RELATIVE EFFECTS OF WATER CHEMISTRY ON ASPECTS OF IRON CORROSION

Yan Zhang

Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE
In
Environmental Engineering

Dr. Marc Edwards, Chair

Dr. Andrea Dietrich

Dr. Peter Vikesland

September 13, 2005
Blacksburg, Virginia

Keywords: iron corrosion, red water, disinfectant, nitrate, sulfate/ chloride ratio, phosphorus, microbial re-growth, nutrient, iron pipe, corrosion

RELATIVE EFFECTS OF WATER CHEMISTRY ON ASPECTS OF IRON CORROSION

Yan Zhang

ABSTRACT

The net present replacement value of all publicly and privately owned potable water pipes in the U.S. is on the order of $2.4 trillion dollars, and costs associated with deteriorating iron pipes is billions of dollars per year. Problems arising from iron corrosion include reduced lifetime of the material, scale buildup and energy loss, non-uniform corrosion and leaks, catastrophic failure, "red water," disinfectant loss and bacterial re-growth. Iron corrosion is a very complicated process and is affected by many factors. This research focused on the effect of disinfectant type, sulfate/chloride ratios, nitrate concentration, and magnesium hardness on iron corrosion. For the waters tested, chlorine better controlled red water and microbial activity in the bulk solution than chloramine. Changes in the sulfate/chloride ratio did not have a large effect on iron corrosion. High levels of nitrate increased the rate of chlorine decay as a result of free ammonia formation, and also increased the release of iron. Increased magnesium and zinc decreased the red water caused by high silicate.

Microbiological activity is important in iron corrosion, and control of re-growth in water distribution systems is a major challenge for water utilities. A separate study examined the inter-relationship between iron corrosion and bacterial re-growth, with a special focus on the potential of iron pipe to serve as a source of phosphorus. Under some circumstances corroding iron and steel may serve as a source for all macronutrients

necessary for bacterial re-growth including fixed carbon, fixed nitrogen and phosphorus. Conceptual models and experimental data illustrate that levels of phosphorus released from corroding iron are significant relative to that necessary to sustain high levels of biofilm bacteria. Consequently, it may be more difficult to limit re-growth on iron surfaces by limiting phosphorus in the bulk water.

ACKNOWLEDGEMENTS

I would like to give special thanks to my advisor, Dr. Marc Edwards for his guidance and insight and his confidence in me in this field. I also want to thank the members of my committee, Dr. Andrea Dietrich and Dr. Peter Vikesland for their advice and assistance. And I also would like to thank Dr. Siyuan Chen Morton, who taught me many good research skills. Additionally, I would like to thank all the members of my research group for their laboratory assistance, advice, and friendship.

And finally, thanks to my family and friends for their support and encouragement to accompany me through the good and hard times in these two years.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

AUTHOR'S PREFACE

This study investigated several important factors affecting iron corrosion and the inter-relationship between iron corrosion and microbial regrowth in two separate studies. The author's focus was on Chapter 1- investigating the effect of disinfectant, sulfate/chloride ratios, nitrate concentration and magnesium hardness on iron corrosion. As part of the author's master's work, for Chapter 2, the author's work was building the theoretical nutrient comparison model and assisting in experimental and data analysis, but it must be recognized that Dr. Siyuan Chen Morton was the major contributor to this work, who did the data interpretation, comprehensive understanding, and overall summarizing and writing.

Chapter 1 further explored the existing knowledge of the influential factors on iron corrosion, including disinfectant, sulfate/chloride ratio, nitrate, natural organic matter, calcium, magnesium and zinc. Saturated and low oxygen conditions; with and without the inoculation of sulfate reducing bacteria were investigated to better illustrate different iron corrosion behavior under different circumstances.

Chapter 2 brought forward an innovative idea that iron pipe could serve as the nutrient source for microbiological regrowth in distribution system. Conceptual models and experimental data illustrated that levels of phosphorus released from corroding iron are significant relative to that necessary to sustain high levels of biofilm bacteria.

CHAPTER I: EFFECT OF SULFATE: CHLORIDE RATIO, MAGNESIUM HARDNESS, ZINC, NITRATE AND DISINFECTION ON IRON CORROSION AND RED WATER.

Yan Zhang and Marc Edwards

ABSTRACT

This study investigated the effect of disinfectant, sulfate/chloride ratios, nitrate concentration and magnesium hardness on iron corrosion. For the waters tested, free chlorine better controlled red water and microbial activity in the bulk solution. Surprisingly, sulfate/chloride ratio changes did not have an effect on iron corrosion. High levels of nitrate increased the rate of chlorine decay and released more iron, but had no effect on chloramine decay rates. Increased magnesium and zinc can decrease the red water caused by silicate.

INTRODUCTION

The net present replacement value of all publicly and privately owned potable water pipes in the U.S. is on the order of $2.4 trillion dollars (1). Unlined iron mains, lined iron mains with coatings that have deteriorated over years of use, and galvanized pipe in homes are representative of iron pipe surfaces that can corrode via direct contact with potable water. Problems arising from iron corrosion include reduced lifetime of the material, scale buildup and energy loss, non-uniform corrosion and leaks, catastrophic failure, "red water," disinfectant loss and bacterial re-growth (2).

The total corrosion rate of the iron metal is best represented by overall weight loss of the pipe. To the extent that the weight loss is non-uniform over the surface, the useful lifetime of the pipe can be further decreased, since pits can form holes more quickly in the pipe and cause leaks. Corroded iron can either be released to the water as dissolved or particulate iron (e.g., red water), or it can remain on the pipe surface as a scale (e.g. rust).

Chlorine versus Chloramine

Chlorine disinfectants have been widely and effectively used to protect the safety of drinking water since 1913 in the U.S. (3). Generally, increased concentrations of disinfectant (oxidants) would be expected to increase iron corrosion rates (2, 4). But older work by Baylis (5) and more recent work by others (6, 7) suggest that increased oxidant (including chlorine disinfectant) concentration can reduce the amount of iron released to water if corrosion scales are present. The more recent work did not address the effect of disinfectants on corrosion rate.

Due to concern over suspected carcinogens formed by chlorine use, water utilities are increasingly switching from chlorine to chloramine (e.g., chlorine combined with ammonia) for residual disinfection. In relation to the critical and costly issue of infrastructure degradation, there is concern in the water industry about the effect of the switch on the lifetime of distribution system assets. Substantial economic losses or gains will be accrued dependent on whether chloramines increase or decrease performance of pipes relative to free chlorine.

Conflicting trends have been reported in the few studies that examined the role of disinfectants in iron corrosion rates to date. LeChevallier et al., 1990 (8) reported a

beneficial effect of chloramines versus chlorine on iron corrosion rates, Treweek et al., 1985 (9) reported no visual and weight loss difference between chlorine and chloramines, but Eisnor and Gagnon et al., 2004 (10) found chloramines caused a higher corrosion rate than free chlorine. The Eisnor study also measured iron release to water and found that both chlorine and chloramines increased total and dissolved iron compared to no disinfectant, and the increase is more significant with chlorine.

This consideration should not be construed as criticism of the earlier work, but only as an attempt to place the conclusions in proper perspective. All corrosion testing has limitations and it is worthwhile to consider these relative to the above research (Table 1). LeChevallier's focus was on disinfection of biofilms and the work was conducted with a synthesized water containing very high assimilable organic carbon (as glucose), very low nitrogen, relatively high phosphorus, very low calcium, and no silica (Table 1). There is also the possibility that inclusion of copper pipe in the test rig exerted some influence on the results obtained, since cupric ions can sometimes accelerate iron corrosion via deposition corrosion reactions that are poorly understood (2). The authors also purposefully used a very high molar ratio of NH_3: Cl_2 of 3:1 to form monochloramine exclusively, as opposed to the 1:1 ratio more commonly used in practice. Finally, iron corrosion rates were tracked electrochemically, an approach which can have relatively high error relative to weight loss measurements (11). The Treweek and Eisnor studies were of longer duration, but used real water and temperature was also varied (Table 1-1). In terms of pipe material, the LeChevallier study used new iron pipes, whereas old tuberculated pipes were used in the Eisnor's study and new black iron was used by Treweek et al. (Table 1-1).

Table 1-1: Different test conditions on the effect of disinfectants on iron corrosion

	Lechevallier et al. 1990(8)	Treweek et al. 1985 (9)	Eisnor and Gagnon et al. 2004 (10)
Corrosion Rate	Free chlorine is more corrosive than monochloramine	No difference between free chlorine and monochloramine	Monochloramine had higher corrosion rate than free chlorine
Iron Release	Not measured	Not measured	Total and dissolved iron
Metal type	New 0.5 inch iron pipes in a rig connected to galvanized, copper and PVC pipes by PVC couplings.	New black iron pipe inserts	100 years old, heavily tuberculated cast iron pipes, 2.4 inch diameter
Test duration	2 weeks	18 months, 0.6 m/s flow velocity,	220 days, 0.3 m/s flow rate
Monochloramine preparation recipe	3:1 molar ratio of ammonia to chlorine	Not mentioned	1ml 5% sodium hypochlorite and 216mg NH4Cl (about 1:1 molar ratio)
chlorine dose	4 mg/L	1 mg/L	0.5-1 mg/L/L
chloramine dose	4 mg/L	around 1 mg/L	1.0-2.0 mg/L
Water chemistry	Synthesized water with 0.57 mg/L-TOC as glucose, 0.52 mg/L- PO_4, 0.01 mg/L-$MgSO_4 \cdot H_2O$, 0.01 mg/L $(NH_4)_2SO_4$, 0.01 mg/L NaCl, 1 µg/L $CaCl_2$, 0. 1 µg/L $FeSO_4$, no silica	Real water with <15 mg/L $CaCO_3$ hardness, < 20 mg/L $CaCO_3$ alkalinity, 9 mg/L silica, < 2.5 mg/L-chloride, <5 mg/L- sulfate, < 0.3 mg/L-Fe, < 1.2 mg/L-Mg, unknown PO_4	Filtered real water with polyphosphate-0.8 mg/L, 1.4 mg/L-TOC, 10 mg/L $CaCO_3$ hardness, 0.02 mg/L-Fe, > 10mg/L $CaCO_3$ alkalinity, unknown Silica, magnesium, ammonia, sulfate, chloride.
pH	7	neutral to slightly acidic range	8
Temp	25°C	Seasonal change	10-25°C, increase during the experiment
Measurement of iron corrosion	New carbon steel electrodes	Weight loss and scale morphology	New carbon steel electrodes and iron release

Aerobic and Anaerobic Iron Corrosion.

Iron corrosion can proceed through anaerobic (e.g., via reduction of water and H_2 evolution) and aerobic pathway (e.g., reduction of oxygen), and the aerobic path has always been presumed to be more important (12, 13). But the anaerobic pathway can be also significant. Speller et al., 1951 (14) reported that about 3-5 % of the total iron corrosion can proceed through anaerobic pathway and Rushing et al., 2003 (15) reported a percentage of at least 0.1-5 %. These results were obtained when oxygen was present at saturation with the atmosphere. Both Speller (14) and Rushing's (15) estimates are actually a lower bound to actual percentage of iron corrosion by the anaerobic pathway, because measured H_2 that is produced by the process can be consumed through a variety of reactions. SRB were not present in these studies, which may be significant given the likelihood they accelerate anaerobic corrosion (16).

Biological activity and Natural Organic Matter (NOM)

Microorganisms are found in most pipe materials and have the best growth in reactive surface such as iron pipes (17, 18). Various bacteria exist in the distribution system, including sulfate reducing bacteria, iron bacteria and nitrifying bacteria (19, 20). These bacteria can affect iron corrosion through the following pathways, (1) adsorption of nutrients (including oxygen) resulting in differential aeration and concentration of cells; (2) Liberation of corrosive metabolites (e.g., ammonia, organic acids, carbon dioxide, and hydrogen sulfide); (3) production of sulfuric acid from more reduced sulfur compounds; and (4) corrosion by anaerobic bacteria such as sulfate-reducing bacteria (20). The role of these bacteria in iron pipes is mixed but is generally considered to be detrimental to most

aspects of iron corrosion (2). Higher levels of bacteria are also believed detrimental to water quality.

Natural organic matter (NOM), a potential carbon source for microorganisms, is expected to increase iron corrosion if bacteria present were to increase corrosion (17). But studies found that NOM decreases iron corrosion (21, 22). Two possible reasons include the fact that natural organic matter is mostly composed of relatively non-degradable organics, and NOM has been found to encourage a more protective scales on pipes under some circumstances (21, 23).

Sulfate Reducing Bacteria and Larson Index.

