Water Quality, Aesthetic, and Corrosion Inhibitor Implications of Newly Installed Cement Mortar Lining Used to Rehabilitate Drinking Water Pipelines

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ABSTRACT

For decades, cement mortar relining has been used successfully to extend the life of drinking water pipelines, although, few quantitative data exist on the short-term water quality impacts of this process. This study investigated mortar lining impacts on disinfectant by-product formation, alkalinity, metal leaching, pH and disinfectant consumption, and odor generation shortly after in-situ installation. The experimental design used a 30-day, coupon immersion procedure that simulated a relined 4-inch diameter pipe located in a low-flow system. Four water regimes were utilized; no disinfectant, chlorine (2 mg/L at pH 6 .5 and 8), and chloramines. Flavor Profile Analysis panels evaluated odors of samples and controls. Additionally, the affects of three different phosphate-based corrosion prevention additive regimes were evaluated. Cement mortar leachates impacted water quality significantly during the first week of exposure. Alkalinity, hardness and pH increased dramatically after initial exposure, rising to approximately 600 mg/L as $CaCO_3$ alkalinity, 770 mg/L as $CaCO_3$ hardness, and pH 12 in the first two days. Sharp declines in alkalinity and hardness did not occur until after day 9 when the cement mortar was substantially cured and release of calcium hydroxide lessened. Chlorinated water residual disinfectant decay rate was increased substantially during the initial 24 hours and remained elevated until day 9. After day 1, there was not a significant increase in the formation of regulated haloacetic acids or trihalomethanes. Significant levels of aluminum ($\leq$ 700 ug/L) and chromium ($\leq$ 75 ug/L) were released at various times during the test period but their concentrations did not exceed USEPA water quality standards. Cement odor intensity levels were significantly higher than controls, persisted for 14 days, and were of an intensity that would be readily noticeable to consumers. The polyphosphate-based corrosion preventative resulted in less severe water quality effects than other phosphate additives or water without added phosphate.

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1. LITERATURE REVIEW

1.1. Introduction

In the 1980's and 1990's there was an increase in concern related to the use of cement mortar lining and its impact on water quality. A survey of 33 US water utilities, each of which had significant sections of cement mortar-lined pipe, was completed in 1989 found that seven were experiencing substantial pH increases and four of these were receiving related customer complaints. These complaints were from customers who were in low flow or dead-end areas of the distribution system (Douglas *et al.*, 1991). In the UK, it was determined that excessively high pH levels were being found in cement mortar relined portions of water distribution systems delivering low alkalinity/low hardness source waters. Because these pH levels were violating European Union standards and were accompanied by significant increases in metal concentrations, several research efforts were initiated (Conroy *et al.*, 1993). To better understand the many factors that contribute to this problem and develop an enhanced research effort that can build upon the work previously completed, a literature review was conducted to determine the following:

- The history and technology related to in situ cement mortar relining of water pipelines
- Scope and findings of previous research related to the water quality and aesthetic impacts of in situ applied cement mortar linings
- Scope and findings of previous research related to the implications of corrosion preventative additives on the above mentioned water quality impacts

This review is provided in the following sections.

1.2. History of In-situ Cement Mortar Linings

The rehabilitation of iron and steel water mains using in-situ cement mortar lining was first performed in 1933. In the early years of this rehabilitation approach the smallest diameter pipe that could be relined was 24 inches. This limitation was the result of the cement spraying rig being manually controlled and requiring an operator to travel through the pipe. In the 1950's, remote spray rigs were developed and perfected thus allowing pipes as small as 4 inches in diameter to be relined. Water mains with diameters ranging from 4 inches to 28 feet are now routinely cleaned and in situ relined by utilities throughout the US (AWWA/ANSI, 2006).

1.3 Cement Mortar Lining Technologies and Protocols

In the US, the industry standard for in situ cement mortar relining of water mains is provided by the AWWA as ANSI/AWWA C602-06 – *Cement Mortar Lining of Water Pipelines-4 inches and Larger* (C602-06). The relining process described in C602-06 consists of the following procedural steps:

- The pipe section of interest is thoroughly cleaned and all loose debris removed
- A cement mortar meeting the requirements of C602-06 is prepared (usually a sand to cement ratio of 1:1) and placed in a hopper
- The mortar is fed to a traveling centrifugal spray rig which moves through the pipe such that the rig does not pass over the newly applied mortar
- The fresh mortar is then finished with a mechanical trowel
- For small pipes (4-10 inches in diameter), the finished mortar thickness should be 4.8mm for ductile iron pipe, 6.3mm for new steel pipe and 8.0mm for old steel pipe
- The pipe is filled and the cement is allowed to cure for 24 hours minimum (no hydraulic pressure is applied at this time)

- The relined pipe section if filled with highly chlorinated water (200 mg/L free chlorine) for 30 minutes, rinsed, inspected and placed back into service (ANSI/NSF, 2000)

This procedure provides a smooth, relined surface which reduces hydraulic friction and protects the pipe against chemical corrosion.

1.4 Previous Research on Water Quality Impacts

Several literature sources were reviewed in preparation for this study. Some sources were specifically germane to drinking water-mortar chemical interactions and provided considerable amounts of valuable information. These sources are reviewed in much greater detail than those sources which provided more general information related to the chemistry of the cement mortar curing process. These reviews are provided in the following sections.

1.4.1 Corrosion and Leaching Effects

United States

In the early 1990's, some utilities began reporting water quality problems associated with cement mortar lining corrosion. The American Water Works Association Research Foundation (AWWARF) funded research to investigate the problem's breadth, causes and water quality impacts. A key report, and subsequent AWWA Journal article, presented the results of one such research project ((Douglas, 1991),(Douglas, 1996)).

The first phase of the research involved the previously mentioned surveying of 33 utilities on the frequency and severity of customer complaints related to recently installed, in situ cement mortar linings. Four utilities responded that they had frequent complaints and they considered the water quality problems significant. Two of these utilities agreed to assist the research team in the project's second phase, assessing the chemical water quality impacts of cement mortar lining materials. One utility, the South Central Connecticut Regional Water Authority (SCCRWA), had very aggressive finished water with a pH of 7.19, an alkalinity of 14 mg/L as $CaCO_3$ and a calcium concentration of 13 mg/L as $CaCO_3$. The other utility, the Marin Municipal Water District (MMWD) in California, had less aggressive water with values of 7.82, 71 and 38 for the same parameters/units shown above. The SCCRWA finished water was normally augmented with the corrosion preventive additive (CPA) zinc metaphosphate ($Zn{:}P_2O_5 = 1{:}7.5$, 2 mg/L) and the MMWD water had a zinc orthophosphate additive ($Zn{:}PO_4 = 1{:}3$, 0.3 mg/L as Zn).

The test setup was an assembly of ten pipe sections, arranged vertically, with each pipe being 1m in length and four inches in diameter. Five of the ten test sections utilized conditions germane to this report. Using the section numbers from the referenced report, the test conditions are provided below in Table 1-1.

Table 1-1. Test Conditions, Five Test Pipe Sections (adapted from Douglas et al, 1996)

Section No.	Flow Regime	Lining Method	Cement to Sand Ratio	CPA Type	Portland Cement Type
1	Continuous	In situ, spray/trowel, 24 hour cure	1:1	Normally used at WTP	I
2	Flush daily			Normally used at WTP	I
3	Flush weekly			Normally used at WTP	I
6	Flush weekly			Alternative CPA used[1]	I
8	Flush weekly			Normally used at WTP	II

[1] Alternative CPA at SCCRWA was zinc orthophosphate ($Zn{:}PO_4 = 1{:}3$, 0.3 mg/L as Zn), alternative CPA at MMWD was polyphosphate-orthophosphate at 0.8 mg/L as phosphate

The same test rig was established at each plant and actual finished water tapped and delivered to the rig (except for pipe section 6 which was fed from a storage tank). Water samples were taken frequently and tested for pH, alkalinity and calcium. On a less frequent basis, testing for silica, zinc, magnesium, phosphate, iron and manganese was completed. Table 1-2 provides a summary of the results and conclusions associated with the variables studied using the five lined pipe sections.

Table 1-2. Summarized Results and Conclusions from Cement Mortar Pipe Lining Tests, Five Selected Pipe Sections (Douglas et al, 1991)

Test Variable	Results	Conclusions
Flow	1. Continuous flow water had nearly identical chemical composition as feed water (no pH or alkalinity increase) 2. Daily flush water had pH increase 4-5 units from baseline, alkalinity increase to 390 mg/L as $CaCO_3$, calcium increase to 80 mg/L as $CaCO_3$ 3. Weekly flush water had pH increase more than 5 units from baseline, alkalinity increase to 760 mg/L as $CaCO_3$, calcium increase to 135 mg/L as $CaCO_3$ 4. All of these parameters stabilized at lower levels as the test progressed.	1. Increased water stagnation increases the pH, alkalinity and calcium content of the exposed water. 2. Continuous water flow eliminates observed increases due to dilution 3. All observed values decrease and stabilize after weeks of exposure
Portland Cement Type	1. Over the 13-week test, Type II cement resulted in higher pH, alkalinity and calcium values 2. Type II cement resulted in lower values for same parameters early in test period (<3 weeks)	1. Type II cement results in higher pH, alkalinity and calcium levels in long term testing (months) 2. Type II cement does deliver lower values in the short term (<3 weeks)

Test Variable	Results	Conclusions
CPA Type	1. At MMWD, the use of polyphosphate-orthophosphate vice zinc orthophosphate resulted in higher levels of pH, alkalinity and calcium in the short term (<2 weeks) but then performed better after that point. 2. At SCCRWA, zinc orthophosphate was used instead of zinc metaphosphate and resulted in significantly higher levels of pH, alkalinity and calcium throughout the entire test period.	1. Polyphosphates, with or without zinc, perform better than zinc orthophosphate with respect to controlling cement corrosion
Inlet Water Aggressiveness	1. The highly aggressive SCCRWA water returned much higher pH, alkalinity and calcium levels in weeks 1 and 2. 2. The SCCRWA water resulted in only slightly higher values at the test period end.	1. Aggressive waters have significant impacts on the resulting pH, alkalinity and calcium levels in the short term (1-2 weeks) 2. The difference between highly and slightly aggressive waters is reduced significantly over time (>10 weeks)

Additionally, tests for trihalomethanes (THM) were performed on the waters from all ten pipe sections at the MMWD facility. This analysis was done at the 13-week termination of the test period. No significant THM levels were found in any of the ten pipe sections.

Samples of pipe lining material were removed from the pipe sections at both test sites. Lining material was abraded and collected at various depths up to 1.27mm. These samples were then tested for calcium loss and pH. Observations included reduced calcium content in the continuous flow and flushed daily lining sections while the flushed weekly sections showed an increase in calcium content. The latter finding was not explained.

The report by Douglas et al. (1991) provides useful information related to the lining material's effects on pH, alkalinity and calcium concentration. However, there was no information gathered during the test period on organic water chemistry (except for THM data above) or aesthetic impacts. No data related to the leaching of metals was discussed nor was there any discussion on the disinfectant levels at each site.

In another report, various sources of elevated aluminum levels are discussed. Snoeyink et al. (2003) consolidate the available research findings on the topic and highlight newly installed cement mortar linings as a potential aluminum source. The report states that newly installed mortar linings can release significant amounts of aluminum especially when water is low in pH and alkalinity. A specific case, from the Dutch Antilles, where a relined pipeline increased aluminum levels to 550-690 µg/L is put forth as an extreme example (Snoeyink *et al.*, 2003).

United Kingdom (#1) – There has been considerable research performed on the water quality affects of in situ applied cement mortar linings in the late 1980's and early 1990's. This research was spurred by the new regulatory demands promulgated by the European Union which were subsequently embraced and enforced by regulatory agencies within the UK. Although cement mortar lining materials were immune to the new regulations due to their longstanding use, the increased focus on water quality and a more robust regulatory framework prompted government entities to increase research in this area. The UK has many low alkalinity, low hardness water sources which were known to be highly corrosive to cement lining materials and there was empirical evidence to suggest corrosion was occurring (distribution system sampling). In 1990 and 1991, Conroy et al, of the Water Research Centre, were funded to investigate the water quality affects caused by newly applied cement mortar lining with a particular interest in low alkalinity source water applications.

The regulatory test for materials in contact with potable water is British Standard (BS) 6920. Conroy decided to move beyond this standard test and perform controlled field tests at four sites (100m long, 100mm diameter (4-inch) iron pipe, installed sections) and build a substantial test rig (40m long, 100mm diameter iron pipe, above ground rig). The pipes were spray-lined and drag trowel finished using ordinary Portland cement mortar. The lining was allowed to cure for 20 hours followed by chlorine disinfection and rinsing. The paper reviewed provides a summary of their test observations using the described equipment and various source water alkalinities.

Using a one-hour retention time between pipe flushing and a source water alkalinity of 35 mg/L as $CaCO_3$ for the pH testing and a six-hour retention time and an alkalinity of 8 mg/L as $CaCO_3$ for aluminum concentration testing, the observations provided in Figure 1-1 were made. These two parameters were provided in the summary because they exceeded the UK water quality regulatory limits for extended time periods. The pH increases rapidly to 11.3 even with relatively frequent flushing and remains high for many weeks. The aluminum concentration also increases and exceeds the USEPA limit of 200 ug/L for the same duration. The elevated pH and aluminum levels were simply attributed to the leaching of calcium hydroxide and aluminum from the mortar. The water's weak buffering capacity is noted as a contributing factor (Conroy *et al.*, 1991; Conroy, 1993).

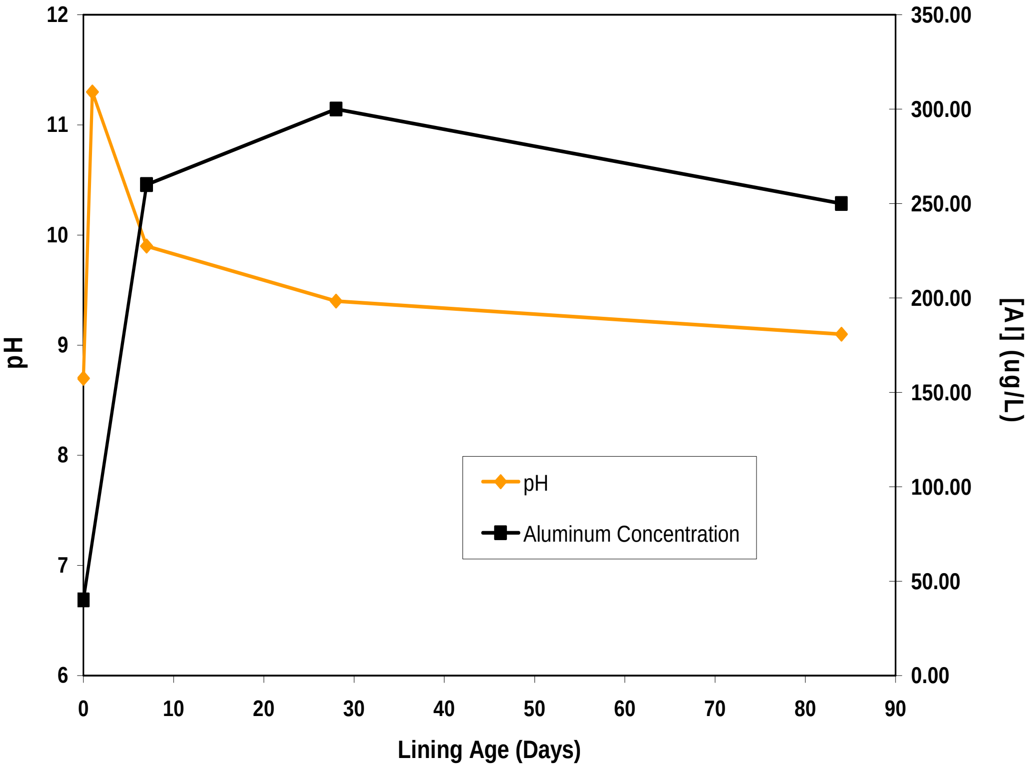


Figure 1-1. pH and Aluminum Concentration vs. Mortar Lining Exposure Time (data from Conroy et al, 1991)

United Kingdom (#2) – As part of a research program to develop a model of cement's resistance to sulfate attack, researchers at the University of Aberdeen in Scotland developed a precursor model to predict the thermodynamic relationships of dominant chemical species when Portland cement and water are mixed(Damidot *et al.*, 1993). They utilized empirical data from previous published sources, known solubility constant data and a computer-based predictive model to determine the solid-phase diagram for the cement-water species interactions. The model provides an analysis of the complex system that is germane to this study for the following reasons:

- It considers gypsum (calcium sulfate) in the calculations and gypsum is an ingredient in the Type II Portland cement used in this study

- It performs the analysis at pH levels ranging from 11.0 to 12.5, the anticipated pH range of this study
- The analysis considers the formation of several calcium and aluminum-based complexes that are not normally considered in discussions related to metal-ligand solubility

Some of these key complexes are as follows:

- Ettringite $(3CaO \cdot Al_2O \cdot 3CaSO_4 \cdot 32H_2O)$
- Monosulphoaluminate $(3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O)$
- Hydrogarnet $(3CaO \cdot Al_2O_3 \cdot 6H_2O)$
- Gypsum $(CaSO_4 \cdot 2H_2O)$

In addition to these complexes, the more commonly considered hydroxides of aluminum (gibbsite) and calcium (portlandite) are key species included in the calculations. All of these compounds would be equilibrating within the aqueous solution found within the pores of the cement liner surface as well as in the bulk drinking water.

The model's key output is the soluble concentration of aluminum at various calcium and sulfate concentrations and an identification of the solid controlling the soluble aluminum level. The resulting two-dimensional (Ca vs. Al at constant sulfate concentration) and three dimensional (Ca vs. Al vs. Sulfate) plots may be very useful tools when interpreting aluminum concentrations within the complex aqueous environment anticipated in this study.

Other Research Work

A significant factor influencing the leaching of inorganic chemical species from the mortar is the material's porosity and related permeability. As the mortar is mixed, the spaces between the calcium silicate granules are filled with water. This water becomes highly saturated with OH^- and Ca^{2+} ions, and other dissolved chemical species, which can pass into the bulk water easily due to the paste's high porosity and permeability (Lewis, 1995). As the cement hydrates, its porosity decreases and the ability for the various chemical species to migrate into the bulk water decreases. Malhotra et al have summarized research findings related to the porosity of cement pastes similar to the composition used in this study and found that porosity on day 1 was 45% and decreased to 34% by day 14. The porosity of the fully cured cement paste falls to 28% (at 180 days). This indicates that 65% of the porosity decrease occurs in the first 14 days followed by a much slower reduction (Malhotra *et al.*, 1987). This suggests that the impacts to water quality induced by the leaching of inorganic chemicals may be significantly reduced after day 14.

In addition to the porosity work shown above, Malholtra reported on the effects that the addition of extremely fine silica particles to the cement paste can have on many cement paste chemical and physical properties. These silica particles are called condensed silica fume and have been extensively studied. The silica fume addition has two important effects:

- A more rapid reduction in the cement pastes porosity due to the silica fume's ability to increase the rate of hydration and produce cured cement with a higher calcium silicate hydrate to calcium hydroxide ratio
- A significant reduction in the calcium hydroxide content within the paste's pore spaces during the hydration process

These data, presented in Figures 1-2 and 1-3, provide the basis for these conclusions (Malhotra, 1987). The cement pastes studied had a water to cement ratio of 0.45 which is very close to the 0.43 ratio used in this study. The silica fume was added such that the water to cement/silica fume ratio remained at 0.45 and that 10% of the cement was replaced by the silica. In Figure 1-3, the reported slope reflects the final slope of the pore size distribution curve developed though mercury intrusion tests. A high slope indicates a higher percentage of smaller pore sizes (10-80nm) versus larger pore diameters (100-600nm).

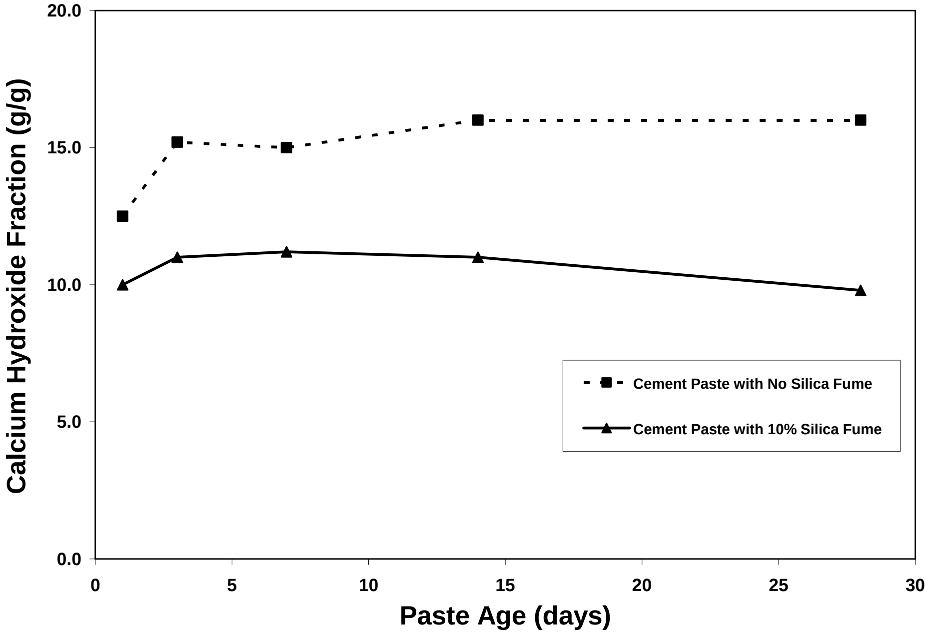


Figure 1-2. Pore Space Calcium Hydroxide Fraction, Cement Paste with 10% Silica and Control (data from Malholtra, 1987)

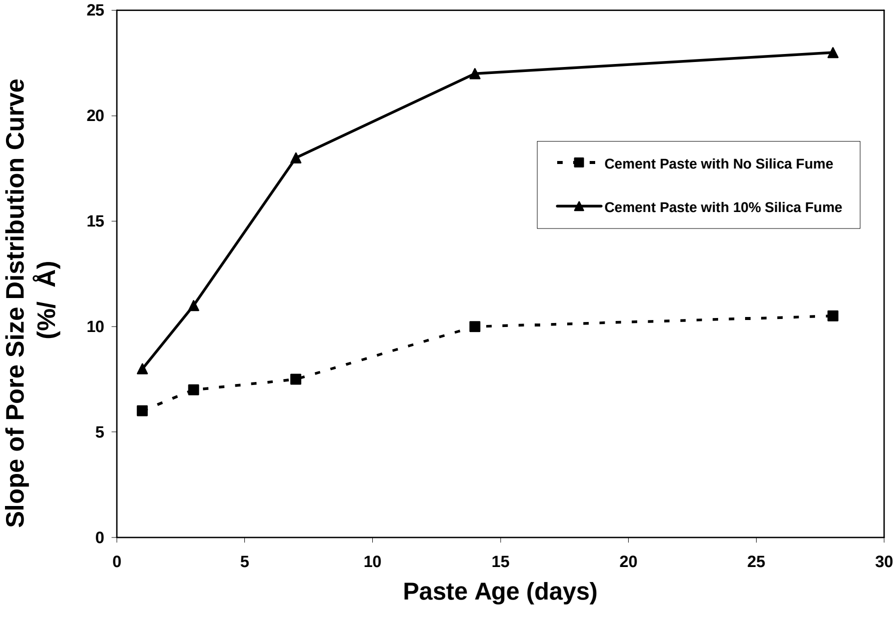


Figure 1-3. Slope of Pore Size Distribution Curve, Cement Paste with 10% Silica and Control (data from Malholtra, 1987)

The silica's ability to reduce the pore space calcium hydroxide content and reduce the pore size may prove to be an effective strategy in reducing some of the adverse water quality effects seen in previous work and anticipated in this study.

1.4.2 Aesthetic Quality Effects

No previous research on the aesthetic effects of cement mortar lining was found but the utility of using Flavor Profile Analysis (FPA), as described in Standard Method 2170, to evaluate drinking water odors resulting from contact with pipe materials is well established. In 2007, Durand and Dietrich used the FPA method effectively to evaluate off odors from drinking water exposed to various types of polyethylene pipe. The waters utilized were disinfected with chlorine or monochloramines and the FPA panelists were able to detect odor differences between the two chlorination types as well as the controls. Also in 2007, Heim and Dietrich used the same FPA method as part of an investigation on the odors imparted by epoxy pipe lining materials. These successful applications of the FPA method speak well to the sensitivity of the method as well as the importance of having a well-trained FPA odor panel((Durand, 2007) and (Heim, 2007)).

