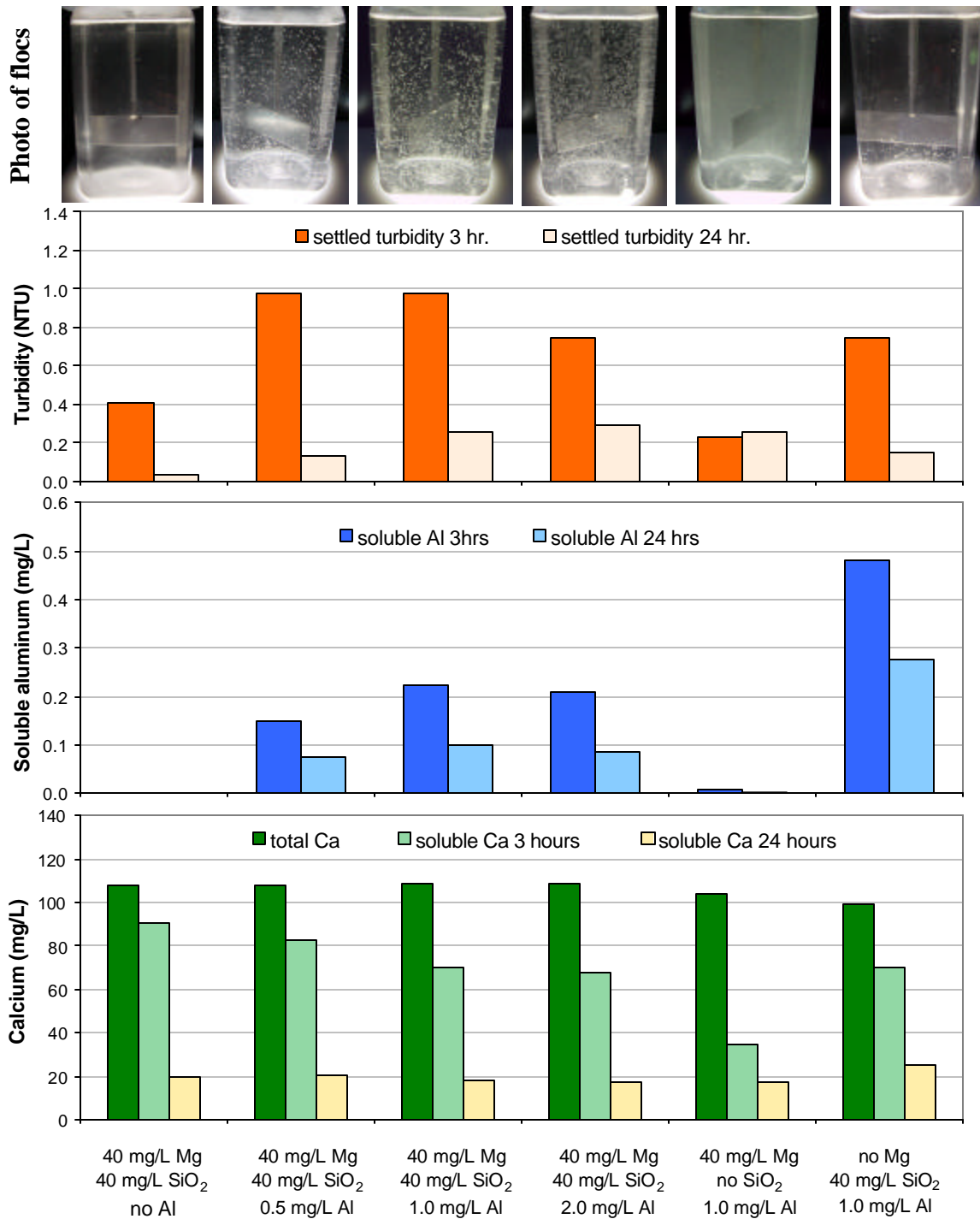


Figure 2-7) Softening jar test results, pH held constant at 9.50 for duration

In general, aluminum addition improved calcium removal significantly at 3 hours (Figure 2-7 & Appendix E). After 24 hours, aluminum showed less control over calcium

solubility. This finding supports addition of aluminum coagulants as softening aids in water treatment practice, since it improved removal of calcium. However addition of Al to solutions with silica led to even greater improvements in Ca removal, settled turbidity and residual Al in the short term. It is possible that aluminum is somehow reducing an interference with calcium removal due to silica. When silica versus calcium removal data is plotted from the data a trend was found that increased silica removal led to increased calcium removal (Figure 2-8).