For over 60 years sulfate-reducing bacteria (SRB) has been regarded as the most important contributor to anaerobic corrosion (24). SRB have been identified in scale layers present on iron pipes in every water distribution system where such tests have been conducted, and there is reason to believe they contribute to iron corrosion. For instance, corrosion scale from the Boston water distribution system contained as much as 3 % S by weight (25), the tubercle deposits collected from Columbus Ohio pipeline contained 26 % S by weight, and 80 % of the samples were positive for SRB (26, 27). More recently Lytle et al., 2004 (28) reported the presence of sulfur in iron pipe scale. These results strongly support the potential importance of SRB and the anaerobic contribution to iron corrosion in water distribution systems.

The studies of Larson (29, 30, and 31) found that the ratio of chloride and sulfate to bicarbonate was practically important to iron corrosion, as expressed in the Larson Index:

$$\text{Larson Index} = \frac{2[SO_4^{2-}]+[Cl^-]}{[HCO_3^-]}$$

where concentrations are expressed in mol/L. A higher Larson Index is believed to indicate a more aggressive water to iron, especially in the context of pitting. Several studies qualitatively confirmed these results by reporting that increased chloride (32, 33) and sulfate (33, 34) caused increased weight loss.

Strong base anion exchange, expected to be installed as a new treatment for arsenic removal at utilities around the country, can remove some bicarbonate, and replace the sulfate with chloride. To the extent that each mole of SO_4^{2-} is replaced by 2 moles of Cl^-, Larson's ratio will remain constant. If HCO_3^- is replaced by Cl^-, Larson's ratio will increase. While a higher Larson's index is generally expected to worsen iron corrosion, if sulfate reducing bacteria were a key contributor to the problem, complete removal of the sulfate required for their growth might be beneficial. Specifically, sulfate reduction by SRB has been reported to stop below a level of 0.48-1.92 mg/L-SO_4 (35). It is therefore speculated that the net effect of strong base anion exchange in a given circumstance could depend on the extent of SRB activity.

Likewise, phosphate and humic substances can also be removed by anion exchange, and lack of these two nutrients might possibly limit SRB and other microbial contributions to corrosion. The results of Okabe et al. 1992 (36, 37) and Weimer et al., 1988 (38) strongly support the general idea that SRB growth and iron corrosion can be limited by availability of organic matter and phosphate, albeit in waters that are unrepresentative of potable waters. Nutrient limitations for SRB in potable water have never been defined (12, 13) as most previous research was conducted in media with extremely high levels of nutrients. It is also possible that the presence of sulfate in the numerator of the Larson's index is unwittingly capturing the role of sulfate in growth of

SRB, which in turn produces adverse consequences for iron corrosion. If that were the case, removal of sulfate, phosphate and the organic matter might benefit overall iron corrosion, even if it were replaced by chloride. The relative importance of chloride and sulfate has never previously been tested in the presence or absence of SRB.

Phosphate

Phosphate based inhibitors have been added to drinking water since the early 1900s to prevent iron corrosion and red water problems (2). However, the actual effect of phosphate inhibitor to iron corrosion varied widely. Some studies found phosphate could prevent corrosion and control red water (2). Others reported the addition of phosphate did not decrease iron corrosion or in fact was detrimental to iron corrosion (39, 40, and 41). A possible explanation proposed by McNeill and Edwards et al., 2000 (41) is that polyphosphate leads to increased scale build-up in stagnant waters thus causing the negative action under this condition.

Zinc

Zinc is blended into phosphate inhibitors to introduce better inhibition performance because the addition of zinc was reported to decrease corrosion compared to regular poly- or orthophosphates (42, 43, 44) However, several studies found no benefit of zinc phosphates compared to regular phosphates(44). No study has been found that demonstrated an effect of zinc alone on iron corrosion.

Calcium and Magnesium.

The presence of calcium and magnesium are thought beneficial to iron pipes. One reason is that the precipitation of a thin layer of calcite (calcium carbonate) and magnesium could protect iron pipes from further corrosion. Many papers have been

dedicated to extolling the virtues of calcite layers (2), although the use of the Langelier index has been largely discredited as a predictor of iron corrosion tendencies (8). Magnesium can form very insoluble compounds with silica (45, 46), which might decrease the red water problems caused by the presence of high silica while in the absence of hardness (15).

Nitrate.

The corrosion reaction between iron metal and nitrate has been used to remediate nitrate contaminated water since the 1990s (47):

$$4\ Fe^{\circ} + NO_3^- + 10\ H^+ = 4\ Fe^{2+} + NH_4^+ + 3H_2O \qquad \text{Equation 1}$$

Nitrate is nearly stoichiometrically converted to ammonia by iron corrosion (48). We note that the ammonia produced could affect the iron corrosion process when disinfectant is applied for the following reasons:

1. Ammonia can react with free chlorine to form chloramine.
2. When ammonia is produced in small amount, breakpoint chlorination could occur,

   $2\ NH_3 + 3\ Cl_2 = N_2 + 6\ Cl^- + 6\ H^+$ (48). Breakpoint chlorination would therefore remove chlorine disinfectant and impact biological activity.
3. Since ammonia is a better source of nitrogen than nitrate for most bacteria, the ammonia produced could trigger microbial growth and iron corrosion.

This work conducted 4 sets of experiments to shed light on the role of the above factors in aspects of iron corrosion in a synthesized potable water.

MATERIALS AND METHODS

Iron sample preparation

The iron samples were cylindrical pieces of cast iron coupons, each 2.5 cm in diameter and 1.9 cm length (Grammer, Dempsey & Hudson, Inc, Newark, NJ). The iron samples were coated with epoxy (Epofix Resin, Struers, Westlake OH), leaving only the top polished surface exposed.

Aerobic and anaerobic iron corrosion (no SRB inoculation)

Iron release and iron corrosion were assessed using an apparatus similar to that described by Rushing et al., 2003 (15). The reactors used for O_2-saturated apparatus were 11 cm tall Cambro 2 L polycarbonate container with 1.6 L solution. The water was continuously stirred with a 61 mm $\times$ 28 mm floating stir bar rotating at 375 rpm.

The reactors used for low O_2 apparatus were 14 cm tall Nalgene 1 L polycarbonate containers with screw on plastic caps. Two sampling ports were opened on each cap and were sealed when not in use. All containers were relatively air tight, as confirmed by a pressure test after filling them with air in a water bath and confirming low rate of gas leakage. The test at low O_2 was undertaken after purging the water and headspace with nitrogen, although no attempt was made to make the low O_2 condition completely anaerobic. The solution volume of each container was 0.8 L. The water was continuously stirred with a 54 mm $\times$ 28 mm floating stir bar rotating at 600 rpm. The reactors were kept in a 20° C constant temperature room.

Eight different conditions were evaluated in tests at saturated and low O_2 conditions (Table 1-2). Also, a separate O_2-saturated experiment was conducted to further investigate the effect of magnesium (Table 1-3). The control waters were synthesized

from nanopure de-ionized water to which the listed reagent grade salts were added. The variations listed from the control in the Table were constituted by adding extra or lesser amounts of the appropriate salts.

The natural organic matter was made by systematically cleaning Aldrich humic acid (50). Humic was first dissolved into 5 N NaOH, centrifuged, and the pellet was discarded. The supernatant was then adjusted to below pH 1 using concentrated hydrochloric acid, centrifuged, and supernatant was discarded. The procedure was repeated 3 times, at the end of which the solid pellet was dissolved in de-ionized water with final pH 4.0. Monochloramine was formed with a 1:1 molar ratio of ammonia and chlorine. DPD testing (USEPA accepted for reporting water and wastewater) confirmed less than 0.2 mg/L free chlorine and 4 mg/L total chlorine initially present in the water for this condition. Initial pH was adjusted to 8 ± 0.2 using 1 N hydrochloric acid or 1 N sodium hydroxide. Water in each reactor was replaced weekly and the chlorine/chloramine residual was maintained daily.

Table 1-2: Test conditions for water with saturated and low oxygen, no SRB inoculation

Reactor	Water Chemistry
1.1	control (100 mg/L as $CaCO_3$ alkalinity + 100 mg/L- SO_4^{2-} + 100 mg/L Cl^- + 20 mg/L-Si)
1.2	control + 0.2 mg/L natural organic matter (NOM)
1.3	control + 0.2 mg/L NOM + 20 mg/L Ca^{2+} (substitute for same mol of Na^+)
1.4	control + 0.2 mg/L NOM + 20 mg/L Ca^{2+} + Na_2HPO_4 as 1 mg/L-P
1.5	control + 0.2 mg/L NOM + Mg^{2+} (substitute for same mol of Na)
1.6	control + 0.2 mg/L NOM + 20 mg/L Ca^{2+} + 1 mg/L Zn^{2+}
1.7	control + 0.2 mg/L NOM + 20 mg/L Ca^{2+} + 3 mg/L Cl_2
1.8	control + 0.2 mg/L NOM + 20 mg/L Ca^{2+} + 5 mg/L monochloromine

Table 1-3: Test conditions to examine effects of magnesium, no SRB inoculation

Reactor	Water Chemistry
2.1	control (100 mg/L as Ca CO_3 alkalinity + 100 mg/L- SO_4^{2-} + 64 mg/L Cl^- + 20 mg/L-Si + 0.2 mg/L-C natural organic matter)
2.2	control + 3 mg/L-Mg $MgCl_2$
2.3	control + 12 mg/L-Mg $MgCl_2$
2.4	control + 25 mg/L-Mg $MgCl_2$
2.5	control + 25 mg/L-Mg $MgCl_2$ + 20 mg/L-Ca $CaCl_2$
2.6	control + 25 mg/L-Mg $MgCl_2$ + 20 mg/L-Si
2.7	control + 20 mg/L-Ca $CaCl_2$
2.8	control - 20 mg/L-Si + 25 mg/L-Mg $MgCl_2$

Iron in the water was measured by collecting samples daily from each reactor. "Soluble" iron was operationally defined by filtration though a 0.45 μm pore size filter,

but it is understood that this method does not remove all colloidal species from the soluble fraction. The samples were digested with 4 % hydrochloric acid and 2 % hydroxylamine before quantifying iron on an Inductively Coupled Plasma Emission Spectrophotometer (ICP-ES) according to standard method 3120 B (51). The O_2 saturated experiment lasted 77 days, the test on Mg effect lasted 35 days and the test at low O_2 lasted 46 days. Scale morphology and composition and weight loss were determined at the end of the test. After drying the iron coupons in a 90°C oven for 48 hours, scales were removed from the coupons with scraping tool and Dremel tool and collected from the coupons. 100 mg of scale from three coupons in each reactor was placed in 100 ml water and digested with 4 % hydrochloric acid and 2 % hydroxylamine at 90 °C until all the insoluble particles became soluble and invisible. Digested samples were analyzed on the ICP-ES for determining major constituents in the scale.

Iron corrosion with active SRB

The same apparatus and general procedure as above were used, but with inoculation of SRB isolated from an 80 year old iron pipe from the distribution system of the Washington Surburban Sanitation Commisssion (WSSC). This utility has always used free chlorine disinfectant. The WSSC pipe had been exposed to Blacksburg tap water for 5 months at low DO, at which time scale from the pipe was removed to isolate and culture SRB using SRB-BART test kits from Droycon Bioconcepts. Inc. The cast iron coupons were exposed to different waters for 153 days total duration. Postgate medium G (36) was first used to cultivate SRB with iron samples present. Oxygen was consumed by adding 0.375 g Na_2S to 1 L medium. After the dissolved oxygen was reduced to below

1 mg/L, SRB culture was inoculated into each reactor, and SRB were established on the coupons. 16 reactors were used at the beginning of the test, with six iron coupons in each 1 L reactor. After 35 days, scale from two iron coupons from each reactor was removed and weight loss recorded. Any of the reactors with iron coupons that had a different color or different weight loss were discarded at this point, since it implied that some difference in oxygen or SRB inoculation occurred.

Twelve reactors remained and 4 new coupons were added into each reactor. These are representative of iron coupons without the 35 days pre-exposure to the SRB and Postgate medium G. The assumption was that comparing the two sets of coupons in the same reactor would be useful in determining the effect of heavy SRB colonization on the pre-exposed sample. All coupons were then exposed to a range of waters (Table 1-4). After two weeks' acclimation, sulfate/chloride ratios were varied and 4 different disinfectant types were added a week later (Table 1-5). The four disinfectant types are **a.** free chlorine, **b.** chloramines, **c.** free ammonia (representing water after chloramine-chlorine decays, and **d.** no disinfectant (representing water after chlorine decays). Also, nitrate concentrations were changed during the experiment, specifically, when the new coupons were first added (35 days after the experiment started), the initial nitrate concentration was 20 mg/L-N, after 32 days, the nitrate concentration was changed to 0.03 mg/L-N, and then 79 days later, the nitrate concentration was changed back to 8 mg/L-N until the end of the experiment.