1.4.3 Impacts of Corrosion Preventatives on Cement Mortar Lining Effects

There has been limited research work performed on the influence of corrosion prevention additives (CPA) on the lining material's leaching behavior. Many water utilities use phosphate-based CPA to reduce the corrosion of the distribution system's metallic components. There is potential for the various phosphate forms to combine with the mortar leachates and coat the liner surface thus affecting subsequent leaching behavior. The work by Douglas et al. (1996) discussed above did address the subject in a limited manner. Their work observed that polyphosphate-based CPA limited pH and alkalinity increases more effectively the zinc orthophosphates after two weeks of exposure time.

A comprehensive theoretical examination of the very complex interactions between CPA-augmented water and cement mortar was presented in a 1981 AWWA Journal article. The research, led by Schock et al. (1981), was sponsored by the AWWARF and USEPA in response to asbestos fiber release concerns due to the corrosion of asbestos-cement (A-C) pipes. Although the research did not specifically consider cement mortar relined pipes, the chemical species and their interactions are very similar to those seen in a relined pipe. A central research objective was to create a computer-based model that could predict the chemical speciation and respective specie solubility levels present when waters of various alkalinity, pH and calcium content are exposed to the pipe's cement binder (Schock *et al.*, 1981). The solubility constants used were obtained from previous research literature. The model also considered the inclusion of zinc orthophosphate CPA as part of the system. The model was applied to systems with pH levels ranging from 5 to 10 but the solubility trends are predictive for higher pH levels. Of the 19 different water type/CPA systems modeled, two were germane to this study. One system had a total carbonate level of 40 mg/L as $CaCO_3$ while the other was 100 mg/L as $CaCO_3$. Each had zinc orthophosphate added at 0.5 mg/L as Zn added. The model provides a logarithmic Saturation Index (SI) for each chemical species with an SI>0 suggesting a precipitate forming. The model also provides a predicted dissolved concentration for zinc, calcium and phosphate. The most pertinent conclusions were drawn from the derived curves with some interpolation to the higher pH levels anticipated during this study. These conclusions are summarized below:

- At pH levels of 8.5 and greater, calcium (from calcium carbonate) and phosphate concentrations begin to decrease rapidly with increasing pH due to precipitation of hydroxyapatite ($Ca_5(PO_4)_3OH$) and $CaCO_3$, with the hydroxyapatite being the leading precipitate (SI=5.8 at pH 10)

- The dissolved zinc level is at its minimum at pH 9, then increases rapidly as pH increases due to the increased solubility of all zinc complexes

Thus, at high pH levels, the dissolved concentration of phosphate should be relatively low due to precipitation and zinc concentrations relatively higher due to increased solubility. Schock and Buelow indicate that calcium levels may be influenced greatly by the solubility of the tricalcium and dicalcium silicates present in the cement before it is hydrated. Based on the theoretical Gibbs free energy values for these solids, it was determined that they would be highly soluble in drinking water and could contribute significantly to the level of dissolved calcium at least until they were fully hydrated. This behavior may mask the model-predicted low calcium levels. They also stated that aluminum levels would be elevated due to the similar dissolution of calcium aluminate.

1.5 Need for Further Research

The dominant water chemistry effects of in situ applied cement mortar linings, namely pH, alkalinity and hardness, have been studied in significant detail. There is a need to expand our knowledge-base related to cement mortar linings and their drinking water impacts. The areas most in need of further study are as follows:

- Organic chemistry effects such as disinfectant by-product and other organic chemical formation since these have become highly regulated parameters and of great concern to water utilities,

- Enhanced understanding of potential metals leaching which can have both health and aesthetic effects, the latter resulting in increased consumer complaints,

- The potential effects, both positive and negative, of corrosion prevention chemicals on the leaching behavior of cement mortar linings,

- The impacts on the decay rate of disinfectant residuals since this is an important factor in ensuring that microbial growth within the distribution system is controlled thus preventing any drinking water-related health concerns,

- Sensory impacts which may result in consumer complaints

This study’s objective is to further the collective knowledge base in these areas and uncover additional opportunities for subsequent research work.

2. MATERIALS AND METHODS

This research project investigated the water quality and aesthetic impacts of cement mortar lining materials by utilizing a coupon immersion regime followed by various testing methods to achieve the research objectives. The following sections describe the materials and methods used to manufacture the coupons, execute the immersion tests and evaluate the chemical and aesthetic impacts caused by the leaching of various coupon constituents.

2.1 Test Apparatus and Water Types

2.1.1 Cement Mortar Coupons

The fabrication of the cement coupons was performed in two phases, prototype and final production. The prototype phase was an opportunity to prove out the cement mortar recipe, mold design, mold filling process and determine if appropriately sized coupons would result. There were two iterations of mold design, fabrication and filling completed during this phase. The original mortar recipe, meeting the requirements of AWWA C602, *Cement Mortar Lining of Water Pipelines in Place – 4 In. and Larger*, and recommended by Dr. Richard Weyers, a Virginia Tech professor, performed successfully in all cases (AWWA/ANSI, 2006). The coupon size also proved to be appropriate. The final production recipe, design and process that resulted are described in more detail below.

2.1.1.1 Cement Mortar Recipe

The cement mortar recipe was determined by following the guidelines listed in the AWWA publication listed above and conversing with Dr. Richard Weyers, a professor at

Virginia Tech and an expert in cement chemistry and construction applications. The following recipe, Table 2-1, was used successfully throughout the prototype and production phases:

Table 2-1. Cement Mortar Recipe

Ingredient	Amount
Sand (Medium Grade, Washed)	1:1 ratio with cement
Cement (Type II Portland cement)	As needed
Water (Tap)	0.43 weight fraction of cement weight (no adjustment made for sand absorption)

2.1.1.2 Coupon Molds

The two production molds consisted of a plywood base that was covered with a thin Teflon® sheet upon which a one centimeter high grid was affixed. Each wooden member of the grid was wrapped in Teflon® film. Each mold grid produced 50 of the 8cm x 8cm x 1cm coupons. The design allowed for easy filling and mortar leveling during the fabrication process.

2.1.1.3 Coupon Manufacture

The coupon production process consisted of the following steps:

1. <u>Mortar mixing</u> – the mortar was mixed in an electric drum mixer using the recipe shown above. Dry ingredients were mixed initially followed by the slow addition of water. The mortar was mixed for approximately 15 minutes. Two batches of mortar mix were produced, one for each mold assembly, over a 90-minute timeframe.

2. Mortar placement – the mortar was transferred to each grid segment using aluminum scoops. The mold was placed on a vibrating table to aid in distributing the mortar. The mortar was initially leveled using a wooden screed. Low spots were filled with fresh mortar and final leveling was accomplished using steel cement finishing trowels. A photograph of a filled mold is provided in Figure 2-1:

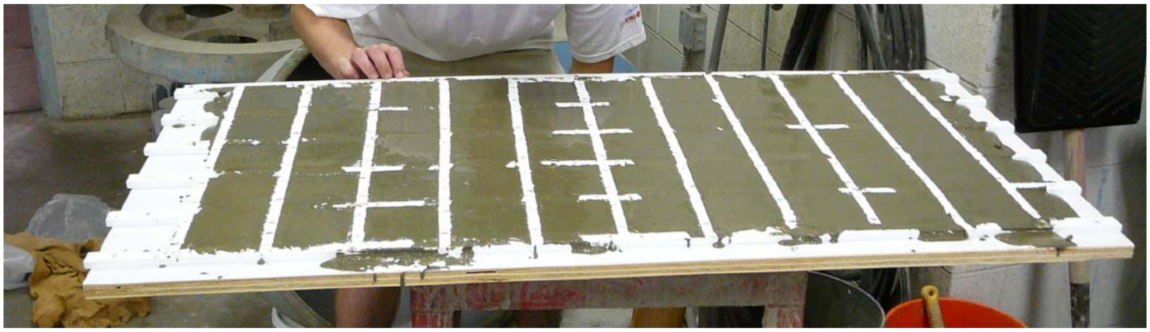


Figure 2-1. Filled Coupon Mold Ready for Curing

3. Coupon curing – the filled molds were placed in a humid room and covered with one layer of polyethylene sheet to preserve moisture during the curing process. The coupons were cured for 24 hours.

4. Coupon removal – the molds were removed from the humid atmosphere and examined for anomalies. Each grid member was then removed thus allowing the coupon to release. The coupons were easily removed due to the Teflon surfaces. All coupons were found to be acceptable and were transported back to the testing lab so that they could be immersed in the test waters.

2.1.1.4 Cement Coupons for CPA and THM Formation/Sorption Testing

For the CPA effects testing, the fabrication of the cement coupons was performed using the same procedures, raw materials, mortar recipe and coupon mold as was used during the leaching tests. The coupons were also dimensionally identical. There were no problems encountered in producing the cement coupons in the same manner as the original coupon set. The coupons were cured for 24 hours before being immersed in the sample waters.

The additional evaluation of THM formation/sorption was conducted using coupons manufactured using the identical procedures described above. A total of seven coupons were fabricated. Five coupons were used to support the THM formation test and two were used within the THM sorption testing. The two sorption coupons were cut into six equal segments during the initial 24-hour curing period so that the individual pieces could fit into the 40mL vials that were used as immersion vessels. There were no problems encountered in producing the cement coupons in the same manner as the original coupon set. As before, the coupons were cured for 24 hours before being immersed in water.

2.1.2 Immersion Test Vessels

The vessels in which the coupons were immersed were fabricated from 173mm diameter, borosilicate serum jars. The jars were reduced in height and a ground glass lip was formed around the top opening. Glass lids were fabricated which, when placed on the filled vessel, formed a headspace-free, airtight seal. The vessels were approximately three liters in volume. Each vessel had Teflon® holding racks which supported six coupons vertically. The coupon surface area to water volume ratio was calculated to be 0.39cm^{-1} which is equivalent to a 4-inch diameter pipe. Triplicate vessels, each with six coupons, were utilized for each of the four water types. One control vessel, with empty Teflon racks, was utilized as the control for each water type. This resulted in 16 vessels being used for this research project. Figure 2-3 provides a photograph of the coupon immersion setup. All vessels contained a magnetic stir bar to aid in mixing the contents before sampling.

Figure 2-2. Coupon Immersion Test Setup

The test vessels used for the corrosion preventative additive (CPA) evaluation were approximately one-sixth in size when compared to those used during the primary leaching tests. They were square, plastic, one-liter containers with open tops. The use of plastic containers and the presence of headspace were acceptable since there were no organic chemical tests planned as part of this experimental section. The vessels were filled with 410mL of prepared sample water and one coupon was immersed in the water. The coupon was supported at an angle by a small glass cylinder. This ensured that all coupon surfaces were in contact with the water. The surface area to volume ratio created by this procedure was $0.39cm^{-1}$ which is the same ratio created by the original setup described above.

There were duplicate test vessels used for each water type (control, orthophosphate (OP), polyphosphate (PP) and orthophosphate with zinc (OPZn)) resulting in eight test vessels being used. The vessels were stored in a dark cabinet except when being sampled and having the water changed. Each was covered with plastic wrap to minimize evaporation.

The additional THM formation testing was performed by first placing five coupons in one of the 3-liter immersion vessels for seven days. This vessel was maintained headspace-free for the duration of the coupon immersion. This created water containing the leached organic compounds that could be expected when water was in contact with the lining material.

2.1.3 Water Types

For the cement mortar lining test, the coupons were immersed in four different water types. The four water types were selected to determine the effects of disinfectant presence, disinfectant type and pH level with the most common disinfectant (chlorine). All the test waters were made by starting with a base water recipe which is provided below in Table 2-2. This base water represented a low alkalinity, low hardness water with a composition similar to treated drinking water. The salts listed in Table 2-2 were added to Nanopure® water.

Table 2-2. Base Water Recipe

Chemical	Molarity
$MgSO_4$	0.000329218
$NaHCO_3$	0.0006773
$CaSO_4*2H_2O$	0.000145197
$CaC1_2*2H_2O$	0.000141477
$Na_2SiO_3*9H_2O$	9.14849E-05
KNO_3	9.89022E-05
HCl	0.0002

The other test waters were made by adding the appropriate concentration of disinfectant and adjusting to the desired pH. The description of the four manufactured test waters is as follows:

1. pH = 8.0, low alkalinity/hardness, no disinfectant (base water)
2. pH = 6.5, low alkalinity/hardness, 2.0 mg/L chlorine.
3. pH = 8.0, low alkalinity/hardness, 2.0 mg/L chlorine.
4. pH = 8.0, low alkalinity/hardness, 4.0 – 6.0 mg/L monochloramine.

In support of each water change, 11-liter glass bottles of each water type would be prepared. The chlorine was added as NaOCl after which the pH was adjusted using hydrochloric acid. The monochloroamine was added by adding NH_4OH followed by NaOCl. These additions were made with the water constantly stirred. Once these were added, five minutes was allowed to elapse and then the water was vigorously shaken for 30 seconds. The pH was then adjusted using hydrochloric acid.

The same low alkalinity, low hardness base water recipe was used for the CPA experiments as was used for the original coupon immersion experiments. The base water was augmented with the CPA of interest and adjusted to a pH 8.0 for CPA test samples or only pH adjusted when used as a control. There were three CPA water types created for use in the test and their recipes are provided in Table 2-3. The CPA dosage levels are representative of corrosion prevention programs used throughout the potable water treatment industry.

Table 2-3. CPA Test Water Recipes

Water Type	CPA Added	CPA Addition Form	Resulting CPA Concentrations
Base (Control)	None	NA	NA
Orthophosphate (OP)	Na_3PO_4	Stock aqueous solution	1.0 mg/L as P
Polyphosphate (PP)	$Na_8P_6O_{19}$	Stock aqueous solution	1.0 mg/L as P
OP and Zinc (OPZn)	Na_3PO_4 and $ZnCl_2$	Both stock aqueous solutions	1.0 mg/L as P 0.3 mg/L as Zn

The base water was used for the THM formation coupon leaching. It was also used as the initial water that was spiked with chloroform in support of the THM sorption test. In both cases, the pH was adjusted to 8.

2.2 Laboratory Procedures

2.2.1 Leaching and THM Formation/Sorption Test Procedures

Primary Mortar Lining Impact Evaluation – The leaching test procedures were adapted from the test procedures provided in ANSI/NSF-61 which has been the industry-standard protocol for evaluating the potential leaching of organic and inorganic compounds from materials in contact with drinking water (ANSI/NSF, 2000). This leaching test was 30 days in duration with water change/sampling occurring in accordance with the schedule provided in Table 2-4. The schedule was developed to collect early data frequently (three changes in days 1 through 4) and then provide for variable sampling frequencies later in the test period.

The water change process consisted of placing the immersion vessel on a magnetic stirrer for no less than one minute to homogenize the water. This was followed by removing the coupons and racks as a single unit from the immersion vessel. The water was then transferred from the vessel to the various sample vials using a clean glass beaker. The coupons/racks were then placed back into the empty vessel and the correct replacement water was poured into the vessel until the glass lid could be positioned with no air bubbles present. The vessel was then placed in a dark cabinet until it was to be sampled again. Nitrile gloves were worn during all of these procedural steps.

Table 2-4. Cement Coupon Leaching Test Sampling/QC Schedule

Parameter	Frequency (Day)	Method Blank	Check Sample	Matrix Spike Duplicate	Surrogate Standards
TOC	1, 2, 4, 9, 11, 14, 15, 19, 24, 30	X	X		
Disinfectant Residual	1, 2, 4, 9, 11, 14, 15, 19, 24, 30	X			
Hardness	1, 2, 4, 9, 11, 14, 15, 19, 24, 30	X	X		
Alkalinity	4, 9, 11, 14, 15, 19, 24, 30	X	X		
pH	1, 2, 4, 9, 11, 14, 15, 19, 24, 30	X			
Temperature	1, 2, 4, 9, 11, 14, 15, 19, 24, 30	X			
Odor	1, 4, 9, 14	X	X		X
THMs	1, 4, 9, 14	X	X	X	
HAA5	1, 4, 9, 14	X	X	X	
SVOCs	1, 4, 9, 14	X	X		X
Metals	2, 4, 9, 11, 14, 15, 19, 24, 30	X	X	X	

Corrosion Preventative Additive Evaluation – The procedures for water changes were the same as the primary testing except that the test period lasted 19 days instead of 30 days. The water changes occurred on days 1, 2, 4, 9, 11, 14, 15 and 19 with samples taken for the tests listed in Section 2.2.1.1. The water was agitated before sampling to improve the homogeneity of the obtained sample. The shorter testing period was selected because the previous results indicated, for the three tests being performed, that little change occurred after day 19.

THM Formation Testing – The water resulting from the five-coupon, seven-day immersion was analyzed for TOC content and found to be 11.9 mg TOC/L. This TOC level was considerably higher than what would normally be observed in a treatment plant so it was diluted to 3.44 mg TOC/L with base water. This water was then chlorinated, using dilute NaOCl solution, to a free chlorine level of 10.3 mg/L. This high level of chlorine ensured there was ample chlorine available for the entire 72-hour test period.

The chlorinated, TOC-laden water was immediately transferred to twelve 40mL glass, amber vials and stored at room temperature in a dark cabinet. At 0, 24, 48 and 72-hour intervals, three vials were pulled and had an excess of sodium thiosulfate added. This immediately halted the formation of any THM. The vials were then placed in refrigerated storage until testing. During the same test period, four vials with clean base water were chlorinated in the same manner as the test samples (no additional TOC) and tested for free chlorine at the same intervals. This was done to monitor the chlorine residual decay in the absence of the added TOC. Three control vials were established with TOC-laden water but no chlorine added. These were sampled and immediately tested at 24, 48 and 72-hour intervals for the presence of THM (chloroform). The chemical analysis for THM content was the same method used for the THM content in the primary leaching experiments (chloroform only).

THM Sorption Testing – a one liter, glass jar was filled with base water and spiked with a chloroform standard resulting in a chloroform content of 12.2μg/L. This spiked water was then distributed to fifteen 40mL amber glass vials each containing a coupon segment. The coupon segments were 1.0cm x 1.25cm x 8.0cm with approximately 5% dimensional variability between segments. The vials were then stored at room temperature in a dark cabinet. Three vials each were then sampled at the 8, 24, 48 and 72-hour interval. There were three vials of chloroform-spiked water that did not contain a coupon which served as controls. Three vials of un-spiked water containing no coupons served as the method blank. The chemical analysis for THM content was the same method used for the THM content in the primary leaching experiments (chloroform only) and determined the loss in chloroform concentration due to sorption on the coupon surface.

2.2.2 Water Chemistry Test Procedures

All of the detailed information related to the referenced test procedures is available in Standard Methods for the Examination of Water and Wastewater, 21st Edition (APHA, 2005). This reference is widely used throughout the drinking water treatment community to establish testing protocols/procedures in both research and commercial applications. The term "Standard Method #" refers to test procedures found in this reference. Specific information related to the actual test equipment used, sample preservation/storage and any calibrations is provided in Appendix A.

2.2.2.1 Inorganic Chemical Tests

Primary Mortar Lining Impact Evaluation – Table 2-5 provides a list of the inorganic chemical analyses performed on the sample waters collected at each water change interval. The QC sample protocols for each analytical test are listed in Table 2-4.

Corrosion Preventative Additive Evaluation – The CPA testing required only pH, hardness, alkalinity and metals analysis be performed. The same methods and protocols listed in Table 2-5 were utilized.

Additional Cement Analysis – An additional analysis of the cement's chemical composition was accomplished by having the Portland cement used in producing the coupons chemically tested per ASTM C 114-07, a standard test procedure for hydraulic cement composition. A sample of dry cement was taken from the same cement bag used to manufacture the coupons and sent to Construction Technologies Laboratory (CTL), a private analytical lab supporting the construction industry. The results were used to aid in identifying the source of metals observed in the coupon-exposed waters of both the primary leaching and CPA experiments.

THM Formation Testing – The THM formation testing required the use of the disinfectant residual test shown in Table 2-5. This test was used to determine the initial chlorination level and track the chlorine control samples throughout the test period. See Table 2-4 for the QC sample protocols.

Table 2-5. Inorganic Chemical Test Methods and Sample Protocols

Parameter	Standard Method[1]	Instrument Used	Preservation and Storage
Disinfectant Residual	2350	HACH colorimeter	4°C ± 2°C
Ammonia	4500	HACH colorimeter	H_2SO_4 to pH<2, 4°C ± 2°C
Hardness	2340b	ICP-MS[2]	HCl or H_2SO_4 to pH<2, 4°C ± 2°C
Alkalinity	2320	HACH colorimeter	4°C ± 2°C
pH	2310	pH meter	N/A
Temperature	2550	Thermometer	N/A
Metals	3125	ICP-MS	HNO_3 to pH<2, 4°C ± 2°C

[1] Standard Methods for the Examination of Water and Wastewater, APHA. AWWA, WEF, 2005

[2] Hardness = [Ca] + [Mg]

NOTE: All these tests utilized triplicate samples that were placed in appropriately sized glass vials and tested well before sample hold times expired

2.2.2.2 Organic Chemical Tests

Primary Mortar Lining Impact Evaluation – Table 2-6 provides a list of the organic chemical analyses performed on the sample waters collected at each water change interval. The sample container material, the number of samples taken for each test and sample handling protocols are also provided. Table 2-4 provides the QC sample protocols for these tests.

THM Formation and Sorption Testing – The THM formation testing required the use of the TOC test shown in Table 2-6 as well as the THM test method. The sorption testing required only the THM analysis. See Table 2-4 for the QC sample protocols.

Table 2-6. Organic Chemical Test Methods and Sample Protocols

Parameter	Standard Method[1]	Instrument Used	Preservation and Storage
TOC	5310c	TOC analyzer	In dark, 4°C ± 2°C
THMs	6232D	Purge & Trap	Ascorbic Acid (20mg/ 40 mL), 4°C ± 2°C
HAA5	6251	Extraction	Dechlorinate, 4°C ± 2°C
SVOCs[2]	6410	GC/MS	Dechlorinate, 4°C ± 2°C
Metals	3125	ICP-MS	HNO_3 to pH<2, 4°C ± 2°C

[1] Standard Methods for the Examination of Water and Wastewater, APHA. AWWA, WEF, 2005

[2] The SVOCs were extracted according to Std. Method 6410 and analyzed by GC/MS. The intent of this procedure was to identify and semi-quantify specific SVOCs that are related to the lining material being tested. The intent was not to quantify every SVOC (PAHs, pesticides, etc) listed in Method 6410.
NOTE: TOC, THM and Metals were sampled in triplicate, placed in appropriately sized glass vials and tested well before the sample hold times expired

Additional Sand Analysis – Additional testing was performed in an effort to determine if the sand was a significant source of TOC. Specifically, the sand was tested to determine if it released significant amounts of TOC when mixed with Nanopure® water. A clean glass flask was filled with 100mL of water and 20.0g of the sand (same bag used for coupons) was added. The mixture was vigorously stirred for one hour and then placed in a cabinet for seven days. The mixture was then stirred and sampled. Six samples were tested for TOC per the method shown in Table 2-6.

2.2.3 Odor Testing Procedures

Odor analysis was performed using the Flavor Profile Analysis (FPA) method described in Standard Method 2170. This method uses specially trained human panel members to assess the odor of the various test samples. The administration of these panels was performed by Ms. Heather Johnson and Dr. Andrea Dietrich both of whom received approval from the Virginia Tech Institutional Review Board for Research Involving Human Subjects. The use of human panel members necessitated these approvals. These approvals are provided in Appendix B.

At each water change, composite samples of the triplicate water types were collected and prepared in accordance with the method by the panel leader. The blind samples, in closed glass flasks, were randomly presented to 3-4 panel members who assessed both the intensity and description of each sample's odors. An odor-free blank and a standard intensity odor sample were presented as QC samples. After all panel members had assessed each sample, individual panel member's assessments were recorded and the panel then discussed their assessments. The final assessments were recorded and used to develop the results presented.

2.3 Statistical Analysis

The statistical analysis of data was performed using an analysis of variance (ANOVA), Tukey multiple comparison tests and/or t-tests. The analyses were executed using the GraphPad Prism® statistical analysis software. An alpha value of 0.05 ($\alpha=0.05$) was used to determine significance. Any statistical analysis that returned a p-value of less than 0.05 was deemed significant.

In cases where triplicate samples (three samples for each water type on each sampling day) were taken and analyzed individually it was possible to compare the individual water types against the control group. The controls, one for each water type, were not triplicate sampled so there is only one data point for each water type on each day. In order to perform an analysis, the four controls were taken as a group so that a mean and standard error could be calculated. This was the only feasible approach to data analysis since there was a limited number of control samples tested. The initial comparison was performed by using a one-way ANOVA with water type as the one factor. If a significant difference in means was found, Tukey multiple comparison tests were run to determine which water types were significantly different from one another or the control. In cases where composite samples were taken resulting in only one data point for each water type on each day, a non-parametric t-test known as a Mann-Whitney test was performed. It compared the exposed samples as a group to the control group. The results for these tests are provided graphically within each Results/Discussion subsection.

The CPA testing resulted in two data points for each CPA-augmented water samples and two data points for the control samples. This allowed for the same ANOVA-Tukey test strategy described above.