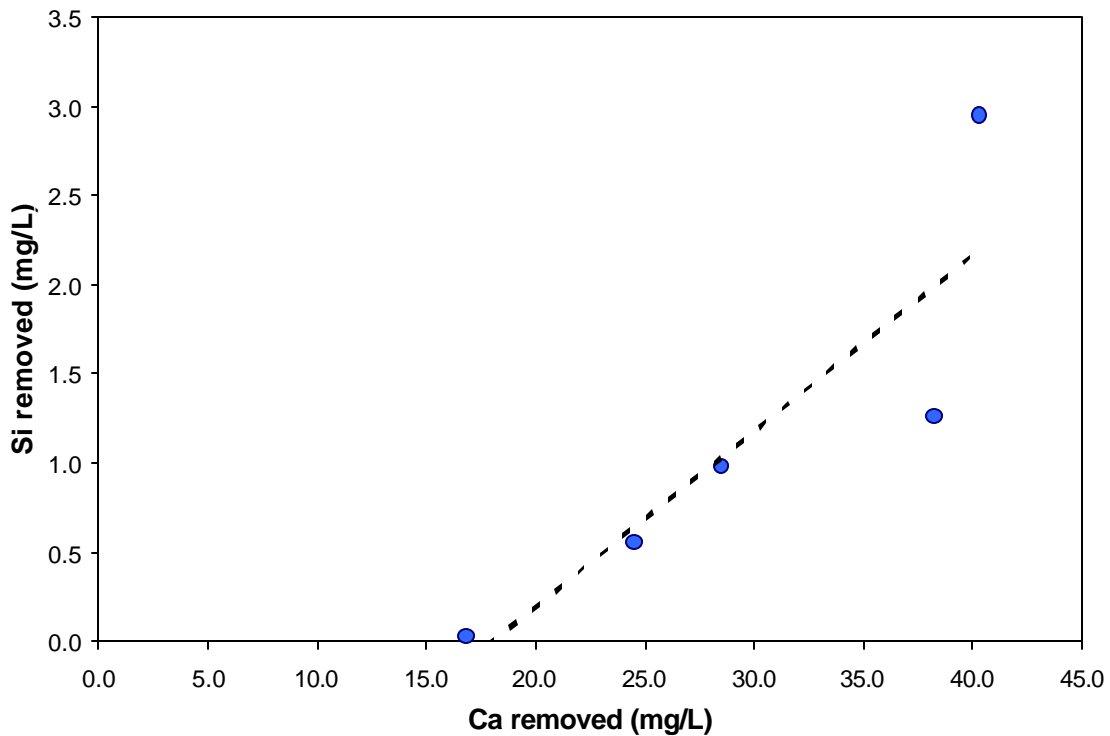


Figure 2-8) Silica removal versus calcium removal in jar tests, pH held constant at 9.50

Previously, in systems without Ca^{+2} or CO_3^{-2} , Al-Mg solid suspensions were found to be very stable, exhibiting little to no settling over time (Table 2-3). However, in the second jar test, with Ca and CO_3^{-2} , this system had the lowest settled turbidity after 3 hours of mixing (Figure 2-7). Even though the combination of silica with aluminum increased floc size, there are some caveats in that these solutions tended to have higher settled turbidities, more residual soluble Al and less efficient calcium removal than when silica was absent.

It is important to note that the pH control approach used in the second jar test, might not be practical in a typical water treatment softening operation. A continuous input of hydroxide was required to maintain pH. In the jar test without pH maintained during flocculation, which may more closely mimic an actual treatment situation, calcium removal was not improved in the suspension without silica over other solutions with silica, aluminum and magnesium. Even though calcium removal was improved with any level of added Al in the experiment where pH drifted, pH control during flocculation could significantly improve overall softening efficiency.