Stock solution preparation:

At first, stock solutions were made for each sulfate/chloride ratio at 10 times the targeted concentration including all elements except for the disinfectant. CO_2 was purged into the stock to better dissolve the solid and keep the stock pH below 7. pH was adjusted to 8 $\pm$ 0.2 by purging CO_2 using Coleman 99.99% compressed CO_2 gas. This method was modified after it was clear that some precipitates were forming. In the second approach, the stock solution was made 5 times targeted concentration without initially containing sulfate, chloride and silicate which were then added from separate stocks just before use in experiment.

Chlorine and monochloramine residuals were maintained twice everyday and water was replaced in each reactor every 4 days. Iron sample was collected at each water change and measured on Inductively Coupled Plasma Mass Spectrophotometer (ICP-MS) according to standard method 3125-B (51). Microbiological activity is monitored through the experiment by ATP, which is the energy transfer molecule found only in living cells. Half milliliter bulk water from each reactor is sampled fresh and tested by ATP unit from AMSA, Inc. The activity of SRB was monitored using a RapidCheck II SRB immunoassay from Strategic Diagnostics Inc. RapidCheck II SRB test employs purified antibodies to detect the enzyme adenosine-5'-phosphosulfonate (APS) reductase which is common to all strains of SRB.

Scale morphology and composition and weight loss were determined at the end of the test. A scanning electron microscope equipped with electron dispersive spectroscopy (SEM-EDS) was used to analyze the surface of two coupons for elements with molecule weights greater than carbon; one of the coupons was from reactor 3.10 (no sulfate, no disinfectant residual), and the other was from reactor 3.8 (highest sulfate, no disinfectant

residual).

The scales from two older coupons and two newer coupons from each reactor were analyzed for nitrifying bacteria and sulfate reducing bacteria using BART test kits from Droycon Bioconcepts Incorporate and RapidCheck II SRB test kits. BART test contains ferrous iron, which can react with H_2S produced by SRB and form a black precipitate.

Table 1-4: Acclimated water chemistry after adding new iron coupons

Constituent	Conc. mg/L
sulfate	14.4- SO_4^{2-}
chloride	34.6- Cl^-
Lactate	0.3-C
NH4-N	1
Phosphate	20
Nitrate-N	0.03
Other Trace nutrient and Vitamin solution	1/20 Postgate Medium G
Ca	20
Mg	20
Si	20
alkalinity	100- $CaCO_3$

Table 1-5: Water chemistry conditions in different reactors for test with SRB inoculated

reactor	Disinfectant type	Cl_2, mg/L	NH_2Cl, mg/L- Cl_2	NH_3, mg/L-N	SO_4, mg/L	Cl^-, mg/L
3.1	Chlorine present	4	0	0	14.4	19.88
3.2		4	0	0	7.68	24.85
3.3		4	0	0	0	30.53
3.4	Chloramines present	0	4 (1:1 ammonia to chlorine molar ratio)	0	14.4	19.88
3.5		0	4 (1:1 ammonia to chlorine molar ratio)	0	7.68	24.85
3.6		0	4 (1:1 ammonia to chlorine molar ratio)	0	0	30.53
3.7		0	4 (3:1 ammonia to chlorine molar ratio)	0	7.68	24.85
3.8	No residual	0	0	0	14.4	19.88
3.9		0	0	0	7.68	24.85
3.10		0	0	0	0	30.53
3.11	Free ammonia	0	0	1	14.4	19.88
3.12		0	0	1	0	30.53

RESULTS AND DISCUSSION

Weight loss

Effect of Disinfectant

Surprisingly, for the tests with SRB inoculation, the overall weight loss difference between chlorine, chloramines, no residual and free ammonia additions was not significant at 90% confidence (Figure 1-1 and A-1-1). For the tests without SRB inoculation, reactors with chlorine addition had either about 10％ lower or the same weight loss compared to the same water without disinfectant. Reactors with chloramine addition had the same weight loss compared to no residual and free chlorine conditions at 90% confidence (Figure 1-2 and A-1-2).

In the experiments without SRB inoculation, the scale recovery of the iron mass lost from the metal samples was different in saturated and low oxygen conditions. About half is recovered in oxygen saturated condition and almost all is recovered in low oxygen condition (Figure 1-2 and A-1-2). Chloramine had slightly more iron present in the scale than did the case with chlorine in both conditions, but not statistically different, indicating that disinfectant had little effect on scale accumulation (Figure 1-2 and A-1-2).

The overall weight loss for the test with the addition of SRB includes the old coupons which were exposed 153 days and the new coupons which were exposed 118 days. It was expected that the old coupons have greater weight loss since they were exposed to the water longer and had very heavy SRB inoculation at the beginning, but interestingly, the new coupons had similar weight loss to the old coupons, some might even show slightly higher weight loss, like reactors with chloramine disinfectant when sulfate is present, though this difference is not significant at 90% confidence (Figure 1-1 and A-1-1). This suggests that a protective scale had formed on the old coupons in Postgate medium G (see section Scale Morphology).

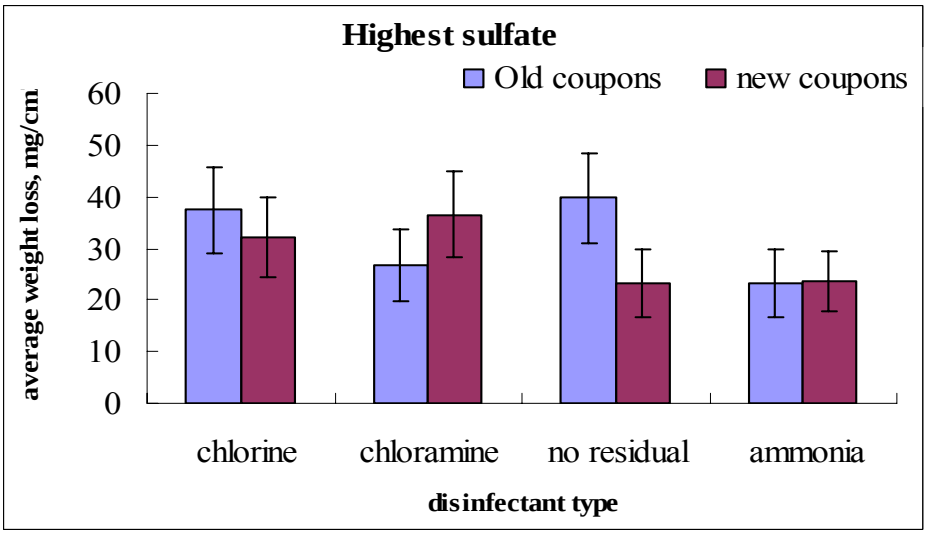


Figure 1-1: Weight loss after 153 days (old coupons) and 118 days (new coupons), in the conditions of highest sulfate, lowest chloride, SRB inoculated. Error bars represent 90% confidence intervals. (Reactors 3.1, 3.4, 3.8, 3.11)

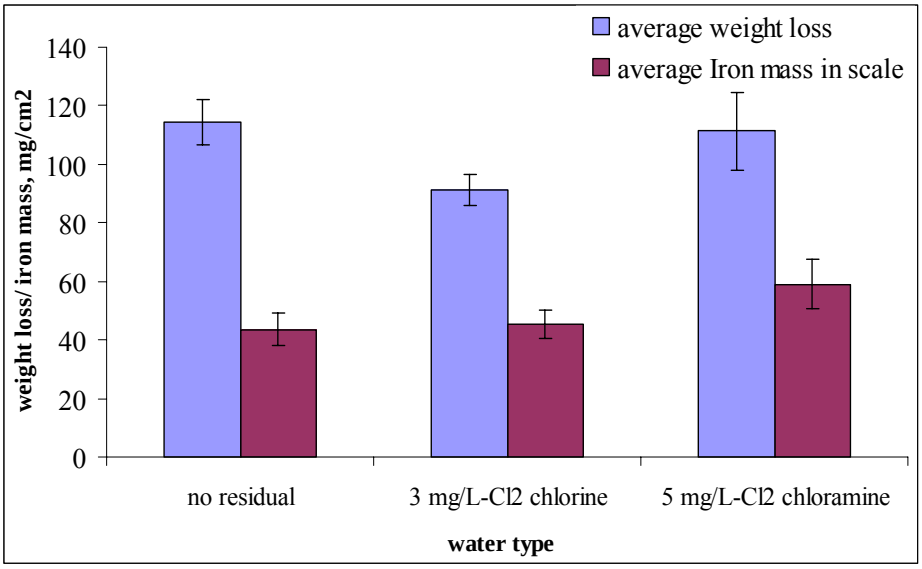


Figure 1-2: Weight loss and iron mass after 77 days under O_2–saturated condition, no SRB inoculation. Error bars represent 90% confidence intervals. (Reactors 1.3, 1.7, 1.8)

Sulfate/chloride ratio

With 90% confidence, the weight loss at all three sulfate/chloride ratios was the same. This is not surprising because very low and similar SRB activity was detected in most iron scales (see Microbiological activity section), indicating that SRB is not a major factor affecting corrosion under this situation. A constant alkalinity and thus a constant Larson's ratio produced the same weight loss.

Magnesium and Silica

After a short term exposure, presence of magnesium without regard to the concentration decreased weight loss in the presence of silica (Figure A-1-4). Though this decrease is significant at 90% confidence, it is very small. Interestingly, the combination of higher silica (40 mg/L versus 20 mg/L) and 25 mg/L magnesium present decreased weight loss by about 10% and iron mass by about 20%. If there was any, we speculate that the slight benefit from magnesium and silica to iron corrosion rates might be due to formation of magnesium silicates.

Natural Organic Matter (NOM), Calcium, Phosphorus and Zinc

In this study, the addition of NOM did not have an effect on weight loss, under both O_2 saturated and low O_2 condition. Calcium is thought to be beneficial to iron corrosion because of the precipitation of a protective scale-calcite (calcium carbonate) (2). But in this study, calcium either slightly increased weight loss or had no effect relative to the condition without calcium at 90% confidence. This might be because the benefit of 20 mg/L calcium was overcome by the negative effect of 35.5 mg/L chloride as calcium is added as calcium chloride. Corrosion inhibitor ions- phosphate and zinc were also investigated, which decreased weight loss by about 45% and 10% respectively, thereby proving they have certain short term benefits. Mechanistically, phosphate can prevent

corrosion and red water by forming a protective film (53); the mechanisms by which zinc reacts are uncertain at this time (Figure 1-3 and A-1-5).

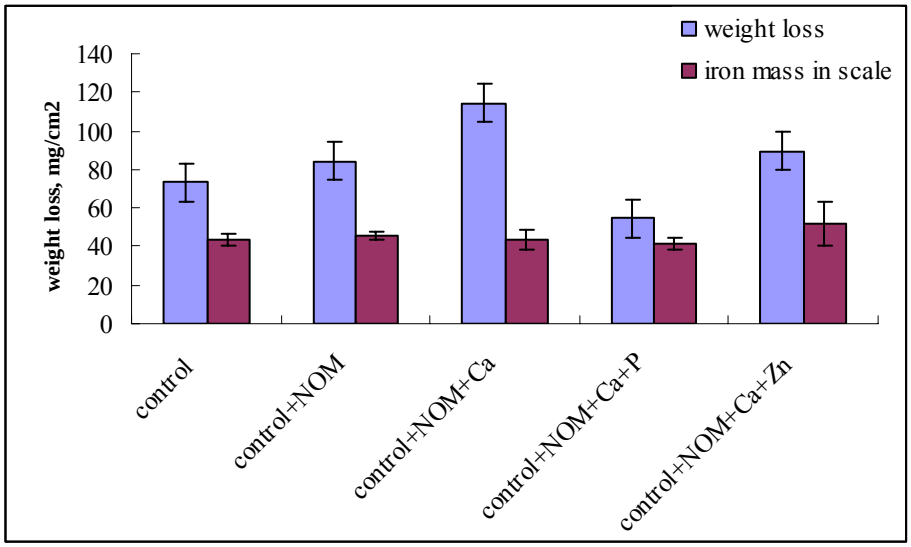


Figure 1-3: Weight loss and iron mass after 77 days under O_2–saturated condition, no SRB inoculation. Error bars represent 90% confidence intervals. (Reactors 1.1, 1.2, 1.3, 1.4, 1.6)

Iron release and red water

Eisnor and Gagnon et al. 2004 considered elevated release of iron to water to be indicative of high corrosion rates in new pipe or the release of older metal deposits into solution (10). But McNeill and Edwards et al. 2001 point out there is little or no relationship between iron release to water and iron corrosion rates, primarily due to the scale on the surface of the pipe that can serve as a larger reservoir of corrosion by-products (2). Nonetheless, the concentration of iron in water is an important water quality parameter because it can reflect potential "red water" complaints. Findings related to red water are discussed below.