3. RESULTS AND DISCUSSION

3.1 General Leaching Test Observations

A key visual observation made during the primary leaching tests was the presence of a white precipitate in all of the vessels containing coupons until day 9. This precipitate was crystalline in appearance but was gelatinous in feel. The precipitate settled to the container's bottom surface after being mixed to a temporarily suspended state. It is suspected that this precipitate was either calcium hydroxide or calcium carbonate. The results will show that the both of these salts are released into the water at high rates until day 9 of the test period. However, the solubility constants and solubility index curves provided in previous literature suggest strongly that this precipitate was calcium carbonate (Schock, 1981). Significant decreases in both the alkalinity and hardness occur simultaneously at day 9 with a modest decrease in pH. As the coupons cured, the rate of calcium release slowed and the water, after day 9, was no longer supersaturated with the carbonate salt (See Equations (1) and (2) below).

3.2 Inorganic Chemical Testing

The following sections provide the inorganic chemistry test results for the primary leaching experiments. The tests were performed in accordance with the procedures outlined in Section 2 and using the test equipment listed in Appendix A.

3.2.1 pH

The pH of all test waters increased rapidly after cement coupon immersion (Figure 3-1). There was no marked difference between the different test waters. The control waters, which were test vessels without cement mortar coupons, were able to maintain their initial pH values throughout the test period.

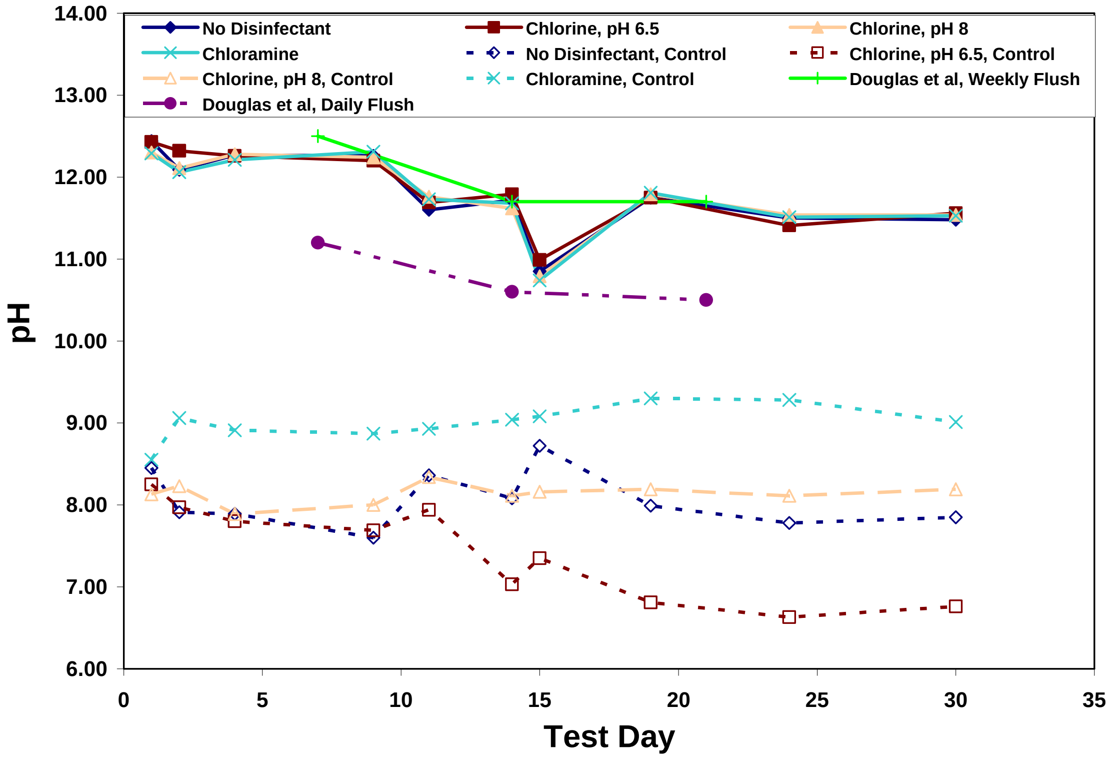


Figure 3-1. pH vs. Testing Day, All Water Types and Controls with data from Douglas et al, 1991

As shown in the Figure 3-1, the pH for the all four test water conditions increased from either 6.5 or 8 to 12 – 12.4 during the first four water changes. The pH was measured only on days that the water in the vessels was changed meaning that the length of time the coupons were in contact with the water is reflected by the number of days between water changes. For sampling days 1, 2, 4 and 9, the pH was consistently above 12. This large increase in pH can be attributed to the leaching of the major cement hydration reaction product, calcium hydroxide, and its subsequent dissolution. This reaction and dissolution rate is highest early in the test period. The key reactions that form the calcium hydroxide are the hydration of tricalcium and dicalcium silicates, the major constituents of non-hydrated cement (Douglas, 1996):

$$2(3CaO \cdot SiO_2) + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 \quad (1)$$

$$2(2CaO \cdot SiO_2) + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 \quad (2)$$

The calcium hydroxide dissolution reaction is as follows:

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \quad (3)$$

The water change on day 11 (48-hour contact time) showed a reduction in the pH rise to about 11.6. After a contact time of 72 hours, when the water was changed on day 14, the pH had risen again to approximately 11.6 in spite of the longer contact time. This suggests that the reaction and dissolution process was slowing. When the water was changed 24 hours later on day 15, the pH declined sharply to approximately 11.0. During the latter stages of the test, days 19 through 30, the longer times between water changes resulted in an elevated pH between 11.4-11.6.

These results are similar to those in the AWWA report by Douglas et al. (1996). The results from their study are plotted on Figure 3-1. The data is from test days 7, 14 and 21 and is adapted from the referenced report. Their test apparatus was an actual 4-inch steel pipe lined with cement mortar which was then flushed at the frequency indicated. Note that their daily flush data agrees well with this experiment's pH values when the period between water changes is 24 hours while their weekly flush data is similar to the values observed after longer exposure periods. This agreement suggests that the coupon immersion test apparatus, designed with a surface area to volume ratio characteristic of a 4-inch diameter pipe, was a reasonable approximation of the actual 4-inch, cement lined pipes used in the Douglas study.

Statistical analysis using the ANOVA/Tukey tests showed that while there were no significant differences between water types, all of the water types had significantly higher pH levels than the control group. This is represented graphically in Table 3-1 with the statistically different populations indicated by a dark block. In this case, all the blocks are dark but when other test parameters are discussed this will not be the case.

Table 3-1. Statistically Significant Differences for pH, All Days, $\alpha = 0.05$

Comparison	Day 1	Day 2	Day 4	Day 9	Day 11	Day 14	Day 15	Day 19	Day 24	Day 30
All Water Types vs. Control Group	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨

3.2.2 Alkalinity

As mentioned earlier, the target total alkalinity for the reference water was 35 mg/L as $CaCO_3$. The average total alkalinity for the all the control waters throughout the test period was 39.4 mg/L as $CaCO_3$, indicating satisfactory agreement between prepared and measured concentrations.

Figure 3-2 indicates that the sample water alkalinity levels were dramatically higher than the control waters and that the disinfection type had little impact on the difference magnitude. The graph also indicates that the total alkalinity was driven very high on days 4 and 9 which corresponds to the days that pH was also very high. The rise in both parameters is a result of the pH being driven higher by the dissolution of calcium hydroxide produced by reactions (1) and (2) above. The total alkalinity can be represented by the following equation (4) with the concentrations expressed in meq/L:

$$Alk_{total} = (HCO_3^-) + 2(CO_3^{-2}) + (OH^-) - (H^+) \qquad (4)$$

It can be calculated that, at these high pH levels, the H^+ and HCO_3^- levels are negligible. The observed range of pH values for day 1, 2 and 4 is approximately 12.00 to12.25 which, with the following conversion, gives the following hydroxide alkalinity range:

$$[OH^-] = 10^{-2.00} = 1.00 \times 10^{-2} \tfrac{mol}{L} OH^- = 10.0 \tfrac{meq}{L} = 500 \tfrac{mg}{L} \text{ as CaCO}_3 \text{ (hydroxide alkalinity)}$$

$$[OH^-] = 10^{-1.75} = 1.78 \times 10^{-2} \tfrac{mol}{L} OH^- = 17.8 \tfrac{meq}{L} = 889 \tfrac{mg}{L} \text{ as CaCO}_3 \text{ (hydroxide alkalinity)}$$

The observed total alkalinity values for day 4 were nearly 600 mg/L as $CaCO_3$ which fall within this predicted range. This calculation suggests that the vast majority of the total alkalinity is the water's hydroxide alkalinity and that the carbonate concentration is quite low. The low carbonate concentration is most likely the result of the low initial carbonate concentration in the base water (i.e. 35 mg/L as $CaCO_3$) and the low solubility of calcium carbonate particularly at these elevated pH levels.

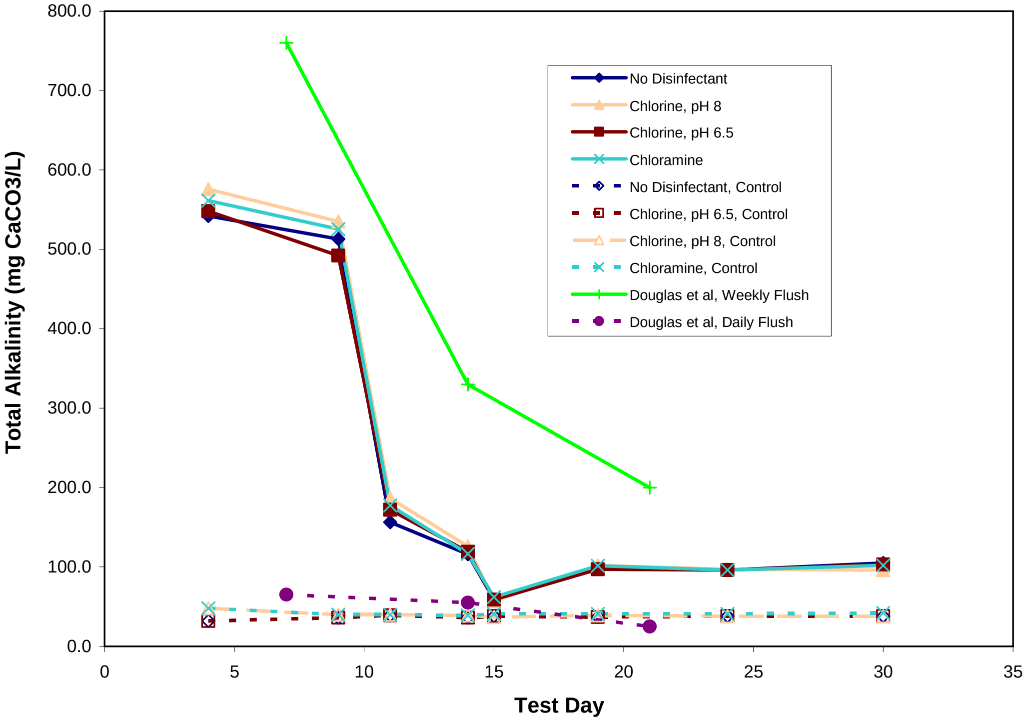


Figure 3-2. Total Alkalinity vs. Testing Day, All Water Types and Controls with data from Douglas et al. (1996)

The data from Douglas et al (1996) are also plotted on Figure 3-2. Once again, this study's alkalinity results fall within the weekly and daily flush results from their study. Note that on the one day where the two studies are most similar, day 15 (one day residence time for this study, daily flush for Douglas et al.), the data are in very close agreement.

The rate of total alkalinity increase over the test period, referred to as total alkalinity flux rate, is shown in Figure 3-3. The figure shows that the rates of total alkalinity increase also declines significantly over the test period. This suggests that the available calcium hydroxide for dissolution is greatly reduced as the cement cures (hydration rates and permeability decreases) and/or as a coating of calcium carbonate forms on the coupon surface. The carbonate coating impedes the dissolution process and reduces the affects on pH and alkalinity.

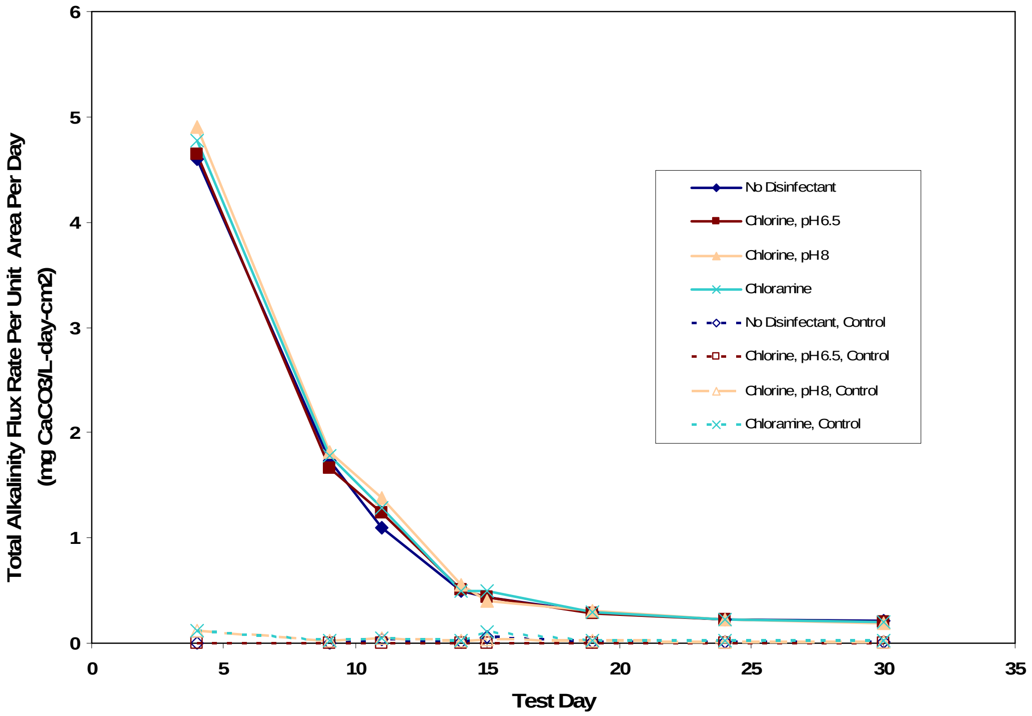


Figure 3-3. Total Alkalinity Flux Rate vs. Testing Day, All Water Types and Controls

The statistical analysis of the alkalinity results follows the same pattern as the pH results with the sample waters all being significantly higher than the control water (shown) but not different from one another (not shown). This is presented in Table 3-2.

Table 3-2. Statistically Significant Differences for Alkalinity, All Days, $\alpha = 0.05$

Comparison	Day 1	Day 2	Day 4	Day 9	Day 11	Day 14	Day 15	Day 19	Day 24	Day 30
All Water Types vs. Control Group	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨

3.2.3 Hardness

The graph provided in Figure 3-4 shows that total hardness (Ca and Mg cations) increases dramatically early in the test period. This increase is due to the release of Ca^{2+} ions from the cement curing process (see reaction equations (1) through (3)) and the solubility of the uncured cement's calcium silicates. The calcium levels reach these high values early in the test period because there is a limited amount of carbonate alkalinity available with which to form calcium carbonate precipitate and the high solubility of calcium hydroxide. Table 3-3 provides some supporting data for this behavior. The data in Table 3-3 is based on observations of the pH 8, no disinfectant water and assumes that all metals were present as free ions. There are also no corrections for ionic strength. While calcium carbonate precipitation occurred throughout the test period, these two assumptions can only be applied to data collected after day 11 since before that time precipitate was readily visible in the water and not filtered out before the samples were tested. On day 15, the calcium hardness drops below the control levels due to the progression of the cement cure process and the significant reduction in the calcium hydroxide production. The control waters had an average calcium hardness of 28 mg as $CaCO_3$/L and while the test samples attained levels as low as 16 mg as $CaCO_3$/L at day 24. At this point in the testing, precipitation of calcium carbonate removes a significant fraction of the available calcium ions and controls the overall calcium concentration. The general observation of increased water clarity was also noted at this same point in the test which was likely due to the relatively small amount of calcium carbonate settling on the coupons.

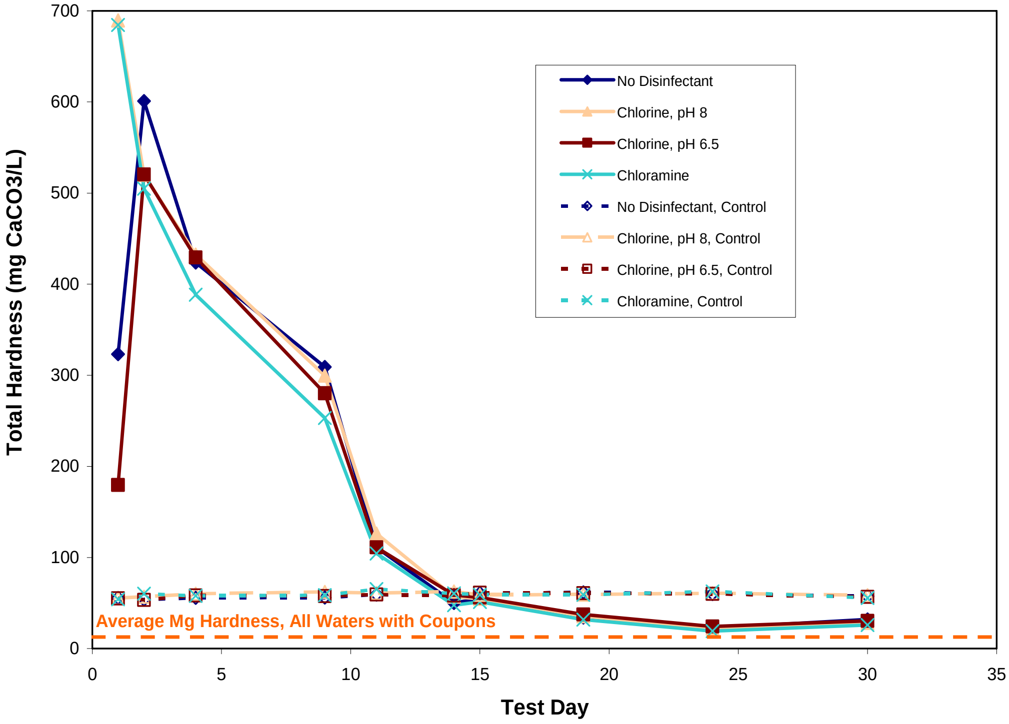


Figure 3-4. Total Hardness (mg $CaCO_3$/L) vs. Testing Days, All Water Types and Controls

The magnesium concentration actually drops from the control water levels in all water types. This suggests that the high pH and available hydroxide ions are creating conditions which allow the magnesium to precipitate as magnesium hydroxide. This precipitation-induced level is represented by the orange dashed line which represents the average magnesium hardness seen throughout the test period. The magnesium hardness in the control waters averaged 31 mg $CaCO_3$/L but dropped to the indicated value of approximately 11 mg $CaCO_3$/L in the test samples. Since magnesium levels are not augmented appreciably by the cement hydration reactions, the precipitation of magnesium hydroxide controls the overall magnesium level throughout the test period. Table 3-3 indicates this for the period from day 11 to day 30.

Table 3-3. Solid Controlling Calcium and Magnesium Concentration, pH 8, No Disinfectant, Based on K_{sp} Values

Day	Measured Concentrations (M)				Saturated per K_{sp} Value?			
	$[Ca^{2+}]$	$[Mg^{2+}]$	$[OH^{-}]$	$[CO_3^{2-}]^1$	$CaCO_3$ $K_{sp}=10^{-8.5}$	$Ca(OH)_2$ $K_{sp}=10^{-5.3}$	$MgCO_3$ $K_{sp}=10^{-7.5}$	$Mg(OH)_2$ $K_{sp}=10^{-10.7}$
11	1.05E-3	5.68E-5	3.98E-3	6.77E-4	Yes	No	No	Yes
14	3.97E-4	1.04E-4	5.25E-3	6.77E-4	Yes	No	No	Yes
15	2.41E-4	3.10E-4	7.08E-4	6.77E-4	Yes	No	No	Yes
19	2.45E-4	9.76E-5	5.62E-3	6.77E-4	Yes	No	No	Yes
24	2.10E-4	1.50E-5	3.16E-3	6.77E-4	Yes	No	No	Yes
30	2.21E-4	9.88E-5	3.02E-3	6.77E-4	Yes	No	No	Yes

[1] Initial carbonate added to base waters was 40.6 mg/L

[2] K_{sp} values at 25°C from Schock, et al. (1981)

The statistical analysis results indicate that all water types were different than the control group until day 14 when there were no significant differences between any of water types or controls. Differences between the sample water types and the controls reappear at day 19. The analysis software did return significant differences between water types for days 24 and 30 but the range in total alkalinity values amongst the water types was 25 to 33 mg/L as $CaCO_3$ and this was not seen as significant in a practical sense (not shown). Table 3-3 presents the statistical analysis results.

Table 3-4. Statistically Significant Differences for Total Hardness, All Days, $\alpha = 0.05$

Comparison	Day 2	Day 4	Day 9	Day 11	Day 14	Day 15	Day 19	Day 24	Day 30
NODIS vs ClpH8									▨
NODIS vs ClpH65							▨		
NODIS vs MCpH8								▨	▨
NODIS vs CONTROL	▨	▨	▨	▨			▨	▨	▨
ClpH8 vs ClpH65									
ClpH8 vs MCpH8							▨		
ClpH8 vs CONTROL	▨	▨	▨	▨		▨	▨	▨	▨
ClpH65 vs MCpH8							▨	▨	▨
ClpH65 vs CONTROL	▨	▨	▨	▨			▨	▨	▨
MCpH8 vs CONTROL	▨	▨	▨	▨			▨	▨	▨

3.2.4 Metals Concentrations

Of the metals tested, only the concentrations of aluminum and chromium were consistently higher in the coupon-exposed waters than their respective controls. This was the case for all pH and disinfection combinations. The aluminum and chromium results are presented in Figures 3-5 and 3-6, respectively. The aluminum concentration exceeded the EPA secondary standard of 0.2 mg/L (USEPA, 2008) until day 11, when its drops significantly. The chromium concentration never exceeds the EPA primary maximum contaminant level of 0.1 mg/L (USEPA, 2008) although it increases rapidly on day 1 and then continually decreases during the test period. As with hardness, there is a reduction in metals release when the concrete matures (about day 9), after which the quantities of aluminum and chromium became negligible and within EPA limits (though still slightly higher than the corresponding controls).

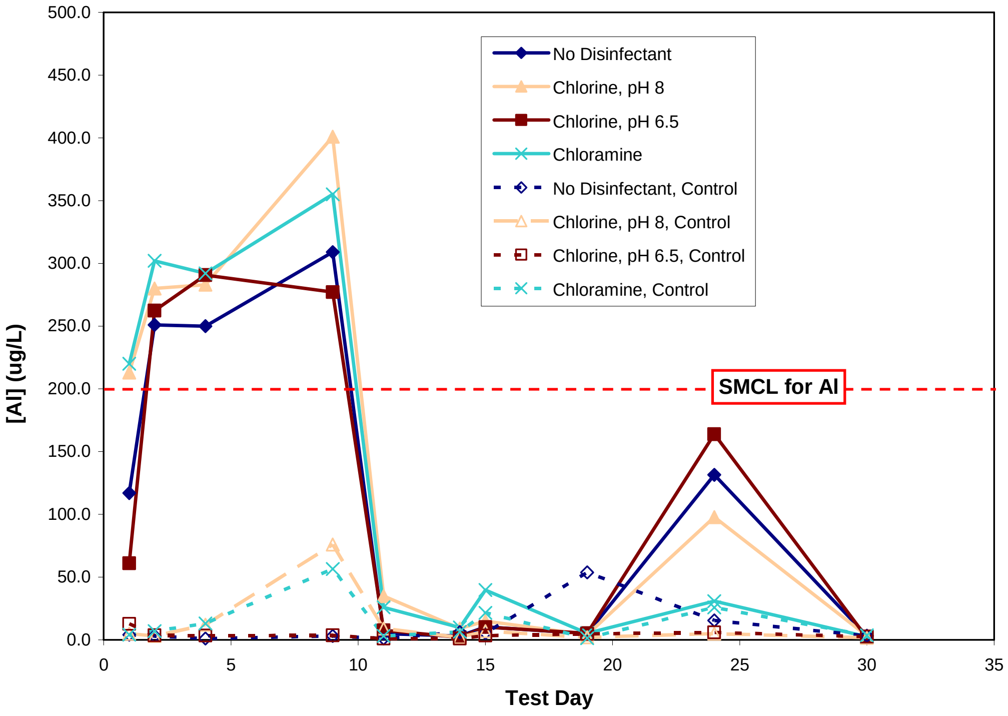


Figure 3-5. Aluminum Concentration vs. Testing Days, All Water Types and Controls

The source for the aluminum is the cement's tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) both of which are slightly soluble in water and release aluminum as they hydrate (Schock, 1981). The chromium source was also thought to be the cement but to confirm this and the aluminum results, additional cement analyses were performed as described in Section 2.2.1.1, and results are provided in Table 3-4. The complete analysis results are provided in Appendix C.