Assuming it is deemed beneficial, when could Al be dosed to waters undergoing precipitative softening without exceeding 0.2 mg/L final Al? Assuming the three solids discussed previously are forming along with calcite and controlling Al solubility, conditional K_{sp} values for these solids can be used to predict when soluble Al will be above and below 0.2 mg/L at a given pH with known concentrations of soluble Mg and SiO_2 . This plot can be used to define a water quality region where soluble Al would be greater than 0.2 mg/L (Figure 2-9). For example, assuming the $\text{AlMg}_2(\text{OH})_7$ solid forms and is at equilibrium if the total soluble Al is 0.2 mg/L aluminum, the hydrolysis constants can be used to predict Al^{+3} . Since OH^- is known the Mg^{+2} can be determined to be equal to 29 mg/L. Mg^{+2} values above this will have soluble Al below 0.2 mg/L and Mg^{+2} values below this will have soluble Al above 0.2 mg/L (Figure 2-9). A similar analysis can be conducted for the other solids.

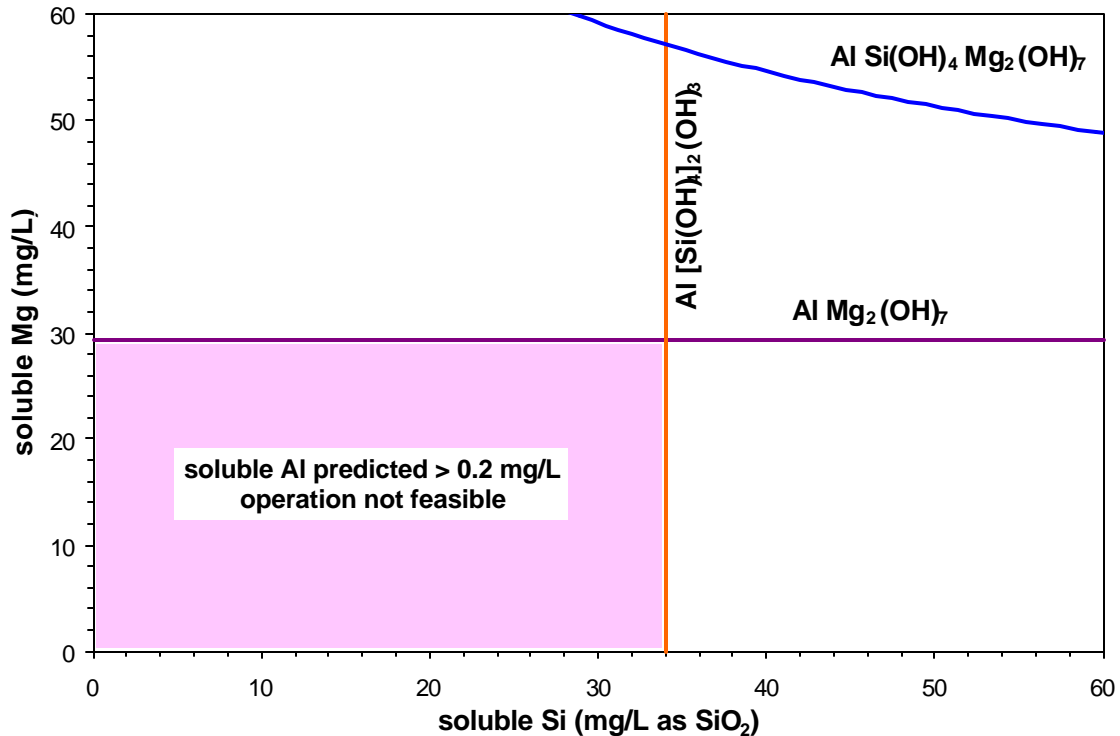


Figure 2-9) Conceptual graph indicating water qualities where Al dosing will not exceed 0.2 mg/L soluble Al at pH 9.5

It is noted at pH 9.5 that very few waters are likely candidates for enhanced softening by Al addition. However, repeating the analyses at higher pH (Figure 2-10) indicates that the required level of Mg in a water to maintain less than 0.2 mg/L Al should decrease sharply at higher pH.

Jar test experiments at pH 10.0 and 10.5 were carried out to verify these trends. Several combinations of Mg and SiO₂ concentrations were selected for testing both inside and outside of the regions predicted in Figure 2-10. At pH 10.0, soluble Al levels as low as 0.2 mg/L were not reached at any test condition, although as Mg and SiO₂ concentration increased soluble Al concentrations did decrease significantly. At pH 10.5, very low levels of soluble Al were found if the water contained slightly over 5 mg/L Mg and 0 mg/L SiO₂, consistent with the model prediction. Elevated levels of silica resulted in more soluble Al at pH 10.5. The major reason for the difference between the model prediction and actual results in Figure 2-10 is that the conditional K_{sp} values were

determined at 24 hours, whereas soluble Al in the jar tests was determined at 3 hours. It is evident that the interplay between aluminum, magnesium and silica is complicated and varied as pH increases above 9.5. To better understand these interactions more study is necessary, but the trends reported in this work are a useful guide.