Effect of Disinfectant

For coupons not inoculated with SRB, the presence of chlorine always decreased iron leaching relative to the same condition without disinfectant. Generally speaking, when saturated levels of oxygen were present, about 60% less iron was in the water with chlorine disinfectant than for the same condition with chloramines (Figure 1-4). But in the condition at lower DO, over the first two weeks of the test, chloramines had distinct advantages relative to the situation either without disinfectant or with free chlorine (Figure 1-5). This trend was completely reversed after two weeks; iron release in the presence of chloramines continued to rise whereas it continued to decrease in the presence of free chlorine (Figure 1-5). By the end of the test with low DO water, the condition with chloramines and no disinfectant were indistinguishable, whereas the condition with chlorine leached more than 3 times less iron to water than did the same water with chloramine (Figure 1-5).

When SRB are added and at very low nitrate concentration-0.03 mg/L-N nitrate, water with chlorine almost always had the lowest total iron concentration; only 3 exceptions out of 51 data points (Figure 1-6 and A-1-6). Note that from the 10th water change onwards, the iron concentration increased significantly in all tests. In addition, the relative performance of chloramines, no residual and ammonia changed; this is attributed to the change in making up the test water as detailed in the materials and methods.

A paired t-test was conducted comparing the head to head results for total iron leaching, and the ranking chlorine < chloramines < no disinfectant was confirmed at > 95% confidence for all tests, and the exceptional case was with middle sulfate/chloride ratio (reactor 3.2, 3.5, 3.7, 3.9), for which total iron in the reactors with chloramines and no

disinfectant was not different at 95% confidence. The benefits of chlorine might be due to its better disinfectant efficiency and reduced microbiologically mediated corrosion or because chlorine is a stronger oxidant and would therefore decrease iron release according to Sarin et al. 2004 (6). The result of reactors with free ammonia had lower iron release than those with no residual is quite perplexing, since free ammonia was observed to stimulate bulk water microbiological activity and expected to worsen iron corrosion (see Microbiological activity section).

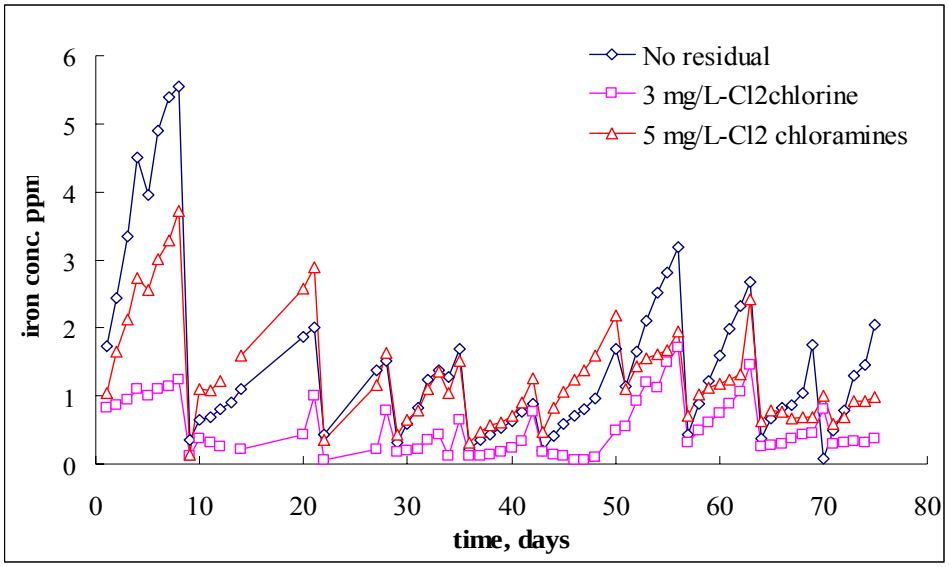


Figure 1-4: Total iron released to water under O_2-saturated condition, no SRB inoculation. The gradual increase of iron represents iron accumulation during the test and the sudden drops represents of a new water change (reactor 1.3, 1.7, 1.8)

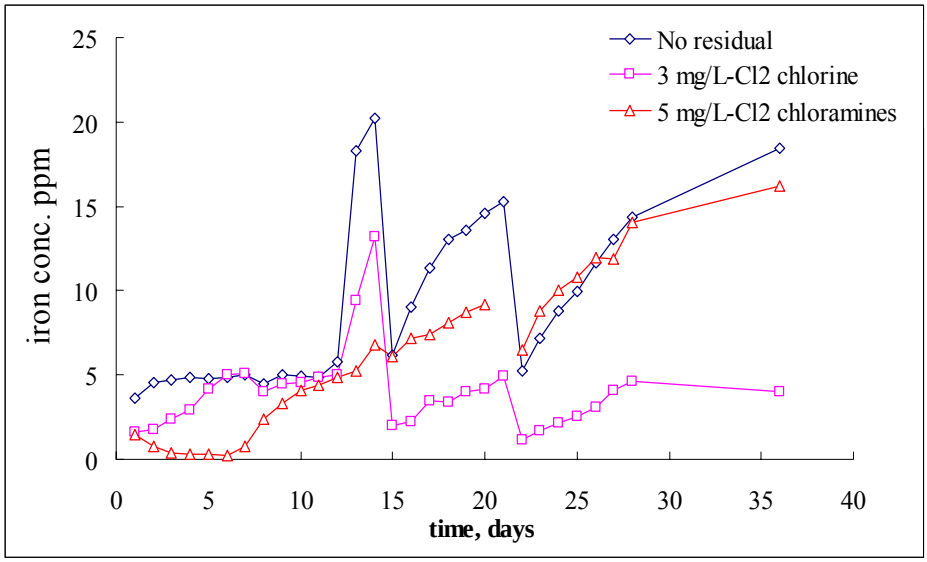


Figure 1-5: Total iron released to water under low O_2 condition, no SRB inoculation. The gradual increase of iron represents iron accumulation during the test and the sudden drops represents of a new water change (reactor 1.3, 1.7, 1.8)

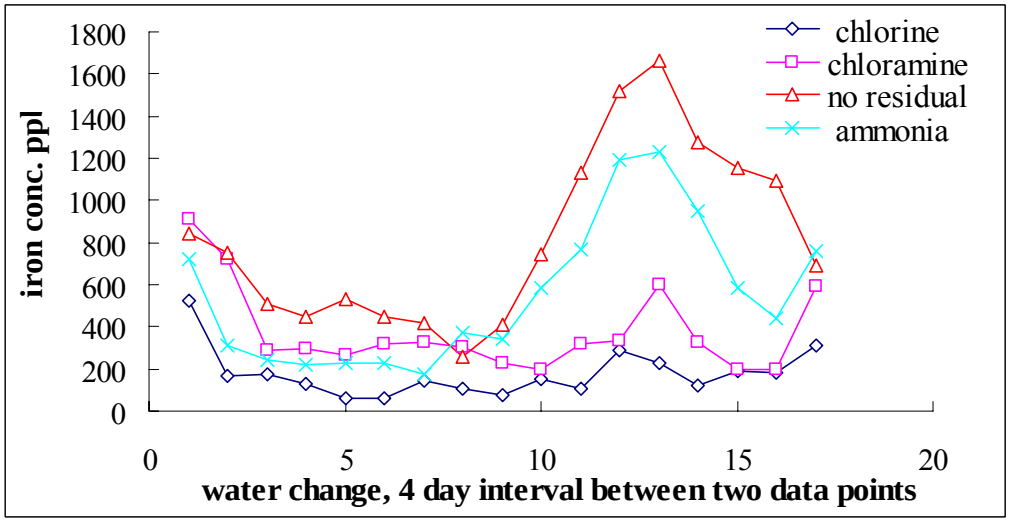


Figure 1-6: Total iron release with highest sulfate/chloride ratio and at low nitrate concentration (0.03 mg/L-N nitrate), SRB inoculated. (Reactors 3.1, 3.4, 3.8, 3.11)

Nitrate

Nitrate is infrequently considered as a key factor in iron corrosion (2, 54), although there are studies indicating nitrate can inhibit pitting corrosion (55, 56) and has no effect on general corrosion in neutral solution (56), the short term nature and high concentration (hundreds to thousands mg/L nitrate) used in these studies don't apply to drinking water systems (56). In this study, the switch from 20 mg/L-N nitrate to 0.03 mg/L-N nitrate caused a sudden drop of total iron release in the reactors with chlorine, but total iron concentration in the reactors with chloramines did not decrease immediately after the switch (Figure 1-7). However, at the final stage of the test, increasing the nitrate concentration back to 8 mg/L-N did not increase iron concentrations in reactors with chlorine as expected. This might be because iron corrosion is low after 5 months exposure, or 8 mg/L-N nitrate is not high enough to cause an effect at this pH value.

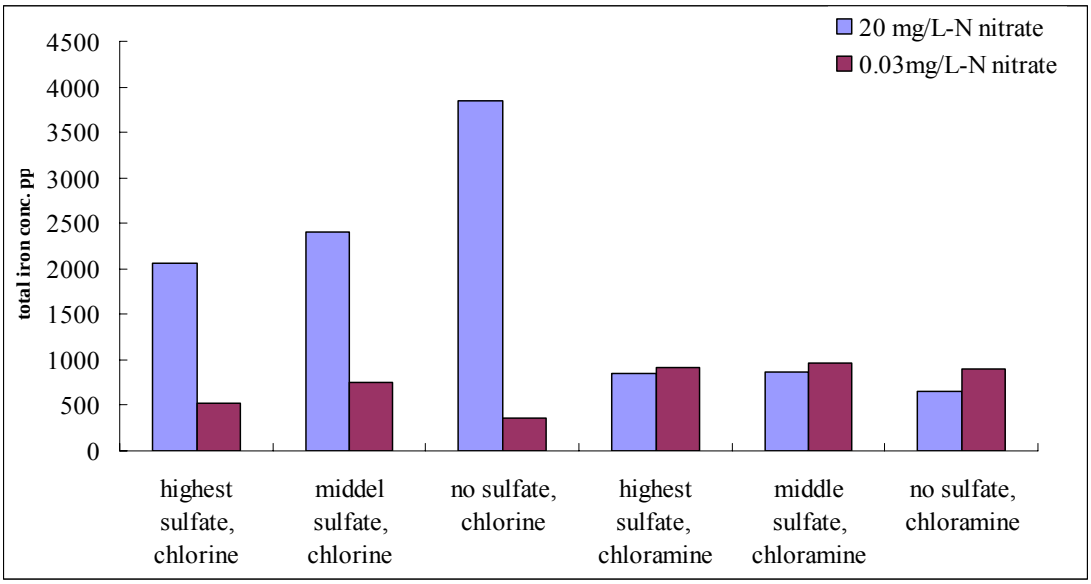


Figure 1-7: Immediate total iron concentration response caused by nitrate concentration change from 20 mg/L to 0.03 mg/L, SRB inoculated.

Sulfate/chloride ratio

Generally speaking, sulfate/chloride ratios did not have a significant effect on total iron release. For a student paired t test, the highest sulfate had the lowest iron concentration except for the case with no residual, in that instance-the condition with the highest sulfate had the highest iron concentration (A-1-7).

Magnesium and Silica

High levels of silica (20 mg/L) without the hardness ions released highest level of iron; when magnesium was present, the reactor with no silica had the lowest total iron and the reactor with highest silica (40 mg/L) had highest total iron most of the time; this is consistent with the results of Rushing et, al. 2003, which proved high silica increased red water (Figure 1-8 and A-1-8) (15). Total and soluble iron concentration decreased as magnesium concentration increased from 0 to 12 mg/L-Mg, but further addition of magnesium up to 25 mg/L did not have additional benefits. A reactor with 20 mg/L calcium (0.5Mm) also reduced iron release. So hardness ions are seen to reduce the adverse effect of silica. This may be because Magnesium can reduce the negative surface charge on iron scale particles caused by silica (60, 63), thus would reduced the electrostatic repulsion force and the scale particles are less likely to disperse into the water (15).