Table 3-4. Composition Analysis of Portland Cement used in This Research

Cement Chemical Compound or Parameter	Weight %
Tricalcium silicate (C_3S)	59
Dicalcium silicate (C_2S)	13
Tricalcium aluminate (C_3A)	7
Tetracalcium aluminoferrite (C_4AF)	9
Dichromium trioxide (Cr_2O_3)	0.04
Loss on Ignition (LOI)	1.69

As shown, the C_3A content by weight was found to be 7% while the C_4AF content was found to be 9%. Based on information found in the literature, it is expected that approximately 65% of the C_3A would be hydrated after 24 hours but only 35% of the C_4AF would have hydrated in the same timeframe (Bye, 1999). At day 11, the levels of hydration have reached 98% and 80% for C_3A and C_4AF, respectively (Bye, 1999). This indicates that from day 1 to day 11, aluminum release is occurring at a reasonably high rate but slowing as time progresses. With the source of the aluminum defined as C_3A and C_4AF, it is necessary to determine what possible precipitation mechanisms might be controlling the concentration. Initially, the possibility of gibbsite ($Al(OH)_3$) precipitation being the controlling factor was explored. Gibbsite solubility curves indicated that at the pH levels encountered during days 1 through 9 (~11.5-12) the soluble aluminum concentrations should be approximately 0.001M or 27000 μg/L (Snoeyink, 2003). The maximum value during the period was 400 μg/L so gibbsite solubility alone was ruled out as the limiting solid.

The work by Damidot (1993) indicates that the more complex mix of species present in the aqueous phase in contact with the cement coupons afforded an opportunity for a more comprehensive analysis. First, three separate days during the test period were selected as samples to be evaluated. Days 2, 11 and 19 were selected and only non-disinfected water was considered since it would be most similar to the systems considered in the Damidot's work and also representative of the disinfected waters in this study. Key data inputs, the measured molar calcium and sulfate concentrations, were converted to the units utilized by Damidot (1993) (mM/L). These data are provided in Table 3-5. The calcium concentrations are also shown raised to the one-fifth power as these values will be necessary when interpreting the solubility diagrams in Figures 3.6-3.8.

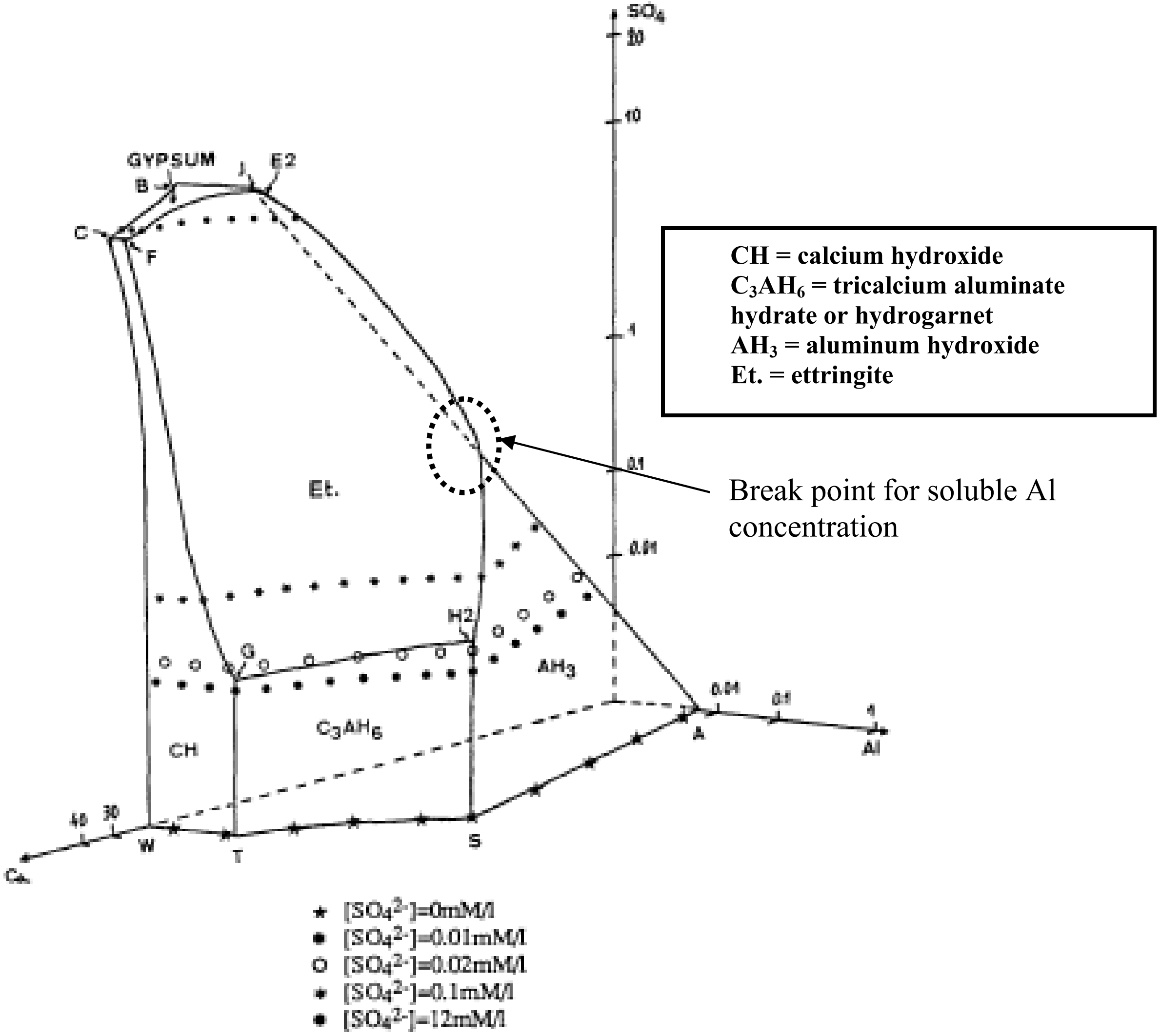
Table 3-5. Sulfate, Calcium and Aluminum Concentrations for No Disinfectant Water in Contact with Cement Coupons (converted to units for Damidot (1993) model)

Day	$[SO_4]$ (mM/L)	[Ca] (mM/L)	$[Ca]^{1/5}$	[Al] (mM/L)
2	0.16	5.93	1.42	0.011
11	0.33	1.05	1.01	0.0002
19	0.27	0.25	0.75	0.00019

The Damidot model is applicable within a pH range of 10.5 to nearly 13, a range which includes all of the pH levels encountered in this study. The three-dimensional solid-phase diagram for the cement-water system is provided as Figure 3-6. The alphanumeric labels on the various solid phase surfaces require clarification:

- CH is calcium hydroxide
- C_3AH_6 is tricalcium aluminate hydrate or hydrogarnet $(3CaO \cdot Al_2O_3 \cdot 6H_2O)$
- AH_3 is aluminum hydroxide
- Et. is ettringite $(3CaO \cdot Al_2O \cdot 3CaSO_4 \cdot 32H_2O)$

The three dimensional graph was created by interpolating between the actual model results shown by the various dashed lines which represent five constant sulfate concentrations ranging from 0 to 12 mM/L as SO_4^{2-}. There were model runs at a sixth sulfate concentration, 1.0 mM/L, but it is not shown on Figure 3-6. The Damidot paper also provides two-dimensional plots at each of these six constant sulfate concentrations which represent Ca-Al planar sections through the volume shown in Figure 3-6. This study's sulfate concentrations shown in Table 3-5 range from 0.16 to 0.33 mM/L as SO_4^{2-}



CH = calcium hydroxide
C_3AH_6 = tricalcium aluminate hydrate or hydrogarnet
AH_3 = aluminum hydroxide
Et. = ettringite

Break point for soluble Al concentration

Figure 3-6. Three-dimensional representation of solubility limiting solid mineral types present when cement is in contact with water, denoted as the $CaO-Al_2O_3-CaSO_4-H_2O$ system. The x, y, and z axis represent the log aqueous concentration of aluminum, sulfate and calcium. (from Damidot, 1993 by fair use, Appendix D)

making the Damidot, two-dimensional plots at 0.1 mM/L and 1.0 mM/L the most useful in interpreting this study's data. They are provided as Figure 3-7 and 3-8, respectively. It should be noted that the Ca and Al concentration values on each axis are actual concentrations raised to the one-fifth power. Superimposed on both plots is the day 2 calcium to aluminum relationship, using the data from Table 3-5 (calcium concentration raised to the one-fifth power). The dashed lines indicate a predicted aluminum concentrations at these sulfate levels. This provides an estimated range for the aluminum concentrations for day 2. After raising the approximate values shown on the aluminum axis to the fifth power (0.50 and 0.22 mM/L Al), the resulting estimated range is 0.005 to 0.03 mM/L Al. The actual measured aluminum concentration was 0.011 mM/L (see Table 3.5) which falls into the range predicted by Damidot (1993).

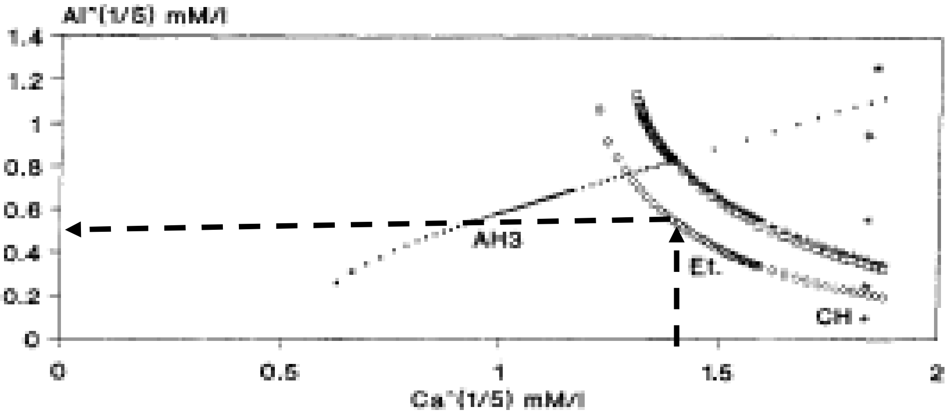


Figure 3-7. Phase Equilibrium Curves of AH_3, C_3AH_6, ettringite and $Ca(OH)_2$ in the calcium-aluminate plane at $[SO_4]$ = 0.1 mM/L (from Damidot, 1993 by fair use, Appendix D). Vertical dashed lined for Ca represents measured concentration on Day 2 of this study.

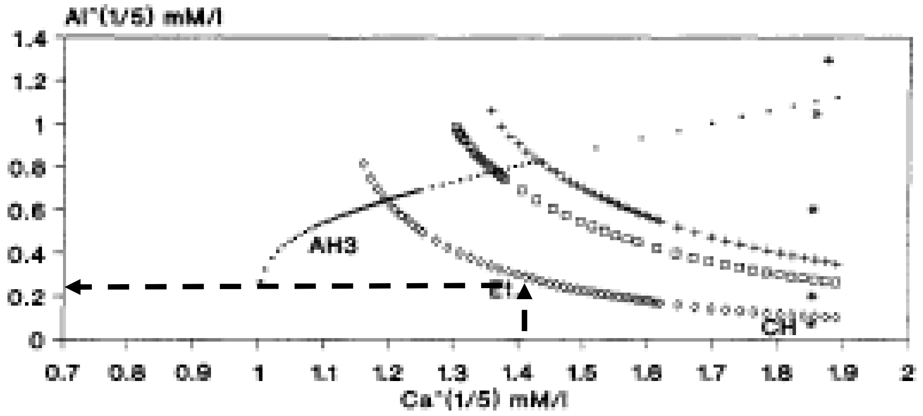


Figure 3-8. Phase Equilibrium Curves of AH_3, C_3AH_6, ettringite and $Ca(OH)_2$ in the calcium-aluminate plane at $[SO_4]$ = 1.0 mM/L (from Damidot, 1993 by fair use, Appendix D). Vertical dashed lined for Ca represents measured concentration on Day 2 of this study.

If the same procedure is followed for day 11 an interesting situation is observed. The $[Ca]^{1/5}$ value is 1.01 which in Figure 3-8 is at a critical breakpoint in the aluminum hydroxide solubility curve. The equilibrium soluble aluminum concentration drops precipitously near this calcium concentration. This breakpoint can be viewed in Figure 3-6 and is annotated with the dashed oval. As the calcium concentration decreases, the controlling solid is the ettringite until the calcium level reaches approximately 1 mM/L at which point the controlling solid become aluminum hydroxide and the soluble aluminum concentration falls to very low levels. In support of this, Figure 3-5 shows a very steep drop in aluminum concentration on day 11, reaching 0.0002 mM/L or, when raised to the one-fifth power, 0.18 on the Figure 3-8 aluminum axis. It must be noted that Figure 3-8 provides solubility curves at a higher sulfate concentration than was observed on day 11 but a close inspection of Figure 3-6 suggests that the day 11 sulfate concentration, 0.33 mM/L, is sufficiently high for the breakpoint to be reached. On day 19, calcium levels have dropped further (0.75 when raised to the one-fifth power) and the system has moved further towards the sulfate-aluminum ordinate plane and well past the breakpoint. The aluminum levels are predicted to remain very low. The observed data supports this with an actual value of 0.00019 mM/L (see Table 3.5).

The increase in aluminum content on day 24 is not easily explained. The day 24 calcium levels remain low and sulfate concentrations do not change significantly from the values presented in Table 3-5. These conditions would suggest a continued low aluminum concentration. On day 24, magnesium levels drop from an average of 3 mg/L on day 19 to an average of 0.4 mg/L. This may suggest another metal-ligand complex is controlling the aluminum levels, with magnesium precipitation occurring preferentially over aluminum precipitation. On day 30, magnesium levels return to 2.3 mg/L and the aluminum concentration decreases to the levels predicted by the Damidot model. The mechanism that resulted in the day 24 aluminum concentration increase was not identified in this study but likely involves an alternate magnesium salt precipitation that results in the increased solubility of an aluminum precipitate.

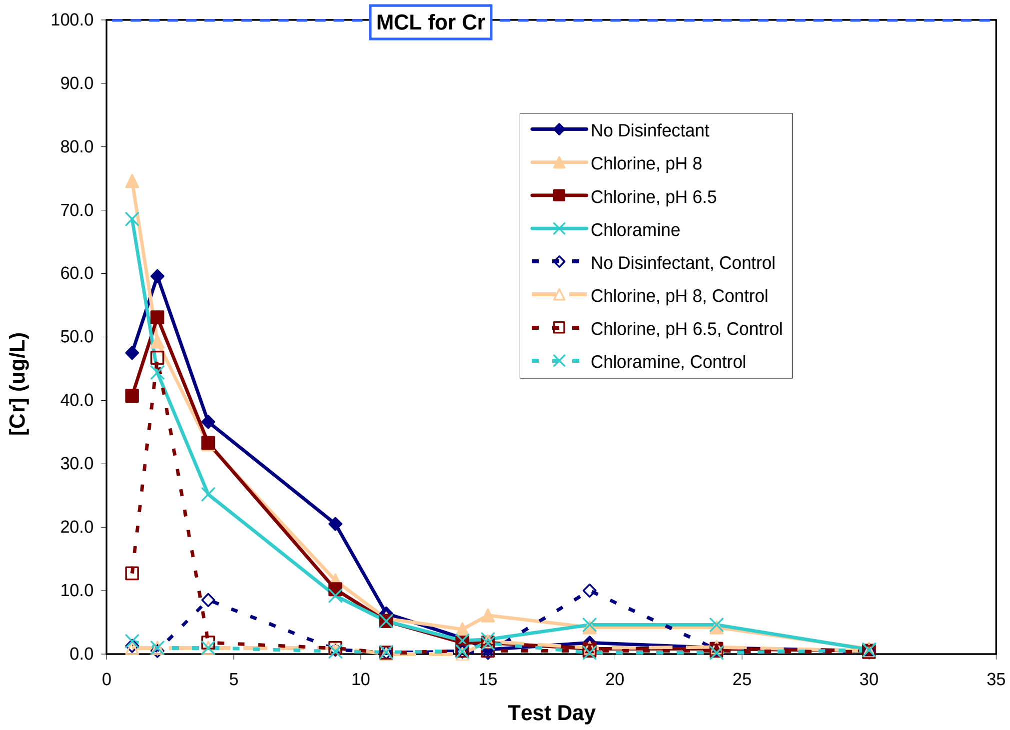


Figure 3-9. Chromium Concentration vs. Testing Days, All Water Types and Controls

As shown in Table 3-4, the cement's dichromium trioxide (Cr_2O_3) concentration was found to be 0.04% or 0.027% as chromium when subjected to the additional chemical analysis described in Section 2.2.1.1. Although this is a small percentage it does represent nearly 100 milligrams of chromium in a test vessel considering that approximately 340 grams of cement were used to produce the six immersed coupons. Dichromium trioxide is considered insoluble in water but if even a very small portion of this compound exists as CrO_3, which is highly soluble, the chromium could easily pass into the water column. Less than 0.2% of this chromium would need to leach to result in the highest observed chromium levels. The chromium levels decrease as the test progressed due to the increasing degree of hydration, which binds the metal in the maturing matrix, and the formation of the carbonate coating. After this point, the test samples behave much like the controls. Additionally and possibly most importantly, the solubility of chromium is very pH dependent with solubility increasing with pH (Hoffland, 2006). The lower pH levels seen later in the test period would reduce chromium solubility significantly. In summary, this additional testing suggested that the raw cement was a likely source of the aluminum and chromium found in the sample waters.

Other metals and non-metal elements were monitored during the test period including sodium, phosphorus, sulfur, chlorine, iron, manganese, nickel, zinc, potassium, and copper; the concentrations of these metals were similar in all of the test waters and the controls indicating that they were not leached from the cement mortar in significant amounts.

The statistical analysis of the aluminum results are provided in Table 3-6 which is larger than previous statistical tables due to the complexity of the results. All water types were significantly different from the controls until day 11. At this point there is no difference between any of the samples or controls. On day 24, the differences appear between the water types and controls described above are shown as significant. The pH 6.5, chlorinated water had significantly higher aluminum content than all other waters except the no disinfectant water. It was also different than the control group. The non-disinfected water was significantly different than all other water types (except pH 6.5) and the control.

Table 3-6. Statistically Significant Differences for Aluminum Concentration, Days 2 through 30, $\alpha = 0.05$

Comparison	Day 2	Day 4	Day 9	Day 11	Day 14	Day 15	Day 19	Day 24	Day 30
NODIS vs ClpH8								▨	
NODIS vs ClpH65									
NODIS vs MCpH8								▨	
NODIS vs CONTROL	▨	▨	▨					▨	
ClpH8 vs ClpH65								▨	
ClpH8 vs MCpH8									
ClpH8 vs CONTROL	▨	▨	▨						
ClpH65 vs MCpH8								▨	
ClpH65 vs CONTROL	▨	▨	▨					▨	
MCpH8 vs CONTROL	▨	▨	▨						

The statistical analysis results for chromium are provided in a similar form as Table 3-7. The significant differences noted after day 9 are somewhat questionable since the values are less than 10 ppb and in many instances, with only three data points, the standard error was zero (all values equal).

Table 3-7. Statistically Significant Differences for Chromium Concentration, Days 2 through 30, α = 0.05

Comparison	Day 2	Day 4	Day 9	Day 11	Day 14	Day 15	Day 19	Day 24	Day 30
NODIS vs ClpH8						▨			
NODIS vs ClpH65									
NODIS vs MCpH8									
NODIS vs CONTROL	▨		▨	▨					
ClpH8 vs ClpH65						▨			▨
ClpH8 vs MCpH8						▨			
ClpH8 vs CONTROL	▨			▨	▨	▨			▨
ClpH65 vs MCpH8									
ClpH65 vs CONTROL	▨			▨					
MCpH8 vs CONTROL				▨					▨

3.2.5 Disinfectant Residual Demand

Figure 3-10 below shows the disinfectant loss rate in milligrams per liter per day for both chlorinated waters, the chloramine disinfected water and their respective controls. The water with no disinfectant is not shown. The data for the controls are shown as both chlorine and monochloramine decay spontaneously even without the presence of cement mortar.

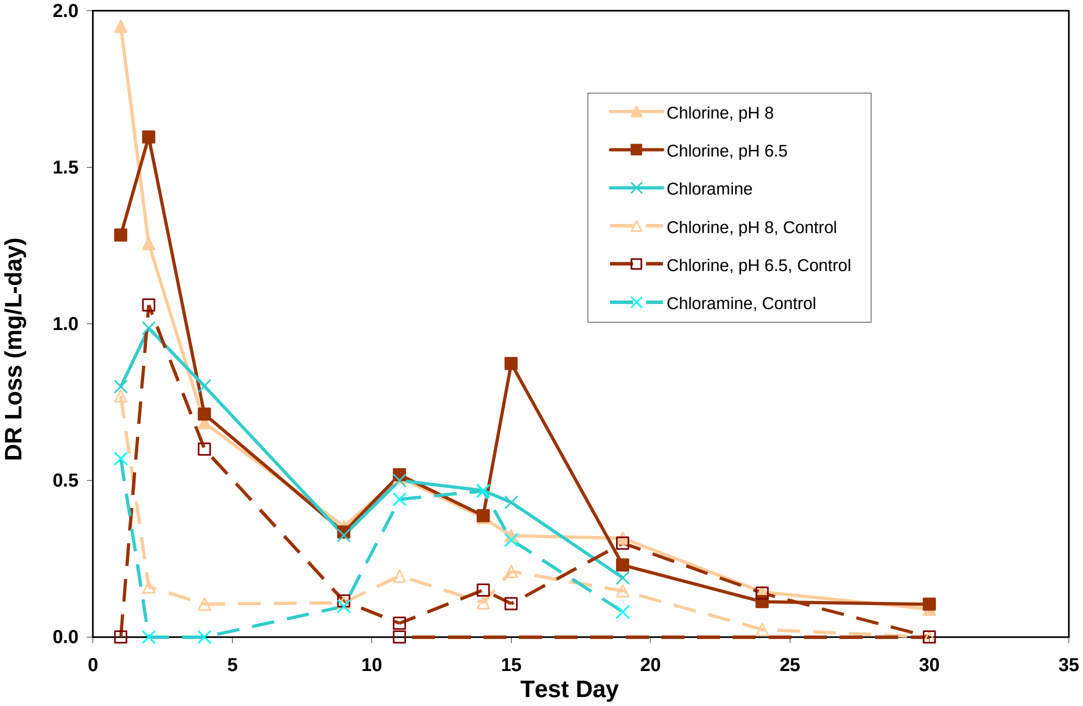


Figure 3-10. Disinfectant Residual Loss Rate vs. Testing Days, Disinfected Water Types and Respective Controls

The decay rate for both chlorine and monochloramine was enhanced by the presence of cement mortar. This higher rate of decay was maintained until Day 9, after which the cement mortar performed more similarly to the controls. This pattern is similar to that observed for pH and alkalinity. This trend also corresponds well with the available TOC (Figure 3-8) which may indicate that the TOC was creating a residual demand and this demand subsided with the reduction in TOC levels.

The statistical analysis results for disinfectant residual loss is provided in Table 3-8 and shows that the differences between various water types were not significant at anytime during the test period. Variances in the control waters on days 1 and 11-15 prevented a significant result.

Table 3-8. Statistically Significant Differences for Disinfectant Residual, Disinfected Water Types, All Days, $\alpha = 0.05$

Comparison	Day 1	Day 2	Day 4	Day 9	Day 11	Day 14	Day 15	Day 19	Day 24	Day 30
ClpH8 vs ClpH65										
ClpH8 vs MCpH8										
ClpH8 vs CONTROL		▨	▨	▨				▨	▨	▨
ClpH65 vs MCpH8										
ClpH65 vs CONTROL		▨	▨	▨					▨	▨
MCpH8 vs CONTROL										

3.3 Organic Chemical Testing

The following are the organic chemistry test results for the primary leaching experiments. The tests were performed in accordance with the procedures outlined in Section 2 and using the test equipment listed in Appendix A.

3.3.1 Total Organic Carbon (TOC)

Figure 3-11 shows the TOC concentrations present in the test waters and controls throughout the test period. The TOC levels were highest on the day 1, especially for the pH 8 waters (chlorine and chloramines). These highest TOC levels associated with the pH 8 water types decrease rapidly at day 2, followed by a slight increase on days 4 and 9. These increases are most likely due to the longer periods between water changes. The pH 6.5, chlorinated water and the disinfectant free water do not have similarly high initial TOC levels and steadily decrease after day 4. All TOC levels decrease to the control levels after day 15. The control TOC concentrations vary slightly around the base water TOC which was found to be between 0.25 and 0.30 mg/L.