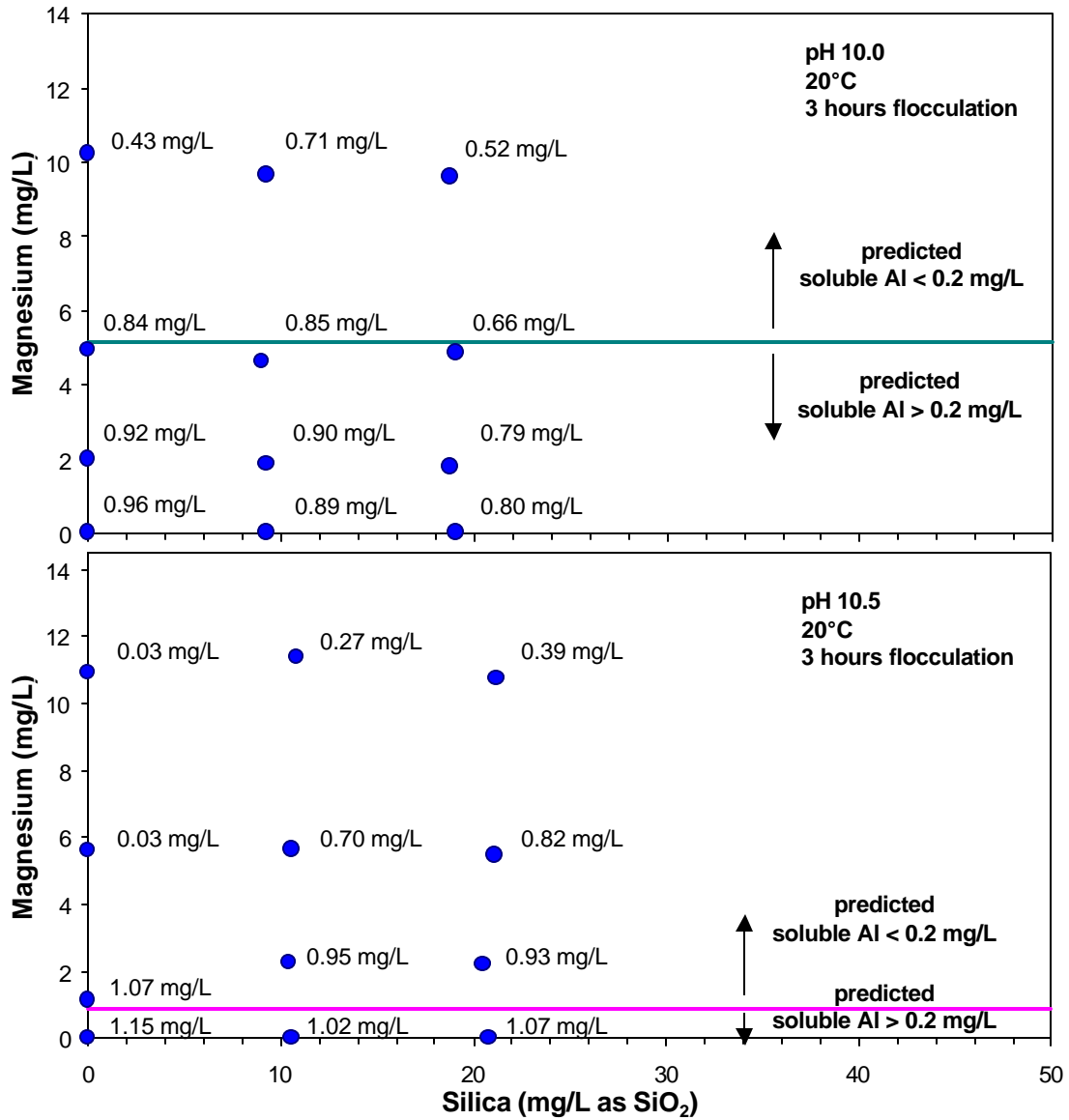


Figure 2-10) Data points indicate soluble Al at the indicated level of total Mg and Si in jar tests at pH 10.0 and 10.5