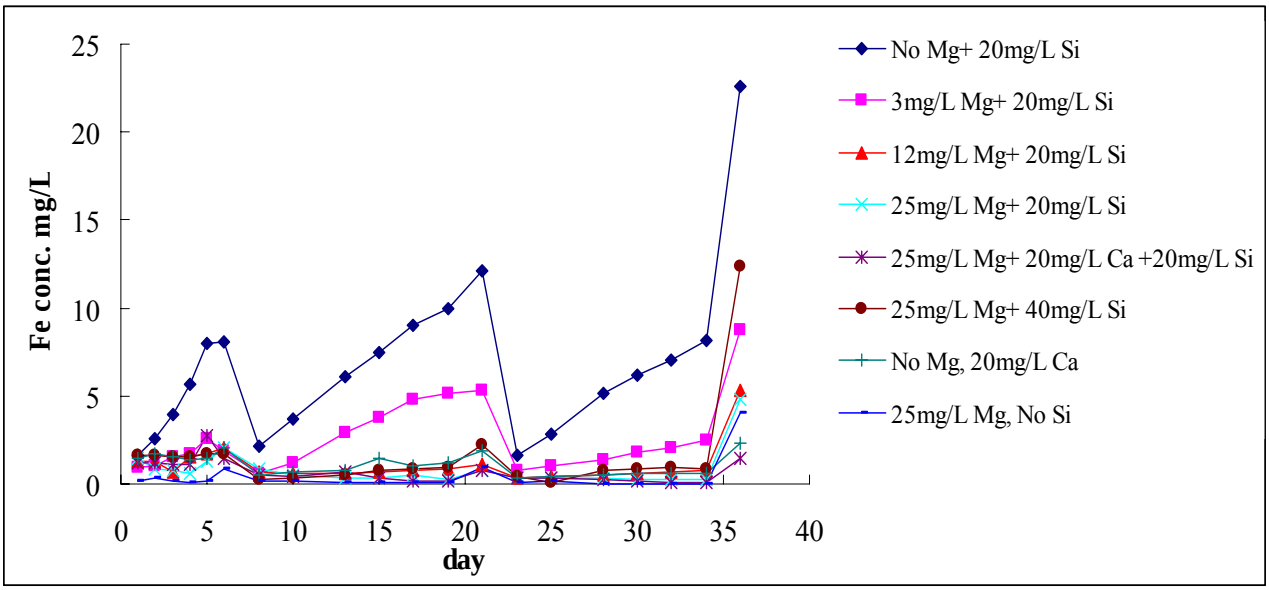


Figure 1-8: Total iron release under O_2-saturated condition, no SRB inoculation.

Natural Organic Matter (NOM), Calcium, Phosphorus and Zinc

Under O_2 saturated condition, NOM increased iron release by about 20% on average. Calcium and phosphate increased iron release over the short term, but decreased iron release at longer term, and zinc decreased iron release by about 40% on average. Under low O_2 condition, NOM, calcium and phosphate had no effect on iron release, and zinc decreased iron release by about 60% on average. The effect of those parameters depend on many factors, so these results might be viewed as valid only under the test conditions reported herein (Table 1-6, Figure A-1-9).

Table 1-6: Effect of different water chemistry parameters on iron corrosion

Parameters	Iron released to water		Iron corrosion rate (weight loss)	
	O_2–saturated	low O_2	O_2–saturated	low O_2
NOM	↑	---	---	---
Ca^{2+}	Short term ↑, long term ↓	---	↑	---
Phosphate	Short term ↑, long term ↓	---	↓	---
Mg^{2+}	↓	↓	---	Slightly ↓
Zn^{2+}	↓	↓	↓	↓
Free Cl_2	↓	↓	↓	---
Chloramines	Short term ---, long term↓	↓	---	---

Note: ↑: increase, ↓: decrease, --- no significant effect

Disinfection Decay Rate

Sulfate/chloride ratio

Normally, chloramine residual is more stable and longer lasting than free chlorine. (59) But in this study, when nitrate concentration was low-0.03 and 8 mg/L-N, chlorine had nearly the same decay rate as chloramine at highest sulfate condition, while the condition with middle and no sulfate, chlorine decayed faster than chloramine (Figure 1-9 and A-1-10). So it is very likely that under certain water chemistry conditions, considering the reduced disinfection efficiency and possible nitrification problem, chloramine might have

relative disadvantage at utilities where chloramines decay was only slightly slower than chlorine.

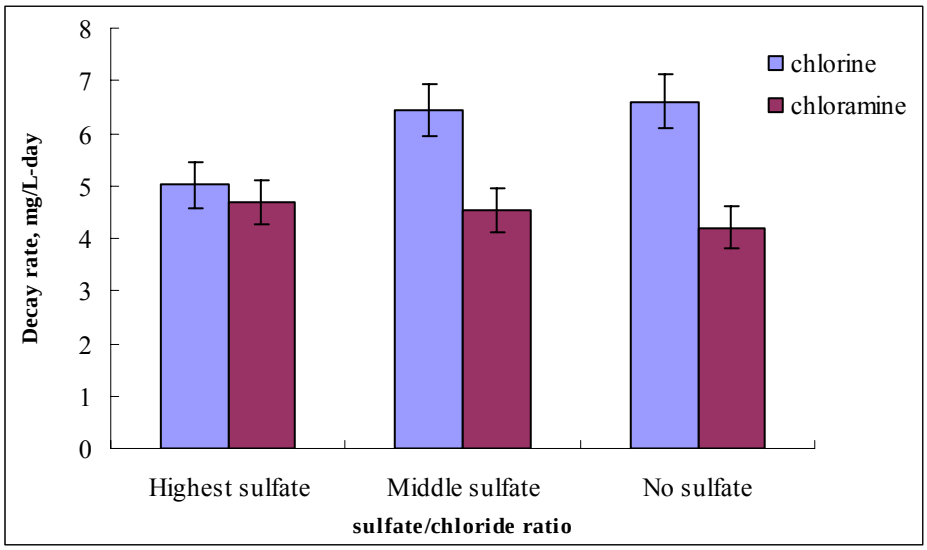


Figure 1-9: Disinfectant Decay Rate with 0.03 mg/L-N nitrate, SRB inoculated. Error bars represent 90% confidence intervals.

Nitrate

Chlorine decay rate increased with increased nitrate concentration, although this increase is only 90% significant when comparing conditions with 0.03 mg/L nitrate and 20 mg/L nitrate. Chloramine decay is not a function of nitrate concentration (Figure 1-10 and A-1-11).

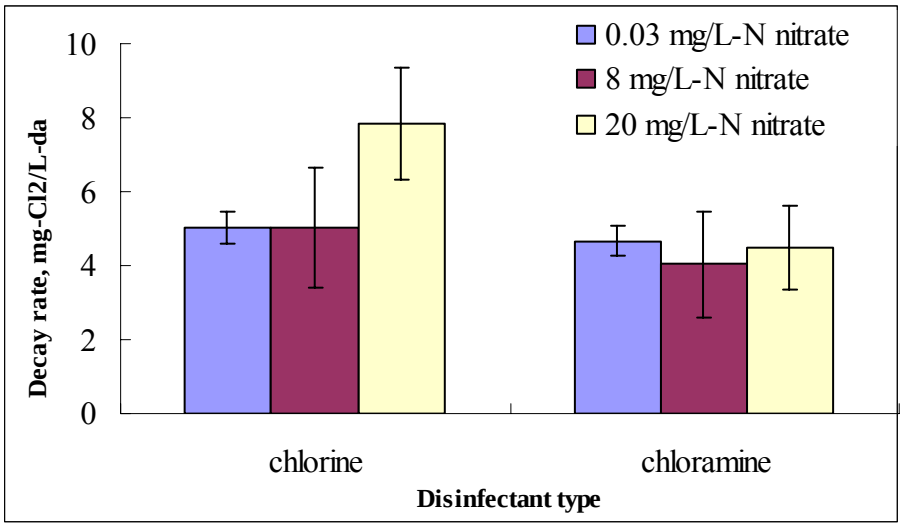


Figure 1-10: Disinfectant Decay Rate with highest sulfate, SRB inoculated.
Error bars represent 90% confidence intervals.

A hypothesis is proposed to explain the higher decay rate and total iron release with chlorine when nitrate concentration is higher (Figure 1-11).

Nitrate is converted to ammonia by iron corrosion (48), expressed with an equation:

$$4Fe + NO_3^- + 10\ H^+ = 4\ Fe^{2+} + NH_4^+ + 3H_2O$$

This reaction is more favorable at lower pH, so the high pH 8 used in this study would tend to reduce the rate of this reaction. The extent of the reaction was assessed in the reactors without disinfectant. With 20 mg/L-N nitrate, 0.3 mg-N/L bulk water ammonia was produced each day, but only about 0.05 mg/L ammonia was produced with 8 mg/L nitrate (Figure 1-12).,

Breakpoint chlorination,

$$2\ NH_3 + 3\ Cl_2 = N_2 + 6\ Cl^- + 6\ H^+ \text{ (49)},$$

if 0.3 mg/L ammonia was formed slowly each day, 1.8 mg/L chlorine would be consumed by this reaction. This explains the higher rate of chlorine decay at high nitrate.

In contrast, formation of ammonia from nitrate in the presence of chloramine would tend to increase the stability of chloramine.

So with 20 mg/L-N nitrate, chlorine decayed very fast, and the reactors with chlorine would stay at low chlorine and no residual mostly before chlorine residual is boosted back to 4 mg/L; with low nitrate concentration, the reactors with chlorine had high chlorine residual mostly. Since no residual was proved to release more iron than chlorine (Figure 1-6), by comparison, high nitrate released more iron than low nitrate.

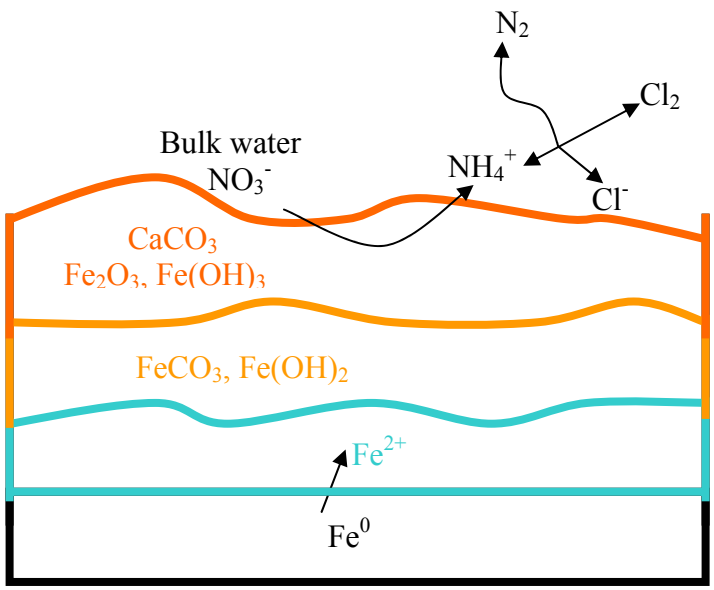


Figure 1-11: Nitrate reduction by iron corrosion and resulting breakpoint chlorination

Practical implication of nitrate effect in drinking water systems

In this study, three conditions are not favorable for the conversion of nitrate to ammonia and consequent faster chlorine decay compared to distribution systems: (1) initial pH 8; (2) iron surface/ water volume ratio is relatively small, similar to a 10 inch pipe; (3) water

movement in these reactors (375 rpm) was relatively fast compared to that in distribution system. The only favorable factor is the higher nitrate concentration-20 mg/L (Table 1-7). Despite the unfavorable conditions in this study, ammonia produced could still consume 1.8 mg/L free chlorine everyday. If this happens, at least 50% of the target chlorine residual in most distribution systems would be removed fast and resulting microbial deterioration. And it is predicted that under circumstances where small diameter pipes are used, under stagnant condition and lower pH water, nitrate effect would occur at relatively low nitrate concentration.

Table 1-7: Comparing the possibility for the occurrence of nitrate conversion by iron corrosion

Favorable Conditions (48)	**This study**	**Distribution systems**	**Where nitrate tend to have an effect**
High surface to volume ratio, like small diameter pipes	Similar to 10 inch diameter pipe	0.5 - 12 inch pipe	Small diameter pipe like pipes in homes
Low flow rate	Relatively fast	Flow rate from 0 – 2 m/s	Stagnant Condition-flow rate 0
Low pH	pH 8	pH 6-9	Lower pH 6-7
High initial nitrate concentration	20 mg/L	0 – 10 mg/L	Higher nitrate concentration

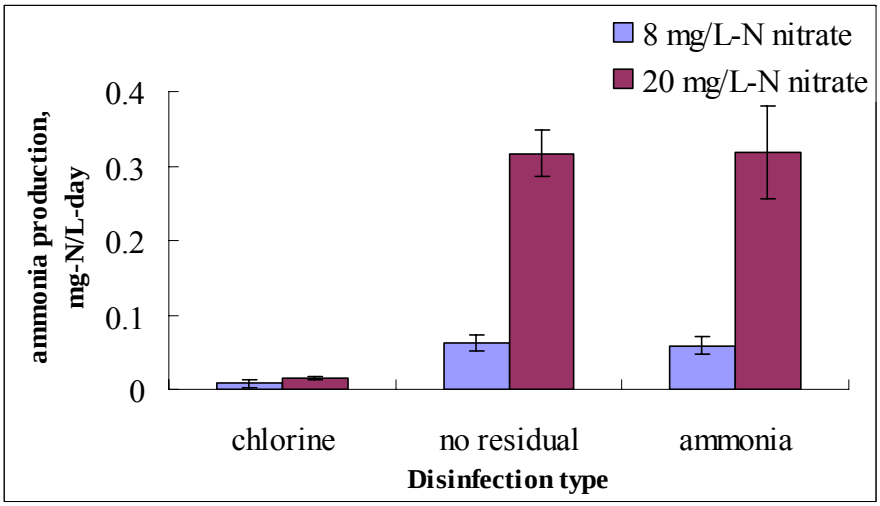


Figure 1-12: Average ammonia production, SRB inoculated.