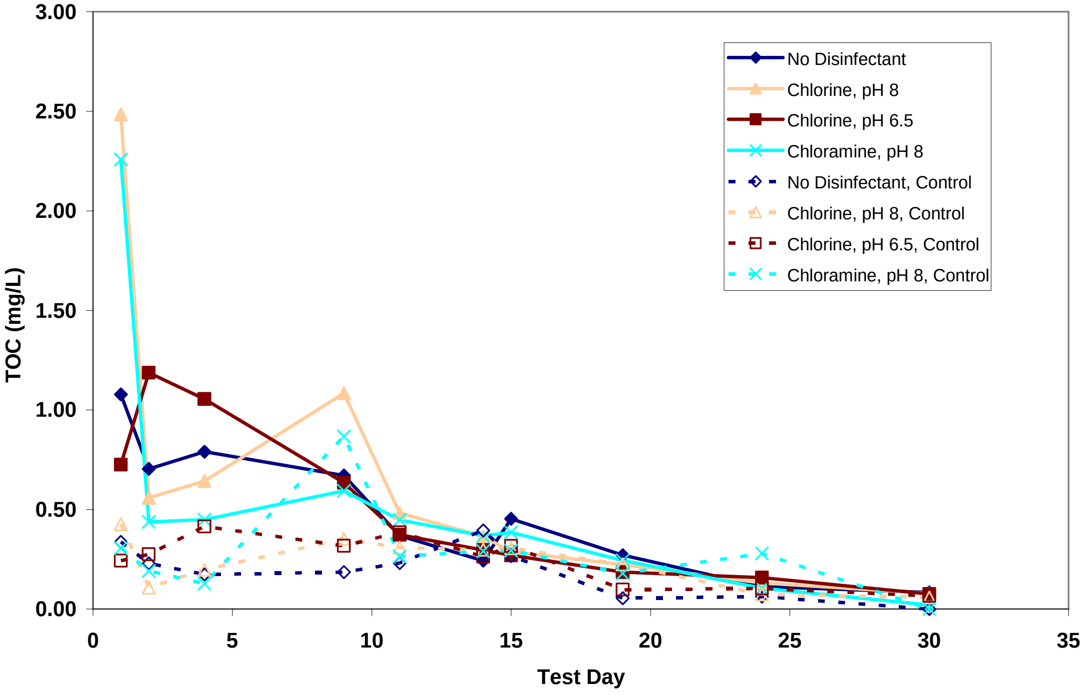


Figure 3-11. TOC Concentration vs. Testing Days, All Water Types and Controls

Figure 3-12 shows the TOC flux in milligrams per liter per day and normalizes the data for the variable exposure time between water changes. The graph also shows a higher flux during the first day followed by a steady and less variable decrease in TOC leaching rates. This suggests that as the cement cures its ability to release TOC drops significantly at day 9 and approaches a “no TOC release” condition by the conclusion of the test period. Additionally, after day 9 the test samples show no significant difference from the controls.

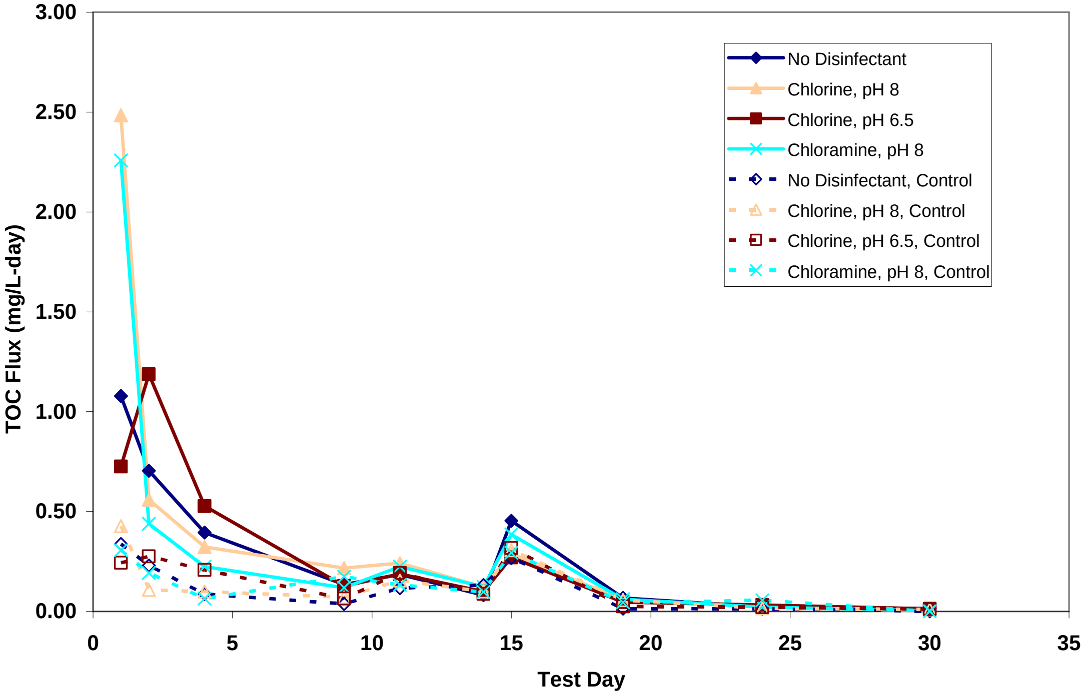


Figure 3-12. TOC Flux vs. Testing Days, All Water Types and Controls

In an effort to determine the TOC source, the sand was tested per Section 2.2.1.2. This testing estimated the amount of TOC released by the sand during the mortar mixing procedure and the first week of coupon curing. The resulting average TOC concentration was 0.75 mg/L which indicates that the sand released 0.075 milligrams of TOC into the 100mL water volume or approximately 0.0038 mg/gram of sand. An average cement mortar coupon weighs 140 grams indicating that six coupons weigh 840 grams. Based on the mortar recipe used, approximately 40% by weight is sand or nearly 340 grams. This suggests that the absolute maximum TOC released from the mortar sand is 1.3 mg. Each vessel contained approximately 2.5L of water after the coupons were in place. This suggests that the sand's maximum TOC contribution was approximately 0.5 mg/L. It would actually be significantly less because only the outer coupon layer is exposed to the water. During days 1 and 2, the cement is rather porous so the water-cement interaction depth maybe significant. If a one millimeter depth is assumed, then two millimeters of the coupon is intimately interacting with the water. That depth represents 20% of the coupons one centimeter thickness. Based on these rather broad assumptions, the sand's possible contribution to the TOC concentration is estimated at 0.1 mg/L, not an unreasonable contribution estimate for the early portion of the test period.

The Portland cement used in producing the coupons was chemically tested per Section 2.2.1.1 with an abbreviated list of results shown in Table 3-4. The test parameter most likely to represent TOC is called Loss on Ignition (LOI). The LOI value represents oxides of carbon, sulfur and nitrogen which are combusted during the 950°C LOI test. The analysis results indicate an LOI of 1.69%. If it is very conservatively assumed that only 1% of this LOI is carbon, then the cement is 0.017% carbon by weight. Also, if it assumed that the total weight of cement within the six immersed coupons is 340 grams then the total amount of carbon is approximately 0.06 grams or 60 milligrams. Using the same depth-of-interaction assumptions presented above, the available carbon may be 20% of this total or 12 milligrams. Using the 2.5L water volume gives a potential TOC concentration of slightly less than 5 mg/L. The highest TOC value observed was only 2.5 mg/L indicating that the actual TOC release rate is lower than the estimated value. However, similar assumptions were used for both the sand and cement and the estimated TOC release rate for the cement was 50 times higher. This suggests that the cement matrix is a much more significant TOC contributor than the sand.

It should also be noted that the coupons were produced using Blacksburg tap water. The controls indicate that the contribution was less than 0.5 mg/L. This is also a likely source of TOC.

The statistical analysis of the TOC results is provided in Table 3-9 and shows that only during day 1 were there any significant differences between the water types, three instances, or with the control group, one instance. There is no particular pattern to the differences that would suggest a reason for these differences.

Table 3-9. Statistically Significant Differences for TOC Concentration, Days 1 through 30, $\alpha = 0.05$

Comparison	Day 1	Day 2 through 30
NODIS vs ClpH8	▨	
NODIS vs ClpH65		
NODIS vs MCPH8		
NODIS vs CONTROL		
ClpH8 vs ClpH65	▨	
ClpH8 vs MCPH8		
ClpH8 vs CONTROL	▨	
ClpH65 vs MCPH8	▨	
ClpH65 vs CONTROL		
MCPH8 vs CONTROL		

In summary, the test waters exposed to the coupons had higher TOC levels than the controls until day 15 at which time the difference became decreased substantially. After day 19, all waters and controls had TOC levels near the base water's background TOC level. The drop in TOC can be attributed to the advancement of cement curing process which restricts the release of TOC as the test period progresses.

3.3.2 Semi-volatile Organic Compounds (SVOC)

There was no significant difference in the SVOC concentrations between the sample and control waters. The liquid-liquid extraction/GC-MS method tested for a variety of compounds including phenols, polyaromatic hydrocarbons, pesticides and industrial chemicals. No graphical presentation for this data is presented due to the unremarkable results.

3.3.3 Trihalomethane (THM) Formation/Sorption

During the primary leaching tests, there was not a significant difference between the coupon-exposed sample waters and the controls with respect to the THM formation rate as shown in Figure 3-13 (p-values comparing test samples and controls ranged from 0.31 to 0.92 for days 1 through 14). The disinfectant-free water type is not shown. The maximum THM concentration obtained was approximately 13 μg/L, well below the USEPA MCL of 80 μg/L.

A key requirement for THM formation is the availability of TOC and all waters had some TOC present (See Figure 3-11). All sample waters had more TOC than the controls but this additional TOC did not result in a significant increase in the observed THM formation rate. The additional TOC available in the sample waters either did not readily form THM compounds in the period between water changes or any additional THM produced was sorbed on the coupon's outer surface and not observed. As mentioned in Section 2, additional THM formation and sorption experiments were performed to gather additional data related to this important water quality parameter. The tests were performed in accordance with the procedures outlined in Section 2. The results of the two tests are presented below.

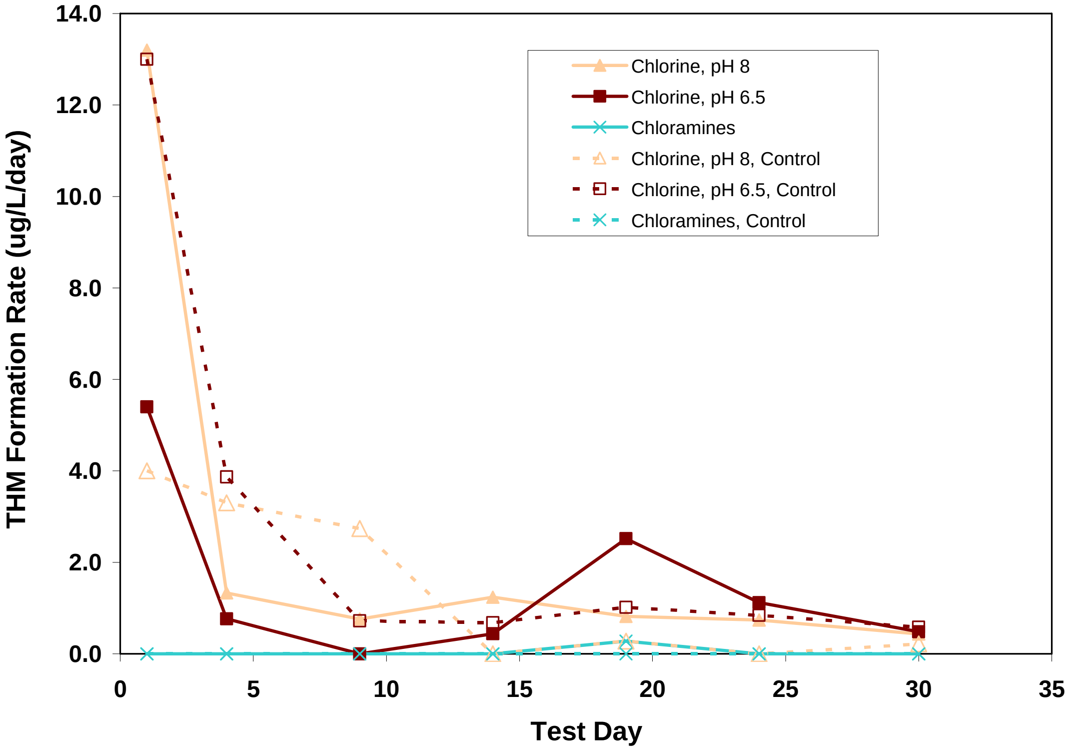


Figure 3-13. THM Formation Rate vs. Testing Days, Disinfected Water Types and Controls

THM Formation Testing Results – The THM formation results are presented graphically in Figure 3-14. The data presented is the average of the triplicate samples analyzed. The figure indicates that the TOC released into the base water by the immersed cement mortar coupons does have the potential to form chloroform, a common THM. At the 72-hour sampling time, approximately 34µg/L of chloroform had formed. Based on the curve shown, the chloroform concentration could have reached between 35 and 40µg/L given additional time. The base water at t = 0 had a chloroform concentration of approximately 3.5µg/L and this value should be subtracted from the total chloroform concentration. The chlorine residual declined as expected as the chloroform reaction progressed, dropping from 10.3 mg/L to 7.8 mg/L. The conditions represented by this test setup are quite severe with high chlorine residual and a relatively high TOC level so actual THM formation would likely be lower in a typical distribution system. However, the results indicate that the cement mortar lining material can generate TOC that has a THM formation potential of at least 30μg/L.

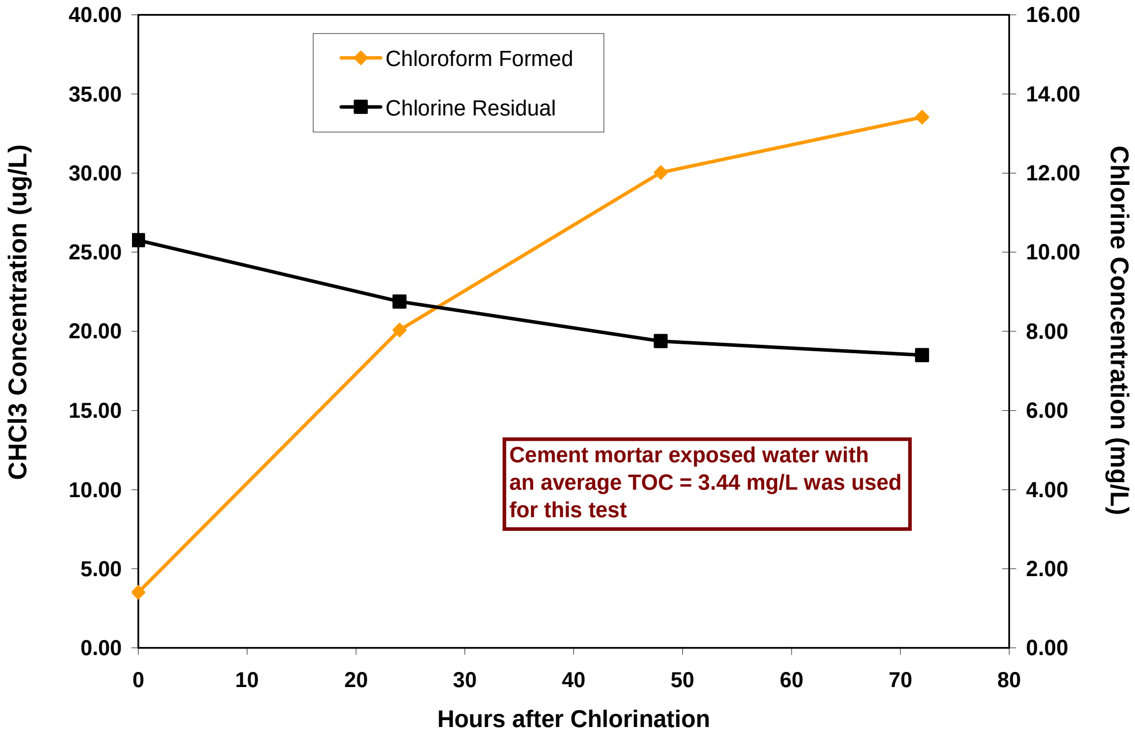


Figure 3-14. $CHCl_3$ and Chlorine Concentration vs. Time, THM Formation Test

THM Sorption Testing Results – The THM sorption results are provide in Figure 3-15 and indicate that the cement mortar lining material does adsorb chloroform. The figure also shows that the sorption rate progresses nearly linearly from 8 to 72 hours after exposure to the coupons. This sorption rate is high in part because of the higher surface area to volume ratio created by the test setup. The vial's 40mL volume is reduced to 30mL due to the insertion of the 10cm^3 coupon section. The sections had an average surface area of 38cm^2 resulting in a surface area to volume ratio of 1.27cm^{-1}. This ratio was 3.25 times higher than the 0.39cm^{-1} ratio used for primary leaching experiments. The dashed line on Figure 3-15 is the sorption rate adjusted for a surface area to volume ratio of 0.39cm^{-1} is characteristic of a 4-inch diameter pipe.

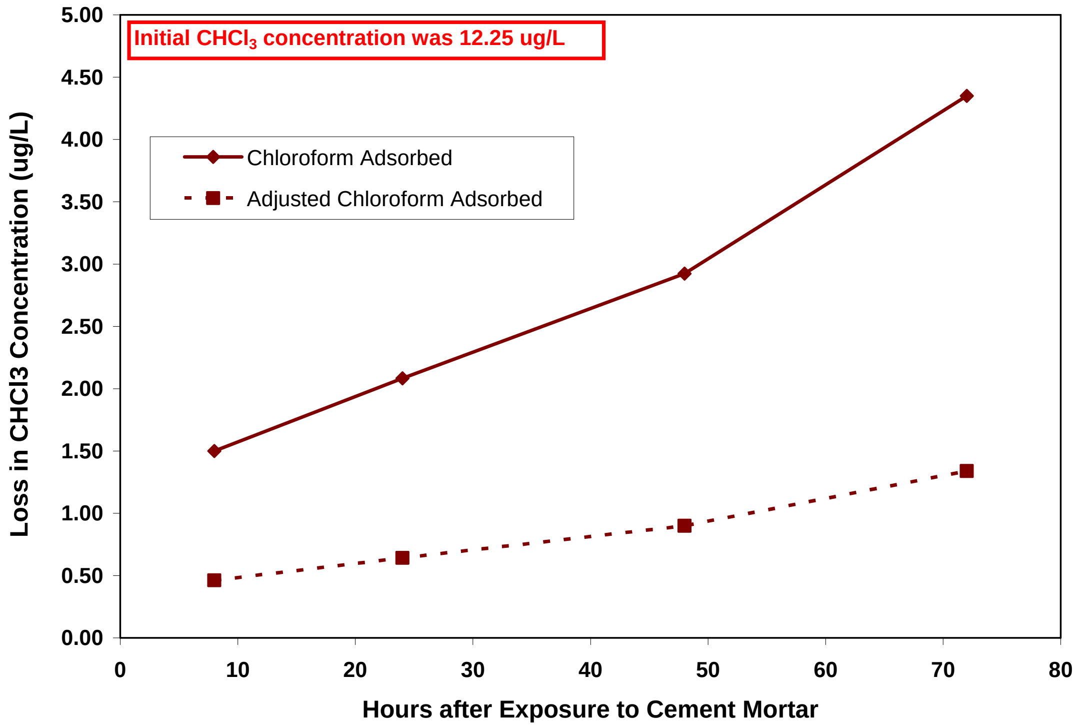


Figure 3-15. Loss in $CHCl_3$ Due to Sorption vs. Time, THM Sorption Test

Since the sorption rate never approaches an asymptote during the test period, a maximum sorption level cannot be predicted. At 72 hours the adjusted adsorbed amount results in a chloroform concentration loss of 1.34µg/L. Based on the surface area of the coupon segment, this equates to approximately 0.035µg/L/cm^2.

3.3.4 Haloacetic Acid (HAA_5) Formation

Figure 3-16 shows that the rate of HAA_5 production within the chlorinated samples was higher than the disinfectant-free and chloramine samples for day 1. This is not unanticipated for two reasons. First, the highest level of organic matter present in the cement mortar would be most available early in the testing period due to the uncured nature of the coupons. The TOC data presented in Figure 3-11 supports this result.

Secondly, chlorine disinfectant is more likely to produce haloacetic acids than chloramine when used in drinking water treatment (USEPA, 2007). On day 4, the HAA_5 production for chloramine and its control increase substantially. This may be an experimental error since the TOC values for the chloramine sample and its control were the lowest of the four sample/control pairs. After day 4, the test sample's HAA_5 concentrations decrease and approach the control values. At no time during the test period did individual HAA_5 levels exceed 14 ug/L and all samples had dropped below 4 ug/L by day 14.

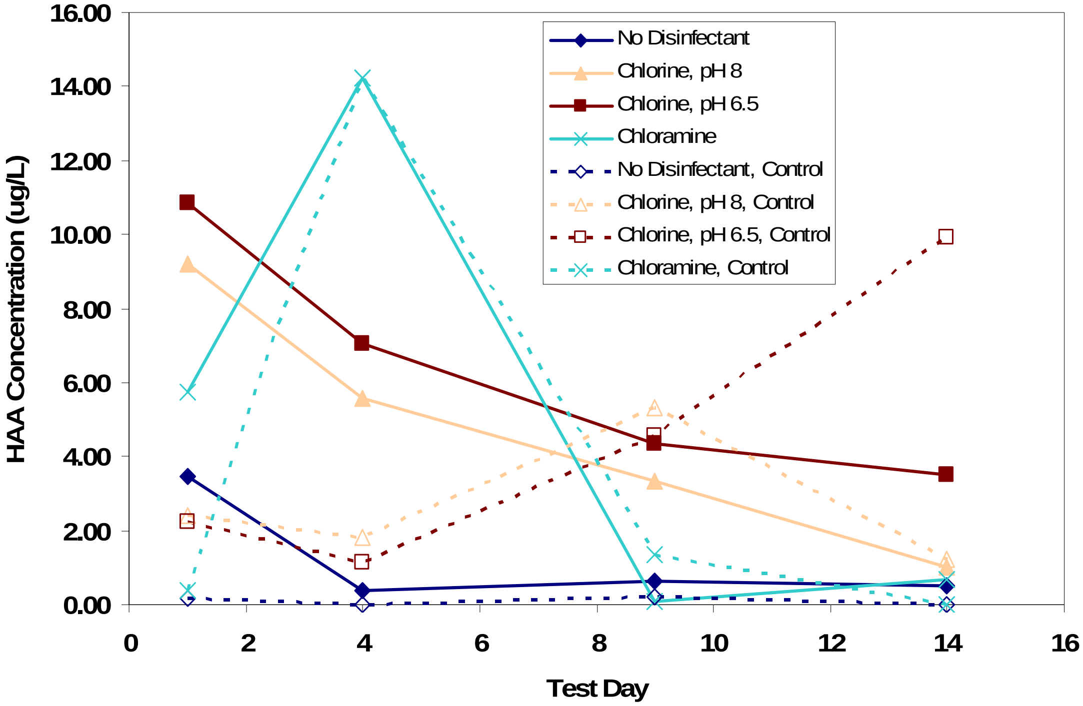


Figure 3-16. HAA_5 Concentration vs. Testing Days, All Water Types and Controls

Figure 3-17 shows the change of HAA_5 concentration on a daily basis. This plot normalizes the data with respect to the number of days between sampling times. It shows that the daily rate of HAA_5 production decreases throughout the sampling period, even for the chloramine sample and control. In summary, the cement mortar lining material did not form HAA_5 compounds at significantly different rates than the controls after day

1 and the HAA_5 production rates decreases rapidly to less than 2 µg/l-day after day 4. Since the test setup is an absolute worst case scenario for an actual distribution system, a small diameter pipe with stagnant water, the risks associated with HAA_5 levels approaching the EPA regulatory limit of 60 µg/L would be minimal.