Conclusions

- Stable $\text{Al}(\text{OH})_3$ colloid formation is prevented by sulfate from pH 5.0 to 6.2, but a specific aluminum sulfate solid is probably not forming.
- Silica and potassium had little effect on Al solubility from pH 4.7 to 5.6 and therefore Al solids containing SiO_2 and K^+ are not expected to form in water treatment situations at low pH.
- A solid with poor settling characteristics of approximate formula $\text{AlMg}_2(\text{OH})_7$ is capable of forming in pH 9.0-10.5 solutions. At long time periods or in the presence of calcite this solid can reduce soluble Al concentrations to near non-detectable levels.
- When silica is present between pH 9.0-10.5 and aluminum is added to water with high Mg^{+2} , two different solids seem to form. The first has the approximate formula $\text{AlMg}_2\text{Si}(\text{OH})_4(\text{OH})_7$, the second $\text{Al}(\text{Si}(\text{OH})_4)_{1.8}(\text{OH})_3$. This combination of solids exhibits rapid agglomeration at any silica level, settles well and reduces Al solubility.
- Aluminum in combination with silica has significant effects on calcium removal during softening jar tests at pH 9.5, 10.0 and 10.5. Dosing of aluminum may cause the soluble Al to exceed the SDWR of 0.2 mg/L at pH below 10.5 and at moderate to high silica concentrations. At higher pH's aluminum solubility is reduced.

Acknowledgement

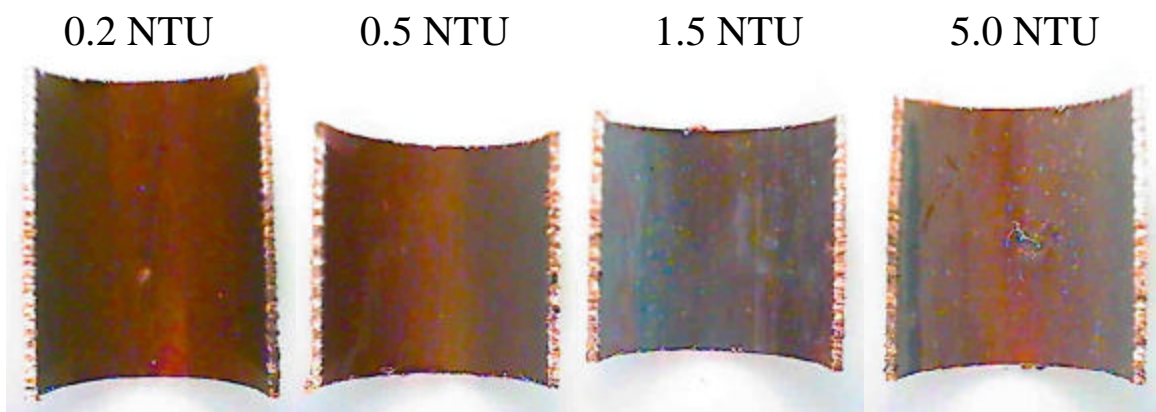
The authors would like to thank Hsiao-wen Chen for her assistance in calculating SO_4^{-2} sorption to $\text{Al}(\text{OH})_3$. This work was supported by the National Science Foundation (NSF) under grant BES-9729008. Opinions and findings expressed herein are those of the authors and do not necessarily reflect the views of NSF.