Error bars represent standard deviation.

Microbiological Activity

Microbiological activity in bulk water

Many microbes are involved in corrosion processes and they are generally considered to be detrimental to iron corrosion (2). In this study, both chlorine and chloramines reduced microbial activity as measured by bulk water ATP, but chlorine out performed chloramines under most conditions. This might partly explain the lower iron release with chlorine, since higher levels of chlorine and lower levels of microbes would tend to keep the surface of the iron scale more oxidizing. Addition of ammonia alone increased microbial activity relative to the condition with no disinfectant consistent with the higher level of nutrient for microbial growth. A student paired t-test illustrates microbial activity with chlorine < chloramines < no residual < ammonia at 95% confidence. (Figure 1-13 and A-1-12)

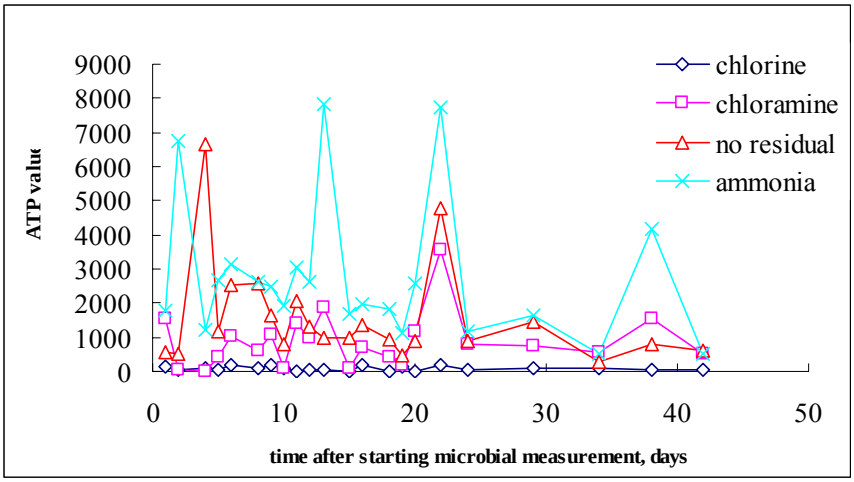


Figure 1-13: Microbiological activity in bulk water based on ATP test at highest sulfate, SRB inoculated.

SRB growth in scale

With Rapid check II method, which detects the enzyme common in SRB, SRB were detected in almost all coupons with and without inoculation of SRB and Postgate medium G exposure, but cell density only ranged from 10^3 to 10^4 cells / ml. The only exception is that at no sulfate, chloramine (1:1 ammonia to chlorine molar ratio) and middle sulfate, chloramine (3:1 ammonia to chlorine molar ratio) conditions, two coupons out of four coupons tested has non detectable SRB.

With the BART test, which detects SRB by identifying the black precipitate formed by ferrous and H_2S when SRB are present, SRB are detected in almost all old and new coupons too. The only exception is that at no sulfate / chloramine condition, three coupons out of four coupons tested have no SRB detected.

Dionized water, which was used to make up the solutions, was used as negative control for both methods and no SRB growth was detected. So the data obtained was valid, but the ubiquitous presence of SRB even in reactors with no sulfate source added was quite

surprising. This indicates that SRB activity was not affected by sulfate/chloride ratios or disinfectant type, so possible sulfur source must have come from the iron to maintain SRB growth. SEM results confirmed that 1.8 ± 1.0 % (average ± standard deviation) sulfur was detected on iron surface in reactor 3.10 (no sulfate, no disinfectant residual).

Scale morphology

The morphology of the scale varied in the tests. Generally speaking, a uniform and dense scale tends to protect iron from further corrosion, while an irregular, loose scale can be less effective at protecting the pipes and contribute to red water problems.

Old coupons versus new coupons:

In the study with SRB added, unexpectedly, the coupons inoculated with SRB and were exposed for 153 days developed a more uniform scale than the coupons without SRB inoculation and were exposed for 118 days (Figure 1-14 and A-1-13). This is attributed to the exposure of old coupons to Postgate Medium G, which has very high calcium (98 mg/L), magnesium (47 mg/L) and phosphorus (45 mg/L), and formed a protective scale on the old coupons. This led to the counter intuitive result that in many cases the new coupons had more weight loss than the old ones.

Old coupons New coupons

Figure 1-14: Scale morphology, highest sulfate, chloramines, SRB inoculated.

Scale differences were observed among different disinfectant types, different sulfate/chloride ratios, but no distinctive conclusion can be draw that one scale is better than the other (A-1-13). Previous research commonly agrees that chloride initiates pits and sufficient sulfate and nitrate inhibit pits initiation (55, 60), and some other authors found chloride caused more pitting than sulfate in steel (52). These studies are always conducted with thousands of mg/L chloride and sulfate concentration (55). In our study, because of the relatively low sulfate and chloride concentration, no obvious pits have been observed, but one interesting finding is that for most old coupons, the reactors with high sulfate, low chloride had more uniform scale than those with low sulfate, high chloride.

In the study without SRB added, NOM, calcium, phosphorus, didn't change the scale morphology much, but with magnesium and zinc, a much more protective scale was developed (A-1-14). Further study of the magnesium effect revealed that the scale became more uniform with higher magnesium concentration and the existence of silica seemed necessary for the formation of a uniform scale (A-1-15). The scale between reactors with chlorine and chloramines are quite different, the one with chlorine was much darker and had gas eruption holes in it visible to the naked eyes, whereas the one with chloramines was thicker and had large turbercles extended outside the coupon surface (Figure 1-15).

Chlorine chloramines

Figure 1-15: Scale morphology after 46 days exposure, no SRB inoculation.

H_2 evolution

H_2 evolution is proportional to the amount of iron corroded via reduction of water. The amount of H_2 evolved was not consistent to iron release or iron corrosion rate (Table A-1). For example, magnesium and chlorine significantly decreased iron release while increased H_2 evolution with 99% and 93% confidence in a student paired t-test. Since H_2 could be a food source to many autotrophic microbes (61, 62, 63); more H_2 would be released if there are less microbes, as in the reactors with chlorine. The higher H_2 evolution with magnesium is quite contradictory to its relatively uniform scale and low iron release; no possible explanation could fit this phenomenon yet.

CONCLUSIONS

This study investigated the effect of disinfectant, sulfate/chloride ratios, nitrate concentration and magnesium hardness on iron corrosion. The basic findings are the followings:

- Chlorine was a better disinfectant than chloramines in the aspect of controlling red water and bulk water microbial activity.
- Sulfate reducing bacteria can maintain their activity after a long time exposure to disinfectant and with no sulfate source added.
- Sulfate/chloride ratio changes did not have an effect on iron corrosion as expected; possibly because SRB activity in this study is very low and iron coupon contain enough sulfur to support SRB growth.
- Chlorine decayed faster and more iron was released at high nitrate condition. Nitrate reduction to ammonia and breakpoint chlorination reactions were proposed to explain this effect. Nitrate change from 0.03 mg/L to 20 mg/L had no effect on chloramines.
- Increased magnesium and zinc can decrease the red water problem caused by silicate. Iron release, weight loss and H_2 evolution result is not always consistent regarding the effect of a certain parameter.

ACKNOWLEDGEMENT

This work was supported by the National Science Foundation (NSF) under grant BES-0201849. The opinions, findings, conclusions or recommendations are those of the authors and do not necessarily reflect the views of NSF.

REFERENCES

1. Edwards, M. (2004) Corrosion Control in Water Distribution Systems. One of the Grand Engineering Challenges for the 21st Century. Edited by Simon Parsons, Richard Stuetz, Bruce Jefferson and Marc Edwards. *Water Science and Technology* 49 (2): 1-8.
2. McNeill, L.S. and Edwards. M.A. (2001) Iron Pipe Corrosion in Distribution Systems. *Journal. AWWA*, July, 2001.
3. Madigan Martinko Parker *Brock Biology of Microorganisms* 9th edition P 975 Southern Illinois University Carbondale Prentice Hall Upper Saddle River, NJ
4. AWWA 1999 *Water Quality and Treatment*, 5th edition. McGraw-Hill, New York.
5. Bayliss, J.R. (1926) Prevention of Corrosion and Red Water *Journal. AWWA*, 15 (6), 598-631.
6. Sarin, P.; Snoeyink, V.L.; Bebee,J.; Jim, K.K.; Beckett, M.A.; Kriven, W.M.; Clement, J.A.(2004) Iron Release from Corroded Iron Pipes in Drinking Water Distribution Systems: Effect of Dissolved Oxygen. *Water Research* 38: 1259–1269
7. P. Sarin; V.L. Snoeyink; D.A.Lytle; and W.M. Kriven (2004) Iron Corrosion Scales: Model for Scale Growth, Iron release, and Colored Water Formation. *Journal of environmental engineering.* April, 2004.
8. LeChevallier, M. W.; Lowry, C.D.; Lee, R.G. (1990) Disinfecting Biofilms in a Model Distribution System. *Journal. AWWA.* July 1990.
9. Trewee, G. P.; Glicker, J.; Chow, B.; Sprinker, M. (1985) Pilot-plant Simulation of Corrosion in Domestic Pipe Materials. . *Journal. AWWA*, October, 1985.

10. Eisnor, J.D.; Gagnon, G. A. (2004) Impact of Secondary Disinfection on Corrosion in a Model Water Distribution System. *Journal of Water Supply.* 53(7): 441.

11. AWWARF, and DVGW-TZW. (1996). Internal Corrosion of Water Distribution Systems. *AWWARF*, Denver, CO.

12. Sun, Y.; and Edwards, M. (2002) Water Chemistry and H_2 Evolution during Anaerobic Iron Corrosion. Proceedings of the AWWA Annual Conference in New Orleans. June 2002. 7-6. 17 pages.

13. Sun, Y.; Morton, S. C.; and Edwards, M. (2002) Equilibrium and Kinetic Aspects of Iron Corrosion in the Presence of Phosphate. Proceedings of the 2002 Water Quality Technology Conference in Seattle Washington. November, 2002. W-11 18 pages

14. Speller F. N. (1951) Corrosion Causes and Prevention, p.39, 3rd ed; McGraw-Hill: New York and London

15. Rushing, J.C.; McNeill, L.S.; Edwards, M. (2003) Some Effects of Aqueous Silica on the Corrosion of Iron. *Water Research* 37: 1080-1090.

16. Evans, Ulick R. (1950) An Introduction to Metallic Corrosion. Butler and Tanner Ltd. Great Britain.

17. Camper, A.K.; Brastrup, K.; Sandvig, A.; Clement, J.; Spencer, C.; Capuzzi, A.J. (2003) Effect of Distribution System Materials on Bacterial Regrowth. *Journal AWWA,* 95: 7: 107.

18. Camper, A.K.; Jones, W.L.; Hayes, J.T. (1996) Effect of Growth Condition and Substratum Composition on the Persistence of Coliforms in Mixed-population Biofilms. *Applied and Environmental Microbiology*, 62, 11: 4014.

19. Lechavallier, M.W.; Babcock, T.M.; Lee, R.G. (1987) Examination and Characterization of Distribution System Biofilms. *Applied and Environmental Microbiology*, 53, 12: 2714.

20. Lee, S.H.; O'Connor, J.T.; Banerji, K. (1980) Biologically Mediated Corrosion and its Effects on Water Quality in Distribution Systems. *Journal AWWA, research and technology,* Nov, 1980 636-645

21. Lind Johansson, E. (1989) Importance of Water Composition for Prevention of Internal Copper and Iron Corrosion. Thesis, Chalmers University of Technology, Goteborg, Sweden.

22. Sontheimer, H.; Kolle, W. & Snoeyink, V.L. The Siderite Model of the Formation of Corrosion-Resistant Scales. *Journal AWWA,* 73:11:572 (1981).

23. Campbell, H.S. & Turner, M.E.D. (1983) The Influence of Trace Organics on Scale Formation and Corrosion. *Journal of the Institute for Water Engineering and Science,* 4:55.

24. Uhlig H.H.; Revie R.W. Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering, 3rd Edition. 419p, 1985, John Wiley, New York, John Wiley and Sons, New York 1985.

25. Sarin P.; Snoeyink V.L.; Bebee J.; Kriven W.M.; Clement J.A. *Water Research.* 2001, 35, 2961.

26. Tuovinen O.H.; Button K.S.; Vuorinen A.; Carlson L.; Mair D.M.; Yut L.A. (1980) Bacterial, Chemical, and Mineralogical Characteristics of Tubercles in Distribution Pipelines. *Journal. AWWA,* 72, 626.