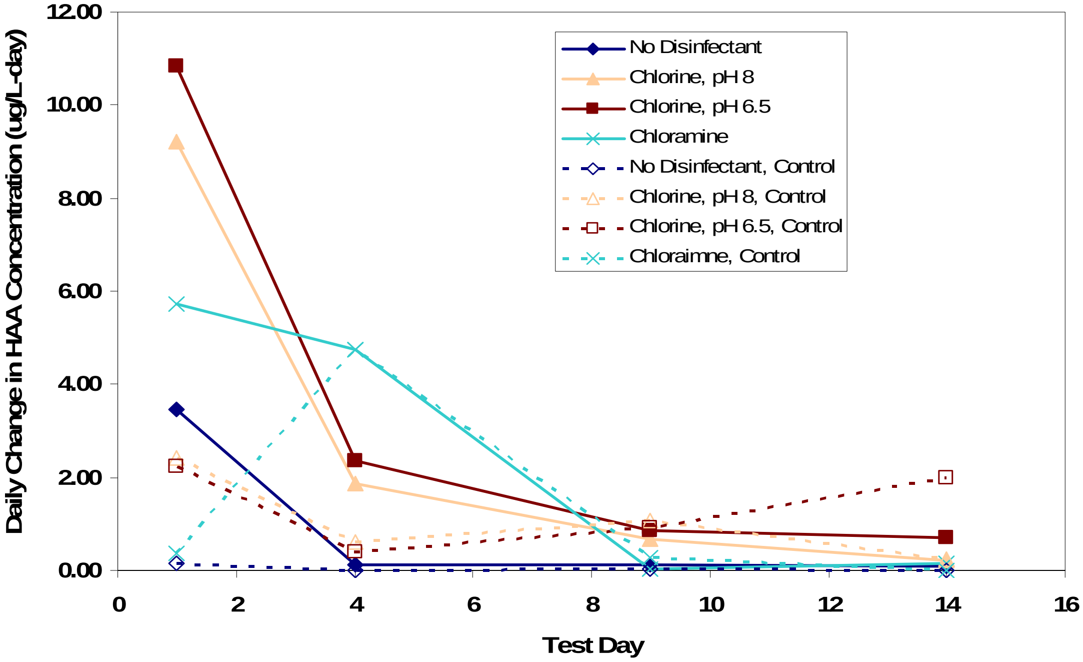


Figure 3-17. HAA_5 Daily Concentration Increase vs. Testing Days, All Water Types and Controls

Statistical analysis of the haloacetic acid data revealed that there was significant difference (p = 0.029) between the coupon-exposed test samples and the controls on day 1 only. This analysis supports the discussion provided above.

3.4 Odor Testing

Composites of the triplicate water samples and controls were evaluated for odor in accordance with Section 2.2.2. As shown in Figure 3-18, a noticeable “cement” odor was imparted to the water by the cement mortar coupons. The cement odor intensity was in the 3.0-4.5 range on the FPA scale of 0-12. This is considered a “weak” intensity (defined as FPA intensity = 4); the weak intensity corresponds to the sweetness of canned fruit (for comparison, FPA intensity of 8 is moderate and corresponds to canned soda while an FPA intensity of 12 is strong and corresponds to syrup or jelly). The odor intensity did not diminish significantly over the 14 day data collection period of that data were collected. Statistical analysis using nonparametric t-test indicated that there was a significant difference between the test samples and the controls on all sampling days.

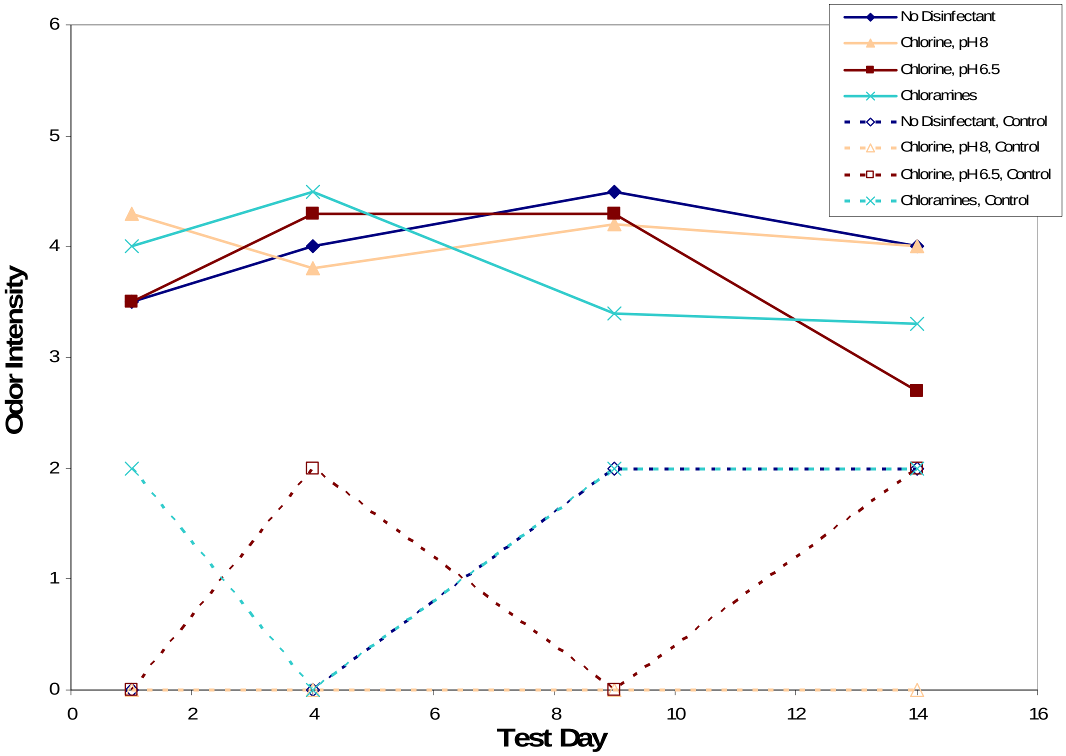


Figure 3-18. Cement Odor Intensity vs. Testing Day, All Water Types and Controls

The cement odor intensity or description was not impacted by the presences of chlorine or chloramine. On day 1, nearly all the residual disinfectant had been consumed in the samples. The sensory panelists detected a chlorine odor (data not shown) on day 14 in the chlorine and chloramine disinfected waters. This is consistent with the chlorine residual loss data (Figure 3-10) which shows that the chlorine and monochloramine were being consumed by the cement mortar early in the test but by day 14 the residual loss was quite small.

3.5 Effects of Corrosion Preventative Additives (CPA)

The objective of this testing was to determine if industry-standard pipe corrosion preventative additives (CPA) had any impact on the water quality effects of newly installed cement mortar lining materials.

The CPA evaluation results are presented with the three CPA types and the control water shown on each figure. The data presented is the average of the duplicates used in the CPA testing. (Note: A very slow leak formed in one of the two control water immersion vessels which resulted in some water loss between days 4 and 9. Approximately 30% of this water leaked over the five day period. The impact of this issue is unknown since the time at which the leak occurred during the period is uncertain. However, the data associated with day 9 control water may be skewed slightly upward.)

3.5.1 pH

The pH results are shown in Figure 3-19 below and indicate that for all samples the pH rises rapidly after exposure to the uncured cement mortar. The three CPA and control water types behaved similarly until day 11 when the polyphosphate (PP) water began to indicate a lower pH. This trend continued throughout the remaining test period with the PP additive showing the largest drop in pH to 10.65, departing from the two other CPA types and the control. The orthophosphate (OP) additive and CPA control behaved very similarly, dropping to pH 11.2 – 11.3 and leveling off. The zinc orthophosphate (OPZn) additive lowered the pH to 11.0, a value which fell in between the PP and OP values. The CPA results showed greater differences between types as the test period progressed.

The rise and overall trend in pH values during CPA testing can be attributed to the same causes that were outlined in the previous section for cement mortar (Section 3.2.1). The exposure time between water changes and the cement's cure progression affect the amount of calcium hydroxide leached into the sample water. Longer exposure times increase hydroxide concentration while cement cure progression dampens the increases in hydroxide concentration due to the more complete hydration of the cement's calcium silicate component. The PP additive's ability to limit the pH increase may be due to its enhanced ability to form a protective layer on the concrete surface thus slowing the movement of calcium hydroxide into the sample water. These results correspond well with the findings reported in Douglas et al (1991).

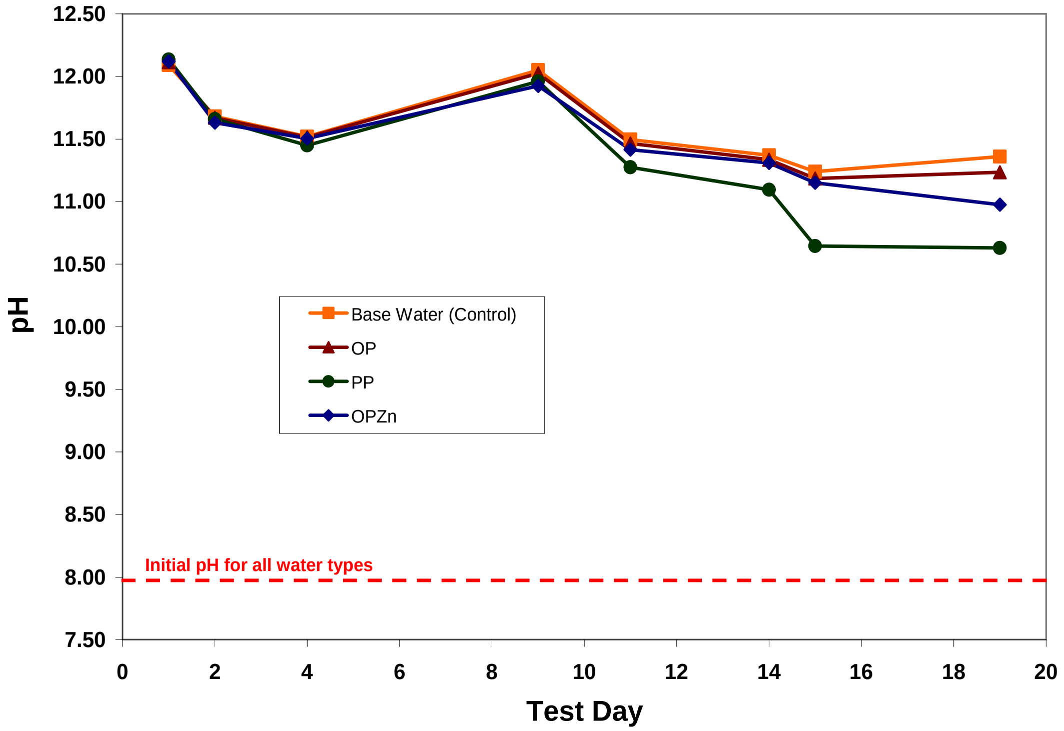


Figure 3-19. pH vs. Testing Day, CPA Evaluation Water Types and Control (OP=orthophosphate, PP=polyphosphate, OPZn=zinc orthophosphate)

Statistical analysis of the CPA pH results are provided in Table 3-10 and it indicates the enhanced ability of the PP additive to control pH increase after day 11. On day 19, the OPZn additive begins to return a significant improvement when compared to the control.

Table 3-10. Statistically Significant Differences for pH, CPA Testing, All CPA Types, All Days, α = 0.05

Comparison	Day 1	Day 2	Day 4	Day 9	Day 11	Day 14	Day 15	Day 19
CONTROL vs PP					▨	▨	▨	▨
CONTROL vs OP								
CONTROL vs OPZn								▨
PP vs OP							▨	▨
PP vs OPZn							▨	
OP vs OPZn								

3.5.2 Alkalinity

The total alkalinity results for CPA tests are provided in Figure 3-20. The total alkalinity values for all samples are very high on day 1 due to a high rate of calcium hydroxide leaching. The alkalinity for all samples then drops rapidly on day 2. Subsequently, the three CPA types and control follow similar trends, only departing from one another on day 9. The data converges for the remainder of the test period with very similar results on day 19. These data suggest that these CPA types at the dosages tested do not have a substantial impact on changes in total alkalinity. Based on the significant differences in pH shown above, larger differences in alkalinity were anticipated since at these elevated pH levels the hydroxyl ion concentration is the key driver in determining alkalinity. One explanation is that the pH levels observed during CPA testing are significantly lower than was seen during the primary leaching tests, in particular the PP additive samples. Since the solubility of carbonate increases rapidly with pH decreases, there are higher levels of dissolved carbonate in the CPA waters which adds to the alkalinity and negates the drop in hydroxide ion concentration.

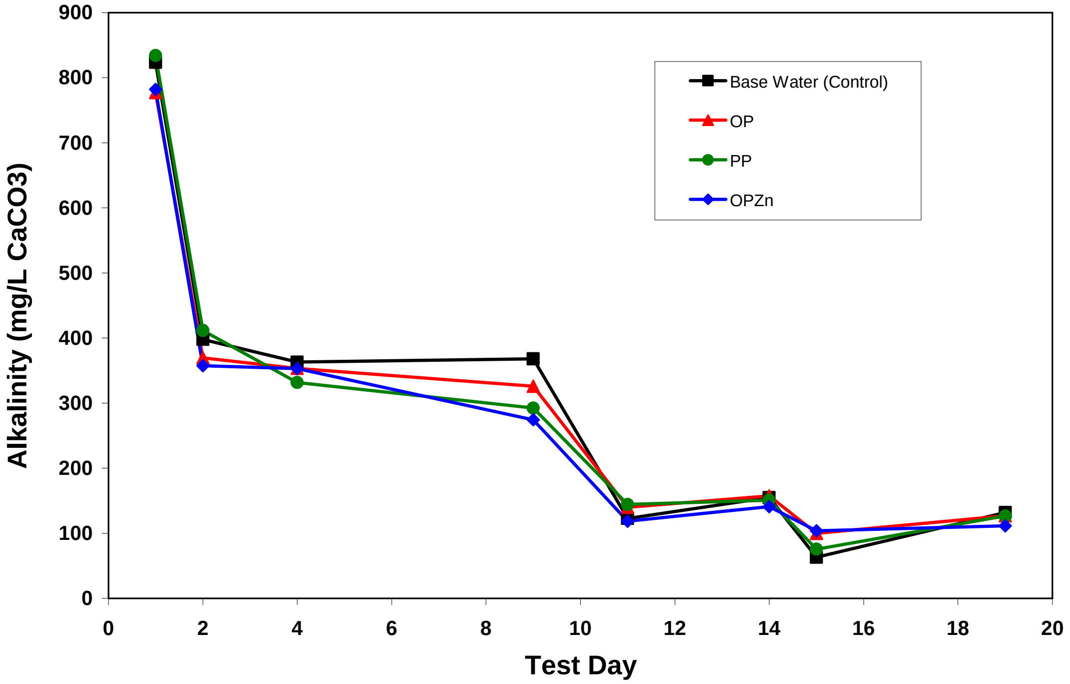


Figure 3-20. Total Alkalinity vs. Testing Days, CPA Evaluation Water Types and Control

Table 3-11 shows the statistical analysis results for CPA testing alkalinity. As mentioned above, significant differences are not observed until day 15. On day 15, the OP and OPZn waters had alkalinity values that were significant higher than the control while on day 19 the OPZn water was significantly lower than all other water types. However, the range of values in question is small. On day 19, the lowest OPZn alkalinity value was 110 mg/L as $CaCO_3$ while the highest control value was133 mg/L as $CaCO_3$. This difference would not be perceptible to the average drinking water consumer and is not considered practically significant.

Table 3-11. Statistically Significant Differences for Alkalinity, CPA Testing, All CPA Types, All Days, $\alpha = 0.05$

Comparison	Day 1	Day 2	Day 4	Day 9	Day 11	Day 14	Day 15	Day 19
CONTROL vs PP								
CONTROL vs OP							■	
CONTROL vs OPZn							■	■
PP vs OP							■	
PP vs OPZn							■	■
OP vs OPZn								■

3.5.3 Metals (including Hardness) and Non-metals

Samples were tested for the content of 17 different metals. This section will discuss the metals testing results for:

- Calcium and magnesium because they are the major constituents of hardness.
- Aluminum because it is a major component of cement in the form of aluminum silicates.
- Phosphorous because the phosphate ion is associated with the corrosion preventative additives that were added to the various test waters.
- Zinc because it was added as a component in one corrosion preventative type and the results showed some significant concentrations in all samples.
- Chromium because of its potential health effects and it was found in significant enough quantities to warrant discussion in the CPA tests and the primary leaching tests.

The other elements that were part of the analysis (Na, Si, S (as SO_4), Cl, K, V, Fe, Mn, Co, Ni and Cu) were either present in very small amounts or did not show any significant variation from the control data or amongst the CPA types. All metal samples were filtered through a 0.45µm glass filter before being tested so as to remove any precipitate.

<u>*Hardness (Ca and Mg)*</u> – The hardness results are provided in Figure 3-21 and show that the hardness is very high on day 1 and then falls asymptotically towards a value of approximately 50 mg/L as $CaCO_3$. This hardness is attributed almost entirely to Ca, the concentration of which is plotted in Figure 3-22, until day 14 for PP samples and day 15 for OP, OPZn and control. After day 14 or 15, Mg begins to make a contribution (See Figure 3-23). The Mg contribution remains small especially for the CPA types other than PP. The high calcium values early in the test period are generated by the same reaction mechanisms that increase pH and alkalinity. As the cement cures, the hydration reactions release calcium hydroxide into the water. The Ca leaching can be further augmented by simple dissolution of free lime and calcium silicates from the mortar to the water. The calcium then reacts with the available carbonate to form calcium carbonate solid. Table 3-12 provides some supporting data for this behavior. The data in Table 3-12 is based on observations of the PP-augmented water and assumes that all metals were present as free ions. There are also no corrections for ionic strength. The carbonate concentrations used to determine these values were calculated by subtracting hydroxide alkalinity from total alkalinity and determining the carbonate ion fraction present at each pH level. Note that calcium carbonate is the controlling solid throughout the test period. Schock et al (1981) suggested that hydroxyapatite ($Ca_5(PO_4)_3OH$) may have been the controlling solid at these elevated pH levels but due to the very low phosphorous levels present (discussed below), this was not the case.

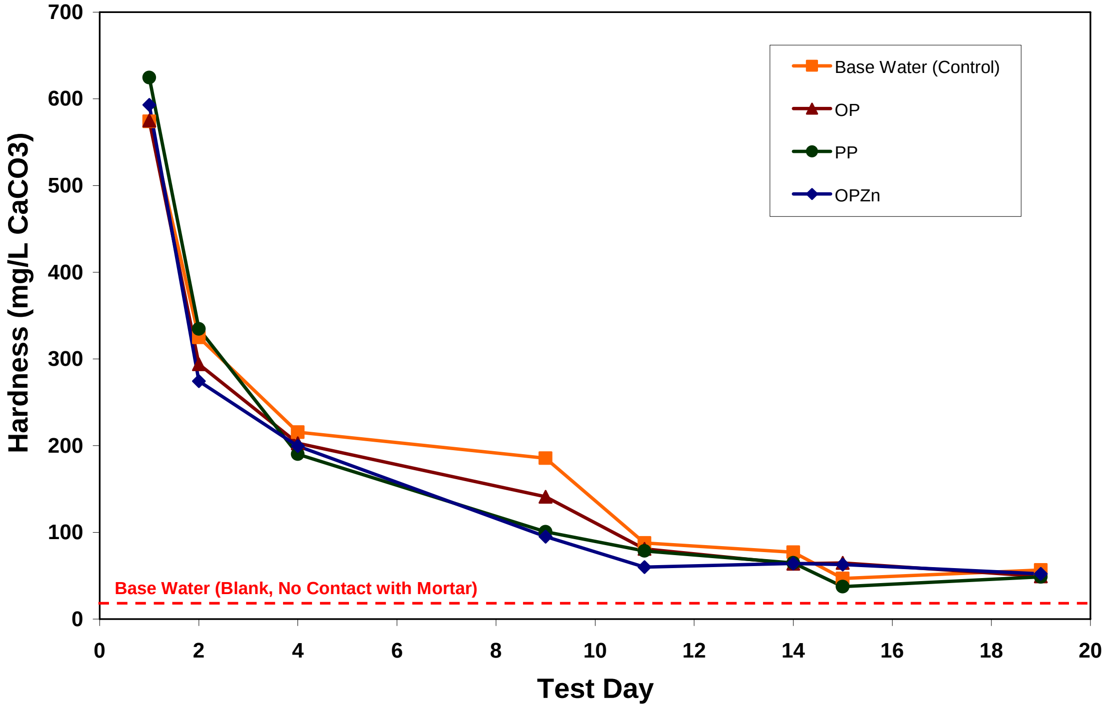


Figure 3-21. Total Hardness vs. Testing Days, CPA Evaluation Water Types and Control

Table 3-12. Thermodynamically Predicted Controlling Precipitate for Ca and Mg Species during CPA Testing (shaded area indicates controlling solid)

Day	**pH**	**Likely Precipitating Solid**[1]						
		$Ca(OH)_2$ $K_{sp}=10^{-5.3}$	$CaCO_3$ $K_{sp}=10^{-8.5}$	$Ca_3(PO_4)_2$ $K_{sp}=10^{-26}$	$Ca_5(PO_4)_3OH$ $K_{sp}=10^{-40.6}$	$Mg(OH)_2$ $K_{sp}=10^{-10.7}$	$MgCO_3$ $K_{sp}=10^{-7.5}$	$Mg_3(PO_4)_2$ $K_{sp}=10^{-25}$
1	12.1		▨			▨		
2	11.7		▨			▨		
4	11.5		▨			▨		
9	12.0		▨			▨		
11	11.4		▨			▨		
14	11.2		▨			▨		
15	10.7-11.5		▨			▨	▨	
19	10.6-11.4		▨			▨	▨	

[1] Calculated based on measured aqueous concentrations of metal cations and anions and solubility parameters at 25°C, K_{sp} values from Schock et al (1981)

The dashed line in Figure 3-23 indicates that the dissolved Mg in all of the water samples is 9.5 mg/L as Mg before placed in contact with the cement mortar. During the period before day 14 for PP and day 15 for the other samples, nearly all of this Mg falls out of solution as a precipitate or as a coating on the cement surface. This precipitate is most likely $Mg(OH)_2$ through day 14. Table 3-12 shows that on days 15 and 19 the $MgCO_3$ may also be a precipitating solid. The calculated aqueous concentrations for each solid are nearly the same so it is unclear which is the controlling species. The hydroxide precipitation occurs due to the high pH seen during the earlier portions of the test period at which the solubility of magnesium hydroxide is very low. It is not until the pH drops below 11.3 that appreciable amounts of Mg are found in solution and the Mg concentration begins to exhibit values comparable to that found with aqueous magnesium carbonate The higher dissolved Mg concentration found in the PP sample is the result of the lower pH values evident in the same samples. It was also noted that the PP water contained much less precipitate than the other samples during this period of lower pH.

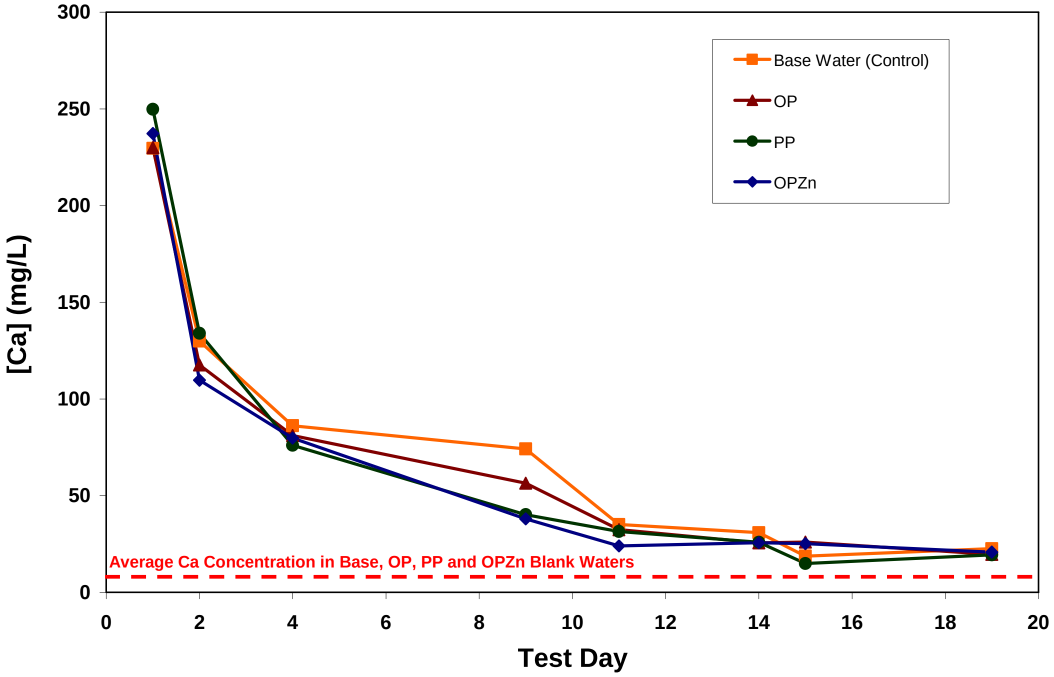


Figure 3-22. Calcium Concentration vs. Testing Days, CPA Evaluation Water Types and Control

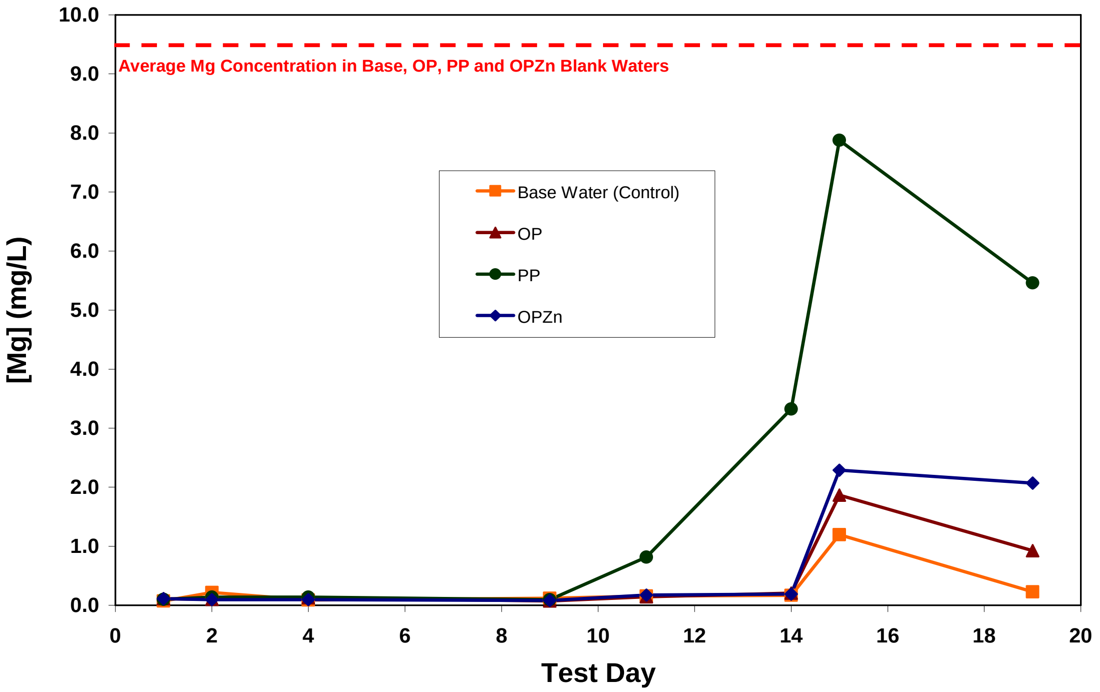


Figure 3-23. Magnesium Concentration vs. Testing Days, CPA Evaluation Water Types and Control

The statistical analysis of CPA hardness data is provided in Table 3-13. It shows that on day 15 there were statistical differences between the some of the water types and some combinations with the control. The OP and OPZn additives had significantly higher hardness values than the PP and control. These differences disappear on day 19. This disappearance may be caused by the longer period between the water changes allowing the system to equilibrate more completely. This would be especially true if the coupon coating, enhanced on the PP additive sample, was slowing the release of calcium. The lower values on the control are not readily explained.

