

# **Effects of water chemistry, temperature, gaseous cavitation & phosphate inhibitors on concrete corrosion**

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## **ABSTRACT**

Concrete corrosion has serious societal and economic impacts and is an important concern in a utility's overall corrosion control strategy. Though concrete based pipes and linings are only restricted to the distribution mains, they still make up a large percentage of the drinking water infrastructure at about 17% of its total length. An improved understanding of the corrosion mechanisms involved steps that can be taken to mitigate concrete corrosion are very important. This study examined the role of phosphate chemicals, water chemistry, temperature and gaseous cavitation on the degradation of cement-based pipes and linings. It also provides information for utilities to make informed decisions regarding the use, effectiveness, and application of phosphate corrosion inhibitors relative to concrete corrosion control.

Under low alkalinity and low pH conditions, considered to be highly aggressive in the literature, we noticed very substantial corrosion of concrete in laboratory experiments. At high pH and high alkalinity conditions, the buildup of scale (e.g., calcium carbonate) on the inside of the pipe is the major concern. The addition of phosphate inhibitors strongly influenced both concrete corrosion and scaling. At low alkalinity the addition of zinc orthophosphate or polyphosphate reduced corrosion of concrete. The addition of orthophosphate under low alkalinity conditions increased aluminum leaching and could push aluminum concentrations above the EPA SMCL threshold. At high alkalinity conditions the addition of orthophosphate is highly effective at reducing scaling, and aluminum leaching was not a concern.

The presence of high concentrations of magnesium and silicon could form magnesium aluminum oxyhydroxides and magnesium silicates which could act as a protective scale on the concrete surface. However, this precipitate forms only at pH values above 9.5. The effectiveness of this protective scale in reducing corrosion of concrete was not established unambiguously in this research. Temperature plays a key role in corrosion of concrete. Calcite solubility increases at lower temperatures however at higher temperatures corrosion

of concrete increases, which implies that corrosion of concrete is not driven by calcite solubility. At higher alkalinities scaling of concrete is higher at lower temperatures. This indicates that calcite solubility controls scaling of concrete at higher alkalinities. Tests with gaseous cavitation indicate that corrosion of concrete does not increase in the presence of gaseous cavitation. Vaporous cavitation is more detrimental to concrete than gaseous cavitation.

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## **AUTHOR'S PREFACE**

This work is presented in Virginia Tech Manuscript format. Each chapter is a separate manuscript formatted for journal submission.

Chapter I compiles an extensive literature review and introduction to the concepts of concrete corrosion and effects of phosphate inhibitors on concrete corrosion. Chapter II looks into the effects of temperature, gaseous cavitation, water chemistry and temperature on concrete corrosion while Chapter III looks exclusively into the effects of phosphate corrosion inhibitors on concrete corrosion. The results in this chapter were based on a series of laboratory studies conducted by the authors at Virginia Tech.

## CHAPTER 1

### INTRODUCTION AND BASIC TESTING METHODOLOGY

Anusha Kashyap, Jeffrey L Parks and Marc Edwards

Corrosion, the degradation of materials through physicochemical interaction with the environment, has profound economic, social, and public health consequences. In the United States it is estimated that the annual cost of corrosion ranges from \$200 to \$271 billion, or about 3.1% of the nation's gross domestic product. According to the AWWA Water Industry Database (WIDB) survey in 1995, the United States has an estimated 1.4 million kilometers of water mains of which 17% are concrete or asbestos concrete mains (FHWA-RD, 2002). Unfortunately, relatively little research expenditure has gone towards the investigation of the processes responsible for the corrosion of concrete drinking water infrastructure. Though concrete based pipes and linings are only restricted to the distribution mains and the service lines are still made of either copper or PVC, concrete pipes still make up a large percentage of the drinking water infrastructure. Thus, an improved understanding of the mechanisms involved and the ultimate mitigation of concrete corrosion is important in light of its social and economic costs (McNeill et al, 2003; Jackson et al, 1992; Dingus et al, 2002).

The corrosion of lead and copper from household plumbing is also a significant problem. In 1991, the EPA issued a regulation to control lead and copper in drinking water (usually referred to as the Lead and Copper Rule or the LCR). Since lead or copper contamination generally occurs from corrosion of household plumbing, it cannot be directly detected by the water utility through testing of the main water distribution system. Instead, EPA requires water utilities to control the corrosiveness of their water if the level of lead or copper at more than 10% of high risk home taps exceeds an Action Level in first draw samples (15 ppb for lead and 1.3 ppm for copper). Many utilities have mitigated lead and copper corrosion by adjustment of pH and/or alkalinity, but others have addressed lead and copper corrosion by dosing orthophosphate (either sodium or zinc) at the treatment plant. The total consumption of all corrosion inhibitors in the United States has doubled from approximately \$600 million in 1982 to nearly \$1.1 billion

in 1998 (FHWA-RD, 2002). It is likely that further increase in the use of corrosion inhibitors in the water industry has occurred over the intervening years since 1998.

Degradation of concrete infrastructure can affect lead and copper corrosion control programs. If treated water pH and alkalinity are too low, leaching of lime to water would be beneficial for reducing lead and copper corrosion (by raising bulk water pH). However, if pH and alkalinity are at levels near their upper range of effectiveness, lime dissolution could be detrimental for some LCR corrosion control programs. In some cases, dissolution of lime from cement can raise the bulk water pH to 10 or even higher and cause problems with lead leaching (Douglas et al, 1996; Conroy et al, 1991). These pH values are far above those deemed effective for orthophosphate inhibition of lead and copper corrosion and amphoteric lead species can become increasingly soluble at high pH.

## **1.1 BACKGROUND**

### ***1.1.1 Characteristics of Concrete***

Concrete is a mixture of two components: aggregate and binder. The aggregate provides the basic structure of the material and is typically either sand or gravel. The binder, or mortar, consists of hydrated cement and is responsible for binding the aggregate together and thus provides the cohesive properties of the material. Dry powdered cement is produced by calcinating calcareous (calcium containing) and argillaceous (clay-containing) rocks with either silica or alumina (AWWARF and DVGW-TZW, 1996). The cement produced by this process contains a number of silicates and oxides of calcium, aluminum, and iron.

The Portland cement commonly employed in water treatment and distribution primarily consists of tricalcium silicate ( $\text{Ca}_3\text{SiO}_5$ ; abbreviated as  $\text{C}_3\text{S}$ ), dicalcium silicate ( $\text{Ca}_2\text{SiO}_4$ ;  $\text{C}_2\text{S}$ ), calcium aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ;  $\text{C}_3\text{A}$ ), iron calcium aluminate ( $\text{Ca}_4\text{Fe}_2\text{Al}_2\text{O}_{10}$ ;  $\text{C}_4\text{AF}$ ), and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). When Portland cement is wetted, these phases undergo a series of hydrolysis, hydration, and ultimately precipitation reactions that produce a hardened material. This process, which can take many years, results in the formation of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ; CH) and poorly crystalline calcium silicate hydrate (C-S-H) gel. Tricalcium silicates on hydration would produce

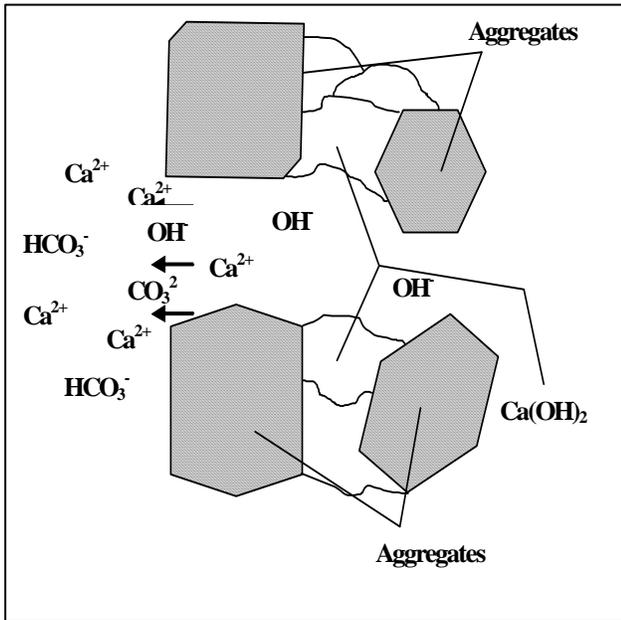
61%  $C_3S_2H_3$  (C-S-H gel) and 39%  $Ca(OH)_2$  while dicalcium silicates produce 82%  $C_3S_2H_3$  (C-S-H gel) and 18%  $Ca(OH)_2$  (Mehta and Monteiro, 2006). These phases are the ‘glue’ that binds the aggregate together and it is their stability that dictates the corrosion resistance of concrete (Deng et al, 2002).

During the hardening period, the interstitial water within a hydrated cement matrix is in equilibrium with the precipitating phases and as such contains high concentrations of calcium, magnesium, sodium, and hydroxide. The hardening period for concrete is a continuous process and happens over many years.

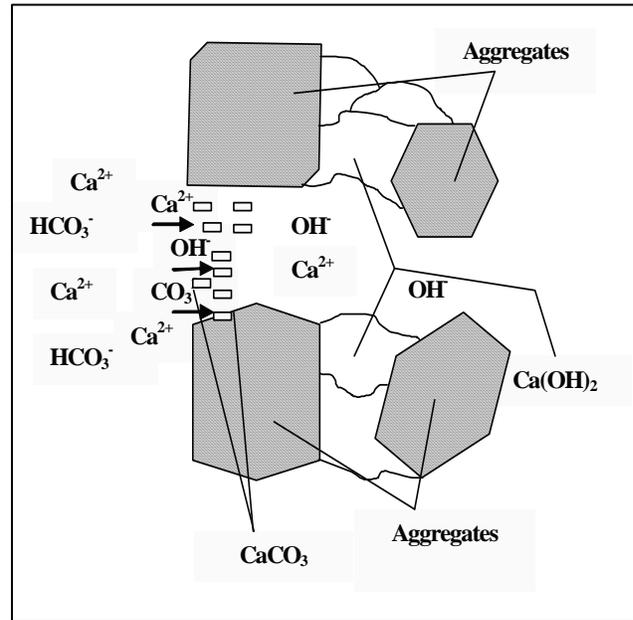
### ***1.1.2 Corrosion of Concrete***

The corrosion of concrete in water infrastructure is a function of the water chemistry and chemical equilibria with the various hydration phases. Corrosion due to improper hardening of concrete can be avoided by proportioning and mixing concrete according to ASTM C-109 “Standard Test Method for Compressive Strength of Hydraulic Cement Mortars”. The other concern is that of water chemistry. The degree of calcium carbonation saturation and the carbonation speciation of water control the degradation of cement materials. This is generally called the carbonic aggressivity (AWWARF and DVGW-TZW, 1996).

In waters having low pH and low alkalinity (i.e. highly aggressive waters), the conditions are not suitable for calcite precipitation and thus concrete is susceptible to corrosion/lime leaching (Figure 1.1). However, in waters with high carbonate concentrations and at a higher pH, calcium carbonate ( $CaCO_3$ ) precipitates readily, both at the concrete-water interface and within the micropores that extend from the concrete interior to the interface (Figure 1.2). In general, this precipitated  $CaCO_3$  (typically presumed to be the mineral calcite, although the  $CaCO_3$  polymorphs aragonite or vaterite are also possible) has been assumed to protect the underlying concrete from degradation (Douglas et al., 1996). Excessive precipitation of calcite can lead to scaling problems which might occur in passive water conditions (i.e. high alkalinity and high pH).



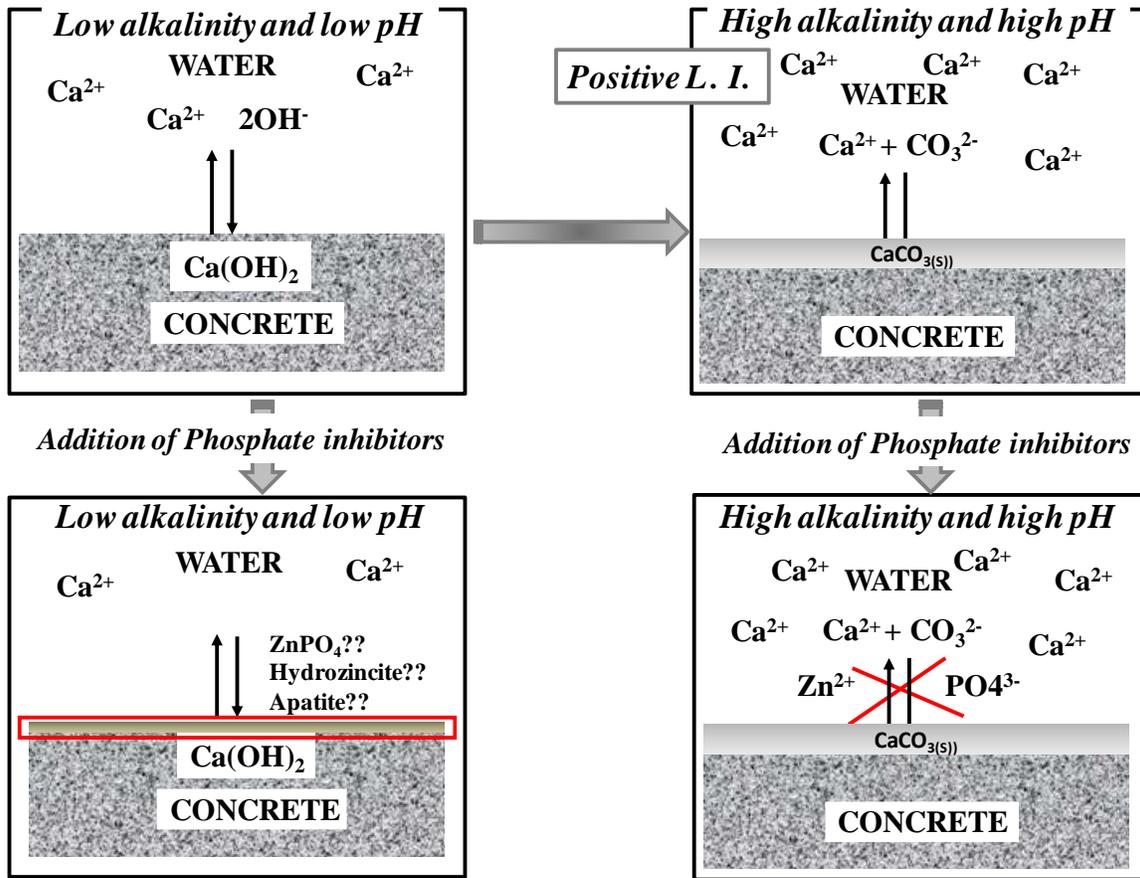
**Figure 1.1. Depiction of corrosion of concrete surface/micropores in low alkalinity and low pH waters (After AWWARF and DVGW-TZW, 1996).**



**Figure 1.2. Depiction of corrosion of concrete surface/micropores in high alkalinity and high pH waters (After AWWARF and DVGW-TZW, 1996).**

### 1.1.3 Corrosion inhibitors

The corrosion of lead and copper from household plumbing has also been mitigated by many utilities by dosing phosphate inhibitors. Addition of phosphate inhibitors could have a positive effect on the corrosion of concrete based on water chemistry. In aggressive water conditions, the addition of phosphate inhibitors can reduce corrosion of concrete by forming a protective layer on the concrete surface (Figure 1.3). However in passive water conditions, phosphate can also be beneficial by inhibiting calcite precipitation (scaling) on the surface (Lin and Singer, 2006) (Figure 1.3).



**Figure 1.3. Effects of phosphate corrosion inhibitors on concrete corrosion.**

**1.1.3.1 Phosphate corrosion inhibitors**

While some utilities adjust pH and/or alkalinity for corrosion control to mitigate lead and copper corrosion others add phosphate corrosion inhibitors. Sodium orthophosphate, zinc orthophosphate (ZOP) and polyphosphate are commonly used corrosion inhibitors. Blends of poly/orthophosphate are also used for corrosion control. A survey conducted in 2001 showed that 57% of the participating 264 utilities began dosing inhibitors to meet the LCR, and 84% of utilities currently use inhibitors to partly control lead and copper corrosion. In addition 10% of the utilities add phosphate corrosion inhibitors to prevent concrete corrosion and an additional 10% add phosphate inhibitors to prevent calcite precipitation (McNeill and Edwards, 2002). Phosphate salts, especially polyphosphates, are known to inhibit calcite precipitation.

#### 1.1.3.1.1 *Orthophosphate*

A shift of inhibitors from poly/orthophosphate blends to orthophosphate was observed from 1994 to 2001 (McNeill and Edwards, 2002). Orthophosphates are generally used in the form of orthophosphoric acid ( $H_3PO_4$ ), or neutralized orthophosphoric acid -- monosodium phosphate ( $NaH_2PO_4$ ), disodium phosphate ( $Na_2HPO_4$ ), and trisodium phosphate ( $Na_3PO_4$ ) -- to mitigate lead and copper corrosion. Orthophosphate chemicals form passivating films on anodic sites to suppress electrochemical reactions. Orthophosphate is effective at controlling lead solubility at slightly alkaline pH (7.1 – 7.8) by the formation of a lead phosphate scale layer (AWWARF and DVGW-TZW, 1996). Orthophosphate has similar benefits in control of copper corrosion. However, earlier research proved that the role of orthophosphate in protecting concrete from corrosion is minor/irrelevant (Schock and Buelow, 1981).

#### 1.1.3.1.2 *Polyphosphate*

Under certain conditions of water quality polyphosphates have been shown to increase soluble lead and copper concentration through complexation (McNeill and Edwards 2002). This was the main reason for the shift of inhibitors from poly/orthophosphate blend to orthophosphate. Nevertheless 20% of the 264 U.S. water utilities surveyed by McNeill and Edwards in 2001 used polyphosphate for corrosion inhibition.

#### 1.1.3.1.3 *Zinc*

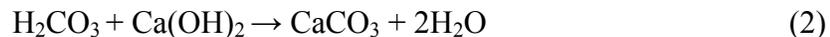
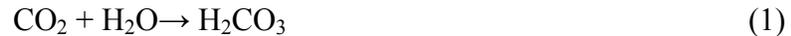
Many utilities use zinc along with orthophosphate, polyphosphate and poly-orthophosphate blends to mitigate lead and copper corrosion. Zinc has been thought to incorporate into some scales to provide cathodic protection whereas orthophosphate provides anodic protection (AWWARF and DVGW-TZW, 1996), which could be important for some metal plumbing. However, while one report suggests that zinc is incorporated into protective films (AWWARF and DVGW-TZW, 1996), others have either claimed that zinc does not play a role (Hatch, 1973 reported in AWWARF, 1990) or that zinc adversely affects lead release (Karalekas et al., 1983 reported in AWWARF, 2001). As a result, most of the zinc added to prevent metallic corrosion is thought to pass

through the distribution system and ultimately end up in wastewater. Zinc eventually becomes concentrated in the wastewater and can become an environmental concern.

However in the work conducted by Schock and Buelow, it was established that zinc is an active agent in mitigating concrete corrosion of asbestos-cement (A-C) pipes by forming a zinc hydroxy-carbonate precipitate over the pipe surface (Schock and Buelow, 1981). Earlier work conducted by Mah and Boatman (1978) noted that a zinc level of 0.3 mg/L and a lime plus orthophosphate level of 5 mg/L reduced leaching of calcium and silicon from A-C pipes. They also noticed some zinc and iron deposition. But there is nothing definitive in the literature proving cause and effect relative to zinc protection, or a mechanism of zinc protection. Also, it is believed that polyphosphate may attack cement and prevent the formation of zinc-based protective coatings (AWWARF and DVGW-TZW, 1996).

#### **1.1.4 Carbonation of Concrete**

Alkaline hydroxides (calcium hydroxide) in the concrete interact with carbon dioxide from the atmosphere forming calcium carbonate. This neutralization of the alkalis in the concrete pore water by carbonic acid is called carbonation and can be described by the following equations:



Carbonated concrete is dramatically weakened compared to regular concrete. Carbonation can be tested easily using a phenolphthalein indicator test; however, there is no standard method for testing carbonation. In this method phenolphthalein is sprayed onto the surface of concrete. If the surface turns pink then there is no carbonation of the surface as the pH is still above 9. But if the surface does not turn pink, then this shows the pH is less than 9 indicating carbonated concrete (Neville, 2003). Phenolphthalein can be sprayed along a cut depth of the concrete surface to determine the extent/depth of carbonation.

## 1.2 OBJECTIVE

In this study an in-depth examination of the interaction of water chemistry, temperature, gaseous cavitation and phosphate corrosion inhibitors on concrete corrosion was conducted. The objectives were to:

- Determine the impact of phosphate chemicals, water chemistry, temperature and gaseous cavitation on the formation of protective scales, lime leaching, and water quality for cement-based pipes and linings.
- Evaluate implications for LCR optimization and corrosion control.
- Provide information for utilities to make informed decisions regarding the use, effectiveness, and application of phosphate corrosion inhibitors on cement-based pipes and linings.

## 1.3 MATERIALS AND METHODS

Eight mortar blocks 12" (305 mm) x 3 ½" (89 mm) x 2 ¾" (70 mm) in dimension were proportioned and mixed as per ASTM C-109 "Standard Test Method for Compressive Strength of Hydraulic Cement Mortars". The mixed mortar was made using fine aggregate as per ASTM C-109 specifications and Type II Portland cement (Table 1.1).

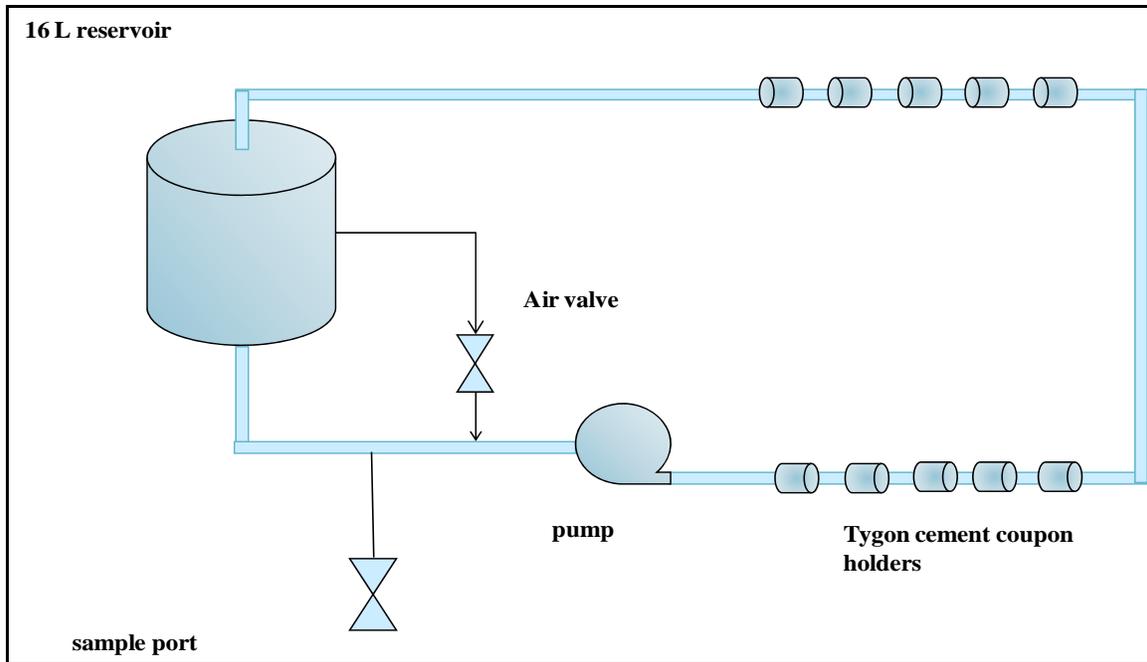
The water quantity was adjusted to compensate for the aggregate absorption. Assuming an entrapped air content of 2.5%, the ultimate yield of this mix was 133.0 pcf (pounds per cubic foot), which is well within the commonly accepted range. The cast specimens were placed in a moisture-controlled room to cure for a period of 28 days. The specimens were left in the casting moulds for the first 2 days of this curing period after which they were removed from the casting mold and cured for the remaining 26 days.