27. Tuovinen O.H.; HSU, J.C. (1982) Aerobic and Anaerobic Microorganisms in Tubercles of the Columbus, Ohio, Water Distribution System. *Appl. & Environ. Microb.* 44(3), 761-764.

28. Lytle, D., Gerke, T., and J.B. Maynard. (2004) Geochemistry of Sulfur in Iron Corrosion Scales found in Drinking Water Distribution Systems. Proceedings of the 2004 AWWA WQTC. 15 pages.

29. Larson, T.E. (1975) Corrosion by Domestic Waters. State of Illinois Department of Registration and Education, Illinois State Water Survey, Bulletin 59.

30. Larson, T.E. & Skold, R.V. (1957) Corrosion and Tuberculation of Cast Iron. *Jour. AWWA*, 49:10:1294.

31. Larson, T.E. & Skold, R.V. (1958) Laboratory Studies Relating Mineral Quality of Water to Corrosion of Steel and Cast Iron. *Corrosion*, 14:285.

32. Hedberg, T. & Johansson, E. (1987) Protection of Pipes against Corrosion. *Water Supply*, 5:3/4: SS 20.

33. Veleva, L.; Castro, P.; Hernandez-Duque, G. & Schorr, M. (1998) The Corrosion Performance of Steel and Reinforced Concrete in a Tropical Humid Climate. A Review. *Corrosion Reviews*, 16:3:235.

34. Riddick, T.M. (1944) The Mechanism of Corrosion of Water Pipes. *Water Works and Sewerage*, 91: Reference and Data: R-133-138.

35. Ingvorsen, K.; Zehnder, A.B.; Jorgensen, B.B. (1984) Kinetics of Sulfate and Acetate Uptake by Desulfobacter postgatei. *Appl. Environ. & Microb.* 47(2): 403-408.

36. Okabe, S., and W.G. Characklis. (1992) Effects of Temperature and Phosphorus Concentration on Microbial Sulfate Reduction by Desulfovibrio Desulfuricans. *Biotechnol. & Bioeng.* V. 39 1031-1042.

37. Okabe, S., P.H. Nielsen, and W.G. Characklis. (1992). Factors Affecting Microbial Sulfate Reduction by Desulfovibrio desulfuricans in Continuous Culture: Limiting Nutrients and Sulfide Concentration. *Biotechnol. & Bioeng.* V. 40 725-724

38. Weimer, J., M. J. Van Kavelaar, C. B. Michel, and T. K. NG. (1988) Effect of Phosphate on the Corrosion of Carbon Steel and on the Composition of Corrosion Products in two-stage Continuous Cultures of Desulfovibrio desulfuricans. *Appl. & Environ.l Microb.* 54(2): 386-396.

39. Rice, O. (1947) Corrosion Control with Calgon. *Journal AWWA,* 39:6:552.

40. Pallo, P.E. (1946) A Study of Corrosion Control with Sodium Hexametaphosphate. *Journal AWWA,* 38:4:499.

41. McNeill, L.S. & Edwards, M. (2000) Phosphate Inhibitors and Red Water in Stagnant Pipes. Journal of Environmental Engineering. 1096-1102 December, 2000

42. Mullen, E.D. & Ritter, J.A. (1974) Potable-Water Corrosion Control. *Journal AWWA,* 66:8:473.

43. Mullen, E.D. & Ritter, J.A. (1980) Monitoring and Controlling Corrosion by Potable Water. *Journal AWWA,* 72:5:286.

44. Swayze, J. (1983) Corrosion Study at Carbondale, Illinois. *Journal AWWA,* 75:2:101.

45. Gill, J.S. (1993) Inhibition of Silica-silicate Deposit in Industrial Waters Colloids and Surfaces A: *Physical and Engineering Aspects*, 74 101-106.

46. Harder, H. (1972) The Role of Magnesium in the Formation of Smectite Minerals. *Chemical Geology* 10: 31-39.

47. Huang, Y.H.; Zhang, T.C. (2005) Effects of Dissolved Oxygen on Formation of Corrosion Products and Concomitant Oxygen and Nitrate Reduction in Zero - valent Iron Systems with or without Aqueous Fe^{2+} *Water research.* 39, 1751-1760

48. Westerhoff, P.; James, J. (2003) Nitrate Removal in Zero-valent Iron Packed Columns. *Water research*. 37, 1818-1830

49. Woolschlager, J. Rittman, B.; Piriou, P.; Kiene, L.; Schwartz, B. (2001) Using a Comprehensive Model to Identify the Major Mechanisms of Chloramines Decay in Distribution Systems. *Water Science and Technology: Water Supply* 1, 4: 103-110.

50. Chin, Y. P.; Gschwend, P. M. The Abundance, Distribution, and Configuration of Porewater Organic Colloids in Recent Sediments. *Geochimica et Cosmochimica Acta* 55: 1309-1317

51. AWWA; APHA & WEF. Standard methods. (1998) 20th ed. Washington, DC: American Public Health Association.

52. http://www.netl.doe.gov/publications/proceedings/03/ucr-hbcu/posters/Brown_p.pdf accessed on 8/18/05

53. Hatch, G.B.; Rice, O. (1945) Threshold Treatment of Water System-Corrosion Control and Scale Prevention with Glassy Phosphate. *Industrial & Engrg. Chem.,* 37:8:710.

54. Lechevallier, M. W.; Lowry, C.D.; Lee, R.G.; Gibbon, D.L. (1993) Examining the Relationship between Iron Corrosion and the Disinfection of Biofilm Bacteria. *Jour. AWWA.* July 1993

55. Gustavo Cragnolino (1983) The Role of Sulfate-reducing and Sulfur-oxidizing Bacteria on Localized Corrosion. Corrosion, 1983. Anaheim, California Paper 244.

56. H.Y. Ma; C. Yang; G.Y. Li; W.J. Guo; S.H. Chen and J.L. Luo (2003) Influence of Nitrate and Chloride Ions on the Corrosion of Iron. Corrosion 59 (12): 1112-1119.

57. Davis, C.C.; Chen, H.W.; Edwards, M. (2002) Modeling Silica Sorption to Iron Hydroxide. *Environ Sci Technol.* 36(4):582-587.

58. Smith, S.; Edwards, M. (2005) The Influence of Silica and Calcium on Arsenate Sorption to Oxide Surfaces. *Journal of Water Supply: Research and Technology.*

59. http://www.epa.gov/region09/water/chloramine.html accessed on 8/15/2005.

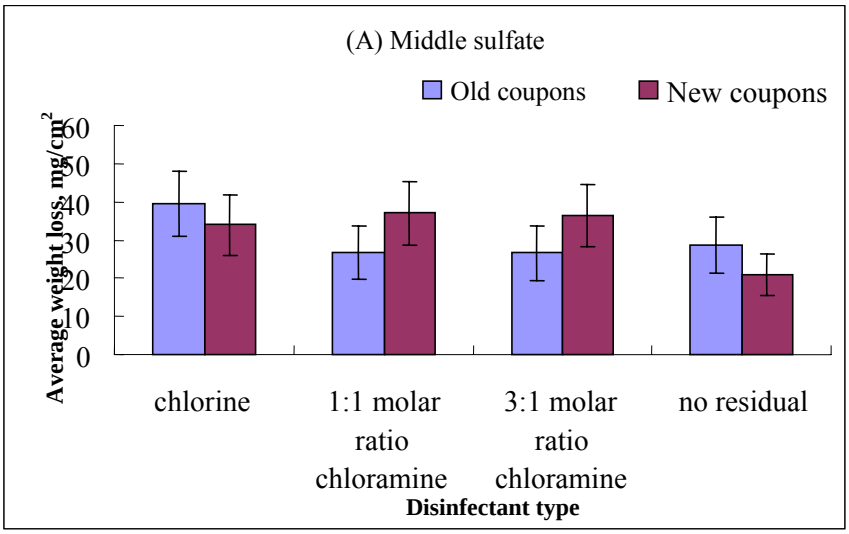
60. Tero J. Hakkarainen (1998) Conditions of Growth of Open Corrosion Pits in Stainless Steels-Electrochemical Experiments on Model Pits. Corrosion, 1998. Paper 310.

61. Ishizaki, A.; Tanaka, K.; Taga, N. (2001) Microbial Production of Poly-D-3-Hydroxybutyrate from CO_2, *Appl. Microbiol. Biotechnol.* 57:6.

62. Van Houten, R.T.; Hulshoff Pol, L.W.; Lettinga, G. (1994) Biological Sulphate Reduction Using Gas-lift Reactors Fed with Hydrogen and Carbon Dioxide as Energy and Carbon Source" *Biotechnol. & Bioeng.,* 44: 586.

63. Wang, H-Y.; Qu, J-H. (2003) Combined Bioelectrochemical and Sulfur Autotrophic Denitrification for Drinking Water Treatment. *Water Research* 37:3767.

APPENDIX-1



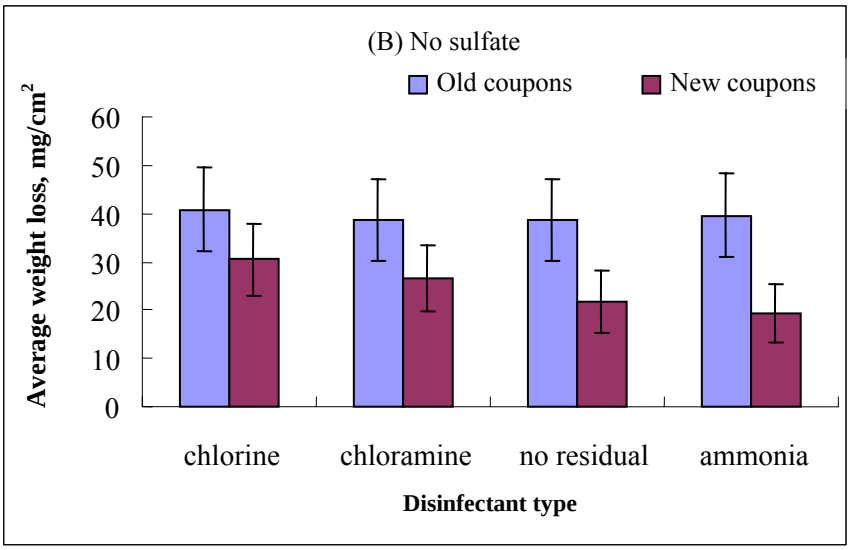


Figure A-1-1: Compare the effect of disinfectant types

Weight loss after 153 days (old coupons) and 118 days (new coupons), SRB inoculated. (A) Middle sulfate (Reactors 3.2, 3.5, 3.7, 3.9); (B) No sulfate (3.3, 3.6, 3.10, 3.12). Error bars represent 90% confidence intervals