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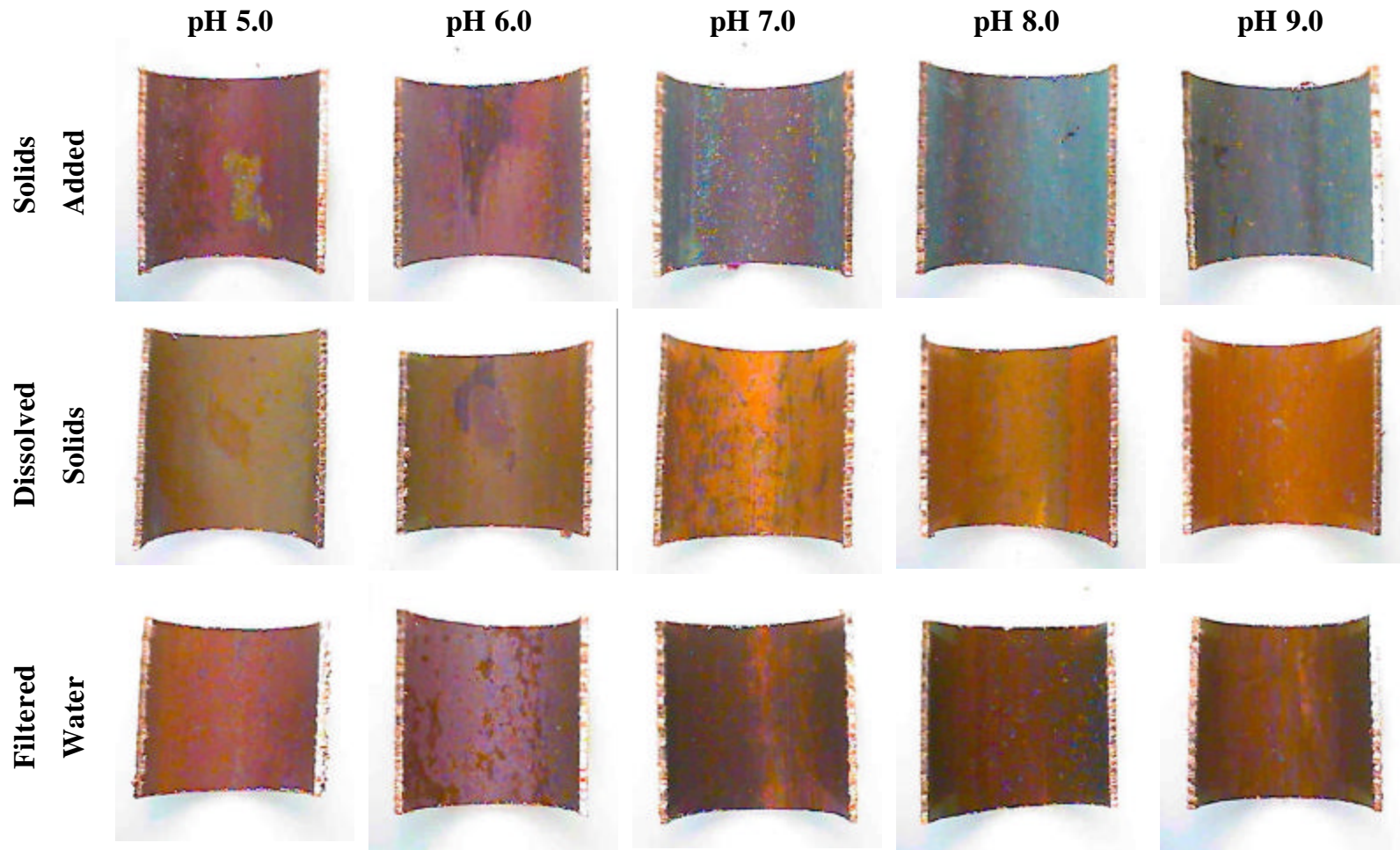