**Table 1.1. Composition of mortar mix.**

Specified parameters As per ASTM C-109-Section 10	Water/cement ratio - 0.4 w/c Cement type - Type II Portland cement Fine Aggregate -100% Passing No.12 Sieve - ≤ 10% Passing No.100 Sieve
Mix parameters	Water/cement ratio - 0.4 w/c Cement type - Type II Portland cement Fine Aggregate - 100% Passing No.12 Sieve - 2.4% Passing No.100 Sieve Aggregate/cement ratio – 1/1
Fine aggregate parameters	SG – 2.61 Absorption – 0.8% Moisture content – 0.2%
Mix quantities (2 ft <sup>3</sup> )	Water – 46.3 lbs. Cement – 114.0 lbs. Sand – 112.4 lbs.

After curing, the specimens were cut into 1" (25 mm) × 3" (75 mm) × ¼" (6 mm) coupons using a bandsaw with a diamond-tipped blade. The specimens were cut dry and phenolphthalein indicator tests showed that the specimens were not pre-carbonated due to dry cutting them. No coarse aggregate was used because our past experience indicated it does not interact meaningfully with the water, it leads to high variability in results from sample to sample, and it increases the experimental time before stable rates of corrosion can be achieved. All tests were conducted with unlined concrete.

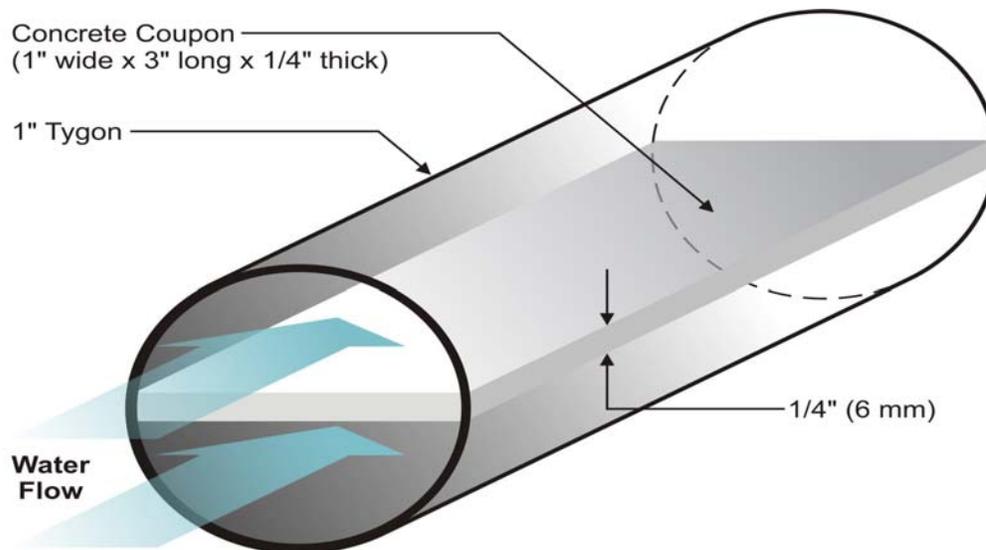
Test rigs were designed to simulate essential features of water hydraulics through a typical distribution system main at small scale, while achieving (1) good corrosion signal-to-noise ratio; (2) representative concrete surface area-to-water volume ratio and water contact times; (3) reasonably aggressive hydraulic conditions; and (4) a range of aggressive water chemistries (Figure 1.4). Ten of the concrete specimens were placed in series as shown in the test rig schematic.



**Figure 1.4. Test rig schematic.**

### 1.3.1 Signal to Noise Ratio

Without high concrete corrosion rates and weight loss (the signal) relative to experimental variability (noise) between rigs and coupons, statistically significant impacts of inhibitors on concrete corrosion will not be discerned. Past experience has shown that 1/4" thick concrete coupons in 1" Tygon coupon holders allows attack to occur on the concrete from two sides simply and realistically (Figure 1.5).



**Figure 1.5. Concrete coupon orientation in test rig.**

### **1.3.2 Surface Area to Volume Ratio and Residence Time**

A 36" OD concrete main with a 28" ID has a surface area to volume ratio (SA/Vol) equal to  $1.7 \text{ ft}^{-1}$  ( $5.6 \text{ m}^{-1}$ ) and a typical distribution system residence time is 2 – 7 days. The test rigs used in this study were designed to have a SA/Vol ratio of  $0.83 \text{ ft}^{-1}$  ( $2.6 \text{ m}^{-1}$ ). Water was completely replaced weekly for a test rig residence time of 7 days. For some reactions, the key effect of concrete on the water is a function of the detention time multiplied by the concrete SA/Vol. For a typical 36" OD main and a residence time of 3.5 days, this product is  $6 \text{ day-ft}^{-1}$ , which compares favorably to our experimental apparatus value of  $5.8 \text{ day-ft}^{-1}$ .

### **1.3.3 Hydraulic Conditions**

Corrosion of concrete results from degradation of material due to the mechanical action of a fluid flowing past its surface as well as chemical attack. Flow in the experimental rigs was maintained at approximately 2 m/s to simulate relatively aggressive conditions across the surfaces of the concrete coupons, which again is essential to producing experimentally significant differences in weight loss. Additionally, the effects of gaseous cavitation were also evaluated in this work, as this has been suspected to be a primary mode of corrosion attack leading to failure in water distribution systems.

To accomplish this, midway through each experimental test (i.e. after 6 weeks) five coupons were removed from each rig and replaced with five new coupons. The five coupons removed from the test rigs were used to evaluate corrosion occurring in the absence of gaseous cavitation. Gaseous cavitation in the experimental rigs was then induced by introducing air into the test loop at the suction end of the pump. Care was taken to ensure that all test rigs had the same amount of air. The flow of air in each test rig was measured and adjusted with a rotameter. At the end of the test the five new coupons were examined to quantify relative corrosion in the presence of gaseous cavitation, while the five coupons that were in place throughout the 12 week test were used to quantify corrosion in a mixture of gaseous cavitation (2<sup>nd</sup> half of study) and normal flow (1<sup>st</sup> half of the study). In this manner, the effect of each corrosion inhibitor

on the different types of attack that are possible including single phase flow, two-phase flow and a combination of the two regimes could be evaluated.

### 1.3.4 Water Chemistry

The relative benefits and detriments of lead and copper corrosion inhibitors on concrete corrosion are dependent on the type of water. Test water chemistries were therefore selected to be representative of extreme conditions that could be encountered in practice. Specifically, baseline water quality parameters for the first two experimental phases (Table 1.2) were selected based on the 5%ile or 95%ile calcium and alkalinity concentrations of treated drinking waters (Snoeyink and Jenkins, 1980; AWWA, 1993; Dodrill and Edwards, 1995). Historically, low pH water with low levels of alkalinity and hardness has been considered highly aggressive to concrete pipeline materials. Not surprisingly, high pH water with high levels of alkalinity and hardness has been thought to be non-aggressive/passive. Each of these water types were evaluated in this study in conjunction with several corrosion inhibitors to determine relative effectiveness of inhibitors in minimizing corrosion in each situation.

**Table 1.2. Baseline water chemistry.**

Constituent	Concentration	Baseline Low alkalinity Test Water	Baseline High Alkalinity Test Water
Calcium	mg/L as Ca	5	120
Alkalinity	mg/L as CaCO <sub>3</sub>	20	200
Magnesium	mg/L	1	1
Sodium	mg/L	7.9	95
Potassium	mg/L	0.6	0.6
Silicon	mg/L	2	2
Chloride	mg/L	8.8	212.3
Sulfate	mg/L as SO <sub>4</sub>	4.5	4.5
Nitrate	mg/L as NO <sub>3</sub>	0.2	0.2
NOM	mg/L as C	0.3	0.3

A total of fourteen experimental rigs were constructed, thereby allowing 52 experimental conditions to be evaluated during the four phases of this study (of the 14 experimental rigs used for testing, 4 were supplemental test rigs that were not constructed until the end of Phase I). Each phase lasted 12 weeks. Phase I utilized the baseline test water at pH 7 with 4 mg/L chloramine disinfectant. Phase II repeated conditions in Phase I except the test water pH was 8.3 (Table 1.3). Phase III was a repetition of Phase II except with the addition of the 95<sup>th</sup>ile magnesium and silicon instead of the 5<sup>th</sup>ile concentration used in Phase I/II. Four types of corrosion inhibitor (plus a control) were evaluated (Table 1.3) giving 10 conditions total (5 levels of inhibitor × 2 levels of aggressiveness).

In a recent survey of 264 water treatment plants in the U.S., 51% were dosing corrosion inhibitors (McNeill and Edwards, 2002). Of those using inhibitors, 72% were dosing orthophosphate, 44% were dosing polyphosphate, and 34% were dosing zinc [note that some were dosing blends so percentages do not add to 100]. Phase IV was a detailed study on the effects of zinc (with and without phosphate) focusing mainly on medium (0.5 mg/L Zn) and high (1 mg/L Zn) levels of zinc in conjunction with either orthophosphate or polyphosphate.

**Table 1.3. Comparison of phases.**

Phase I	10 test conditions(2 alkalinities X 5 inhibitor conditions) at pH 7 Testing period:Total 12 weeks (6 weeks with and w/o gaseous cavitation each)
Phase II	Same 10 test condition as in Phase I at pH 8.3 Testing period:Total 12 weeks (6 weeks with and w/o gaseous cavitation)
Phase III	Same 10 test condition as in Phase II with an addition of 40 mg/L Mg and 20 mg/L Si Testing period: 12 weeks without gaseous cavitation
Phase IV	10 test conditions(2 alkalinities X 5 inhibitor conditions of varying Zinc levels) at pH 7 Testing period: Total 6 weeks(without gaseous cavitation)

**Table 1.4. Inhibitor conditions.**

Condition	Concentration Goal
Control	no inhibitor
Sodium Orthophosphate	2 mg/L (as PO <sub>4</sub> )
Zinc Chloride/Sodium Orthophosphate	0.25 mg/L Zn + 2 mg/L PO <sub>4</sub>
Zinc Chloride	0.25 mg/L Zn
Sodium Hexametaphate	2 mg/L (as PO <sub>4</sub> )

#### 1.4 DATA COLLECTION METHODOLOGY

There is no “perfect” measure of concrete corrosion, as all key parameters can have differing interpretations (Table 1.5). Thus, the extent of concrete corrosion must be tracked by a variety of methods that include losses in weight, thickness, or hardness, as well as leaching of various elements to water including calcium, silicon, or aluminum. Each of these surrogate measures can provide insights to corrosion and their relative accuracy/importance depends on the condition being studied (Table 1.6). The measurements are divided into two types: changes in water chemistry and physical changes to concrete coupons.

Changes in water chemistry can be quantified in many ways. In this study, water quality parameters in each pipe rig were measured prior to contact with cement coupons. These parameters included pH, alkalinity, total inorganic carbon, total organic carbon (TOC), and metals concentrations (including calcium, magnesium, silicon, aluminum, zinc, and phosphorus). Likewise, these same parameters were measured after either one or two week contact time with concrete coupons. By taking the difference in concentration between the initial and final data, the amount of each constituent that has leached into solution from the concrete coupons (or precipitated onto surfaces in the rig) can be calculated.

Physical changes to concrete coupons can also be tracked in several ways. In this study, however, we looked at weight change, thickness change, and hardness change as the primary indicators of corrosion. Weight, thickness, and hardness of concrete coupons were measured before and after contact with waters of varying corrosivity.

#### **1.4.1 Water chemistry analysis.**

The synthetic water re-circulated through the test rigs was analyzed weekly to determine the extent of uptake/removal of elements from the test water. If the concentration of an element decreases with time in the test water, it is an indication of precipitation/deposition on the concrete surface or pipe/reservoir walls. Conversely, if the concentration of an element increases in the test water it is an indication of leaching from the concrete coupons used for testing. The test water was analyzed for anion concentrations by ion chromatograph (IC) and for various element concentrations by inductively coupled plasma with mass spectrometry (ICP-MS). The rest of the measurements/analyses followed techniques outlined in Standard Methods (APHA, AWWA, and WEF, 1998). The anions measured included chloride, sulfate, nitrite and nitrate. Elements which were measured by ICP-MS include calcium, magnesium, silicon, aluminum, zinc and phosphorous. The difference in the concentration of elements in the initial water and the tested water gives the amount leached into water from the coupons or precipitated from water onto the surface of the coupons (or test rig apparatus). Alkalinity was also measured using standardized sulfuric acid (0.0193N) per Standard Methods.

#### **1.4.2 Physical analysis/measurements.**

Physical measurements of the concrete coupons provide some direct measurements of concrete corrosion. All coupons were measured for weight, thickness and hardness prior to testing. The same coupons were then air dried after testing until substantial weight change stopped occurring. That is, coupons were weighed after every four days until the weight change from the preceding measurement was less than 0.2%. The coupons were not oven dried at higher temperatures due to the possibility of decomposing the hydrates. After the air dried coupons were weighed, they were measured for thickness with a micrometer and hardness with a durometer. Hardness and thickness changes proved to be highly variable and these measurements were discontinued for later phases.

**Table 1.5. Summary of strengths and limitations of measurements.**

Measurements	Purpose	Strengths	Limitations
Weight Change	Weight loss indicates Corrosion	Direct measurement of loss of cementitious material due to corrosion	1. Does not take into consideration gain in weight due to carbonation 2. There could be discrepancies in the data due to incomplete drying of coupons 3. Weight gain could be indicative of only clogging of concrete pores by precipitate. There will be no surface protection of concrete.
	Weight gain indicates Scaling	Direct physical measure of gain in weight due to precipitate forming on the cement surface	
Thickness Change	Thickness loss indicates Corrosion	Direct measurement of loss of cementitious material due to corrosion	1. Magnitude of thickness change is too small to make any statistical comparisons 2. Does not take into consideration carbonation depth
	Thickness gain indicates Scaling	Direct measurement of precipitate on concrete surface exempts precipitate within concrete pores	
Hardness Change	The durometer hardness values were related to loss of calcium from pipe as determined by X-ray elemental profile scans of A/C pipe cross section (Millette, J.R et al., 1984)	This measure could have been used to reinforce the calcium change data if the hardness measurements could be replicated	The inability to replicate these hardness values questions the precision of these values
Calcium concentration	Initial concentration of Calcium- Concentration of calcium in bulk water after testing period= Negative (indicates leaching from coupon)	1. This data can be used along with alkalinity or other elements to predict the nature of precipitate formed 2. Does not depend on reproducible drying of coupons 3. The error is much lower (in the order of 2%) than other physical measures	Calcite (or other calcium-containing compounds) might precipitate on other surfaces in the test rigs and measurement of calcium concentration does not take this into consideration
	Initial concentration of Calcium- Concentration of calcium in bulk water after testing period= Positive (indicates precipitation)		
Fate of inhibitor	Initial concentration of Zinc/Phosphate added to water - Concentration of Zn/P in water after test = Positive (indicates precipitation of inhibitors)	This is the only measure that can predict the fate of inhibitors like Zinc and Phosphate	Zinc and Phosphate might not precipitate on the concrete surface forming a protective layer, but instead precipitate on other surfaces in the test rigs
Aluminum concentration	Concentration of Aluminum in water after test period indicates leaching from cement matrix	Direct measure of cement corrosion	The amount of aluminum in hardened cement is less than 2% of the total mass so only small amounts are leached into bulk water
Magnesium and Silica Concentration	Initial concentration in water- Concentration after test period= Positive indicates precipitation while negative indicates leaching	These measures can be used in conjunction with Calcium and Aluminum data to indicate corrosion	As in the case of aluminum, only a small amount of magnesium is present in hardened cement. Corrosion of cement could be occurring via lime dissolution without breaking down calcium silicate hydrate matrix.

**Table 1.6. Summary of analysis and procedures.**

Parameter/Procedure	Standard Method	Instrument	Precision	QC Method	Frequency
Temperature		NBS approved thermometer	± 1 °C	n/a	n/a
pH	4500 - H <sup>+</sup> B	Corning Model 313 w/ Accumet Ag/AgCl electrode	± 0.1 pH units	Calibrate with standards	Daily
Chloramine concentration	4500-G	Hach Spectrophotometer	0.1 mg/L	Zero with DI water	Daily
Weight loss		Denver APX-60 analytical balance	± 0.0001 g	Repeat measurements at regular intervals	At the start and end of each run (6 weeks)
Thickness		Micrometer	± 0.01 mm	Verify with test block	At the start and end of each run (6 weeks)
Hardness		Durometer	± 1 point	Verify with test block	At the start and end of each run (6 weeks)
Alkalinity	2320 - B	Titration using standardized Sulfuric acid	± 0.1 3 mg/L as CaCO <sub>3</sub> , or 5%, whichever is greater	Ran duplicate samples	At the start and end of each weekly water change
TOC/TIC	5310 - C	Sievers 800 Portable TOC Analyzer	± 1 mg/L C	Blank	At the start and end of each weekly water change
				Verify standard concentrations	
Anions (chloride, sulfate, nitrate, nitrite)	4110	Dionex DX 120 ion chromatograph	Varies, but typically ± 10%	Calibrate with standards	Twice per weekly water change
				Blank	10%
				Verify check standard concentration	10%
Cations/metals (calcium, magnesium, silicon, phosphorus, zinc, aluminum)	3500 - B	Thermo Electron X-Series ICP-MS	Varies, but typically ± 2%	Calibrate with standards	Twice per weekly water change
				Blank	10%
				Verify check standard concentration	10%
Water flow rate	Mfg instructions	Blue-White Industries Model F-1000-RB electronic flow meter	± 2% full scale (± 1.4 lpm)	n/a	n/a
Air flow rate (for bubble/cavitation testing)	Mfg instructions	Dwyer Model MMA-5 rotameter	± 4% full scale (± 0.4 scfh)	n/a	n/a

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## CHAPTER 2

# EFFECT OF WATER CHEMISTRY, TEMPERATURE AND CAVITATION ON CONCRETE CORROSION

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### 2.1 INTRODUCTION

Concrete and cement-lined pipes are used extensively in potable water distribution systems where they are especially cost effective and durable in large diameter piping. Moderate diameter pipes are often ductile iron lined with cement as a protective coating, whereas smaller diameter pipes and service lines are lead, copper, PVC, PEX, polybutylene or galvanized iron. It is therefore important to consider the impacts of distributed water quality on corrosion of concrete pipes and linings.

### 2.2 BACKGROUND

#### 2.2.1 *Langelier Index to Predict Corrosion and Scaling*

Corrosion of concrete is an exceptionally complex process dependent on water chemistry, type of concrete and physical flow conditions. It has been noted that under suitable conditions a  $\text{CaCO}_3$  precipitate forms a protective layer at the concrete-water interface. However, at low alkalinity and low pH water conditions, lime leaches from the cement to water. Accordingly, one of the key factors used to evaluate the potential for concrete degradation is the Langelier Index (LI; AWWARF and DVGW-TZW, 1996; McNeill and Edwards, 2003):

$$\text{LI} = \text{pH}_a - \text{pH}_s \quad (1)$$

$$\text{pH}_s = \text{pK}_s - \log [\text{Ca}^{2+}] - \log [\text{HCO}_3^-] - \log \gamma_{\text{Ca}^{2+}} - \log \gamma_{\text{HCO}_3^-} \quad (2)$$

where  $\text{pH}_a$  is the measured bulk water pH,  $\text{pH}_s$  is the pH at which the solution is saturated with  $\text{CaCO}_3$ , and  $\text{pK}_s$  is the solubility product constant for calcite at a given temperature. Waters with positive LI values are typically deemed non-aggressive towards concrete, while those with negative LI values are labeled aggressive (Douglas et al., 1996).

The Langelier Index is based on the effect of pH on the equilibrium solubility of  $\text{CaCO}_3$  (Letterman, 1999), and there is scant evidence that it actually predicts waters which are

aggressive to concrete. Although waters that are highly aggressive towards  $\text{CaCO}_3$  (i.e., negative LI values) are often also highly aggressive towards concrete, it is possible to find some waters with positive LI values that can corrode concrete. In fact, a recent literature review suggests that Langelier indices do not always correlate with practical concrete corrosion data that has been gathered in the field (McNeill and Edwards, 2003). This is because the LI values dramatically oversimplify the concrete corrosion process. In particular, it does not account for the extreme stratification in pH that can exist between ‘bulk water’ and the concrete pore water. Concrete corrosion can initiate deep within the concrete matrix and measurements of bulk water pH may not reflect the pH of the region where corrosion is occurring. The corrosion processes occurring at the surface may be quite different from those that occur within the concrete matrix. Finally, the protective layer on concrete might not be calcite.

The Langelier Index does provide relatively good mechanistic insight into trends associated with scaling problems due to excessive deposition and build-up of calcium carbonate. Deposition of thick calcium carbonate layers on pipe is a substantial concern given head loss, reduced flow rates and associated aesthetic concerns due to sloughing of white particulates.

Another significant drawback to the use of Langelier indices is that they do not consider the potential effects of other ions such as sulfate, chloride, magnesium, silicon, zinc, or phosphate on corrosion. Changes in the concentration of each of these ions have the capability to affect concrete corrosion rates (McNeill and Edwards, 2003), presumably by formation of important solids other than calcite on the concrete surface that can protect the underlying pipe.

### ***2.2.2 Effects of Magnesium and Silicon on Concrete Infrastructure***

The role of magnesium in concrete corrosion has not been well addressed in the literature. It is known that  $\text{Mg}^{2+}$  can act in concert with sulfate and is more aggressive than  $\text{Na}^+$  (Dewah et al, 2002; Rasheeduzzafar et al, 1994). It is hypothesized that the  $\text{Mg}^{2+}$  ion readily reacts with  $\text{OH}^-$  ions present in the concrete pore-water to form the mineral brucite ( $\text{Mg}(\text{OH})_2$ ). This process leads to a decrease in pore-water pH that can enhance lime and C-S-H dissolution, thus leading to concrete degradation. Additionally, Kvech et al. (2002) discovered that magnesium-aluminum oxyhydroxides were highly insoluble near pH 9.5. Since the pH near the surface and within pores of concrete is often higher than that of bulk water, it is likely that similar compounds could form on concrete via reaction between aluminum (from the dissolving

cement) and magnesium (from the water). Magnesium silicates are also known to form during water softening processes and coat pipes in some distribution systems, and therefore could be influential in corrosion of cement as well (Kristiansen, 1977; Price et al, 1997).

Recent unpublished work in Europe has determined that aqueous silicate (Slats, 2002) tends to decrease aluminum leaching to potable water from the cement. The implication is that aluminum silicates, or perhaps aluminum magnesium silicates (Kvech and Edwards, 2002) are forming in pores, and that these silicates can be protective to concrete. Trussell and Morgan in 2006 proposed another saturation index which predicts when wollastonite ( $\text{CaSiO}_3$ ) will precipitate and be protective to cement surfaces.