The statistical analysis of the calcium results, shown in Table 3-14, provides additional evidence of calcium hydroxide dissolution as the main source of alkalinity and calcium. The results show that significant differences are evident between the same populations as were indicated for alkalinity. This similarity is due to the dissolution of calcium hydroxide releasing proportional amounts of calcium and hydroxide ions into the water. This proportional release, along with its magnitude relative to other potential release mechanisms, means that their concentrations vary similarly in all of the CPA water types.

Table 3-13. Statistically Significant Differences for Total Hardness, CPA Testing, All CPA Types, All Days, $\alpha = 0.05$

Comparison	Day 1	Day 2	Day 4	Day 9	Day 11	Day 14	Day 15	Day 19
CONTROL vs PP								
CONTROL vs OP							▨	
CONTROL vs OPZn							▨	
PP vs OP							▨	
PP vs OPZn							▨	
OP vs OPZn								

Table 3-14. Statistically Significant Differences for Calcium Concentration, CPA Testing, All CPA Types, All Days, $\alpha = 0.05$

Comparison	Day 1	Day 2	Day 4	Day 9	Day 11	Day 14	Day 15	Day 19
CONTROL vs PP								
CONTROL vs OP							▨	
CONTROL vs OPZn							▨	▨
PP vs OP							▨	
PP vs OPZn							▨	▨
OP vs OPZn								▨

The statistical analysis of the magnesium data are provided in Table 3-15. The solubility of magnesium hydroxide and/or carbonate is very pH dependent, the pH variability shown in Figure 3-19 is the key driver for these results. Note that on days 14, 15 and 19, the pH levels seen with the PP additive are markedly lower than the other three samples. Magnesium salt solubility increases as the pH decreases. Hence the highest magnesium levels for the PP additive.

Table 3-15. Statistically Significant Differences for Magnesium Concentration, CPA Testing, All CPA Types, All Days, $\alpha = 0.05$

Comparison	Day 1	Day 2	Day 4	Day 9	Day 11	Day 14	Day 15	Day 19
CONTROL vs PP						▨	▨	▨
CONTROL vs OP								
CONTROL vs OPZn								▨
PP vs OP						▨	▨	▨
PP vs OPZn						▨	▨	▨
OP vs OPZn								

Aluminum – The Al concentration results are provided in Figure 3-24 and indicate that this metal does dissolve into the water during the cement mortar's curing period. The data also suggests the there are differences between the various CPA types as to the magnitude of this dissolution, mostly due to their varying ability to reduce pH and calcium levels.

The calcium levels are important factors when interpreting this system's behavior using the approach outlined by Damidot (1993) and used to examine the primary leaching data (Section 3.2.4). It should be noted that the test samples that have had CPA added to them are slightly modified with respect to the systems considered by Damidot due to the addition of phosphates and zinc. The impacts of these additional compounds have not been determined as part of this study but since their concentrations are quite low it is assumed that Damidot model is still applicable. A review of the aluminum results, from the perspective of the Damidot model, is provided below:

- Early in the test period, higher calcium levels keep aluminum levels in a moderate range for this study due to the solubility mechanisms described in the Section 3.2.4 and illustrated in Figure 3-6.

- The low aluminum values on day 4 are unexpected when interpreted using the Figures 3-6 through 3-8. The lower calcium levels relative to day 2 should have allowed for an increase in aluminum. The reason for this decline, which occurs in all water types, was not determined in this study.

- On day 9 an increase in aluminum concentration is seen as calcium levels drop further and the system moves further to the right on Figure 3-6.

- On day 15, calcium levels have dropped sufficiently thus allowing the system to reach the aluminum solubility breakpoint (from ettringite to aluminum hydroxide as controlling solid) and the aluminum levels drop substantially.

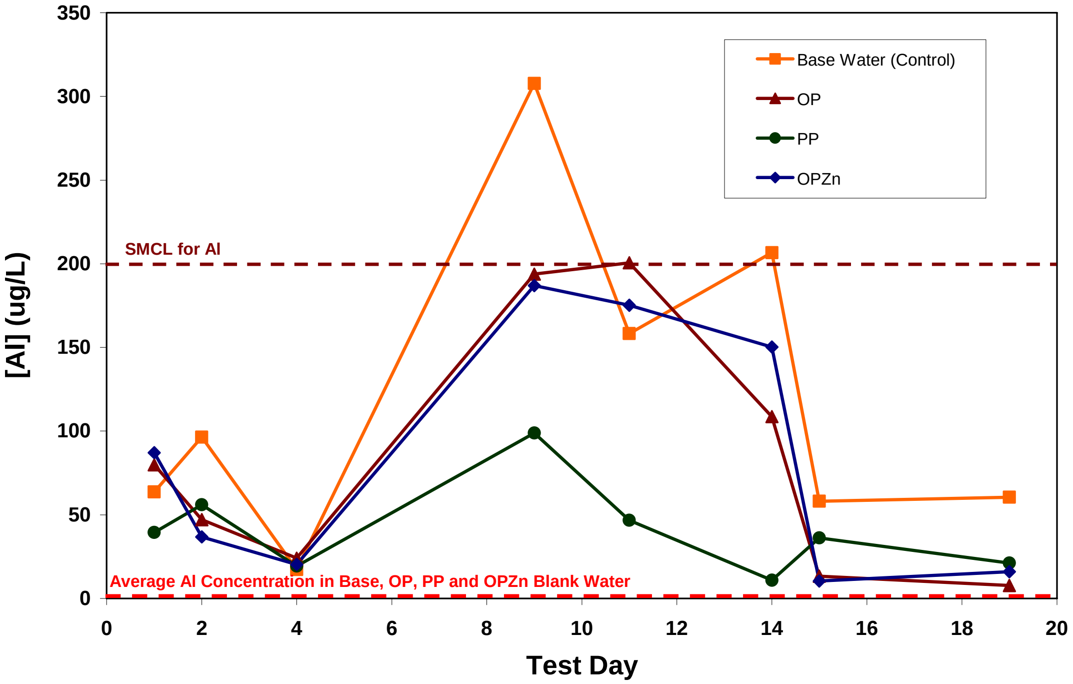


Figure 3-24. Aluminum Concentration vs. Testing Days, CPA Evaluation Water Types and Control

The OP and OPZn additives behaved similarly throughout the test period with both limiting aluminum dissolution better than the control on most days. The PP limited the Al concentration most effectively until day 15 and performed much better at days 9, 11 and 14. At day 19 the three CPA types all limit the Al concentration to substantially lower values than the control.

The statistical analysis of the aluminum data, Table 3-16, showed a significant difference for the OP and OPZn on day 15. The superior performance of the PP additive was not returned as significant on any day, due to the relatively high variability in the aluminum concentrations of the other additive/water combinations.

Table 3-16. Statistically Significant Differences for Aluminum Concentration, CPA Testing, All CPA Types, All Days, α = 0.05

Comparison	Day 1	Day 2	Day 4	Day 9	Day 11	Day 14	Day 15	Day 19
CONTROL vs PP								
CONTROL vs OP							▨	
CONTROL vs OPZn							▨	
PP vs OP								
PP vs OPZn								
OP vs OPZn								

Phosphorous – The phosphorous concentration results are provided in Figure 3-25 and show that the P concentration drops to virtually zero for all CPA types until day 14. The PP water sample shows some P, most likely in the form of phosphate, on day 14 while the others remain at near zero. On day 15, the PP water shows a rapid increase in phosphate content to slightly more than 800µg/L as P while the OP and OPZn show an increase to nearly 60µg/L as P. It should be noted that at the pH levels considered for this study, the phosphate may occur as the phosphate ion (PO_4^{3-}) or monohydrogen phosphate (HPO_4^{2-}). The pK_{a3} of phosphoric acid is 12.4 which means that as the pH decreases below 12.4, the monohydrogen phosphate (HPO_4^{2-}) form is progressively favored over the phosphate ion (PO_4^{3-}). Monohydrogen phosphate does not readily form complexes with magnesium or calcium so the observed phosphate levels must be corrected for this when determining the possible concentrations of dissolved calcium and magnesium phosphate salts. With this in mind, an effort to determine the precipitate responsible for the very low phosphorous levels observed from days 1 to 14 was undertaken using the following data:

- Observed concentrations of carbonate and hydroxide ions
- Corrected phosphate ion values
- Available solubility constants for the most likely precipitating salts (Schock, 1981)

The predicted concentration for metals that form complexes with phosphate and were present within the system was calculated for each day (Ca, Mg, Zn and Al). These calculations do not account for the competing effects of these and other species within the solution but at these low concentrations the effects have little impact on the qualitative determinations presented here. The tabular results of this analysis are provided in Appendix E.

The results indicate that at no point during the test period, for the metals considered, is a phosphate-based salt the controlling precipitate. The mechanism causing the drop in phosphorous level during days 1 to 14 could not be identified. The actual aqueous system is very complex and is probably not well-represented by this simple and ideal approach. Further research could be performed to ascertain the mechanism causing the drop in phosphorous levels.

However, the results shown in Figure 3-25 suggest that at the higher pH values prevalent during the earlier portion of the test period the phosphate was precipitating out of solution or forming a coating on the coupon surface. As mentioned above, the identification of this precipitate was not possible.

Later in the test period, as the pH decreases for the reasons discussed at length in previous sections, the fraction of monohydrogen phosphate increases significantly and does not readily complex with available metals. It remains in solution as an ion and is observed in the phosphorous test results. The lower pH values produced by the PP additive allowed a greater fraction of the added phosphate to remain in solution (approximately 2/3 of the available phosphate).

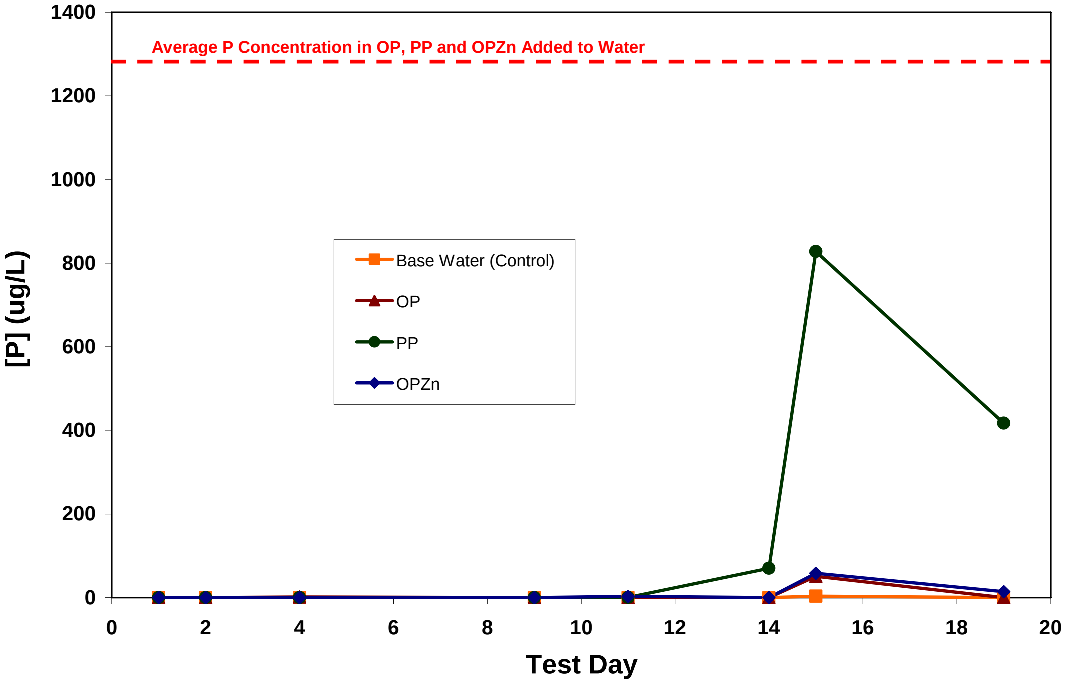


Figure 3-25. Phosphorous Concentration vs. Testing Days, CPA Evaluation Water Types and Control

The dashed line represents the average phosphorous content of the CPA types in each of the conditioned waters before contact with the coupons (1283, 1261 and 1253 µg/L as P for PP, OP and OPZn respectively). The control water which had no phosphate added never shows any phosphate content indicating that the mortar does not contribute phosphate to the water. In summary, with respect to phosphorous content alone, the PP additive allowed a greater fraction of soluble monohydrogen phosphate ion to exist after day 14 due to its ability to limit the pH increases during the same period.

The statistical analysis of the phosphorous data is present in Table 3-17 and it verifies the findings discussed above in that the PP augmented water has significantly higher phosphorous levels due to the lower pH levels evident during the latter portion of the test period.

Table 3-17. Statistically Significant Differences for Phosphorous Concentration, CPA Testing, All CPA Types, All Days, $\alpha = 0.05$

Comparison	Day 1	Day 2	Day 4	Day 9	Day 11	Day 14	Day 15	Day 19
CONTROL vs PP							▨	▨
CONTROL vs OP								
CONTROL vs OPZn								
PP vs OP							▨	▨
PP vs OPZn							▨	▨
OP vs OPZn								

Zinc – The Zn concentration results are provided in Figure 3-26 and show that the CPA type had little impact on the Zn concentrations found in the waters over the entire test period. Even the OPZn water, which had an average of 360 µg/L as Zn before contact with the coupons (red dashed line), had Zn concentration values that were similar to the other two CPA types and the control (these samples had nearly 0 µg/L as Zn before contact with coupons as shown by black dashed line). This suggests that two mechanisms are at work with respect to Zn concentration. First, the cement mortar is contributing Zn to the water sample in all cases. The cement analysis, Appendix C, shows that the cement has a zinc content of 0.01% by weight. This is a small percentage but large enough to contribute zinc at the levels seen in this study. Second, the pH conditions are then controlling the concentration of Zn that remains in solution. Zinc solubility in this system is minimized at pH 9 so as the pH is lowered from above 12 early in the test period, less of the Zn is staying solution (Schock et al., 1981). The Zn is either precipitating as zinc hydroxide, or forming a surface coating at the lower pH values seen later in the test period. Overall, there is little difference in the behavior of the three CPA types and the control with respect to Zn concentration. This conclusion was supported by the statistical analysis of the zinc data which showed there were no significant differences between the CPA additives.

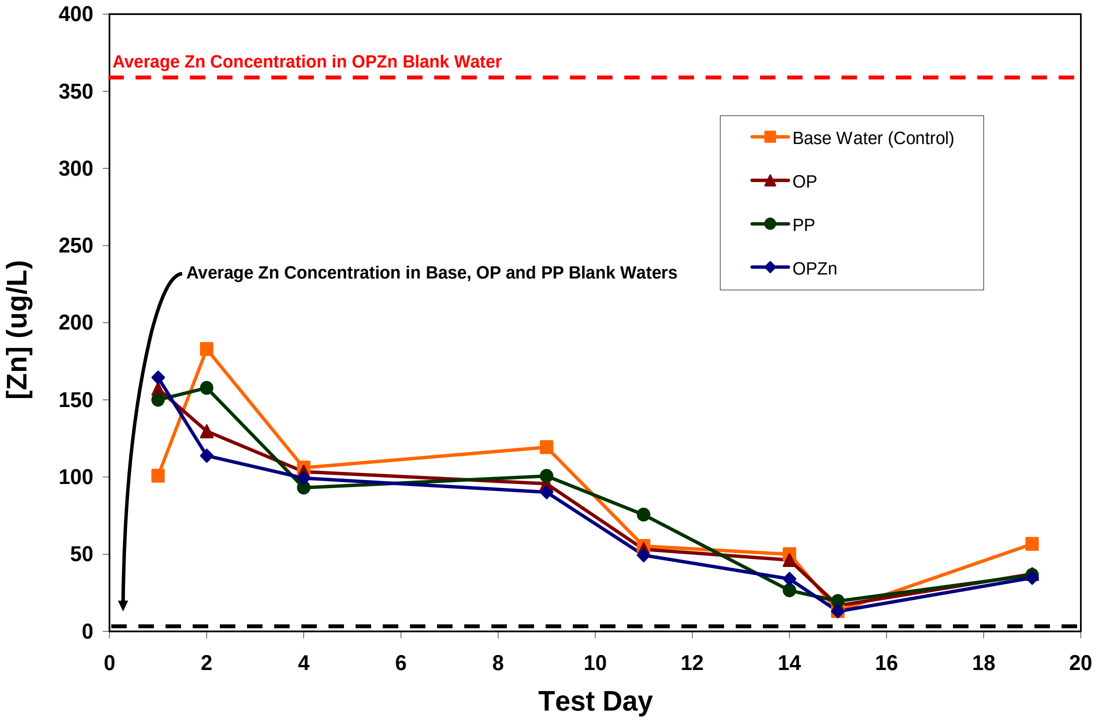


Figure 3-26. Zinc Concentration vs. Testing Days, CPA Evaluation Water Types and Control

Chromium – The Cr concentration results are provided in Figure 3-27 and show that the cement mortar increases the Cr concentration substantially on day 1 for all CPA water samples and the control. As discussed earlier, the analysis of the cement revealed that it contained a small percentage of Cr_2O_3 and constitutes the only available source of chromium. The Cr concentration then declines rapidly for all samples as the cement cures. The PP additive does drive the Cr concentration to a slightly lower value (to

1μg/L) than the other CPA types and the control. The statistical analysis of this data, see Table 3-18, shows that the PP additive did result in significantly lower Cr levels than the control on days 14 and 19 due to its ability to limit pH increases more effectively. The Cr concentration never approaches the EPA MCL of 100μg/L. Overall, the CPA additive samples behaved similarly with respect to Cr concentration.

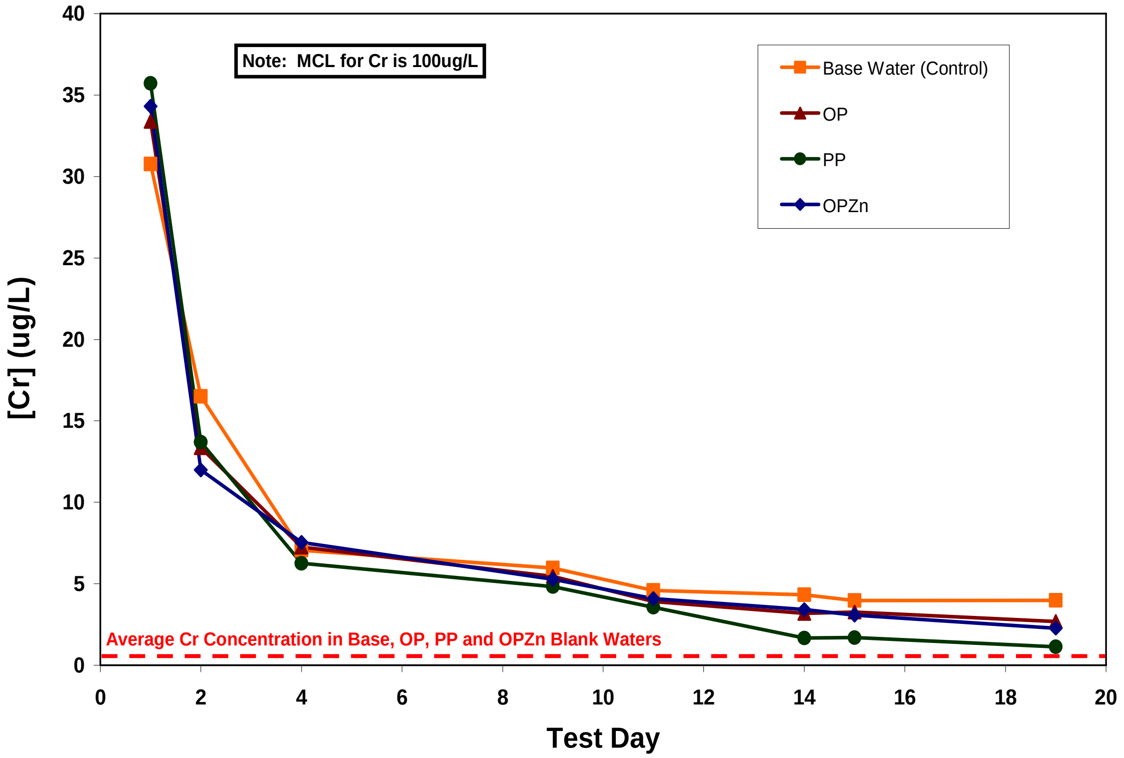


Figure 3-27. Chromium Concentration vs. Testing Days, CPA Evaluation Water Types and Control

Table 3-18. Statistically Significant Differences for Chromium Concentration, CPA Testing, All CPA Types, All Days, $\alpha = 0.05$

Comparison	Day 1	Day 2	Day 4	Day 9	Day 11	Day 14	Day 15	Day 19
CONTROL vs PP						▨		▨
CONTROL vs OP								
CONTROL vs OPZn								
PP vs OP								
PP vs OPZn								
OP vs OPZn								

4. CONCLUSIONS

This study's conclusions are provided below and are based on the results and discussion presented in the previous section. It should be noted that the effects observed were the result of severe conditions that may be anticipated within specific sections of an actual drinking water distribution system. These conditions include a physical arrangement that simulated a small diameter pipe with very low water flow and rather aggressive initial water chemistry due to its low alkalinity and low hardness. These conditions would only be met in limited portions of a distribution system that used similar finished water. The application of these conclusions to an actual distribution requires consideration of these factors.

4.1 Cement Mortar Lining Impacts on Inorganic Water Chemistry

Based on the information garnered during the literature review, it was anticipated that the inorganic chemistry impacts caused by the cement mortar lining would be the most profound. This was indeed the case. The resulting data and its analysis allow the following to be concluded:

- Newly applied cement mortar lining material can cause significant increases in pH. The pH may rise between 4 and 5 pH units initially before falling to 3 to 4 units above the original finished water pH. This latter level may persist for weeks. The increase is the result of dissolution of the calcium hydroxide that is released from the cement during the hydration process. The high porosity of the uncured cement mortar also enhances the release of calcium hydroxide. The type of disinfectant, chlorine or monochloramine, or initial pH have little impact on this increase.

- The new lining material may also increase the water's alkalinity dramatically, to over 800 mg/L as $CaCO_3$ in some situations before declining to approximately 100 mg/L as $CaCO_3$ after two weeks time. The alkalinity may stay at this level for weeks after installation. The alkalinity increase was due to the large increase in the hydroxide ion concentration and not due to elevated carbonate levels. Again, disinfectant type had little impact on the increase.

- The total hardness of the water increased to nearly 700 mg/L as $CaCO_3$ in some cases due in most part to the same calcium hydroxide dissolution reaction that caused the pH increase. An additional source was the solubility of the di- and tricalcium silicates present in the cement before hydration is completed. These increases dropped as the test period progressed with values actually falling below the control levels. This is due to the precipitation of magnesium hydroxide and calcium carbonate, effects that take command of the water chemistry changes late in the test period after the cement's hydration processes have matured. There were no significant differences in this behavior with respect to disinfectant presence or type.