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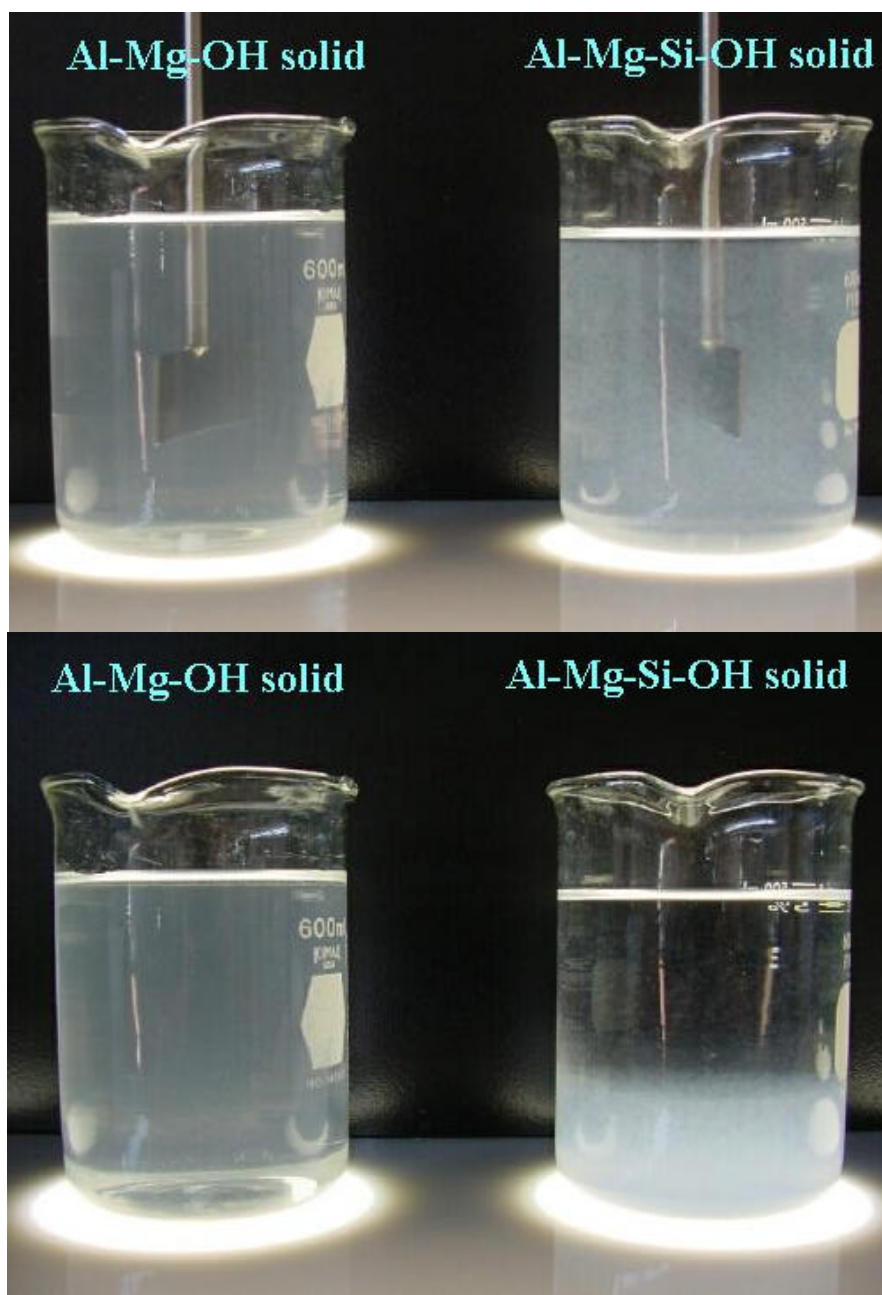
APPENDIX