### ***2.2.3 Role of Cavitation in Concrete Corrosion in Distribution Systems***

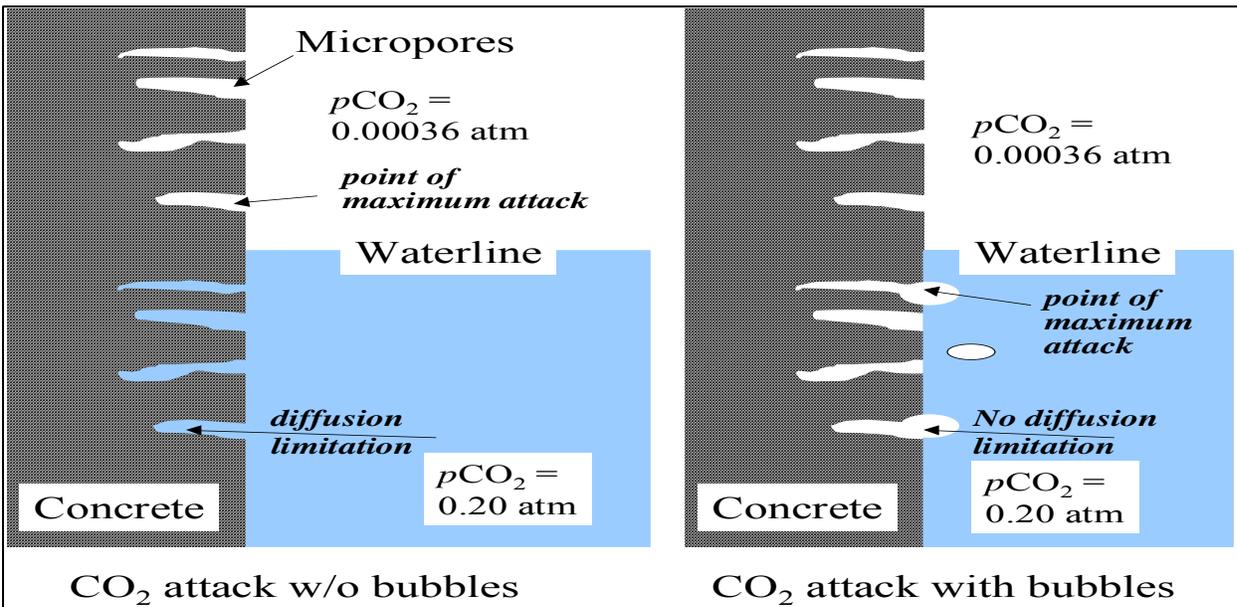
Cavitation is the process by which gas or vapor bubbles nucleate, grow, and then collapse in a liquid. This collapse occurs (sometimes violently) when the local solution pressure drops below the vapor pressure, thus resulting in vaporous cavitation by boiling the water at ambient temperature. Similar collapse can also occur from total dissolved gases, formed by local pressure drop below the saturation pressure of the dissolved gases. The maximum pressure from the bubble collapse is estimated at tens of thousands of pounds per square inch (psi) and the time span of collapse can be less than a millisecond (Konno et al., 2001). These implosions create “microjets” that can travel faster than the speed of sound and cause severe pitting (Siegenthaler, 2000).

Typical vapor pressures of water from 10-40° C range from 0.012 to 0.073 atm, whereas the total dissolved gas pressure of natural water is typically in the range from 0.8 to 1.2 atmospheres (Scardina, 2004). Vaporous cavitation occurs when the vapor pressure is below the dissolved gas pressure. Since the typical system pressure is usually 20 psi (1.36 atm) or greater with typical water main velocities of 2 – 8 fps (0.6 – 2.4 mps), the possibility of vaporous cavitation occurring in transmission lines is expected to be extremely low. Even so, many pump, valve, and pipe failures are often attributed to cavitation.

Cavitation can also arise from gaseous cavitation, in which dissolved gases in the water nucleate to form bubbles, as opposed to vaporous cavitation attributed to bubbles of water vapor as described previously. The formation of gaseous cavitation bubbles is slower than vaporous, since the dissolved gases are present in the water at the part per million level and the bubbles

must grow by diffusion, whereas vaporous cavitation bubbles can arise much more rapidly since water itself is the solvent (Novak, 2005). Indeed, extensive pipeline venting systems are necessary on mains to remove gas that is formed by gaseous cavitation (Novak, 2005). It is possible that the observation of severe cavitation damage in practice, relative to expectations of unlikely cavitation according to simplistic theories, is due to departures from ideal flow as defined by the classic Bernoulli’s equation. Specifically, it is understood that in microeddies, pressures might be much lower than predicted by Bernoulli’s equation due to non-ideal flow (Birkhoff, 1957). In any case, bubbles (vaporous cavitation) and trapped gases (gaseous cavitation) are present in many transmission mains.

**Figure 2.1. Deterioration of concrete immersed in water. If water is undersaturated with respect to dissolved gases, micropores are filled with water and maximum corrosion attack is at the waterline during “normal” corrosion (left). Under the same circumstances but in water supersaturated with respect to dissolved gases, bubbles can grow from concrete micropores, removing diffusion limitations and directly exposing concrete to extremely high CO<sub>2</sub> (right). The moist conditions at the waterline apply to all surfaces in a pipeline contacting bubbles. Moreover, the high pressures would dramatically increase the partial pressure of CO<sub>2</sub> in release gas, which attacks concrete via carbonation.**

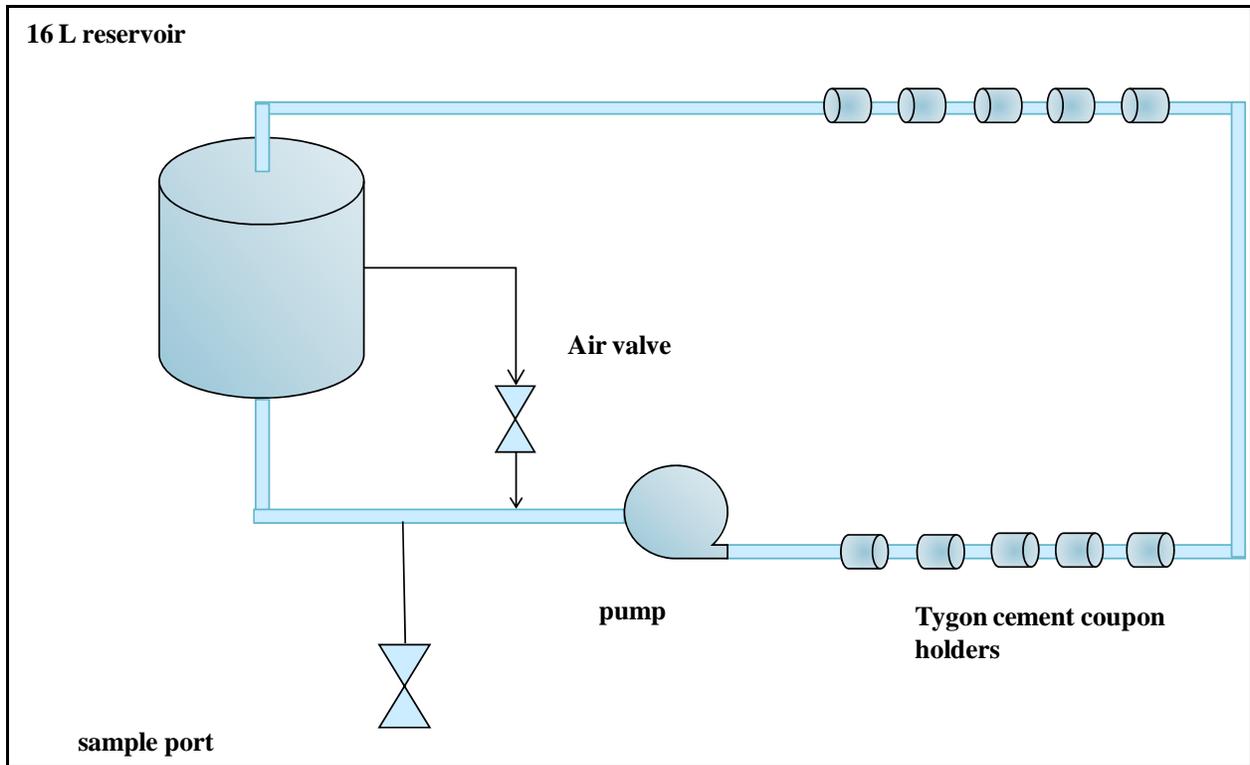


Damage to concrete from gas might arise from a variety of mechanisms. In addition to the intense pressure from collapsing bubbles, damage might be due to indirect effects such as the high CO<sub>2</sub> gas content in bubbles. In fact, in some cases bubble formation is likely to be the rate limiting step to concrete degradation. The adverse impact of “aggressive” CO<sub>2</sub> on drinking water treatment plant infrastructure is well established, and it is worth describing some practical aspects of CO<sub>2</sub> attack as related to concrete infrastructure. First, if concrete is immersed in water, deterioration occurs in three zones depending on whether it is below the waterline, just above the water line or far above the waterline (Figure 2.1). Of these three zones, concrete attack is slowest in the zones below the waterline and far above it. Even though the water can have dissolved CO<sub>2</sub> partial pressures 500 times higher than the atmosphere during enhanced coagulation (0.2 atm CO<sub>2</sub>), the rate of CO<sub>2</sub> diffusion through water filled micropores in the concrete is approximately 3500 times slower than through air, so the net result is that CO<sub>2</sub> is transported more quickly into concrete from air (Masterton and Hurley, 1993; Prins, 1987).

Far above the waterline, the humidity is insufficient to allow degradation to proceed. Thus, the concrete degrades most rapidly just above the water line, where micropores are free of liquid and in contact with the atmosphere and humidity is high (Weyers, 1993). Observations in Galesburg (IL) related to premature degradation of a 36” diameter concrete distribution main along the upper portion of the pipeline is consistent with this mode of failure (Galesburg Register-Mail, 2006). The presence of trapped gas in this system was noted as a serious contributing issue. The research herein attempted to consider the mechanisms of concrete corrosion due to bubble formation in pipelines.

### **2.3 EXPERIMENTAL SETUP**

Ten test rigs (Figure 2.2) were used to study the effects of water chemistry and gaseous cavitation while four additional rigs were used to study the effects of temperature on corrosion of concrete. The design and operation of these rigs is explained in detail in Chapter 1.



**Figure 2.2.** Test rig schematic.

### 2.3.1 Alkalinity, pH and Gaseous Cavitation

Two levels of alkalinity were tested: low alkalinity (20 mg/L as CaCO<sub>3</sub>) and high alkalinity (200 mg/L as CaCO<sub>3</sub>) (Table 2.1). Five inhibitor conditions were also tested for each of two baseline water chemistries (Table 2.2). This study was conducted in two phases. In Phase I a pH of 7 was maintained throughout the testing period (12 weeks). The first six weeks of operation was at typical distribution system hydraulic conditions. That is, no gaseous cavitation was induced and the water velocity was maintained at approximately 2 m/s. After the first six weeks the first five cement coupons in each test rig were removed and evaluated. Replacement coupons were then installed. In the remaining six weeks gaseous cavitation was initiated in the system by introducing air at the suction end of the pump.

Throughout the 12 week operation water was drained from each test rig and replaced weekly. During the first four days of operation each inhibitor was added at three times the concentrations listed in Table 2.2 and NOM was added at 10 times the concentration listed in Table 2.1 to ‘condition’ the cement coupons.

**Table 2.1. Baseline water chemistry for Phase I and Phase II.**

<b>Constituent</b>	<b>Concentration</b>	<b>Baseline Test Water A (Low alkalinity)</b>	<b>Baseline Test water B (High Alkalinity)</b>
Calcium	mg/L as Ca	5	120
Alkalinity	mg/L as CaCO <sub>3</sub>	20	200
Magnesium	mg/L	1	1
Sodium	mg/L	7.9	95
Potassium	mg/L	0.6	0.6
Silicon	mg/L	2	2
Chloride	mg/L	8.8	212.3
Sulfate	mg/L as SO <sub>4</sub>	4.5	4.5
Nitrate	mg/L as NO <sub>3</sub>	0.2	0.2
NOM	mg/L as C	0.3	0.3

**Table 2.2. Inhibitor conditions.**

<b>Condition</b>	<b>Concentration Goal</b>
Control	no inhibitor
Sodium Orthophosphate	2 mg/L (as PO <sub>4</sub> )
Zinc Chloride/Sodium Orthophosphate	0.25 mg/L Zn + 2 mg/L PO <sub>4</sub>
Zinc Chloride	0.25 mg/L Zn
Sodium Hexametaphate	2 mg/L (as PO <sub>4</sub> )

### 2.3.2 Magnesium and Silicon

The ten test rig assembly that was built to study the effects of alkalinity, pH and gaseous cavitation was reused to study the effects of magnesium and silicon on concrete corrosion. It was hypothesized that magnesium silicate and/or magnesium-aluminum oxyhydroxides form at higher pH values thus reducing the corrosion of concrete (see Section 2.2.2).

This research, like Phases I and II, was conducted for 12 weeks. The first six weeks of operation was similar to the first six weeks in Phase II except for the addition of the 95%ile magnesium and silicon (Table 2.3). All five inhibitor conditions were tested without gaseous cavitation. After the first six weeks the first five cement coupons in each test rig were removed and replacement coupons were installed. The second six weeks was a repetition of the first six

weeks. This extended study of the coupons without gaseous cavitation was conducted to evaluate the importance of kinetics on the deposition of precipitate on the concrete coupons. As in the earlier phases, three times the inhibitor dosage and 10 times the NOM dosage were added during the first four days of rig operation to ‘condition’ the cement coupons.

In Phase III the magnesium concentration was 40 mg/L, the silicon concentration was 20 mg/L, and the pH was maintained at 8.3. This pH, however, was most likely too low for magnesium silicate precipitation. The city of Austin (TX) which distributes water ranging from pH 9.4 to 10.1 noticed some magnesium silicate scaling (Price et al., 1997). Austin conditions were mimicked to determine if magnesium silicate precipitation occurs at higher pH (Table 2.3). Austin uses sodium hexametaphosphate (2 mg/L as PO<sub>4</sub>) to control calcium carbonate scale in their distribution system so that was also repeated in this study.

An additional test was conducted to determine if wollastonite precipitates with appropriate amounts of calcium and silicon (without magnesium) and if it can be protective to cement surfaces. Beaker tests and the “Trussell” wollastonite saturation index (Trussell et al., 2006) were used to determine appropriate levels of calcium and silicon, such that a positive index for wollastonite would be achieved (Table 2.3).

**Table 2.3. Baseline water chemistry for tests on magnesium and silicon.**

Constituent	Concentration	Phase III Baseline Low alkalinity Test Water	Phase III Baseline High Alkalinity Test Water	Synthetic Austin (TX)	Synthetic Supersaturated Wollastonite
Calcium	mg/L as Ca	5	120	20	120
Alkalinity	mg/L as CaCO <sub>3</sub>	20	200	60	20
pH		8.3	8.3	10 / 8.5*	10 / 8.5*
Magnesium	mg/L	1	1	20	1
Sodium	mg/L	7.9	95	0	0
Potassium	mg/L	0.6	0.6	0.6	0.6
Silicon	mg/L	2	2	4	20
Chloride	mg/L	8.8	212.3	0	0
Sulfate	mg/L as SO <sub>4</sub>	4.5	4.5	80	60
Nitrate	mg/L as NO <sub>3</sub>	0.2	0.2	0.2	0.2
NOM	mg/L as C	0.3	0.3	0.3	0.3

\* Initial pH of Austin and Wollastonite waters switched to 8.5 during weeks 9 - 12

### 2.3.3 *Temperature*

Concerns over elevated water temperature were identified immediately after starting experimentation. This rise in water temperature was due to the high mechanical energy input to the water by the centrifugal pumps, as well as some heat dissipation from the pump motors. The significance of the effects of temperature on concrete corrosion was studied by building four additional test rigs that could be placed in a constant 10 °C (50 °F) temperature room. During operation the water temperature was approximately 16 – 18 °C (61-64 °F) which is typical of actual distribution systems. This was in contrast to the test rigs operating at room temperature where the water temperature was 29 – 32 °C (84-90 °F).

The four conditions tested at this lower temperature were the low alkalinity and high alkalinity water chemistries (Table 2.1) with no inhibitor and with zinc orthophosphate inhibitor (Table 2.2) at pH 7. The test was conducted for a period of six weeks without gaseous cavitation. The same four inhibitor conditions were tested again at pH 8.3 with the addition of the 95%ile magnesium and silicon (Table 2.3). This test was conducted for a period of 12 weeks without gaseous cavitation.

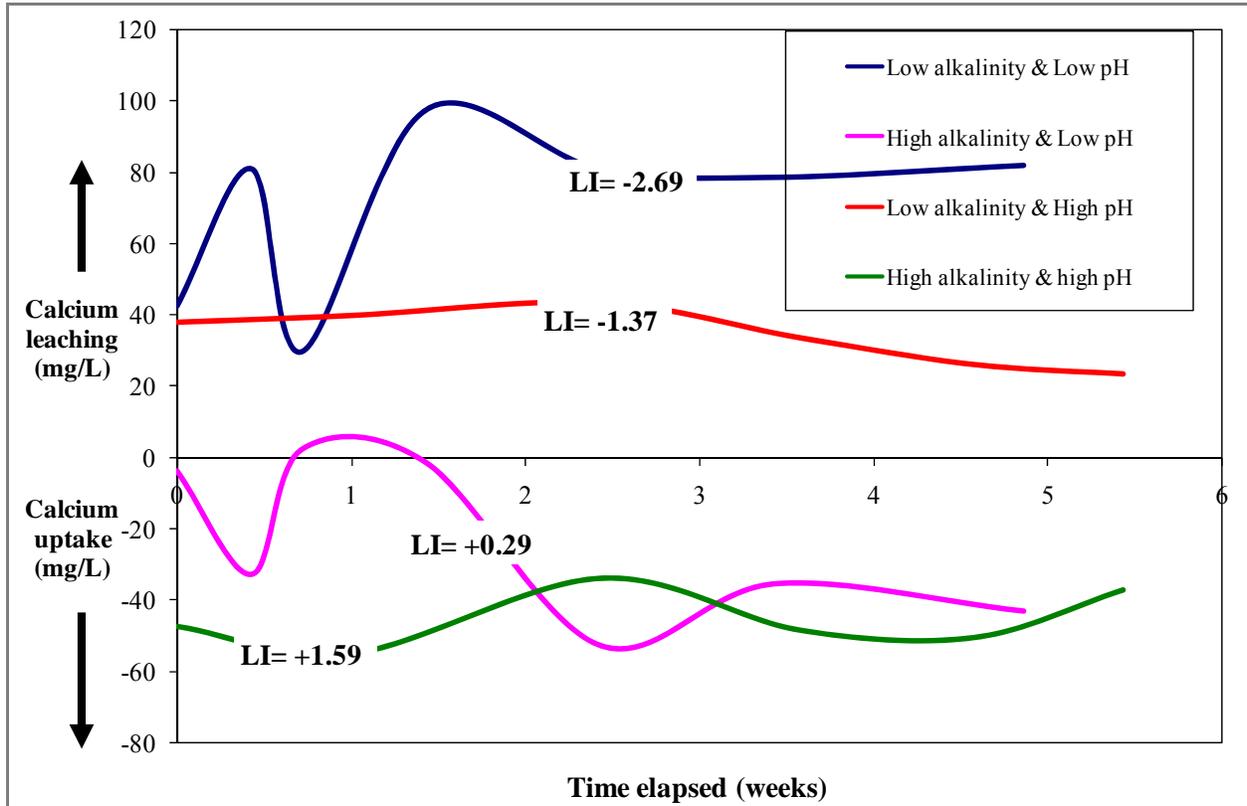
## 2.4 **RESULTS AND DISCUSSION**

The overall objective of this study was to determine if water chemistry, gaseous cavitation and temperature mitigate (or exacerbate) the corrosion of concrete and dissolution of lime. The corrosion of concrete was quantified using two types of measurements. The first was a physical measurement of the weight change of the coupons before and after the test. The second factor considered was chemical in nature. This was the concentration of calcium measured at the beginning and end of each week. The fate of the inhibitors was also monitored regularly. Metals concentrations were determined using inductively coupled plasma with mass spectrometry (ICP-MS).

### 2.4.1 *Alkalinity and pH*

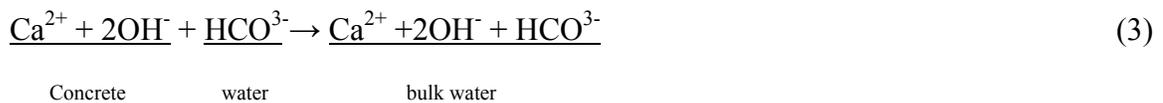
Plots of change in calcium concentration in each test water show that there was considerable calcium leached from the concrete test coupons in the low alkalinity waters and calcium precipitated from solution in the high alkalinity waters (Figure 2.3). An increase in calcium concentration is indicative of lime leaching from the concrete coupons while calcium

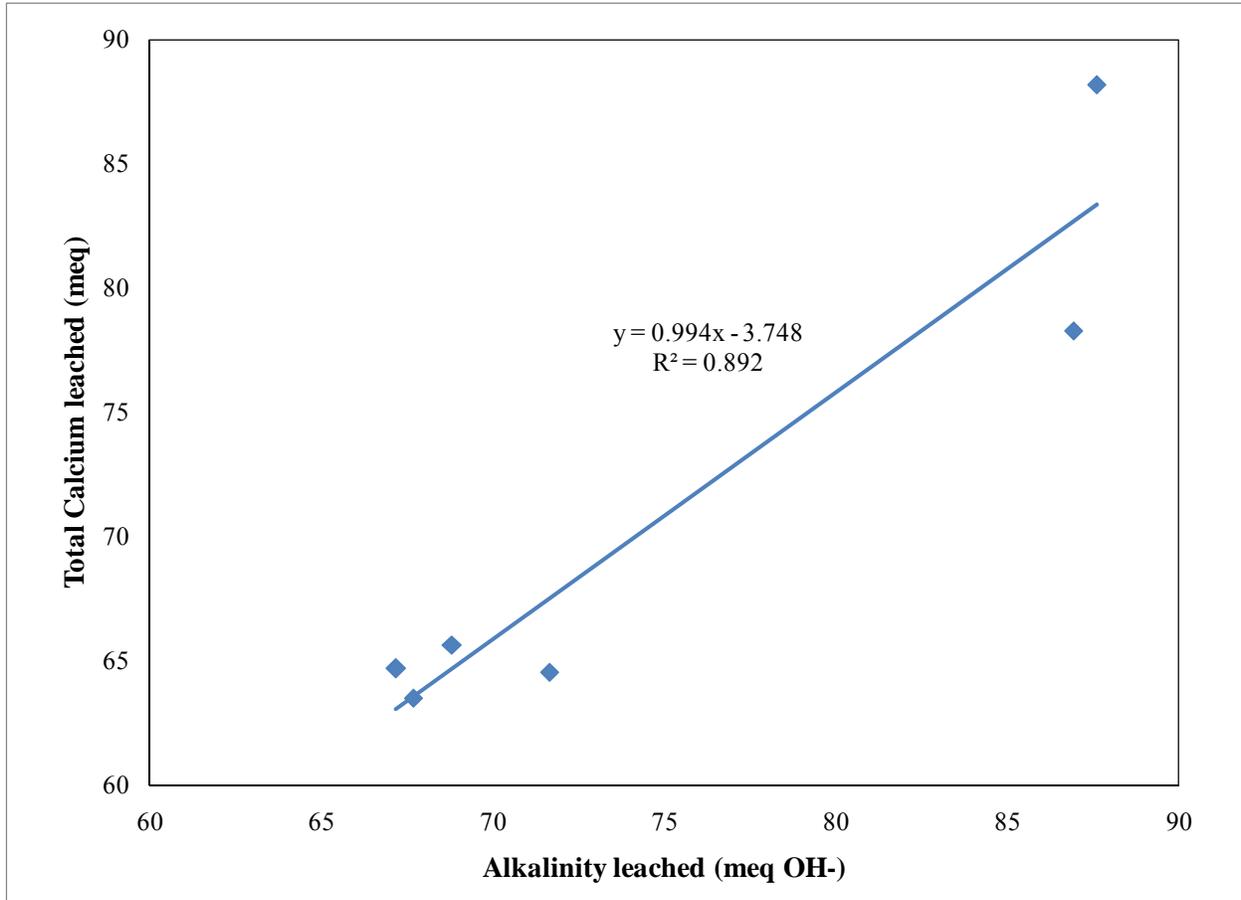
uptake indicates calcite precipitation onto the concrete surfaces. The weight change of the concrete coupons confirms these observations. These measurements were not used for comparative studies between phases because it could not be confirmed that the drying of coupons was reproducible between phases.