- The release of aluminum and chromium to the water will likely occur due to leaching from the cement mortar. The aluminum is the result of tricalcium aluminate dissolution and a by-product of its hydration. The same effects, although to a lesser extent, are the result of tetracalcium aluminoferrite reacting in a similar fashion. Aluminum concentration is controlled by the solubility of various aluminum salts as modeled by Damidot (1993) and applied to this study's results. Aluminum levels can exceed the EPA MCL of 200 μg/L for a period lasting from one week to three weeks after liner installation. Chromium levels never exceed the EPA MCL of 100 μg/L but can reach 75 μg/L in the first day after installation. Chromium levels drop rapidly and reach background levels no later than two weeks after installation. No other metals are released in sufficient quantities to merit discussion.

- The cement mortar lining does initially create a higher demand for disinfectant, particularly when chlorine is used. This relationship is most evident in the day immediately after exposure when TOC levels are elevated due to leaching from the mortar. The differences become less than significant after a few days and all disinfected waters behave similarly to the controls after 15 days. Water disinfected with chloramines exhibited this behavior to a lesser degree.

In general, these conclusions align very well with previously reported studies. This study examined more closely the sources of aluminum and chromium as well as examining the impacts on disinfection residual. There is excellent agreement with the work by Douglas et al with respect to pH, alkalinity and hardness effects.

4.2 Cement Mortar Lining Impacts on Organic Water Chemistry

With little previous work on organic water chemistry effects induced by exposure to newly installed cement mortar linings reported in the literature there were few benchmarks with which to compare this study's findings. The organic water chemistry-related conclusions are as follows:

- The lining material may increase the exposed water's TOC level for up to four days. These elevated TOC levels may contribute to the formation of disinfectant by-products especially if chlorine is in use. The TOC concentrations will likely drop to background levels after four days and more certainly before nine days after exposure.

- The cement mortar linings contribute to both the formation and sorption of trihalomethanes. Chloroform at levels near 35 μg/L can be formed when elevated levels of cement-induced TOC is available in chlorinated waters. This can occur with approximately 72 hours residence time. The liner surface can adsorb slightly more than 1 μg/L during the same time period. These effects are rapidly diminished with even modest water changes and dissipate completely after a few days, following closely the reduction in TOC levels.

- The formation of haloacetic acids was not markedly increased by contact with the cement mortar linings. Elevated levels of approximately 14 μg/L may be evident one day after exposure but these rapidly decline to background levels. This brief response is more likely when chlorination is the disinfection method. The levels never approach the EPA MCL of 60 μg/L but may bear consideration in waters that contain an already elevated level.

- The formation of semi-volatile organic compounds was not enhanced by the water's contact with the mortar lining material. This was true for all disinfection methods.

In summary, the organic chemistry effects resulting from drinking water's exposure to newly installed cement mortar lining material are not as profound or persistent as the inorganic effects. There were no excursions above EPA MCL values for any parameter. The THM results confirm the informal results presented by Douglas et al in that there was not a significant concentration formed, especially after the first day of exposure.

4.3 Cement Mortar Lining Impacts on Water Aesthetics (Odor)

This study may be the first to look closely at this parameter and the findings point to the cement mortar lining imparting a weak (by FPA standards), but readily detectable "wet cement" odor which persists for at least two weeks after exposure. The odor is detectable whether or not the water is disinfected or not. It is likely that this odor would persist for a substantial period in low flow, dead end portions of a distribution system.

4.4 Impacts of Corrosion Preventative Additives

Previous research observed some implications due to the presence and type of CPA used with respect to the inorganic chemistry impacts of newly installed cement mortar linings. This study found that similar conclusions could be outlined and they are provided below:

- The presence of CPA reduced the increases in pH significantly, particularly after two weeks of exposure and even more at 19 days. This affect is of greater magnitude with use of polyphosphate corrosion inhibitors vice using orthophosphate or zinc orthophosphate inhibitors. This may be due to the polyphosphate's enhanced ability to form a protective coating on the coupon. The improved coating may be due to the precipitation of hydroxyapatite which augments the other precipitates normally present in this system.

- The impacts to alkalinity and hardness were not as substantial as the impacts to pH with the differences between the controls and CPA augmented waters being insignificant in a practical sense. Magnesium levels were significantly higher with polyphosphate-augmented waters due to lower pH values but because the overall magnesium levels are quite low, the impact on the overall hardness was small.

- The release of aluminum followed much the same pattern described above in the primary leaching experiments. There was little impact due to the use of CPA until after two weeks of exposure when the CPA-augmented waters had lower aluminum levels. The aluminum levels in CPA-augmented waters did approach the EPA MCL of 200 μg/L after nine days of exposure. The aluminum levels decrease to less than 25 μg/L for the waters with the additives after 19 days.

- The phosphorous content remains very low for the first two weeks of exposure at which time the polyphosphate additive allows a significant increase. This may be due to the higher concentration of hydrogen phosphate present at lower pH levels which does not readily complex and precipitate. The phosphorous release was significantly lower with the other additives due to their inability to minimize pH increases as effectively as polyphosphate. The very low phosphorous levels observed from days 1 to 14 could not be readily attributed to a specific precipitation mechanism.

- Zinc release followed the same pattern as seen in the primary leaching experiments with little differences between the additive types. Even the zinc orthophosphate additive, which was added to produce higher initial zinc concentrations, had similar zinc release levels which may be due to pH-driven precipitation of zinc-ligand complexes.

- Chromium levels followed the same pattern as was seen in the primary leaching experiments, higher earlier in the test period and falling rapidly to very low levels. This is the result of the cement's hydration process maturing and binding the available chromium in the mortar matrix. There were no significant difference between the CPA additives nor did they perform differently than the control.

In summary, the most marked CPA-induced impact observed was the significantly lower pH values, particularly when polyphosphate is used. This conclusion aligns well with the findings of Douglas et al (post two weeks). The resulting lower pH does impact the metals concentrations, particularly magnesium, aluminum and phosphorous, after two weeks of exposure. The impacts to total hardness and alkalinity are not remarkable.

5. RECOMMENDATIONS

The recommendations provided below are divided into two areas, each having a different target audience. The first recommendation set proposes potential actions that can be taken by drinking water providers to minimize the effects observed in the study. The second individual recommendation is a suggested opportunity for further research in this study area and is presented for consideration by the academic community.

5.1 Effect Minimization

When a drinking water utility determines that a significant portion of the distribution system requires rehabilitation and they decide to use cement mortar lining as the method, the following actions may minimize the effects described in this study. These recommendations are especially applicable if the pipelines to be rehabilitated are smaller in diameter and in low flow or dead end portions of the distribution system:

- If possible, allow the cement mortar lining to cure for a longer period of time before placing the pipeline back in service. If four days can be tolerated versus one day, many of the effects described in this report will be reduced. A period of ten days would be optimal but it is unlikely that this delay would be feasible.

- Monitor the water quality frequently for the first two weeks after service is returned so that excessive pH or aluminum levels can be observed and acted upon if found. Continue to monitor on a less frequent basis for 30 days after service restoration or until any observed excursions from normal water quality have subsided.

- If the finished water is extremely aggressive (very low alkalinity/hardness), consider an alternate lining material such as epoxy or a mortar with a lower cement content. The addition of a small percentage of condensed silica fume to the cement has been shown to reduce the concentration of calcium hydroxide in the cement paste's pore space and accelerate the reduction in pore size. Both of these effects may reduce the pH, alkalinity and hardness results observed in this study. (Malhotra, 1987) The UK has been using mortar manufactured with 65% of the cement replaced with silica-rich blast furnace slag as an alternate to conventional cement (Conroy et al., 1993)

- If excessive pH values are observed near dead end portions of the distribution system after return to service, increase flow through the rehabilitated area through the use of a by-pass arrangement. Continue this practice until pH values fall to an acceptable value.

5.2 Future Research Opportunity

This study has increased the collective knowledge related to the potential water quality impacts of newly installed cement mortar linings especially in the areas of organic water chemistry and the further implications of various corrosion prevention additives (CPA). It is the latter of these two areas, the CPA effects, where additional study may prove valuable.

This study showed that the use of polyphosphate-based CPA significantly dampened the pH increases seen in water without the additive and it was proposed that this was due to the existence of an enhanced liner coating. However, the amount of data available was limited and no study of variable dosages was performed. These CPA effects warrant further study, to include the other CPA types considered in this study, so that the favorable mechanisms can be better understood and optimized if possible. While the pH dampening observed in this study may seem modest, they had significant impacts due to the pH sensitivity of the various water quality parameters in question. Further research may allow utilities to optimize their CPA strategy when contemplating large-scale cement mortar rehabilitation projects and improve chronic water quality problems caused by the extensive use of cement-lined pipes. The potential advantages of improved CPA regimes and dosages would be particularly applicable to utilities with highly aggressive finished waters.

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APPENDIX A – Methods of Chemical Measurements

METHODS OF CHEMICAL MEASUREMENTS

The following methodologies are used in chemical analysis of parameters:

pH and Temperature

Temperature and pH were measured using Standard Method 4500-H^+ using a Corning 315 pH/ion probe that was calibrated using standard pH solutions 4, 7, and 11.

Total Alkalinity

Alkalinity was measured using Standard Method 2320. H_2SO_4 (CAS #7664-93-9) with concentration 0.0190 N was titrated into 100-mL samples to pH 4.5.

Disinfectant Residual

Disinfectant residual was measured using Standard Method 2350 with a HACH® kit (HACH, free chlorine CAT #21055-69, total chlorine CAT #21056-69) measuring free and total chlorine. Free chlorine was used to measure the chlorinated sample water. Monochloramine was calculated using free and total chlorine (total – free = chloramine).

Elemental Analysis for Metals, Nonmetals, and Hardness

Selected trace metals (sodium [Na], magnesium [Mg], aluminum [Al], potassium [K], vanadium [V], chromium [Cr], iron [Fe], manganese [Mn], cobalt [Co], nickel [Ni], copper [Cu], zinc [Zn], arsenic [As], molybdenum [Mo], cadmium [Cd], tin [Sn], barium [Ba], and lead [Pb]) , and nonmetals (sulfur [S], phosphorous [P], chlorine [Cl], and silicon [Si], a semi-metal) were measured. Standard Method 3125 was used and the samples were analyzed on a ThermoElectron Corporation inductively coupled plasma mass spectrometer (ICP-MS) X-Series. Hardness, as the sum of calcium and magnesium concentrations, was measured using the elemental analysis results.

Total Organic Carbon (TOC)

TOC was measured using Standard Method 5310C using a Shimadzu TOC-V TOC analyzer. The samples were acidified to < pH 2 using nitric acid (CAS #7697-37-2). Two measurements were taken from each replicate. If the samples were not within 20%, a third sample was taken and an average was calculated to give the TOC concentration for that sample.

Trihalomethanes (THMs)

THMs were analyzed using Standard Method 6232D using a Tre Metrics 9001 gas chromatograph, Tracor 1000 Hall® detector, Tekmar 2016 purge and trap autosampler, and Tekmar 3000 purge and trap concentrator. The column used was a DB-624 with helium as the carrier gas with the initial oven temperature at 45 °C and held for 3 minutes, increasing at 11 °C/min. with a maximum oven temperature of 200 °C. Standard curve was performed for each run unless run sequentially (THM-521-1 Ultra 5000 μg/mL standard).

Haloacetic Acids (HAA5)

The HAA5 extractions were performed following EPA Method 552.3 using liquid-liquid extraction, derivitization, and GC with electron capture detection (ECD). The standard (Methylated Haloacetic Acid Standard, Chem Service, West Chester, Pa.) contained concentrations of HAA5 ranging from 20 μg/L to 60 μg/L. The GC column used was a DB-1701 (30 m length, 0.25 diam., 0.25 μm film) with helium as the carrier gas and nitrogen as the makeup gas. The initial oven temperature was 35 °C, which was held for 10 min. and increased at 5.7 °C/min. to 75 °C and held for 5 min. Temperature was again increased at 5 °C/min. to 100 °C and held for 5 min., then increased at 20 °C/min. to 140 °C and held for 5 min. After being removed and equilibrating to room temperature, the samples were identified and quantified using procedural standard calibration.

Semivolatile Organic Compounds (SVOCs)

SVOCs were measured using Standard Method 6410B, which is a liquid-liquid extraction using methylene chloride and then concentrated using a Kaderna-Danish apparatus at 75 °C water bath. The samples were analyzed using a GC/MS using a DB-5 column (30.0 m x 250 μm x 0.30 μm). The initial oven temperature was 40 °C and was held for 3 min., then increased by 8 °C/min. to 200 °C and held for 1 min. The column was then heated by 10 °C/min. to 300 °C and held for 11 min. The targeted compounds were identified using standard NIST elution times as well as mass spectra. Nontargeted compounds were tentatively identified based on library matching of mass spectra. For selected compounds, chemical standards were purchased and retention times and mass spectra compared to confirm their qualitative identity and measure quantitative amounts.

Odor Analysis

Odor analysis was performed using the Flavor Profile Analysis (FPA) using Standard Method 2170 where FPA participants underwent a 1-day training session to learn the FPA method. The study protocol was approved by the Institutional Review Board for Research Involving Human Subjects at Virginia Tech. The FPA intensity scale is 0: odor free (OF), 1: threshold, 2: very weak, 4: weak, 8: moderate, 10: strong, and 12: very strong. The weak intensity corresponds to the sweetness of canned fruit (for comparison, an FPA taste intensity of 8 is moderate and corresponds to canned soda, while an FPA intensity of 12 is strong and corresponds to syrup or jelly).

THM Sorption/Formation Experiment

An issue for leaching tests, including those described in NSF-61, is that DBPs can form in the water during leaching and then be re-sorbed into the lining material and consequently, not measured. This phenomenon was investigated for selected THMs. The formation of THMs from the reaction of TOC leached from the lining material and added chlorine used for disinfection was investigated by placing coated coupons in reference water with no disinfectant and allowing leaching to occur over a 72- to 96-hour period under headspace-free conditions at room temperature. The TOC was then measured from aliquots of the leached water that were placed in headspace-free VOA vials with the addition of free chlorine. At 0-, 24-, and 72-hour time intervals, 0.0250 N sodium thiosulfate solution was added to quench the THM formation reaction. The samples were then analyzed for disinfectant residual and THMs.

To investigate if THMs could sorb into the lining material, coated coupons were immersed headspace-free for up to 72 hours in reference water containing 15 to 100 μg/L of THMs and no free chlorine. Lining material coupons were placed in the test apparatus with the standard water without disinfectant for 72 to 96 hours under headspace-free conditions. The sorption of THMs into the lining was tested by determining the concentration of THMs in the water over time.

APPENDIX B – IRB Approval Forms

VirginiaTech

Office of Research Compliance
Institutional Review Board
1880 Pratt Drive (0497)
Blacksburg, Virginia 24061
540/231-4991 Fax: 540/231-0959
E-mail: moored@vt.edu
www.irb.vt.edu
FWA00000572(expires 7/20/07)
IRB # is IRB00000667.

DATE: January 23, 2007

MEMORANDUM

TO: Andrea M. Dietrich
Pinar Omur
Heather Johnson

FROM: David M. Moore

Approval date: 2/2/2007
Continuing Review Due Date:1/18/2008
Expiration Date: 2/1/2008

SUBJECT: **IRB Expedited Continuation 1:** "Taste and Odor Testing of Plumbing Materials" , IRB # 06-042

This memo is regarding the above referenced protocol which was previously granted expedited approval by the IRB. The proposed research is eligible for expedited review according to the specifications authorized by 45 CFR 46.110 and 21 CFR 56.110. Pursuant to your request, as Chair of the Virginia Tech Institutional Review Board, I have granted approval for extension of the study for a period of 12 months, effective as of February 2, 2007.

Approval of your research by the IRB provides the appropriate review as required by federal and state laws regarding human subject research. As an investigator of human subjects, your responsibilities include the following:

1. Report promptly proposed changes in previously approved human subject research activities to the IRB, including changes to your study forms, procedures and investigators, regardless of how minor. The proposed changes must not be initiated without IRB review and approval, except where necessary to eliminate apparent immediate hazards to the subjects.
2. Report promptly to the IRB any injuries or other unanticipated or adverse events involving risks or harms to human research subjects or others.
3. Report promptly to the IRB of the study's closing (i.e., data collecting and data analysis complete at Virginia Tech). If the study is to continue past the expiration date (listed above), investigators must submit a request for continuing review prior to the continuing review due date (listed above). It is the researcher's responsibility to obtained re-approval from the IRB before the study's expiration date.
4. If re-approval is not obtained (unless the study has been reported to the IRB as closed) prior to the expiration date, all activities involving human subjects and data analysis must cease immediately, except where necessary to eliminate apparent immediate hazards to the subjects.

cc: File
Department Reviewer: William R. Knocke

Virginia Tech
VIRGINIA POLYTECHNIC INSTITUTE
AND STATE UNIVERSITY

Institutional Review Board

Dr. David M. Moore
IRB (Human Subjects) Chair
Assistant Vice President for Research Compliance
1880 Pratt Drive, Suite 2006(0497), Blacksburg, VA 24061
Office: 540/231-4991; FAX: 540/231-0959
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DATE: February 2, 2006

MEMORANDUM

TO: Andrea M. Dietrich Civil & Environmental Engineering
Pinar Omur

FROM: David Moore

SUBJECT: **IRB Expedited Approval:** “Taste and Odor Testing of Plumbing Materials”
IRB # 06-042

This memo is regarding the above-mentioned protocol. The proposed research is eligible for expedited review according to the specifications authorized by 45 CFR 46.110 and 21 CFR 56.110. As Chair of the Virginia Tech Institutional Review Board, I have granted approval to the study for a period of 12 months, effective February 2, 2006.

Virginia Tech has an approved Federal Wide Assurance (FWA00000572, exp. 7/20/07) on file with OHRP, and its IRB Registration Number is IRB00000667.

cc: File
Department Reviewer: William R. Knocke

APPENDIX C – Analysis of Type II Cement

Analysis of Cement – Cement Mortar Lining Project

Sample: Portland Cement, Roanoke (from Virginia Tech, D. Clark)
Date Tested: 30 October 2008
Tested By: CTL Group Inc., S. Markovic
Test Specifications: ASTM C 114-07
Results:

Analyte	Wt %
SiO_2	19.81
Al_2O_3	4.79
Fe_2O_3	3.11
CaO	62.48
MgO	3.08
SO_3	3.00
Na_2O	0.18
K_2O	0.90
TiO_2	0.23
P_2O_5	0.11
Mn_2O_3	0.23
SrO	0.13
Cr_2O_3	0.04
ZnO	0.01
LOI (950°C)	1.69
Total	99.81
Alkalies as Na_2O	0.77

Calculated Compounds per ASTM C 150

C3S	59%
C2S	13%
C3A	7%
C4AF	9%

APPENDIX D – Fair Use Analysis of Damidot Figures (1993)

Fair Use Analysis Summary

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Please retain for your records.

The information below summarizes your four-factor fair use analysis. This summary is not conclusive, but is intended to help you make your own reasonable and well-informed decision.

A thorough fair use analysis is based on balancing the four factors. As you consider and examine each factor by itself, you also need to weigh the four factors against one another. At times, some factors may weigh more heavily for or against fair use than others. For example, even if the first three factors weigh in favor of fair use, the weight given to the fourth factor may tip the scale against fair use. It is the balance of the four factors that should guide you when deciding whether your use is a fair use.

Document to be copied: Figures 6, 7 and 10 from Damidot, D., et al. (1993).
Date: 02-28-2009

Summary: Favors Fair Use

Your analysis of the four factors suggests that your proposed use **favors fair use.** An analysis that weighs favorably toward fair use supports this use of the material under the circumstances you described without getting permission from the copyright owner.

Detailed Report

In determining fair use there are no simple answers. Each use is dependent on the conditions for that use. After considering and examining the four factors, the factors need to be weighed against each other. No one factor makes the use fair or unfair. And, at times, depending on particular circumstances, some factors may carry more weight than others.

You've analyzed **purpose** to be *somewhat favorable* towards fair use.

You cited the following elements for your analysis:

Favors Fair Use	Weighs Against Fair Use
• Instruction, restricted access course websites, research, and/or personal use	

You've analyzed **nature** to be *strongly favorable* towards fair use.

You cited the following elements for your analysis:

Favors Fair Use	Weighs Against Fair Use
• Published • Factual, non-fiction	

You've analyzed **amount** to be *strongly favorable* towards fair use.

You cited the following elements for your analysis:

Favors Fair Use	Weighs Against Fair Use
• Small excerpt, extract, or clip	
• Only portion needed for favored purpose	

You've analyzed **market** to be *somewhat favorable* towards fair use.

You cited the following elements for your analysis:

Favors Fair Use	Weighs Against Fair Use
• One or few copies made	
• Use stimulates market for original work, no impact on market	

Printer-Friendly Version

Please retain for your records.

APPENDIX E – Analysis of Controlling Solids within CPA Test Waters

Thermodynamically Predicted Controlling Solid – Various Metals and Ligands
CPA Testing Days 1 – 19

Note: Controlling solid concentration is indicated in bold red text, K_{sp} values from Schock et al (1981), all concentrations presented in M/L

1. Calcium solids

Day	pH	CO3 Concentration (M/L)	PO4 Concentration (M/L)	Predicted Ca Conc KSP for Ca(OH)2	Predicted Ca Conc KSP for CaCO3	Predicted Ca Conc KSP for Ca3(PO4)2	Predicted Ca Conc KSP for Ca4H(PO4)3	Predicted Ca Conc KSP for Ca5(PO4)3OH
1	12.14	1.5061E-03	1.75E-10	2.9537E-02	**2.52E-06**	6.9154E-03	4.2286E-02	1.2221E-02
2	11.66	1.7905E-03	5.87E-11	2.6325E-01	**2.12E-06**	1.4327E-02	7.3064E-02	2.9315E-02
4	11.45	1.8407E-03	3.62E-11	6.9241E-01	**2.06E-06**	1.9771E-02	9.3047E-02	4.3161E-02
11	11.28	4.7787E-04	9.37E-10	1.5501E+00	**7.95E-06**	2.2635E-03	7.3282E-03	6.6394E-03
14	11.10	8.2186E-04	1.12E-07	3.5511E+00	**4.62E-06**	9.3421E-05	1.8241E-04	4.0830E-04
15	10.65	4.3576E-04	4.69E-07	2.8207E+01	**8.72E-06**	3.6032E-05	4.8153E-05	2.1293E-04
19	10.63	8.5237E-04	2.28E-07	3.0225E+01	**4.46E-06**	5.8224E-05	8.1952E-05	3.3035E-04

2. Magnesium Solids

Day	pH	CO3 Concentration (M/L)	PO4 Concentration (M/L)	Predicted Mg Conc KSP for Mg(OH)2	Predicted Mg Conc KSP for MgCO3	Predicted Mg Conc KSP for Mg3(PO4)2
1	12.14	1.5061E-03	1.75E-10	**9.6666E-08**	2.32E-05	1.4887E-02
2	11.66	1.7905E-03	5.87E-11	**8.6153E-07**	1.95E-05	3.0844E-02
4	11.45	1.8407E-03	3.62E-11	**2.2661E-06**	1.90E-05	4.2562E-02
11	11.28	4.7787E-04	9.37E-10	**5.0731E-06**	7.32E-05	4.8729E-03
14	11.10	8.2186E-04	1.12E-07	**1.1622E-05**	4.26E-05	2.0111E-04
15	10.65	4.3576E-04	4.69E-07	**9.2315E-05**	**8.03E-05**	**7.7570E-05**
19	10.63	8.5237E-04	2.28E-07	9.8917E-05	**4.11E-05**	1.2534E-04

3. Zinc and Aluminum Solids

Day	pH	CO3 Concentration (M/L)	PO4 Concentration (M/L)	Predicted Zn Conc KSP for ZnCO3	Predicted Zn Conc KSP for Zn3(PO4)2	Predicted Al Conc KSP for AlPO4	Predicted Al Conc KSP for Al(OH)3
1	12.14	1.5061E-03	1.75E-10	**9.2957E-09**	5.5280E-06	3.60E-09	**1.84077E-27**
2	11.66	1.7905E-03	5.87E-11	**7.8191E-09**	1.1453E-05	1.08E-08	**4.89779E-26**
4	11.45	1.8407E-03	3.62E-11	**7.6060E-09**	1.5805E-05	1.74E-08	**2.0893E-25**
11	11.28	4.7787E-04	9.37E-10	**2.9297E-08**	1.8094E-06	6.73E-10	**6.99842E-25**
14	11.10	8.2186E-04	1.12E-07	**1.7035E-08**	7.4679E-08	5.62E-12	**2.42661E-24**
15	10.65	4.3576E-04	4.69E-07	**3.2128E-08**	**2.8804E-08**	1.34E-12	**5.4325E-23**
19	10.63	8.5237E-04	2.28E-07	**1.6425E-08**	**4.6543E-08**	2.76E-12	**6.0256E-23**