Appendix A) Chapter I, Experiment #2, effect of increasing aluminosilicate solids concentration on copper pipe scale



Appendix B) Chapter I, Experiment #3 pipes, effect of pH and aluminosilicate solids fraction on copper pipe scale

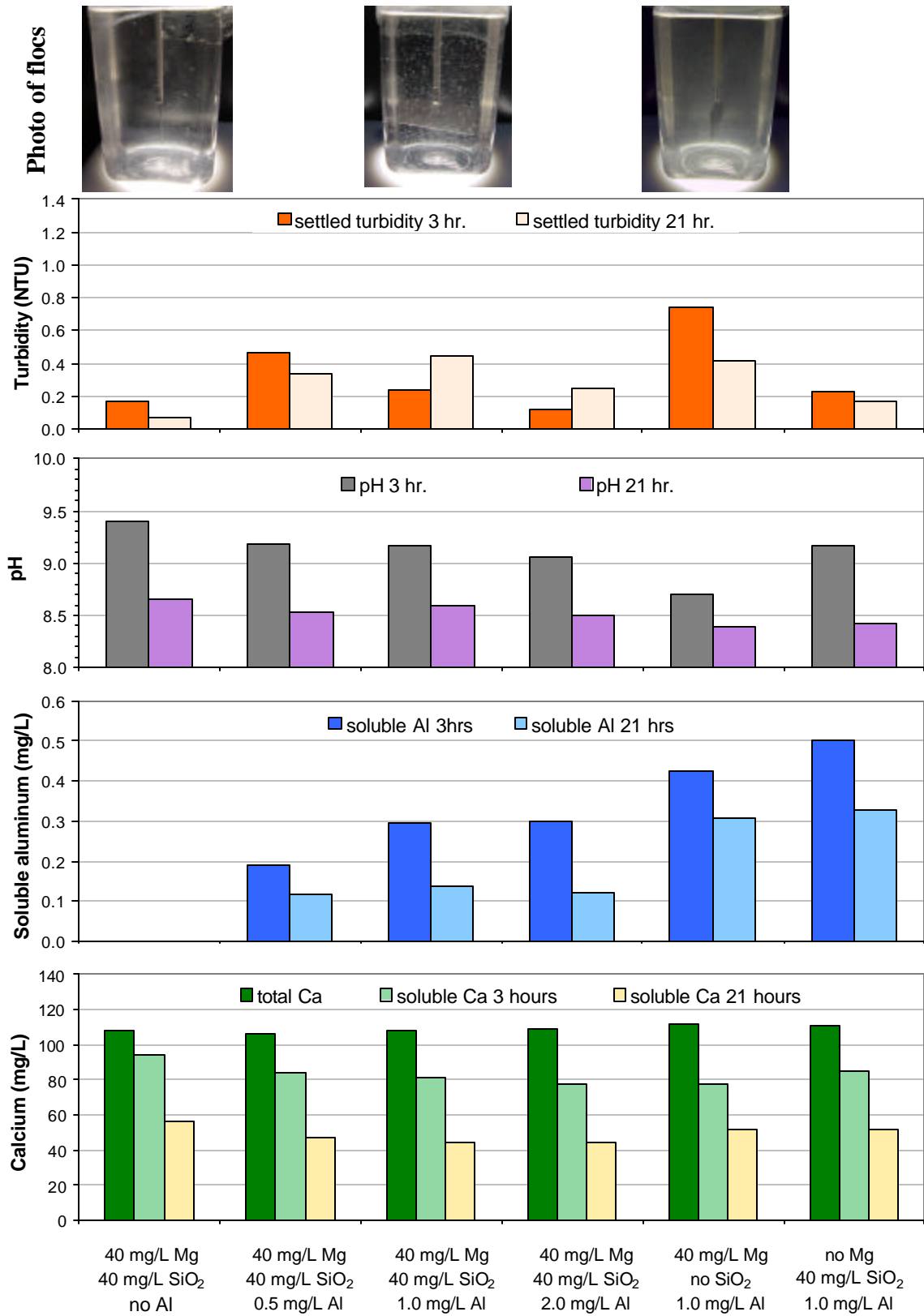


Appendix C) Al-Mg-OH and Al-Mg-Si-OH / Al-Si-OH solids formed at higher concentration for collection of solids and X-ray diffraction. Top shows floc formation after 24 hours, Bottom shows settling after 20 minutes.

Appendix D) Chapter II, Turbidity data for jar tests, during flocculation and post settling

Solution *			pH	time	Flocculation	Settled
Al mg/L	Mg mg/L	SiO ₂ mg/L	control	hours	turbidity	turbidity
					NTU	NTU
0	40	40	drift	3	0.41	0.17
0.5	40	40	drift	3	5.2	0.47
1.0	40	40	drift	3	7.8	0.24
2.0	40	40	drift	3	14.5	0.12
1	40	0	drift	3	6.5	0.74
1	0	40	drift	3	1.0	0.23
0	40	40	hold 9.5	3	0.58	0.41
0.5	40	40	hold 9.5	3	2.8	0.98
1.0	40	40	hold 9.5	3	8.6	0.98
2.0	40	40	hold 9.5	3	22.5	0.75
1	40	0	hold 9.5	3	25.8	0.23
1	0	40	hold 9.5	3	1.4	0.75
0	40	40	drift	21	-	0.07
0.5	40	40	drift	21	-	0.34
1.0	40	40	drift	21	-	0.45
2.0	40	40	drift	21	-	0.25
1	40	0	drift	21	-	0.42
1	0	40	drift	21	-	0.17
0	40	40	hold 9.5	24	0.06	0.04
0.5	40	40	hold 9.5	24	1.4	0.13
1.0	40	40	hold 9.5	24	5.9	0.26
2.0	40	40	hold 9.5	24	15.7	0.29
1	40	0	hold 9.5	24	4.7	0.26
1	0	40	hold 9.5	24	0.37	0.15

* allcontain: 100 mg/L Ca⁺², 150 mg/L HCO₃⁻, 7x10⁻³ M NaNO₃



Appendix E) Chapter II, Jar test results, pH allowed to drift after initially raised to 9.50

AUTHOR'S VITA

STEVEN JOSEPH KVECH

Steve Kvech was born on October 7, 1976 in Baltimore, Maryland and was raised in nearby Linthicum, Maryland. Steve attended Virginia Tech in Blacksburg, Virginia from 1994-2001 earning a Bachelor of Science Degree in Civil Engineering in addition to a Master of Science Degree in Environmental Engineering. He has accepted a position with George, Miles and Buhr Engineers in Salisbury, Maryland.