**Figure 2.3. Comparison of calcium leaching/uptake from concrete coupons for all control rigs. LI=Langelier index at given pH and alkalinity.**

The leaching rate of calcium and alkalinity indicates that in low alkalinity (20 mg/L as CaCO<sub>3</sub>) and low pH (pH = 7) waters the concrete coupons leach lime into the water (Figure 2.4). Leaching of lime from the concrete coupons causes the calcium concentration in the bulk water to go up by 2 meq (Equation 3). The alkalinity of the bulk water also goes up by 2 meq as hydroxide ions leach into solution (Equation 3) indicating a 1:1 ratio of calcium to alkalinity. The slope of the line in Figure 2.4 is close to 1 and therefore appears to confirm this observation.

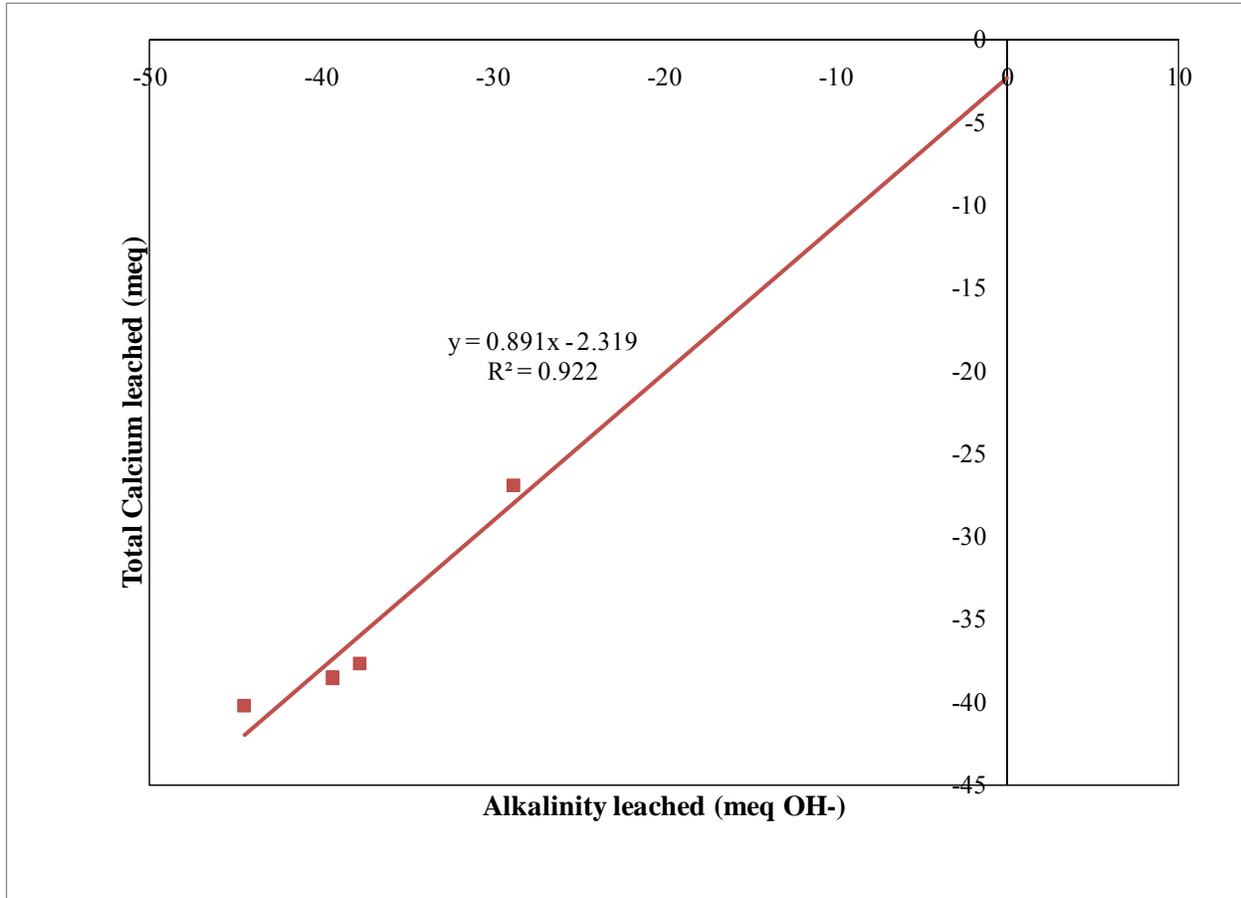




**Figure 2.4. Lime leaching into solution in low alkalinity and low pH control (no inhibitor) conditions.**

In the water with high alkalinity (200 mg/L as CaCO<sub>3</sub>) and high pH (pH = 8.3), the water is supersaturated with calcium (with respect to calcium carbonate). Under these conditions calcite precipitate is formed. Precipitation of calcite causes the calcium concentration in the bulk water to go down by 2 meq (Equation 4 and Figure 2.5)). The alkalinity of the bulk water also goes down by 2 meq since 1 meq of bicarbonate is consumed and 1 meq of H<sup>+</sup> is formed (Equation 4). Equal reduction of calcium and alkalinity concentrations is indicated by the slope of the trend line in Figure 2.5.





**Figure 2.5. Calcite precipitating from solution in high alkalinity and high pH control (no inhibitor) conditions.**

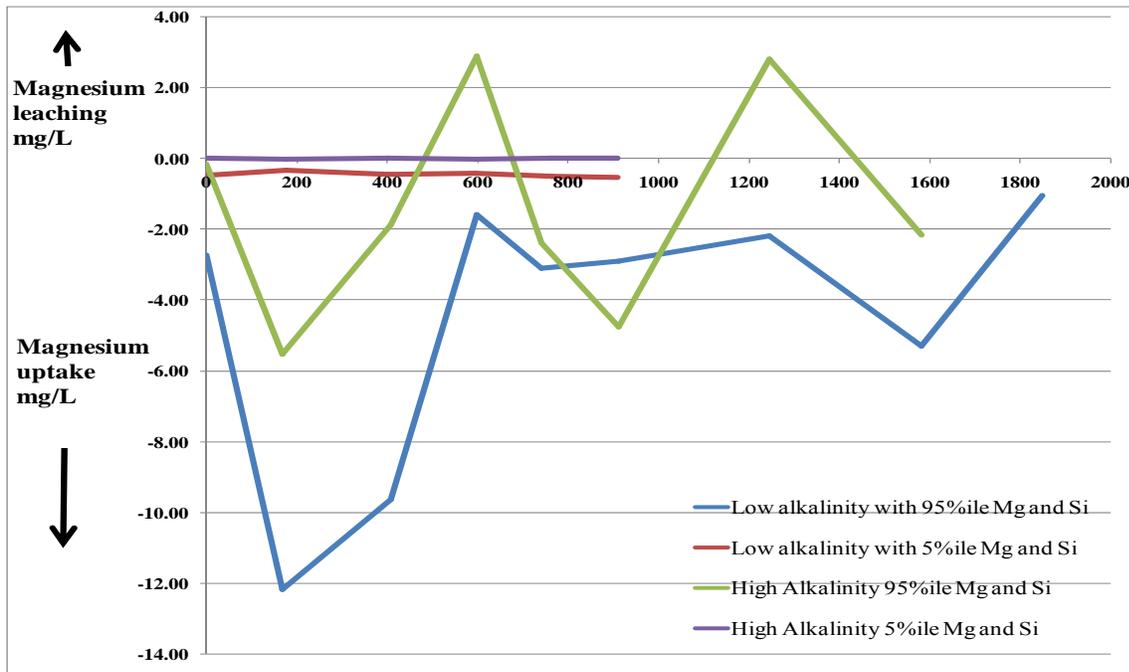
Concerns at low alkalinity conditions are very different from the concerns at higher alkalinity conditions. Low alkalinity lends itself to rapid degradation of the concrete structure due to increased leaching of lime. Elevated weight loss can result. However a higher alkalinity condition tends to cause precipitation of calcite. Thus, a combination of high pH and high calcium carbonate saturation state can lead to scaling of concrete pipes or linings.

#### **2.4.2 Magnesium and Silicon**

Phase III was a repetition of Phase II except for the addition of the 95%ile magnesium and silicon (i.e. 40 mg/L Mg and 20 mg/L Si). This phase was conducted to determine the effects of magnesium and silicon on corrosion of concrete. It was hypothesized that at these levels of magnesium and silicon precipitation of magnesium silicates or magnesium aluminum-

oxyhydrates might occur, forming a protective insoluble layer over concrete that would reduce corrosion.

There was clearly a small amount of magnesium and silicate precipitate formed at the beginning of each test as indicated by the loss of these constituents from the water (Figure 2.6 and 2.7). This is most likely because the pH of the water during the first week was close to 10 due to excessive lime leaching from the coupons during this period. But after the pH stabilized at 8.3 (due to conditioning of coupons), there was relatively little uptake of magnesium and silicon. A comparison of the calcium uptake and leaching in the water with the 5%ile and 95%ile magnesium and silicon shows that calcite precipitation was relatively unaffected compared to previously described behavior (Figure 2.8).



**Figure 2.6. Average weekly concentration of magnesium in water vs. time in hours (Phase III).**

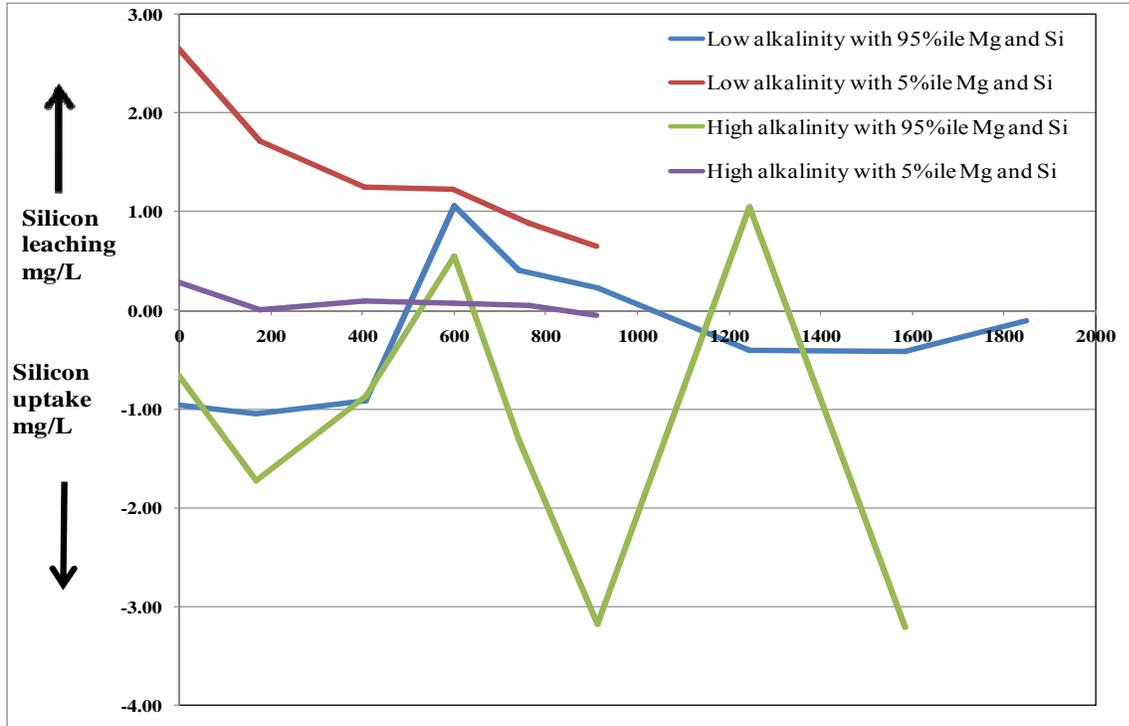


Figure 2.7. Concentration of silicon in water vs. time in hours (Phase III).

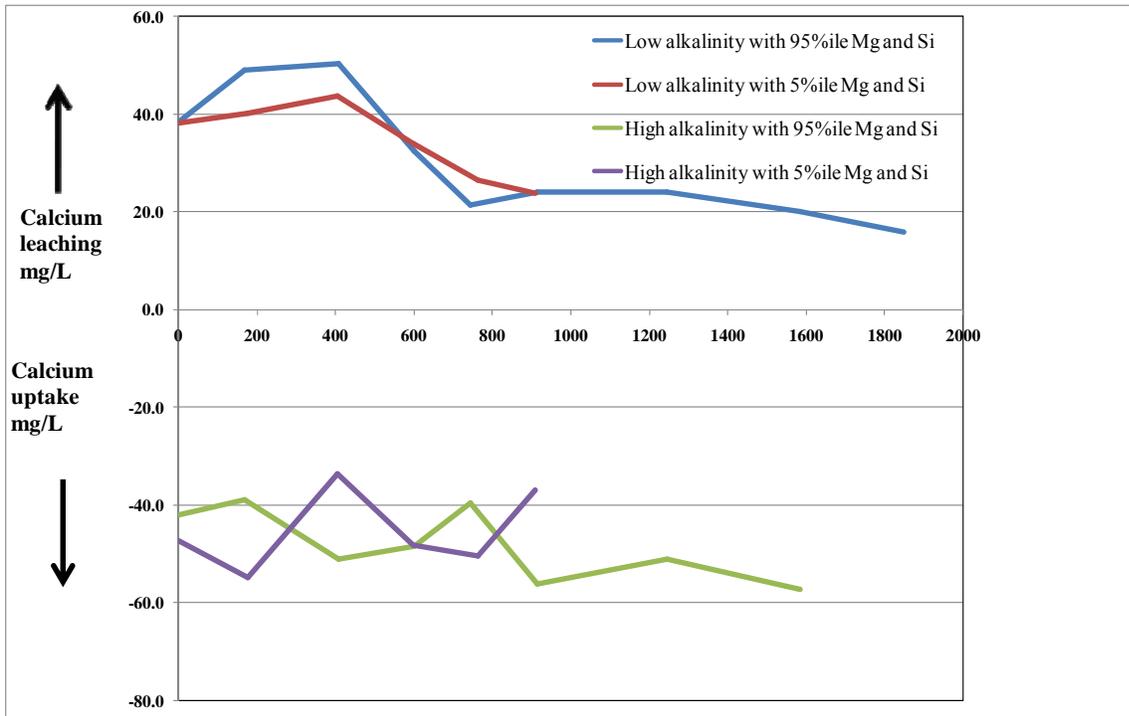


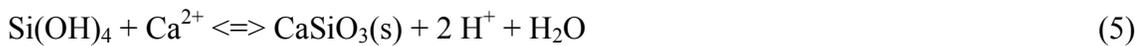
Figure 2.8. Concentration of calcium in water vs. time in hours (Phase III).

In the test of the synthesized City of Austin (TX) water conducted to study magnesium silicon precipitates at higher pH, fairly small amounts of magnesium, silicon, and phosphorus precipitated during the 12 week study (Table 2.4); however, the majority precipitated during the first 6 weeks when the pH was higher. As previously, pH of the test rigs were maintained at around 10 but constantly dropped to the mid-9 range. During the latter part of the test the pH was re-adjusted to 8.5 to observe the effects of pH on magnesium silicate precipitation. The pH remained constant around a value of 8.5 during this part of the test. Calcium leached from the coupons under both pH conditions.

**Table 2.4. Elemental changes associated with synthetic Austin (TX) test. (+ values indicate element leached into solution; - values indicate that element precipitated from solution).**

Water	Change in Mass (mg)			
	Ca	Mg	Si	P
Syn Austin (TX) 1st 6 weeks	372	-217	-35	-14
Syn Austin (TX) 2nd 6 weeks	455	11	12	0
Syn Austin (TX) total	827	-207	-22	-14
Total mass added (for reference)	2,880	2,880	576	94

In the test conducted to study protection of concrete by wollastonite, the rig was operated using water quality parameters that yielded a positive saturation index for the formation of wollastonite, CaSiO<sub>3</sub>. Wollastonite forms per the following equation:



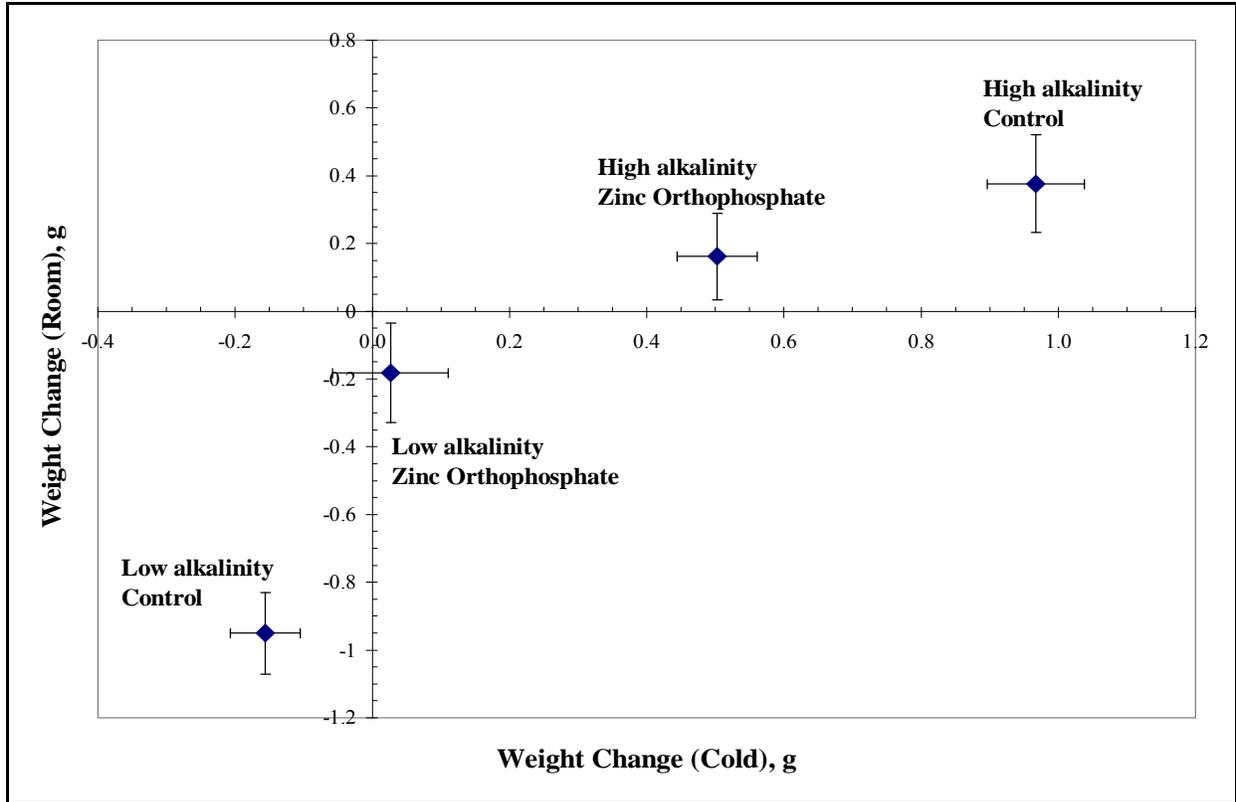
The equilibrium constant for this reaction as given by Trussell and Morgan is 10<sup>-13.05</sup> at 25 °C. A water quality of 120 mg/L calcium, 20 mg/L silicon, and pH 10 results in a saturation index of +0.63, indicating a supersaturated condition with respect to wollastonite. Results from the first six weeks indicate that calcium and silicon did precipitate from solution under these conditions (Table 2.5). During the second six weeks the pH of the test water was lowered to 8.5. This condition results in a wollastonite saturation index of -1.8, indicating a highly under-saturated condition. Results from the second six weeks of testing bear this out, in that no silicon precipitated during this time. Despite this fact, the water was cloudy throughout the 12 weeks of testing; indicating that residual wollastonite or a similar compound was present.

**Table 2.5. Elemental changes associated with synthetic supersaturated wollastonite test. (+ values indicate element leached into solution; - values indicate that element precipitated/removed from solution).**

Water	Change in Mass (mg)		
	Ca	Mg	Si
Syn supersat Wollastonite 1st 6 weeks	-3,867	4	-125
Syn supersat Wollastonite 2nd 6 weeks	-1,420	0	2
Syn supersat Wollastonite total	-5,287	4	-122
Total mass added (for reference)	17,280	144	2,880

### 2.4.3 Temperature

The tests to determine the effect of temperature were conducted at two different time periods. Concrete coupons undergo continuous weight change due to hydration of concrete. Since these tests were conducted at two different time periods the coupons used in the first phase of testing had aged less than those used in the later phase. Thus, a direct and unambiguous comparison of weight change measurements is not possible. The weight change data however, shows that even though weight change is a function of temperature, the rank of the effectiveness of inhibitors remains the same for both 28 °C and 18 °C (Figure 2.9).

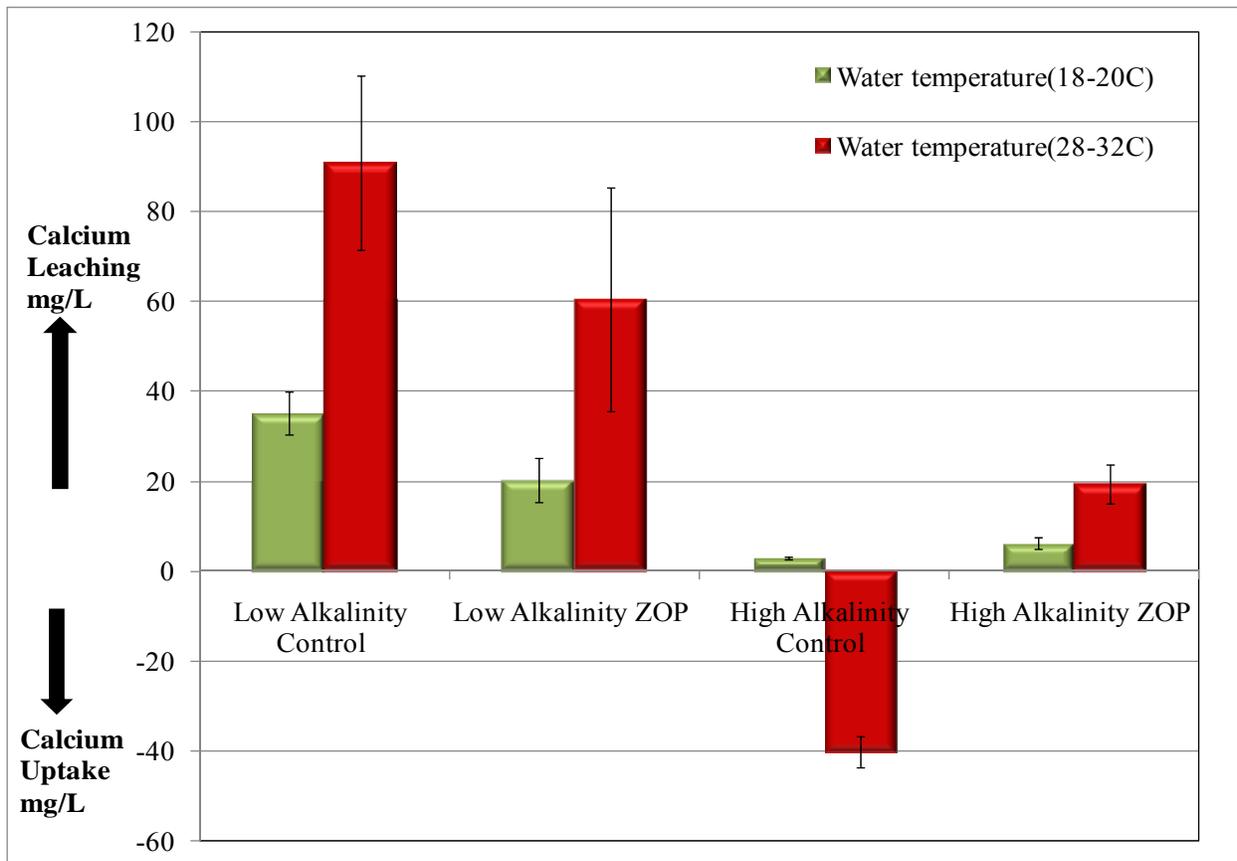


**Figure 2.9. Comparison of weight change at room temperature (water temperature 28 °C-32 °C) and cold temperature (water temperature 16 °C-18 °C). Error bars are indicators of 95% confidence intervals.**

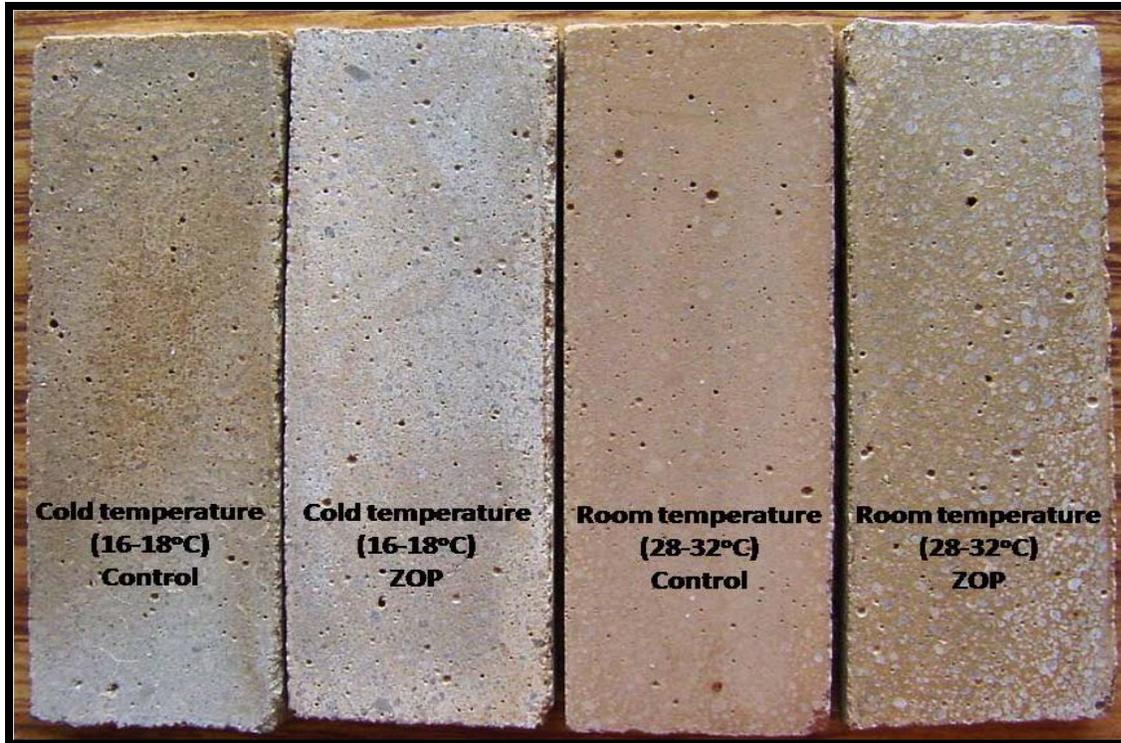
A comparison of calcium concentration in bulk water showed that under low alkalinity conditions calcium leaching is higher at higher temperatures. Calcium leached throughout the six week testing period. Calcite solubility is higher at lower temperatures, and therefore, the expected trend would be that calcium leaching would be greater at higher temperatures, but this was not observed (Figure 2.10). This indirectly proves that corrosion of concrete in low alkalinity waters is not driven by calcite solubility. Instead, the higher weight loss at higher temperature is likely due to increased degradation (concrete corrosion) rates.

At higher alkalinities calcite scaling is the dominant factor. Consequently, calcite solubility and precipitation is more likely to control the fate of the concrete. At lower temperatures there was little precipitation of calcium, which is consistent with the expectation of higher solubility of calcite at lower temperatures (Figure 2.10). The potential role of higher temperatures in accelerating degradation was overwhelmed by the effect of calcite solubility.

The addition of ZOP inhibits calcite precipitation at higher temperatures. Addition of ZOP could be highly detrimental to concrete at high temperature, as it dramatically increases calcium leaching to the water, presumably by preventing formation of protective calcite or analogous scales. At high alkalinity and low alkalinity (pH 7) addition of ZOP at lower temperatures caused calcium leaching to decrease by nearly one-third compared to calcium leaching at higher temperatures (Figure 2.10). The calcite precipitate on the surface of the concrete coupons was visibly obvious as shown in Figure 2.11.



**Figure 2.10. Comparison of calcium leached/precipitated from coupons (last 3 weeks data used) at room temperature (water temperature 28 °C - 32 °C) and cold temperature (water temperature 16 °C - 18 °C). Error bars are indicators of 95% confidence intervals.**



**Figure 2.11. Comparison of coupons tested at 16 - 18 °C and 28 - 32 °C.**

#### **2.4.4 Gaseous and Vaporous Cavitation**

Weight change of test coupons after six weeks of testing under normal flow conditions (without gaseous cavitation) and two-phase flow conditions (with gaseous cavitation) were compared to determine if gaseous cavitation showed a significant effect. Student's t-tests were performed to determine if there were any significant differences in the weight change due to gaseous cavitation.

There were no significant effects of gaseous cavitation on the concrete coupons at either pH 7 or pH 8.3. In Table 2.6 the weight change values with and without gaseous cavitation with p-values above the 95% significance level threshold have been shown. Even so, almost all these statistically different values show *less* weight loss in the case of gaseous cavitation than in normal flow conditions. The calcium concentration with and without gaseous cavitation reflects most of the trends observed in the weight change data. However in cases where there is no statistical significance between weight change with and without gaseous cavitation, the change in calcium concentration is also statistically insignificant. In some cases of significant weight change differences however there is no difference in calcium change. Gaseous cavitation

increased scaling only in one case (zinc chloride at low alkalinity and high pH conditions) and the calcium data reflects the same.

**Table 2.6. Statistical comparison of coupon weight change with and without gaseous cavitation (Highlight indicates gaseous cavitation caused less weight loss).**

Condition	Weight change- Phase I pH 7			Weight change- Phase II pH 8.3		
	w/o gaseous cavitation	With gaseous cavitation	Statistical significance	w/o gaseous cavitation	With gaseous cavitation	Statistical significance
<b>Low alkalinity</b>						
Control	-0.950 ± 0.120	-0.543±0.120	p = 0.02	0.154±0.025	0.113±0.043	no
Orthophosphate	-0.789±0.157	-0.408±0.021	p = 0.01	0.101±0.051	-0.014±0.128	no
Zinc Orthophosphate	-0.446±0.193	-0.129±0.080	no	0.227±0.028	0.180±0.180	no
Zinc Chloride	-0.446±0.051	-0.513±0.108	no	0.091±0.029	-0.070±0.080	p = 0.02
Polyphosphate	-0.181±0.147	-0.422±0.032	no	-0.048±0.057	-0.016±0.101	no
<b>High alkalinity</b>						
Control	0.376±0.144	1.394±0.114	p = 1e-4	1.187±0.218	1.748±0.119	p = 0.001
Orthophosphate	0.256±0.082	0.447±0.019	p = 0.02	0.480±0.048	0.435±0.097	no
Zinc Orthophosphate	-0.039±0.182	0.193±0.121	no	0.501±0.076	0.487±0.053	no
Zinc Chloride	0.210±0.220	1.007±0.073	p = 0.001	0.446±0.087	1.733±0.155	p = 2e-4
Polyphosphate	0.161±0.127	0.177±0.125	no	0.332±0.045	0.401±0.121	no

**Table 2.7 Statistical comparison of weekly change in calcium concentration with and without gaseous cavitation (Highlight indicates gaseous cavitation caused less calcium leaching).**

Condition	Change in calcium concentration (mg/L) Phase I pH 7			Change in calcium concentration (mg/L) Phase II pH 8.3		
	w/o gaseous cavitation	With gaseous cavitation	Statistical significance	w/o gaseous cavitation	With gaseous cavitation	Statistical significance
<b>Low alkalinity</b>						
Control	88.7±10.169	58.1±9.142	p=0.0058	34.4±6.307	23.2±1.974	p=0.0354
Orthophosphate	77.9±9.539	51.6±11.344	p=0.0340	35.2±7.068	27.7±5.572	no
Zinc Orthophosphate	59.7±12.501	47.9±7.065	no	34.0±9.989	24.0±6.813	no
Zinc Chloride	69.9±15.723	53.8±4.654	no	35.9±6.871	29.6±2.107	no
Polyphosphate	39.6±8.279	50.4±6.510	no	37.9±9.612	28.8±6.956	no
<b>High alkalinity</b>						
Control	-35.3±14.687	-13.8±16.214	no	45.2±6.546	-57.0±12.058	no
Orthophosphate	11.8±4.087	11.6±2.821	no	8.0±5.512	-1.4±10.224	no
Zinc Orthophosphate	17.8±2.540	18.4±3.864	no	6.5±6.662	-1.1±9.975	no
Zinc Chloride	9.1±16.355	-10.7±19.219	no	33.0±8.370	-51.4±12.502	p=0.0290
Polyphosphate	8.8±6.339	12.5±3.417	no	11.4±5.251	2.5±13.390	no

Vaporous cavitation is caused by a drop in pressure below the boiling point of water. A short term experiment was conducted where a concrete coupon was subjected to vaporous cavitation produced via a sonic horn. After 24 - 27.5 hours, the effects of vaporous cavitation were obvious in the area of cavitation bubble impingement (Figure 2.12). Vaporous cavitation caused ~5% loss in the weight of the tested concrete coupon and a hole penetrated through the concrete at the point of attack. A typical 5 mm concrete liner would be fully penetrated in less than a day at this rate of attack.



**Figure 2.12. Coupon subjected to vaporous cavitation.**

## 2.5 CONCLUSIONS

- Low alkalinity and low pH conditions are extremely aggressive to concrete and cause rapid degradation of concrete by lime leaching.
- High alkalinity and high pH conditions are non-aggressive to concrete but scaling of pipes by calcite precipitation is a major issue.
- Magnesium and silicon can be effective at preventing corrosion of concrete, but only at higher bulk water pH of around 9.5.
- Kinetics of concrete corrosion degradation reactions increase at higher temperatures, but this effect is countered by reduced calcite solubility in waters with higher pH/higher alkalinity (with no inhibitor added).

- Gaseous cavitation did not increase concrete corrosion, but vaporous cavitation is extremely detrimental to concrete.

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## CHAPTER 3

# EFFECT OF PHOSPHATE CORROSION INHIBITORS ON CONCRETE PIPES AND LININGS

Anusha Kashyap, Jeffrey L Parks and Marc Edwards

### 3.1 INTRODUCTION

Corrosion of lead and copper in drinking water distribution systems is a public health concern. The EPA Lead and Copper Rule requires water utilities to take measures to control the corrosiveness of their water to lead if the “action level” in first draw samples exceeds 15 ppb for lead or 1.3 ppm for copper. Many utilities have mitigated lead and copper corrosion by adjustment of pH and/or alkalinity, but even more have dosed phosphate inhibitors (either orthophosphate salts or polyphosphate blends) at the treatment plant to minimize lead and copper leaching. Although concrete corrosion does not pose a direct health hazard, it nonetheless has large economic and social consequences. This research was designed to examine the effects of phosphate corrosion inhibitors on concrete corrosion.

### 3.2 BACKGROUND

#### 3.2.1 *Phosphate corrosion inhibitors*

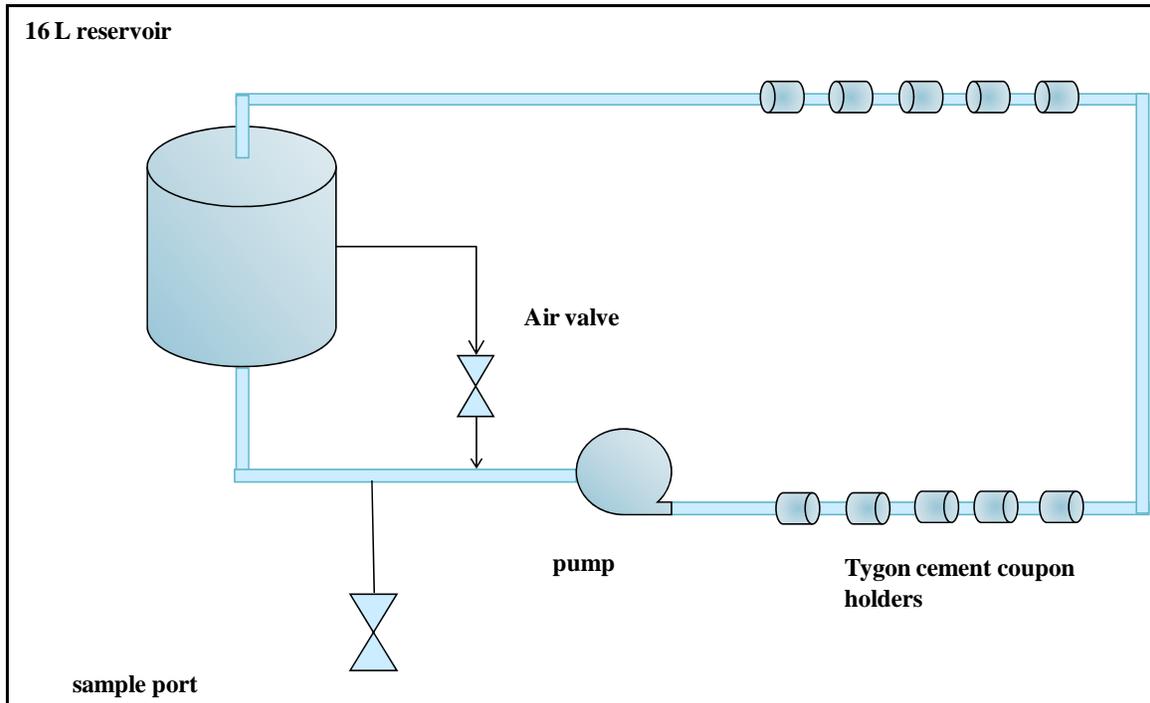
Corrosion inhibitors are dosed to mitigate corrosion of lead and copper from household plumbing. Sodium orthophosphate, zinc orthophosphate (ZOP) and polyphosphate are commonly used corrosion inhibitors. Blends of poly/orthophosphate are also used for corrosion control. These inhibitors have been discussed in detail in Chapter 1.

#### 3.2.2 *Carbonation of Concrete*

Alkaline hydroxides (calcium hydroxide) in the concrete interact with carbon dioxide in the atmosphere forming calcium carbonate. This neutralization of the alkalis in the concrete pore water by carbonic acid is called carbonation. This was previously discussed in Chapter 1.

### 3.3 EXPERIMENTAL SETUP

Ten test rigs (Figure 3.1) were used to study the effects of water chemistry and gaseous cavitation while four additional rigs were used to study the effects of temperature on corrosion of concrete. The operation of these rigs is explained in detail in Chapter 1.



**Figure 3.1. Test rig schematic.**

#### 3.3.1 Phosphate corrosion inhibitors

Five inhibitor conditions were tested at two baseline water chemistries (Table 3.1 and 3.2). Two levels of alkalinity (20 mg/L as  $\text{CaCO}_3$  and 200 mg/L as  $\text{CaCO}_3$ ) and pH (pH 7 and 8.3) were tested. This study was conducted in two phases. In Phase I a pH of 7 was maintained throughout the testing period (12 weeks). During the first six weeks of Phase I, the dosage of polyphosphate was mistakenly six times the concentration in Table 3.1. The first six weeks of operation were at typical distribution system hydraulic conditions; that is, no gaseous cavitation was induced and the water velocity was maintained at approximately 2 m/s. After the first six weeks the first five cement coupons in each test rig were removed and evaluated. Replacement coupons were then

installed. For the remaining six weeks of operation gaseous cavitation was simulated in the system by introducing air at the suction end of the pump.

Throughout the 12 week operation water was drained from each test rig and replaced on a weekly basis. During the first four days of operation each inhibitor was added at three times the doses listed in Table 3.2 and NOM was added at 10 times the dose listed in Table 3.1 to more quickly ‘condition’ the cement coupons.

**Table 3.1. Baseline water chemistry for Phase I and Phase II.**

Constituent	Concentration	Baseline Test Water A (Low alkalinity)	Baseline Test water B (High Alkalinity)
Calcium	mg/L as Ca	5	120
Alkalinity	mg/L as CaCO <sub>3</sub>	20	200
Magnesium	mg/L	1	1
Sodium	mg/L	7.9	95
Potassium	mg/L	0.6	0.6
Silicon	mg/L	2	2
Chloride	mg/L	8.8	212.3
Sulfate	mg/L as SO <sub>4</sub>	4.5	4.5
Nitrate	mg/L as NO <sub>3</sub>	0.2	0.2
NOM	mg/L as C	0.3	0.3

**Table 3.2. Inhibitor conditions for Phase I and II.**

Condition	Concentration Goal
Control	no inhibitor
Sodium Orthophosphate	2 mg/L (as PO <sub>4</sub> )
Zinc Chloride/Sodium Orthophosphate	0.25 mg/L Zn + 2 mg/L PO <sub>4</sub>
Zinc Chloride	0.25 mg/L Zn
Sodium Hexametaphate	2 mg/L (as PO <sub>4</sub> )

### 3.3.2 Zinc inhibitors

An additional phase of experimentation was conducted to study the effects of zinc on corrosion of concrete. In this study varying doses of zinc were used to determine the optimum dosage at which zinc is most effective. The same baseline water chemistry as in

Phase I was used in this study (Table 3.1). Both orthophosphate and polyphosphate were dosed along with zinc (Table 3.3). This test was conducted for a six week period under normal flow conditions (i.e. without gaseous cavitation). Care was taken to ensure that the pH remained at 7 throughout the study period and the flow rate was 2 m/s in all test rigs.

**Table 3.3. Inhibitor conditions for zinc effect study.**

Condition	Concentration Goal
Control	no inhibitor
Zinc Chloride	1 mg/L Zn
Zinc Chloride/ Sodium Orthophosphate	1 mg/L Zn + 2 mg/L PO <sub>4</sub>
Zinc Chloride/ Sodium Orthophosphate	0.5 mg/L Zn + 2 mg/L PO <sub>4</sub>
Zinc Chloride/ Sodium Hexametaphosphate	1 mg/L Zn + 2 mg/L PO <sub>4</sub>

### 3.4 RESULTS AND DISCUSSION

“Corrosion control” can have different goals for concrete dependent on circumstance. From the perspective of protecting the underlying pipe, deposition of solids or formation of “scale” on the coupon is beneficial, since it reduces the rate of attack. However, formation of too much scale can reduce flow and increase head loss. This study examines how phosphate inhibitors (orthophosphate, polyphosphate and ZOP) affect concrete corrosion rate and scale buildup.

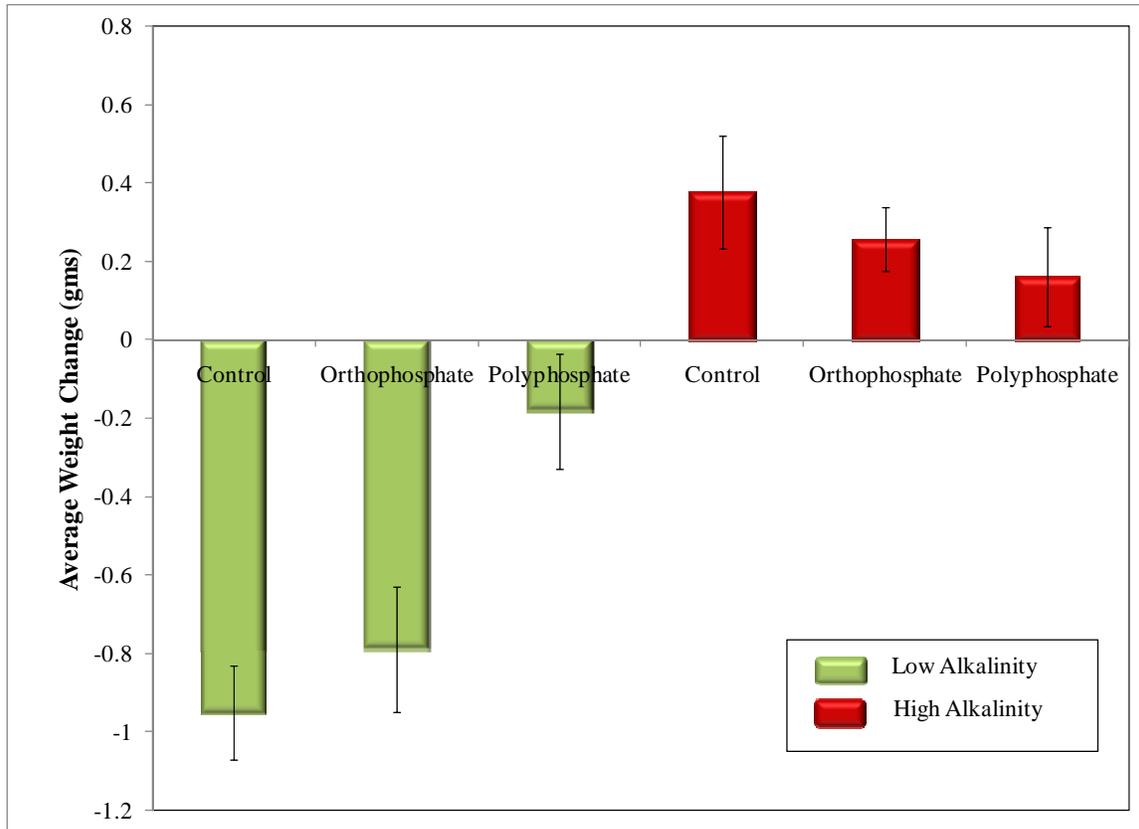
In addition, there is a growing impetus to reduce the concentration of zinc used for corrosion inhibitors in the water industry. In addition to the extra cost, zinc can cause issues related to wastewater sludge land application, sewage treatment operations, and unfortunately there is little evidence that the zinc actively helps to control copper and lead corrosion. On the other hand, there has been some evidence that zinc can sometimes reduce corrosion of concrete. Hence, it was deemed important to examine the impacts of zinc on concrete corrosion, thereby quantifying the possible downside of removing/reducing zinc inhibitor dosing.

#### 3.4.1 Comparison of Orthophosphate and Polyphosphate

Comparison of air dried coupon weight changes shows that of the two phosphate chemicals, polyphosphate was more effective in mitigating concrete corrosion at pH 7. At the low alkalinity and low pH considered most aggressive to concrete, orthophosphate

reduces corrosion by 20% while polyphosphate reduces corrosion by 80% (Figure 3.2). During the first six weeks of Phase I the dosage of polyphosphate was 6 times 2 mg/L and this was corrected to 2 mg/L during the second six weeks. On comparing the weight change and calcium data for first six weeks without gaseous cavitation and second six weeks with gaseous cavitation it was observed that the better performance of polyphosphate was due to overdosing.

At low pH, high alkalinity conditions are less corrosive to concrete than low alkalinity (Figure 3.2). Under these conditions the most calcite precipitated under the control condition and weight gain of the coupons was highest. Addition of orthophosphate and polyphosphate inhibited calcite precipitation and caused reduced weight gain under these conditions.

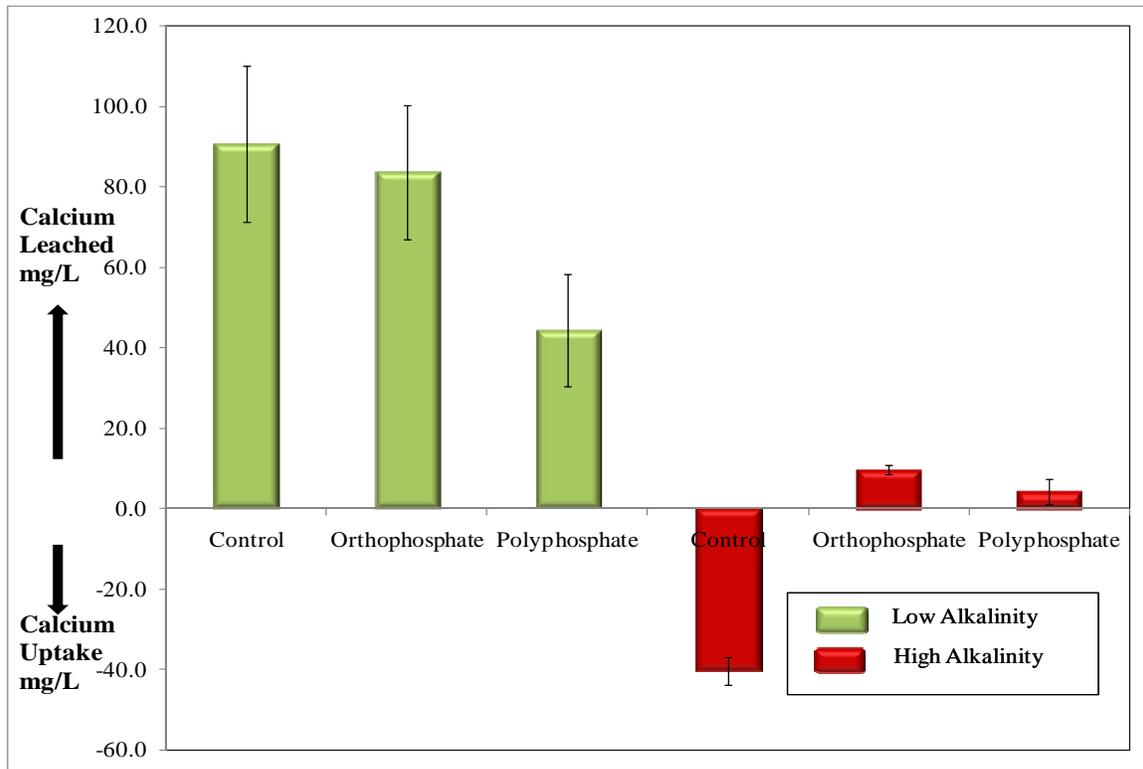


**Figure 3.2. Comparison of average weight change data for phosphate inhibitors at pH 7. Error bars indicate 95% confidence intervals.**

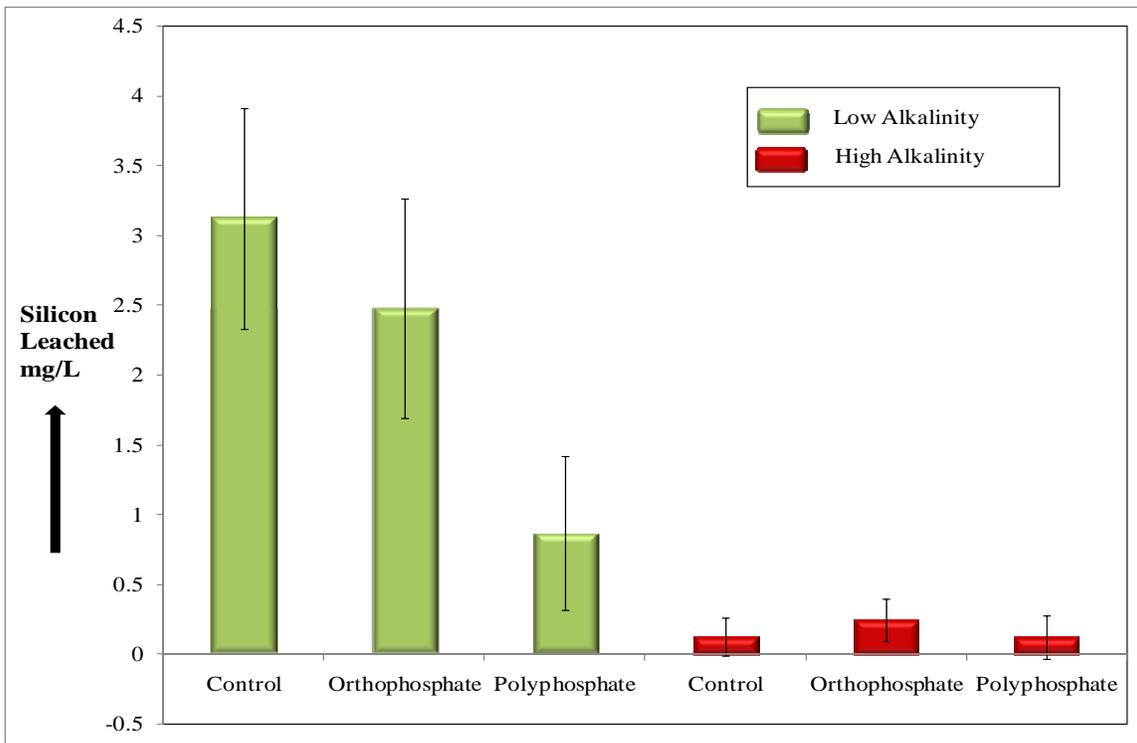
The trends in weight loss or weight gain are reaffirmed by the calcium leaching/uptake data (Figure 3.3). The average calcium leached/precipitated for each of

the last three weeks of testing (Figure 3.3) had a similar trend to that observed for the entire six weeks (data not shown). As evidenced by the weight change data, maximum leaching of calcium occurred in the control (no inhibitor) rigs for low alkalinity and low pH waters. Addition of orthophosphate did not cause any statistical difference in calcium leaching to the water but it reduced silicon leaching from the concrete under these conditions (Figure 3.4). However, addition of orthophosphate increased average aluminum leaching above the secondary maximum contamination level [SMCL for aluminum is 0.05-0.2 mg/L] (Figure 3.5), although the difference with the control was not significant at >95% confidence. As indicated by the weight change data, addition of high levels of polyphosphate reduced leaching of all key elements including calcium, silicon and aluminum (Figure 3.3, 3.4 and 3.5).

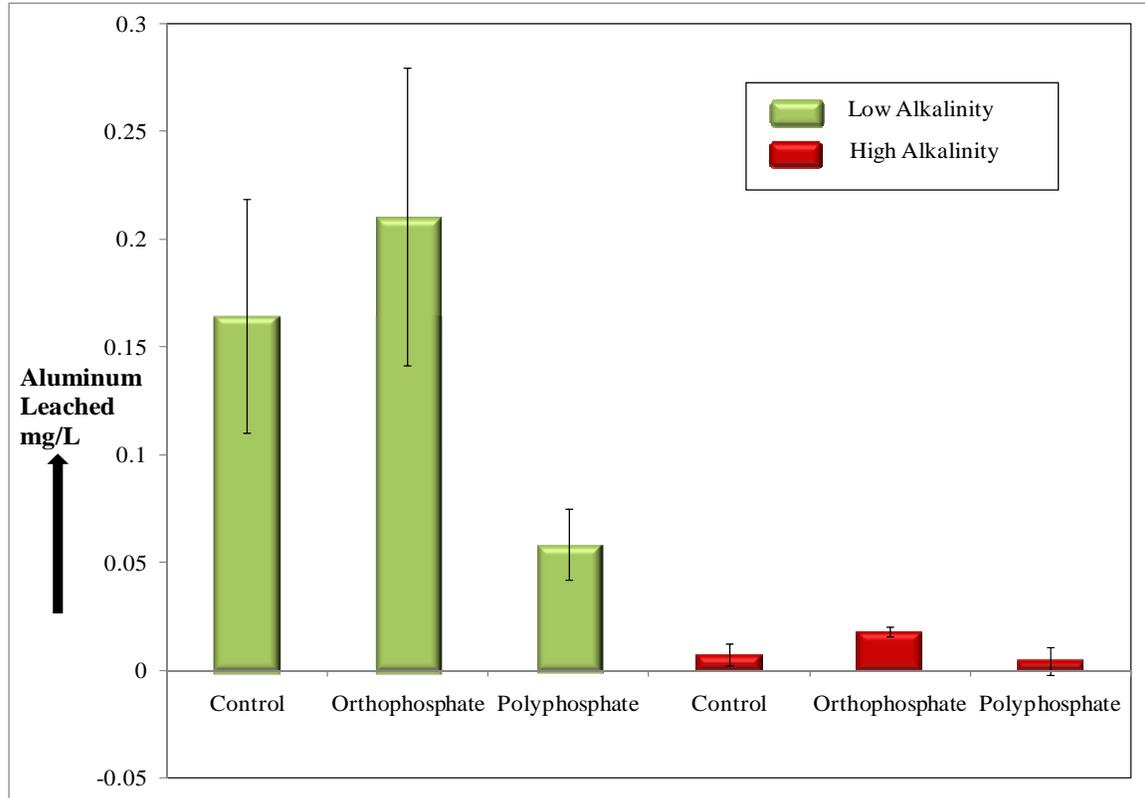
At high alkalinity and low pH, the concrete actually lost calcium to the water in the presence of phosphate inhibitors, versus net calcium uptake from the water observed in the control without phosphate inhibitors (Figure 3.3). Silicon and aluminum leached to the control water without inhibitors, but addition of orthophosphate slightly increased aluminum leaching from concrete (Figure 3.4 and 3.5). It is therefore clear that the use of phosphate inhibitors in scaling water, can not only prevent buildup of scale, but leave the concrete surface open to corrosive attack. Phosphate inhibitors therefore have a significant detrimental effect to concrete longevity in such situations.



**Figure 3.3. Calcium leached/precipitated from coupons over the last 3 weeks of Phase I (pH 7).**

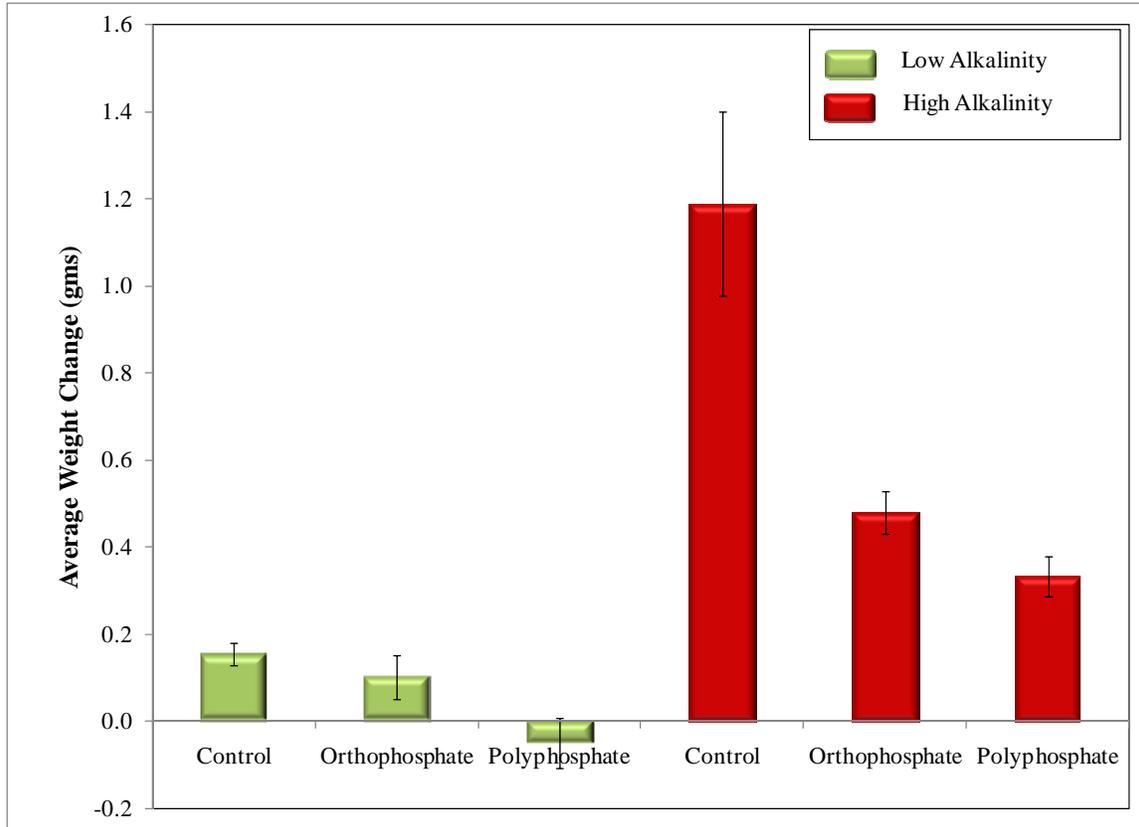


**Figure 3.4. Silicon leached from coupons over the last 3 weeks of Phase I (pH 7).**



**Figure 3.5. Aluminum leached from coupons over the last 3 weeks of Phase I (pH 7).**

Two alkalinity conditions were also tested at a higher pH of 8.3. At high alkalinity and high pH, the water is supersaturated with calcium (with respect to calcite) and these conditions are highly conducive to calcite precipitation. Under these conditions corrosion of concrete is not typically a concern but scaling is. Weight change data for concrete coupons shows that addition of either ortho or poly-phosphate (dosage as in Table 3.2) inhibits calcite precipitation, thus reducing scaling (Figure 3.6).

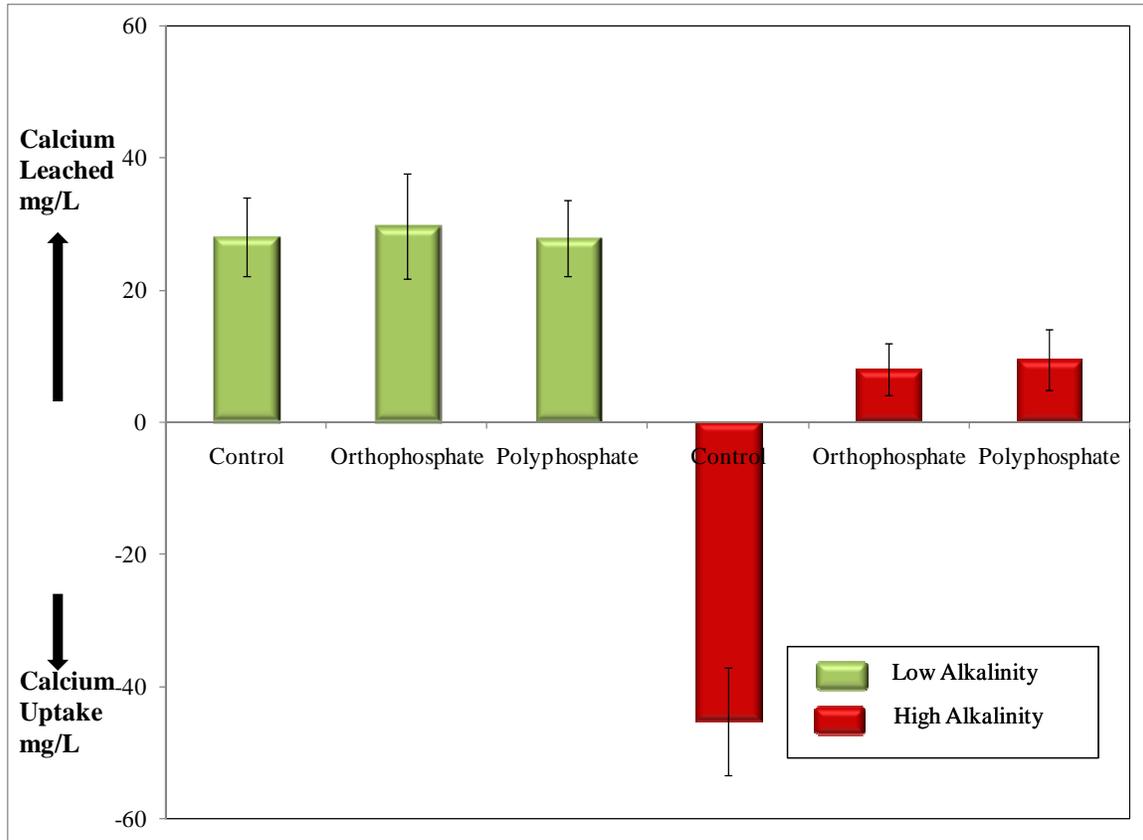


**Figure 3.6. Comparison of average weight change data for Phosphate inhibitors at pH 8.3. Error bars indicate 95% confidence intervals.**

At low alkalinity and high pH, there were small amounts of calcium and silicon leaching (Figure 3.7 and 3.8). In these tests both orthophosphate and polyphosphate (2 mg/L as  $\text{PO}_4$ ) were not very effective in reducing corrosion/calcium leaching in these conditions (Figure 3.7). And addition of orthophosphate did increase aluminum leaching closer to the upper range of the SMCL (Figure 3.9). As before, in scaling waters, the orthophosphate and polyphosphate stopped scaling, but also left the concrete surface subject to corrosive attack.

The slight **increase** in weight under the conditions of higher pH and lower alkalinity (Figure 3.6) seem counter-intuitive, given the extensive leaching of calcium and other constituents from the concrete to the water and the lack of scaling. However, carbonation (uptake of  $\text{CO}_2$ ) by the concrete coupons was highly significant. Phenolphthalein indicator tests were performed on the concrete coupons to determine the extent of carbonation (Figure 3.10). The pink coloration indicates areas of active lime

and little carbonation. At low levels of alkalinity at both pH 7 and 8.3, significant carbonation of the concrete coupons was observed. At highly aggressive conditions of alkalinity and pH, large amounts of corrosion/leaching of calcium was observed which caused an overall decrease in the weight of the coupons, even though there was some carbonation of these coupons as well (Figure 3.10). The true extent of carbonation is difficult to track, although it was undoubtedly occurring and confounds the interpretation of weight loss data as a straightforward indicator of the extent of corrosion.



**Figure 3.7. Calcium leached/precipitated from coupon over last 3 weeks of Phase II (pH 8.3).**

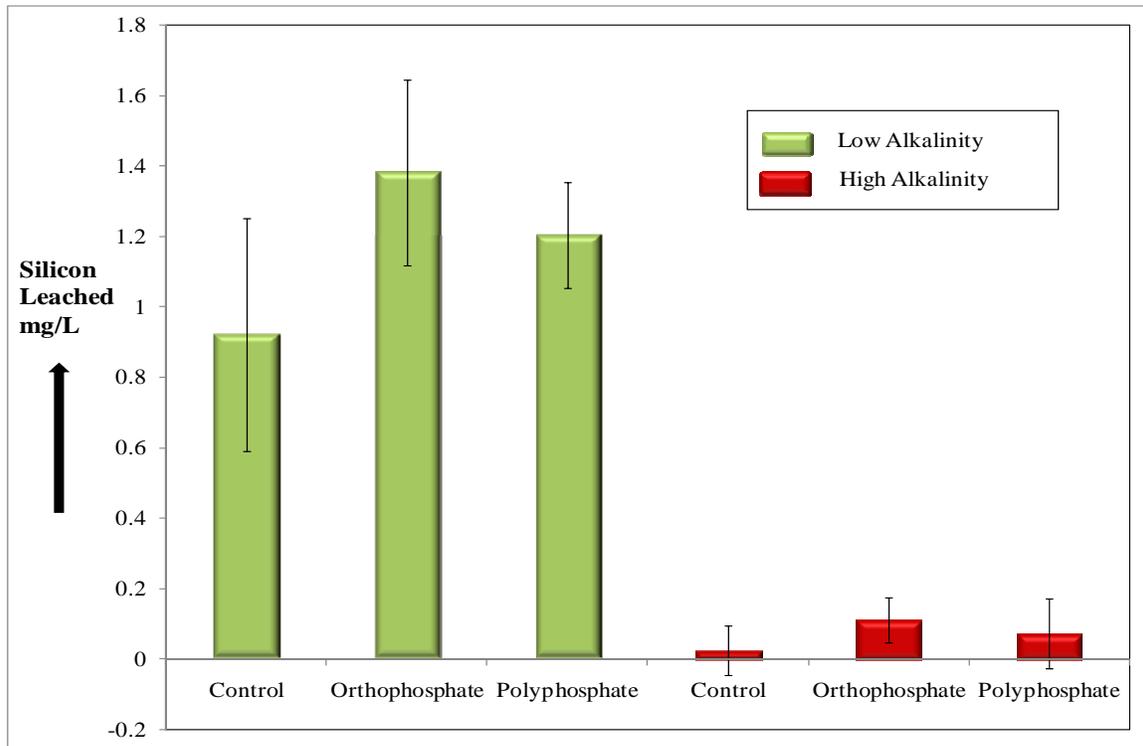


Figure 3.8. Silicon leached from coupons over the last 3 weeks of Phase II (pH 8.3).

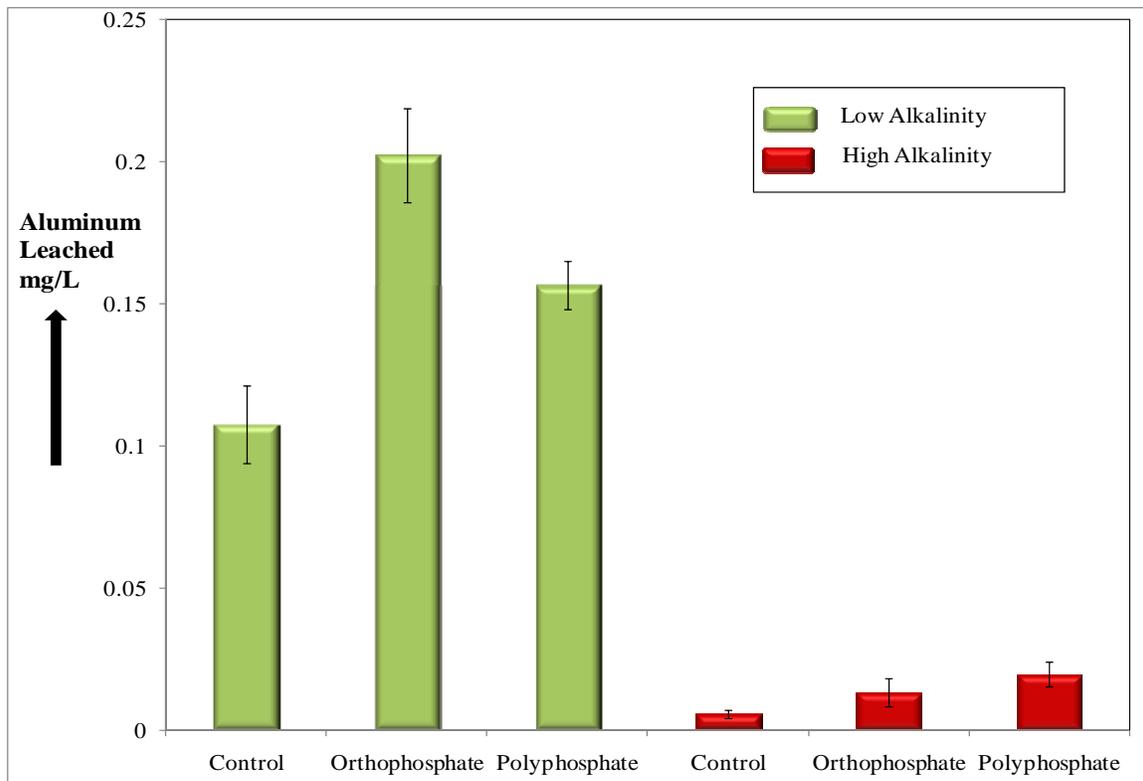
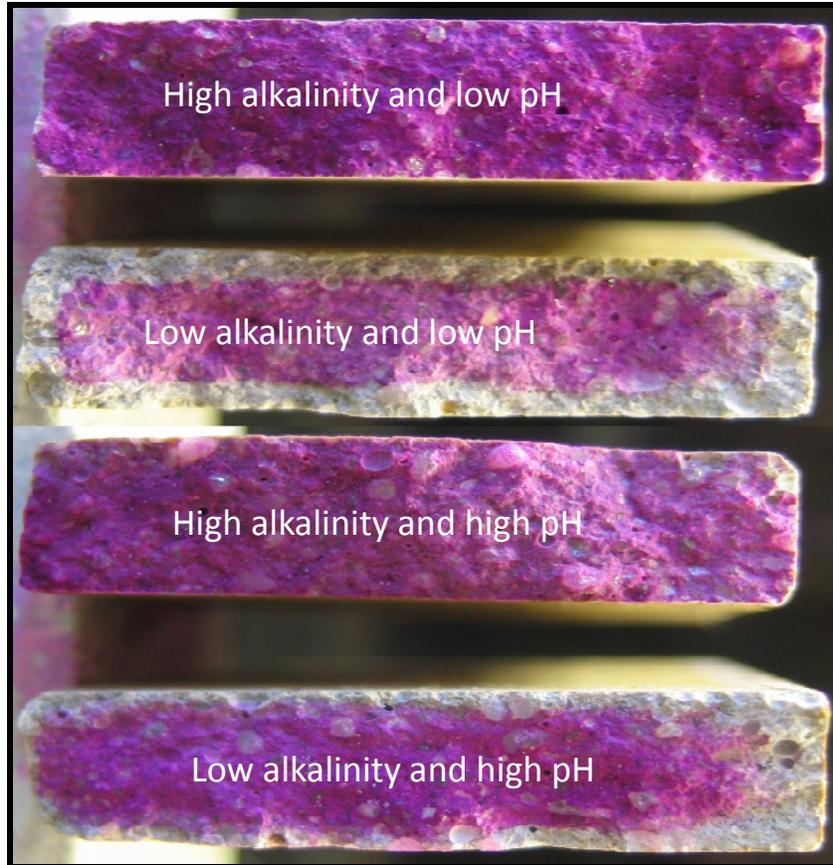


Figure 3.9. Aluminum leached from coupons over the last 3 weeks of Phase II (pH 8.3).



**Figure 3.10. Carbonation of concrete coupons. The most significant carbonation occurred at low pH and low alkalinity, as indicated by the thickness of outermost non-pink layer.**

In summary, the use of phosphate inhibitors not only mitigated concrete corrosion in aggressive low pH-low alkalinity water conditions, but also reduced calcite precipitation and scale build-up under high pH-high alkalinity conditions. But in the scaling waters, the downside of scale prevention is that the use of phosphate left the concrete somewhat more susceptible to corrosion. The addition of orthophosphate also increased aluminum leaching from concrete at levels of concern relative to the SMCL.

#### **3.4.2 Comparison of Zinc and Non-zinc Corrosion Inhibitors**

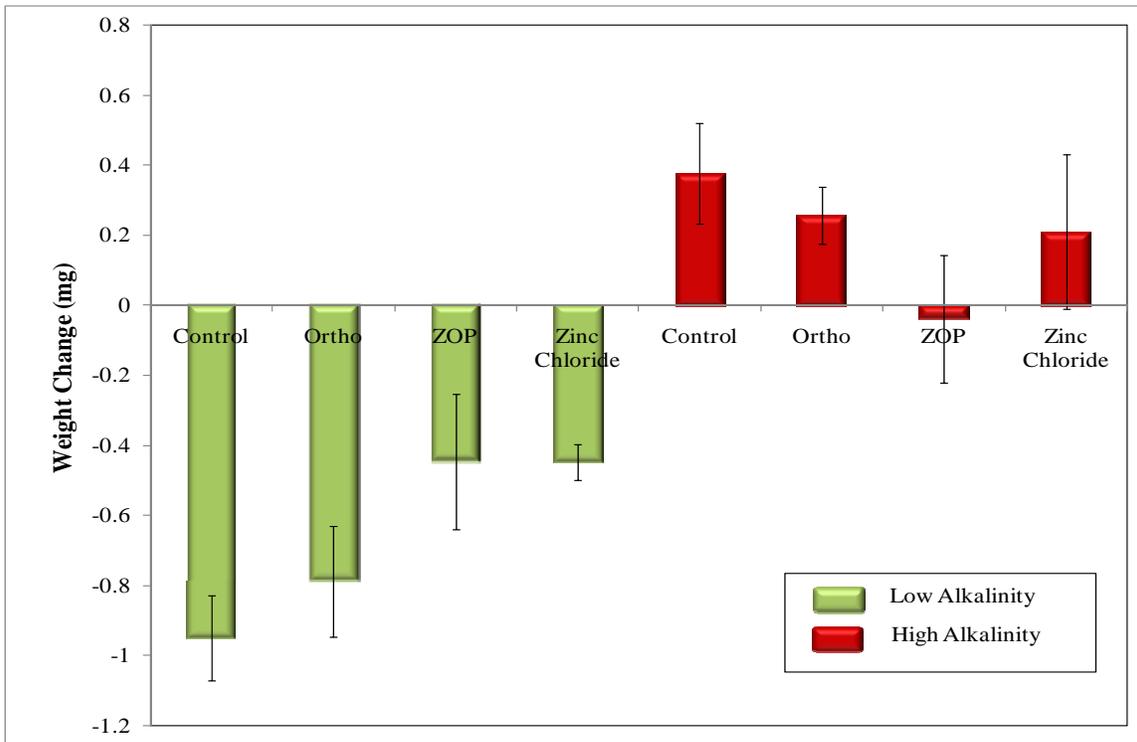
It has been hypothesized that zinc controls concrete corrosion by formation of hydrozincite ( $Zn_5(CO_3)_2(OH)_6$ ). Three zinc inhibitor concentrations (0.25 mg/L, 0.5 mg/L and 1 mg/L as Zn) were tested to better understand the effects of zinc on concrete corrosion (Table 3.2). The concrete coupons were air dried after testing as in the

phosphate inhibitor tests. The concentration of calcium in the test water at the end of the testing period was used as an important secondary indicator to track concrete corrosion.

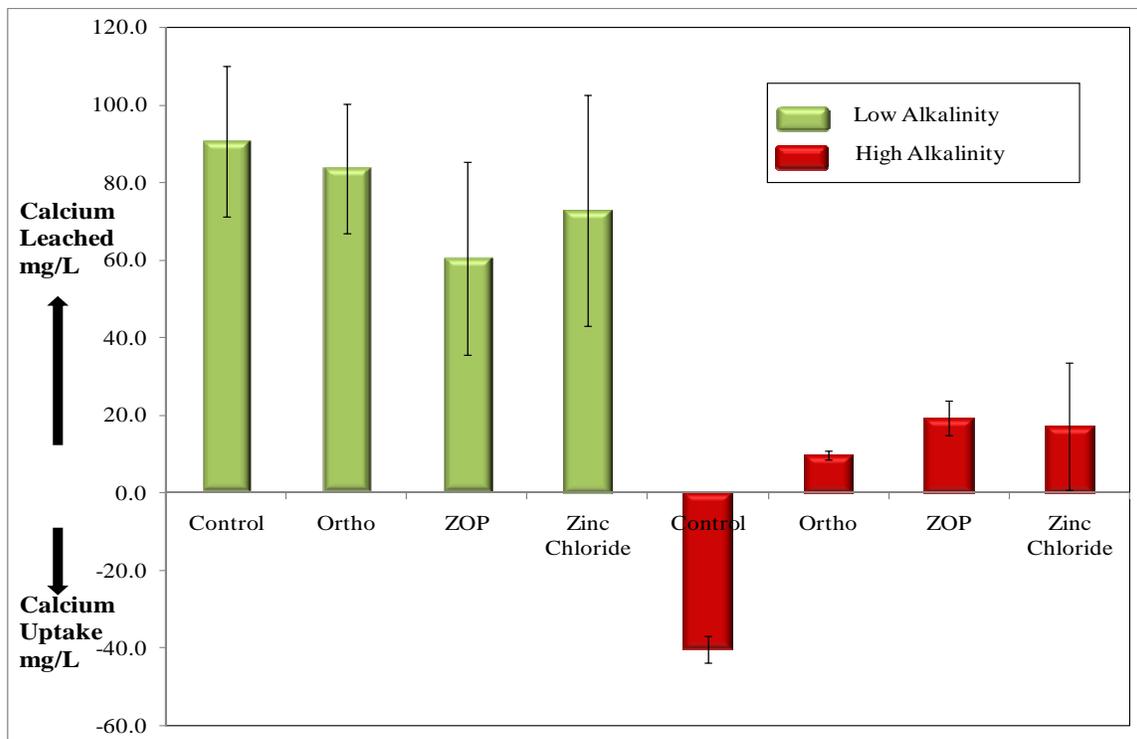
In low alkalinity and low pH waters, ZOP (0.25 mg/L Zn + 2 mg/L PO<sub>4</sub>) and zinc chloride were similar at controlling concrete corrosion. Both zinc chloride and ZOP nearly halved the weight loss of the coupons relative to the situation without inhibitor (Figure 3.11). They also reduced calcium leaching and silicon leaching under these conditions, albeit to a lesser extent (Figure 3.12 and 3.13). Under the same conditions, ZOP ensured substantial (and statistically significant) reduction in the leaching of aluminum (Figure 3.14), dropping the aluminum below the EPA SMCL (0.05-0.2 mg/L). Thus, it is clear that use of zinc does contribute to concrete corrosion control.

Measurements of zinc concentration indicate substantial precipitation of zinc added to bulk water, presumably by uptake to the concrete coupons (Table 3.4). For comparison, over the six week testing period a total of 32 mg zinc was added to the test rigs. Of this, almost three quarters was removed from the water during the low alkalinity test (~22-27 mg). Therefore, a considerable portion of the added zinc precipitated over the course of this study (Table 3.4). Zinc concentrations as low as 0.25 mg/L can help mitigate concrete corrosion in aggressive water conditions.

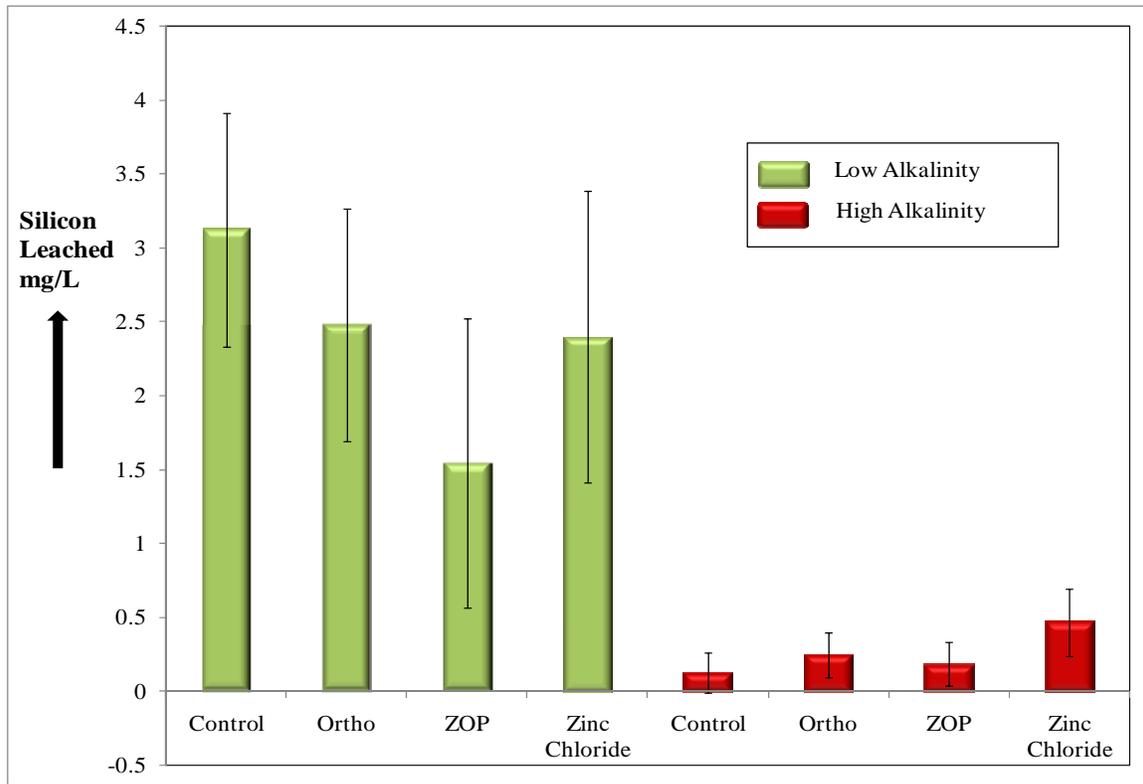
Conversely, at high alkalinity and low pH conditions, there was no significant uptake of zinc from solution. Zinc alone was not as effective as phosphate in inhibiting calcite precipitation. Under these conditions aluminum concentration was always below the lower SMCL limit for aluminum and the addition of inhibitors did not improve or worsen the situation (Figure 3.14). At high alkalinity and low pH conditions, water was not as corrosive as the low alkalinity condition, and there was only a small amount of calcite precipitation. Addition of ZOP under these conditions inhibited calcite precipitation and actually allowed net calcium leaching to the water from concrete (Figure 3.12). Weight change data for these conditions show that addition of ZOP caused greater reduction in calcite precipitation than either zinc or phosphate alone, without detectable weight/loss (Figure 3.11). Overall, addition of zinc under these high alkalinity-low pH conditions could be detrimental to concrete longevity, because it increased calcium leaching.



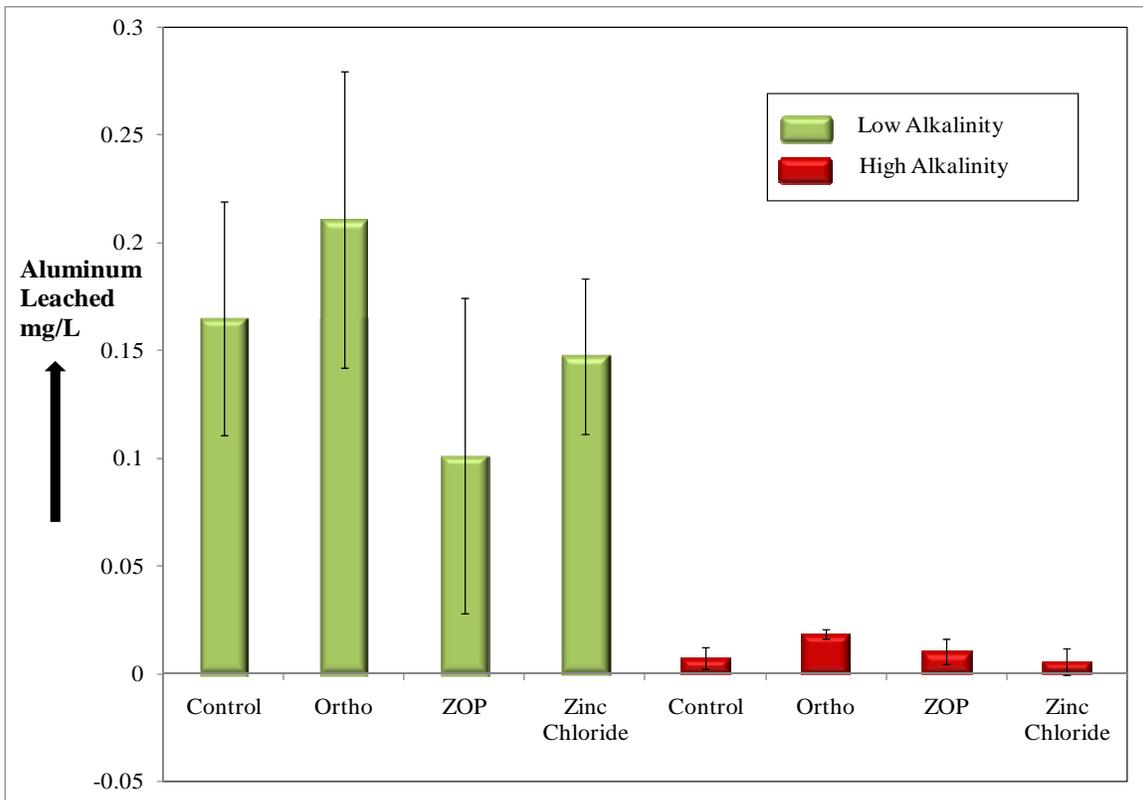
**Figure 3.11.** Comparison of average weight change data for zinc and non-zinc corrosion inhibitors at pH 7. Error bars indicate 95% confidence intervals.



**Figure 3.12.** Calcium leached/precipitated from coupons over last 3 weeks of Phase I (pH 7).

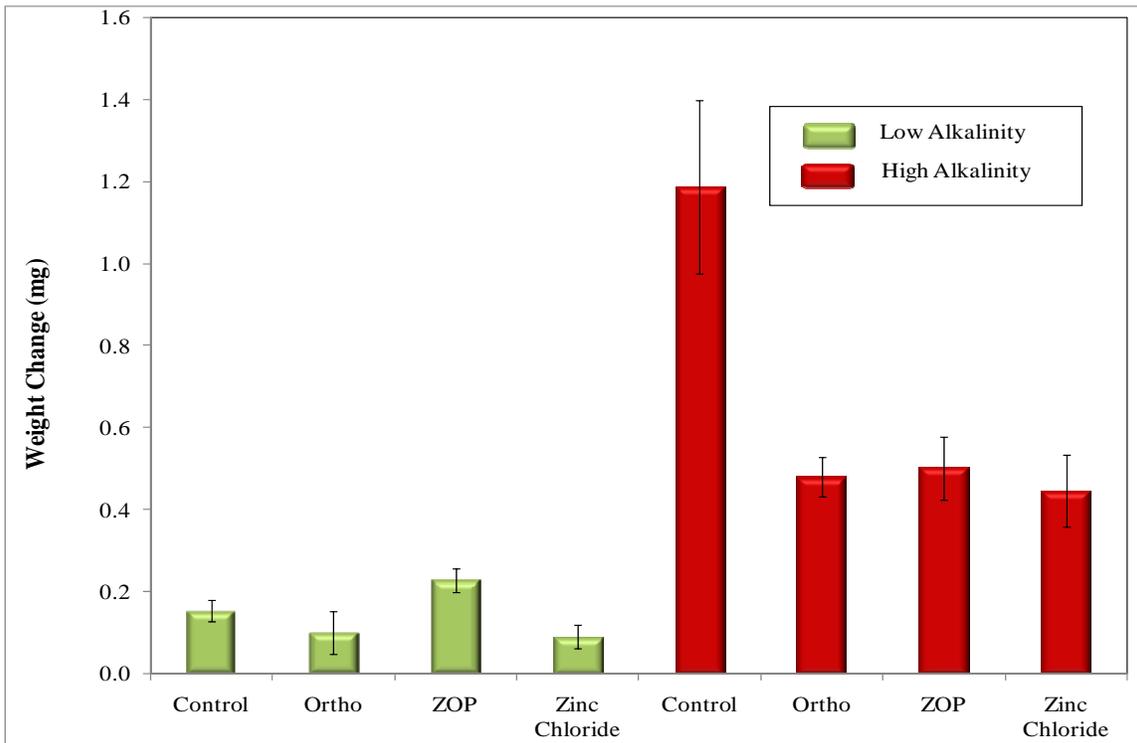


**Figure 3.13. Silicon leached from coupons over last 3 weeks of Phase I (pH 7).**

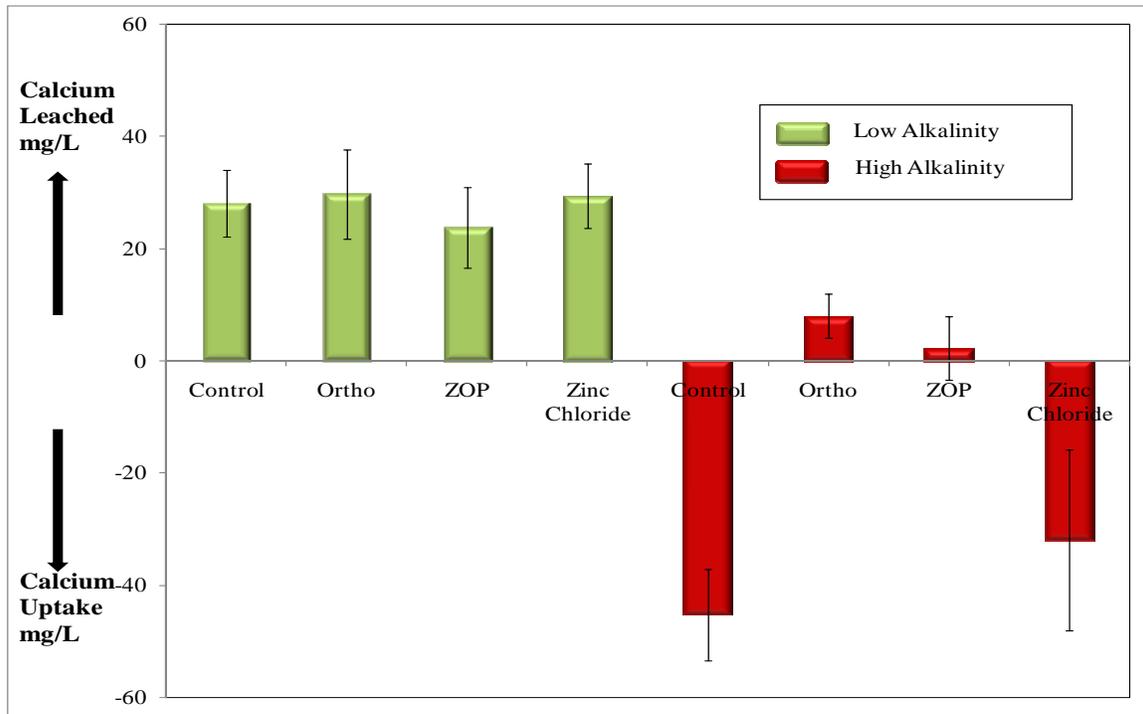


**Figure 3.14. Aluminum leached from coupons over last 3 weeks of Phase I (pH 7).**

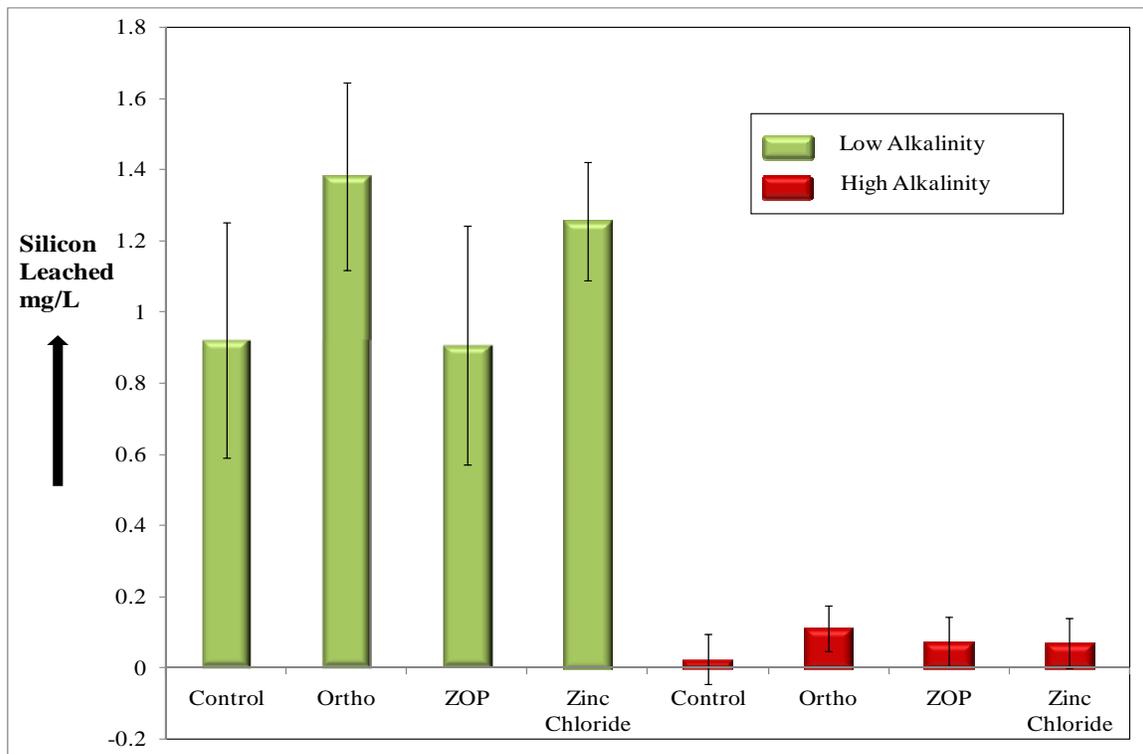
Though a combination of low alkalinity and high pH is not as aggressive to concrete as low alkalinity and low pH, these conditions can nonetheless cause weight loss. However, zinc did not have a significant role in reducing lime leaching/mitigating corrosion of concrete, since orthophosphate, ZOP and zinc chloride behaved similarly (Figure 3.16). In the case of phosphate inhibitors at low alkalinity, carbonation of concrete coupons was observed, causing an increase in the weight of the coupons (Figure 3.15). The same was observed even in the presence of zinc (Figure 3.15). The inference is that at high alkalinity and high pH, zinc has no role in inhibiting calcite precipitation or reducing scaling problems. In high alkalinity and high pH conditions zinc precipitated (~30 mg from Table 3.4) along with calcite and therefore did not inhibit calcite precipitation (Figure 3.16). Calcium leached under passive water conditions in the presence of 0.25 mg/L zinc chloride (~200 mg/L from Figure 3.16). Under high pH and high alkalinity conditions, the concentration of aluminum was always lower than the EPA SMCL limit as in the high alkalinity and low pH conditions (Figure 3.18).



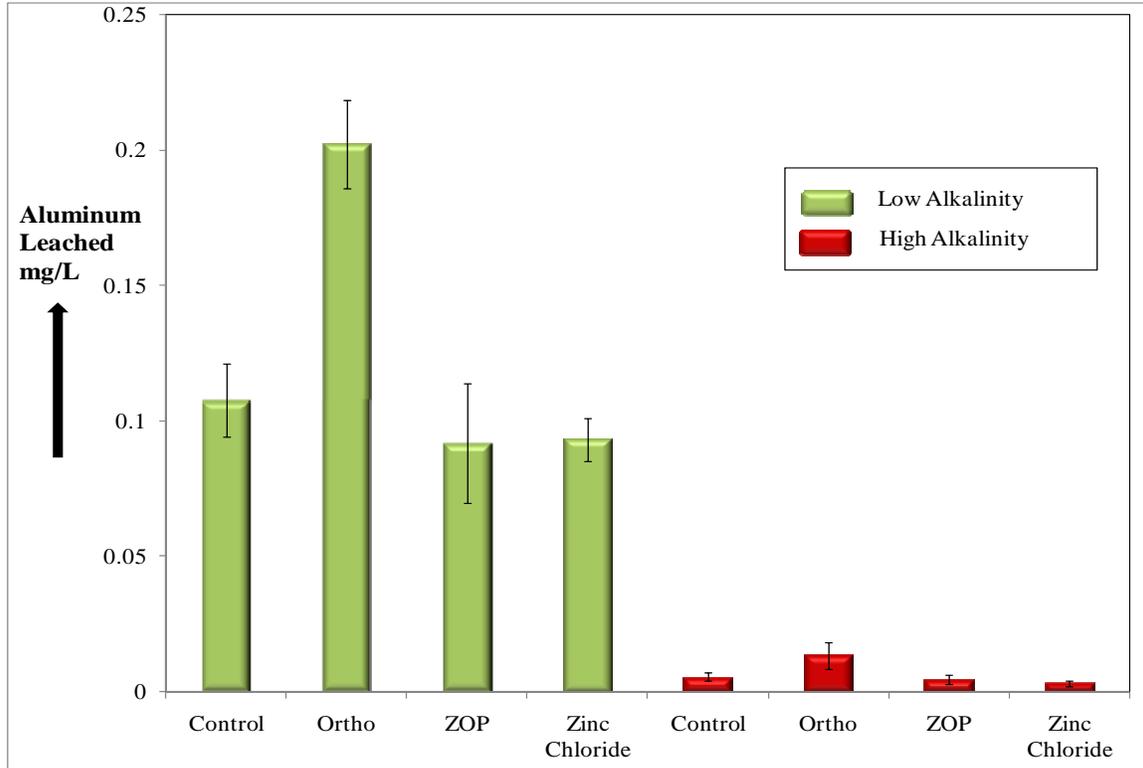
**Figure 3.15.** Comparison of average weight change data for zinc and non-zinc corrosion inhibitors at pH 8.3. Error bars indicate 95% confidence intervals.



**Figure 3.16.** Calcium leached/precipitated from coupon over the last 3 weeks of Phase II (pH 8.3).



**Figure 3.17.** Silicon leached from coupons over the last 3 weeks of Phase II (pH 8.3).



**Figure 3.18. Aluminum leached from coupon over the last 3 weeks of Phase II (pH 8.3).**

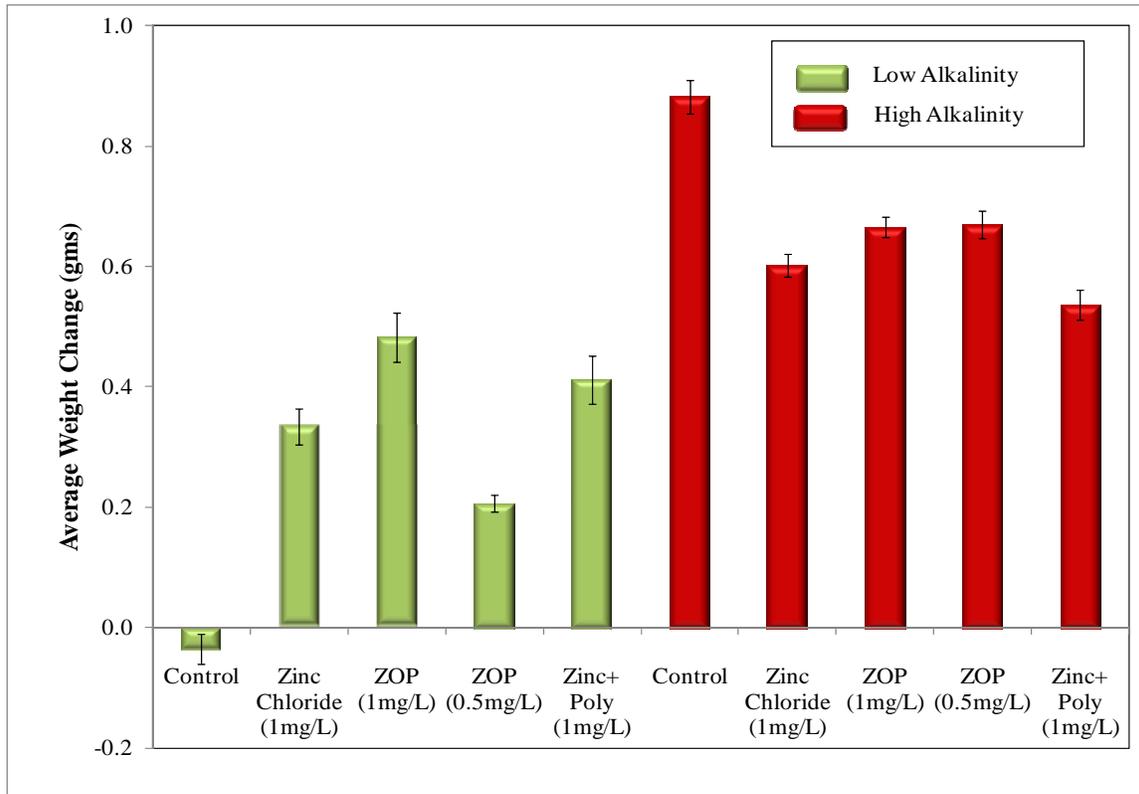
**Table 3.4. Fate of inhibitors (negative indicates precipitation of zinc or phosphate from solution, all positive numbers are very low in comparison to the initial concentration and can be considered to be ZERO for all practical purposes).**

Condition	Phase I (pH 7)		Phase II (pH 8.3)	
	P as mg	Zn as mg	P as mg	Zn as mg
Low alkalinity Orthophosphate	-6.4		-1.6	
Low alkalinity Zinc Orthophosphate	14.4	-24	-1.6	-27.2
Low alkalinity Zinc Chloride		-25.6		-22.4
High alkalinity Orthophosphate	35.2		-1.6	
High alkalinity Zinc Orthophosphate	27.2	3.2	0	-14.4
High alkalinity Zinc Chloride		-11.2		-30.4

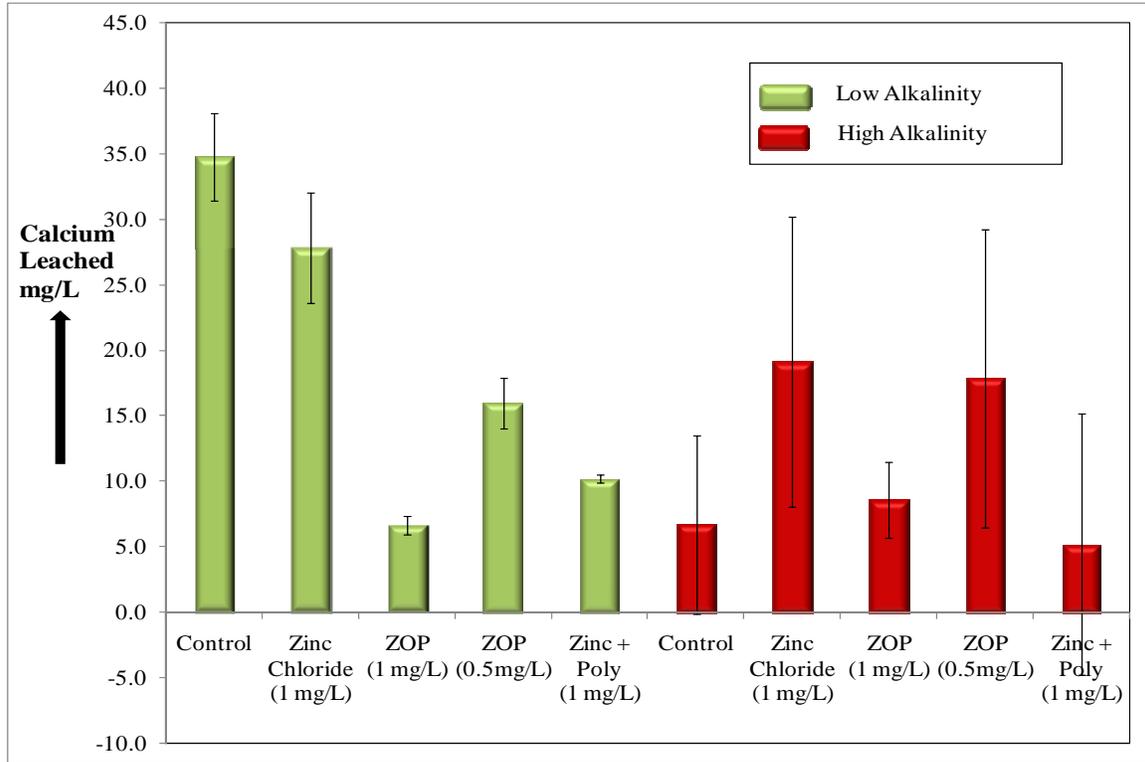
### 3.4.3 Optimal Zinc Dosage

Zinc alone was not more effective than orthophosphate in reducing scaling of calcite in high alkalinity waters at either low or high pH. Thus, it is more appropriate to use zinc inhibitors in low alkalinity waters to reduce corrosion. Two levels of zinc (1 mg/L and 0.5 mg/L as Zn) were tested as part of this study and with increased

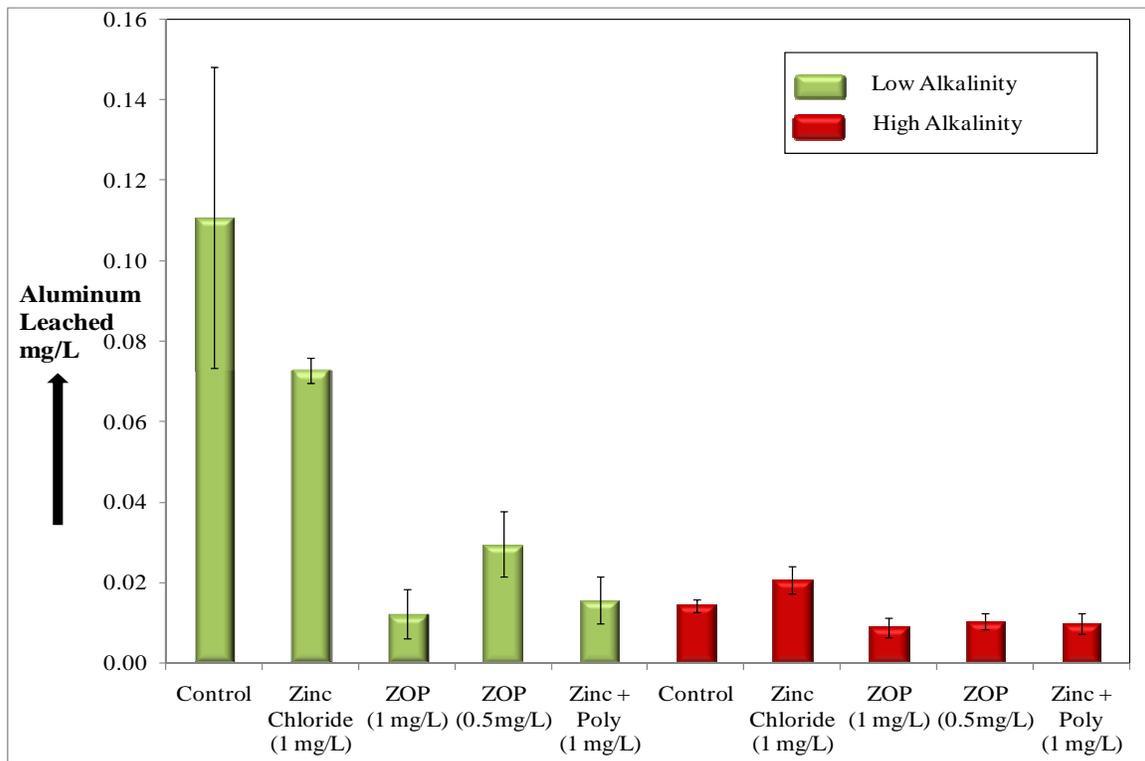
concentrations of zinc, the effectiveness of the inhibitor also improved (Figure 3.19). That is, at higher concentrations weight gain and calcium loss from coupons was less than at lower concentrations. Zinc was most effective when used along with orthophosphate. At higher concentrations of zinc (i.e. 1 mg/L) leaching of key elements like calcium and aluminum was less in comparison to the other inhibitor conditions tested (Figure 3.20 and 3.21). As the zinc dosage increased the amount of zinc precipitating from solution also increased (Table 3.5). This zinc precipitate might protect the concrete from further corrosion.



**Figure 3.19. Comparison of average weight change data for varying dosages of zinc inhibitors at pH 7. Error bars indicate 95% confidence intervals.**



**Figure 3.20. Calcium leached/precipitated from coupon over the last 3 weeks of testing.**



**Figure 3.21. Aluminum leached from coupons over the last 3 weeks of testing.**

The coupons used for this study were allowed to cure (age or harden) for almost two years longer than the coupons used for Phase I. This could also be the reason for reduced leaching and weight loss in this study in contrast to preliminary tests (in detail in sections 3.4.2 and 3.3.1). Therefore, the results from this study are used only for a comparative analysis of zinc inhibitors and control conditions.

Calcium leached from the coupons upon addition of the highest dosage of ZOP (1 mg/L Zn + 2 mg/L PO<sub>4</sub>) was 43% lower than was leached in the absence of any inhibitor (Figure 3.20). However, addition of 0.5 mg/L Zn + 2 mg/L PO<sub>4</sub> of orthophosphate reduced leaching of calcium by nearly 41% compared to the control water (Figure 3.20), while the minimum dosage of ZOP tested (0.25 mg/L Zn + 2 mg/L PO<sub>4</sub>) reduced calcium leaching by about 33% compared to the control water (Figure 3.12). From this perspective the higher zinc doses were better at protecting the concrete. Although calcium leached in all the conditions tested, there was a net gain for all conditions except for the low alkalinity control. As before, this discrepancy is attributed to carbonation of the coupons. Even though all the coupons gained weight there were clear differences in weight gain between inhibitor conditions.

**Table 3.5. Fate of inhibitors (-ive indicates precipitation of zinc and/or phosphate from bulk water).**

Condition	Phase I (pH 7)	
	P as mg	Zn as mg
Low alkalinity Zinc Chloride (1 mg/L)		-98.0
Low alkalinity Zinc Orthophosphate (1 mg/L)	-15.5	-59.4
Low alkalinity Zinc Orthophosphate (0.5 mg/L)	-18.2	-44.7
Low alkalinity Zinc Polyphosphate (1 mg/L)	-20.8	-79.2
High alkalinity Zinc Chloride (1 mg/L)		-14.4
High alkalinity Zinc Orthophosphate (1 mg/L)	-13.0	-22.5
High alkalinity Zinc Orthophosphate (0.5 mg/L)	-9.6	-14.3
High alkalinity Zinc Polyphosphate (1 mg/L)	-11.7	-14.8

### 3.5 CONCLUSIONS

- Of the two phosphate inhibitors (i.e orthophosphate and polyphosphate), polyphosphate was most effective at reducing concrete corrosion and scaling at a higher dosage of 12 mg/L. At higher pH of 8.3 neither orthophosphate nor polyphosphate were very effective at reducing corrosion.
- Zinc is an active compound in reducing corrosion of concrete, but it behaves as a better inhibitor when used in conjunction with phosphate from the perspective of corrosion control and scaling. The addition of 0.25 mg/L Zn produced a 33% reduction (in comparison to control) in calcium leaching relative to use of orthophosphate alone. .
- Increased dosing of zinc (0.5-1 mg/L Zn) provided increased protection to concrete.

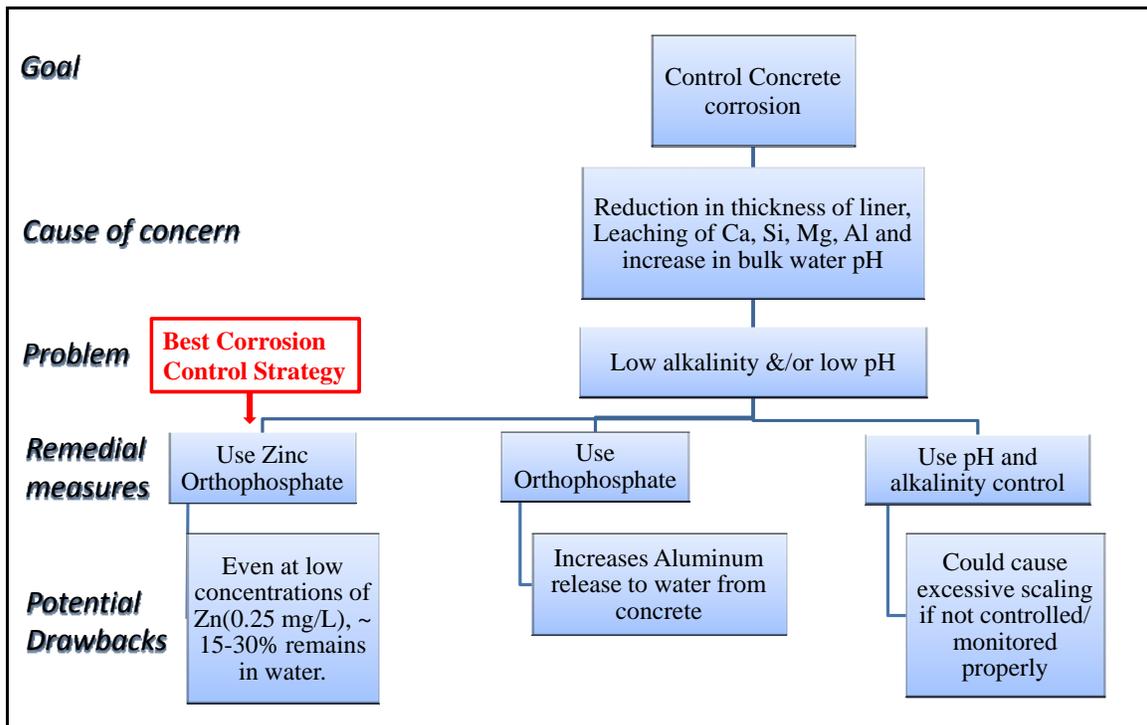


Figure 3.22. Decision tree for corrosive/ highly aggressive water conditions.

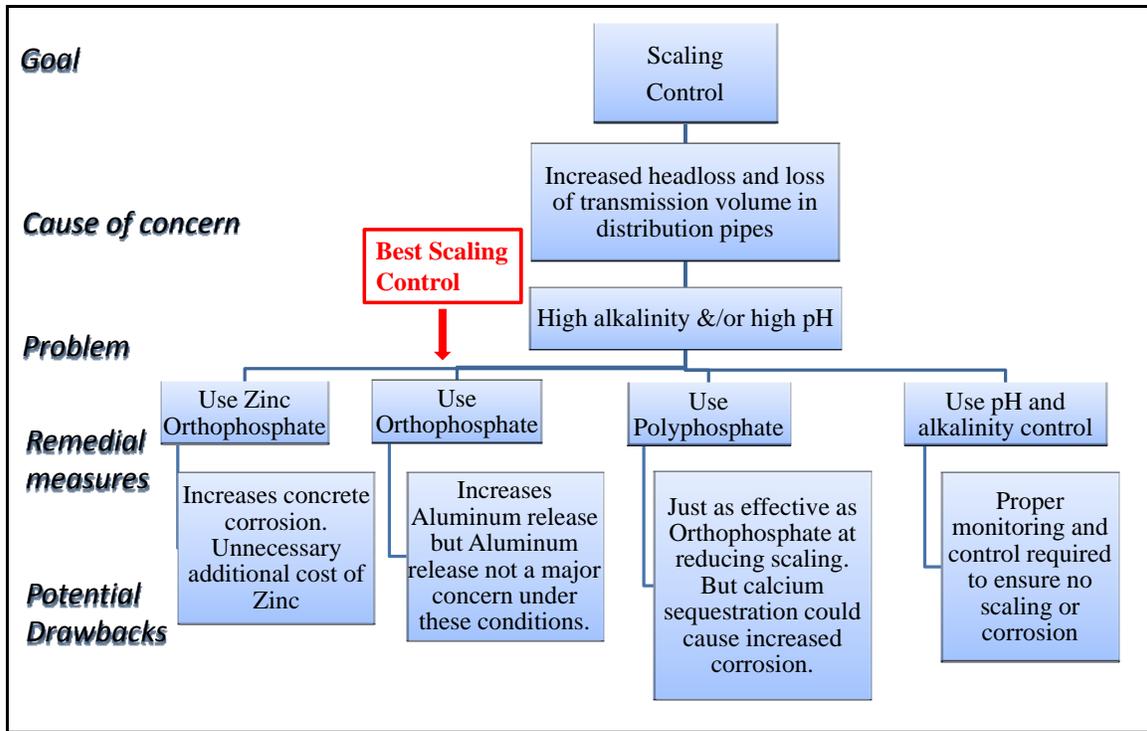


Figure 3.23. Decision tree for scaling/ passive water conditions.