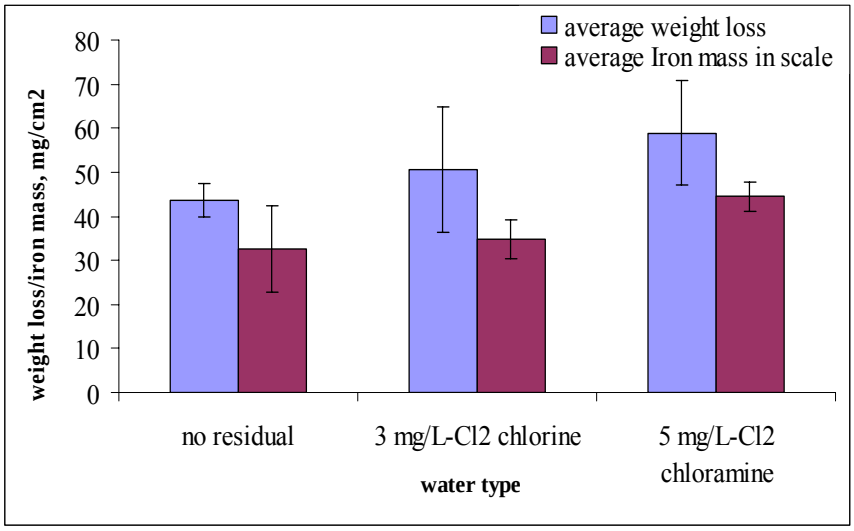
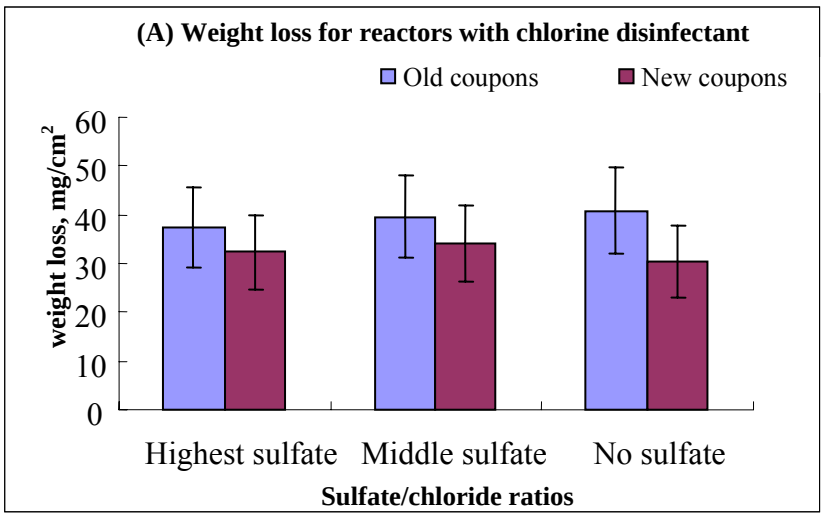
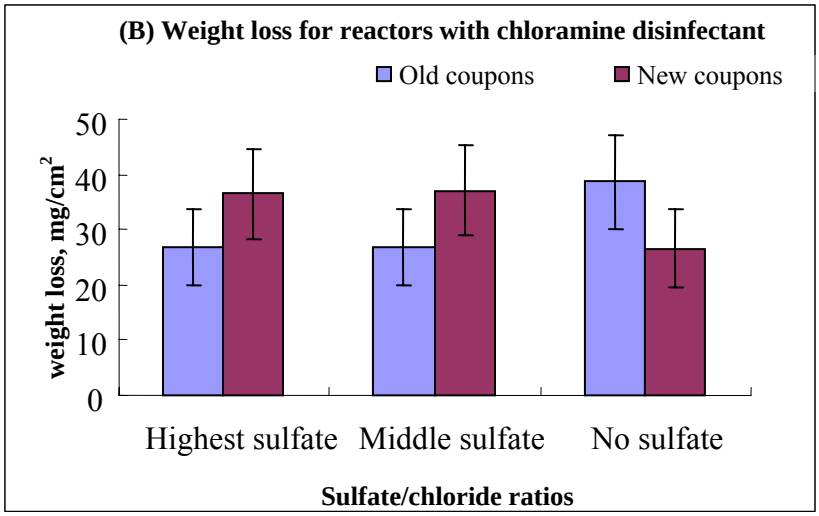


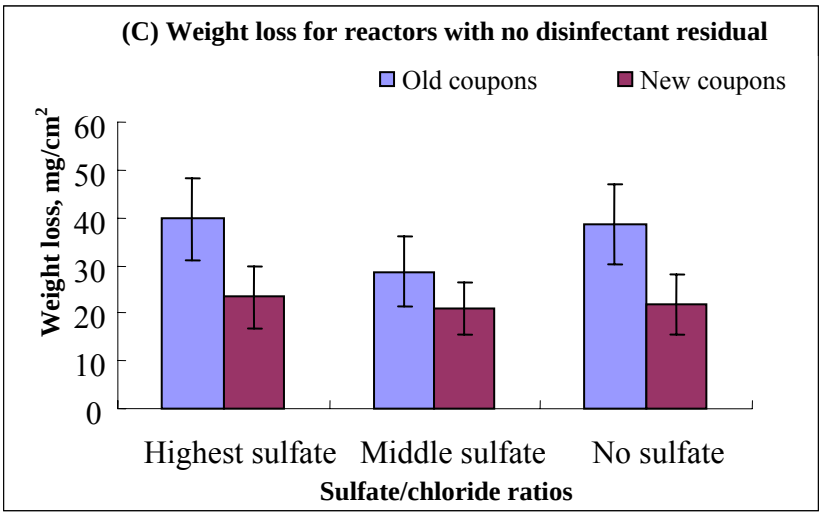
Figure A-1-2: Compare the effect of disinfectant types

Weight loss and iron mass after 46 days under low O_2 condition, no SRB inoculation.

Error bars represent 90% confidence intervals. (Reactors 1.3, 1.7, 1.8)


(A) Weight loss for reactors with chlorine disinfectant
Old coupons
New coupons
weight loss, mg/cm2
60
50
40
30
20
10
0
Highest sulfate
Middle sulfate
No sulfate
Sulfate/chloride ratios


(B) Weight loss for reactors with chloramine disinfectant
Old coupons
New coupons
weight loss, mg/cm2
50
40
30
20
10
0
Highest sulfate
Middle sulfate
No sulfate
Sulfate/chloride ratios



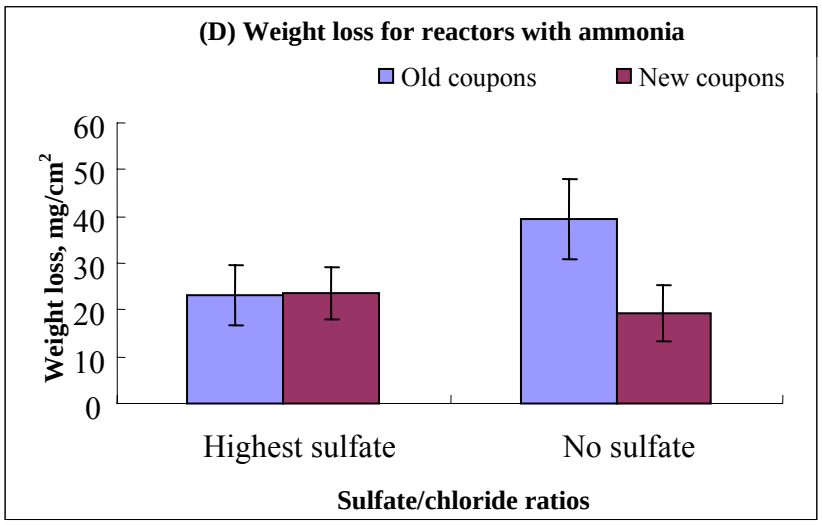


Figure A-1-3: Compare the effect of sulfate/chloride ratios

Weight loss after 153 days (old coupons) and 118 days (new coupons), SRB inoculated. (A) Chlorine (Reactor 3.1 - 3.3); (B) Chloramine (Reactor 3.4 - 3.7); (C) No residual (Reactor 3.8 - 3.10); (D) Ammonia (Reactor 3.11, 3.12). Error bars represent 90% confidence intervals

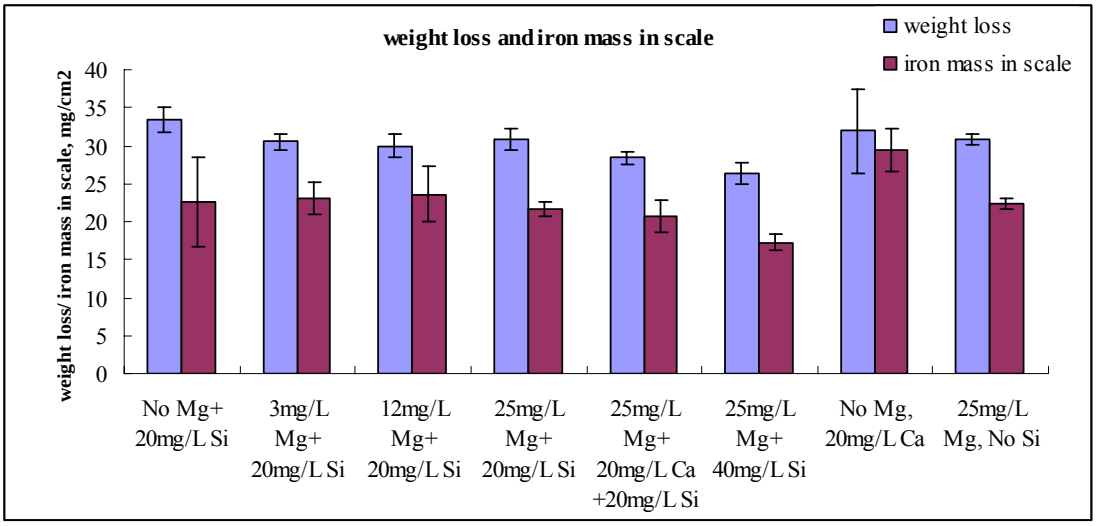


Figure A-1-4: The effect of Mg and Si on iron corrosion. Weight loss after 37 days, no SRB inoculated. Error bars represent 90% confidence intervals

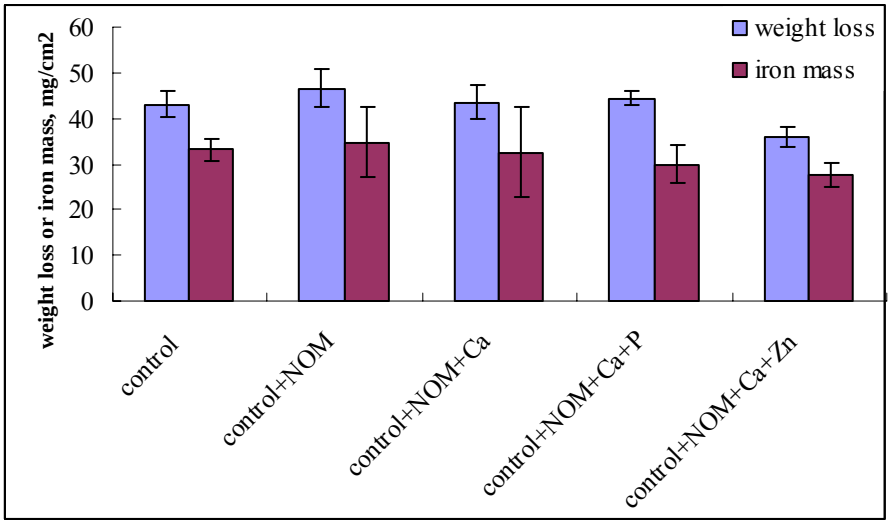
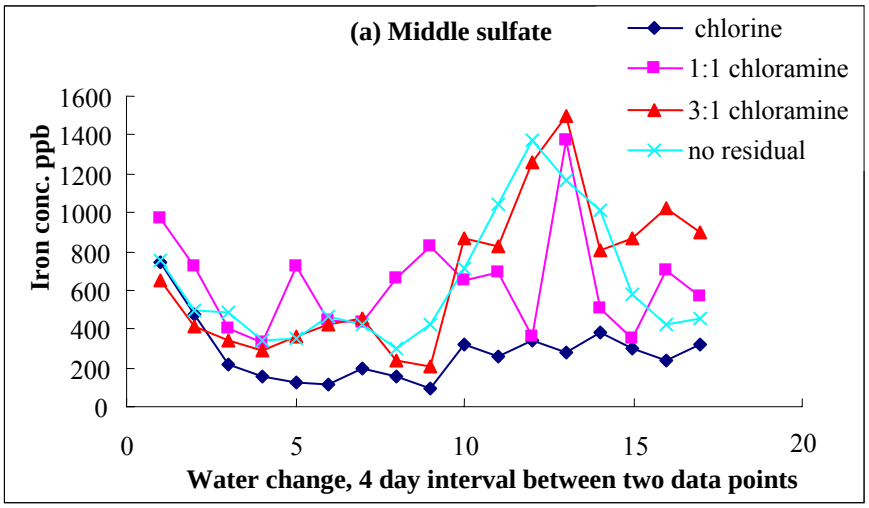


Figure A-1-5: Effect of NOM, calcium, phosphorus, magnesium, and zinc. Weight loss and iron mass after 46 days under low O_2 condition, no SRB inoculation. Error bars represent 90% confidence intervals



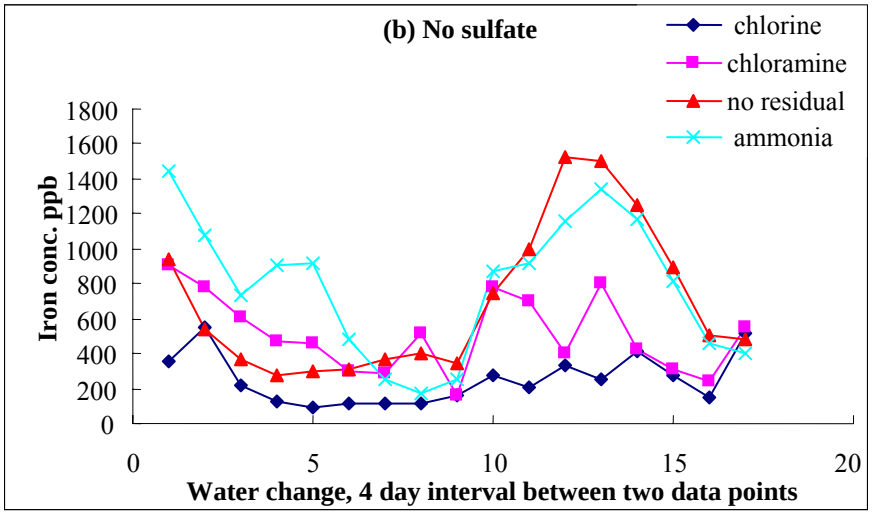
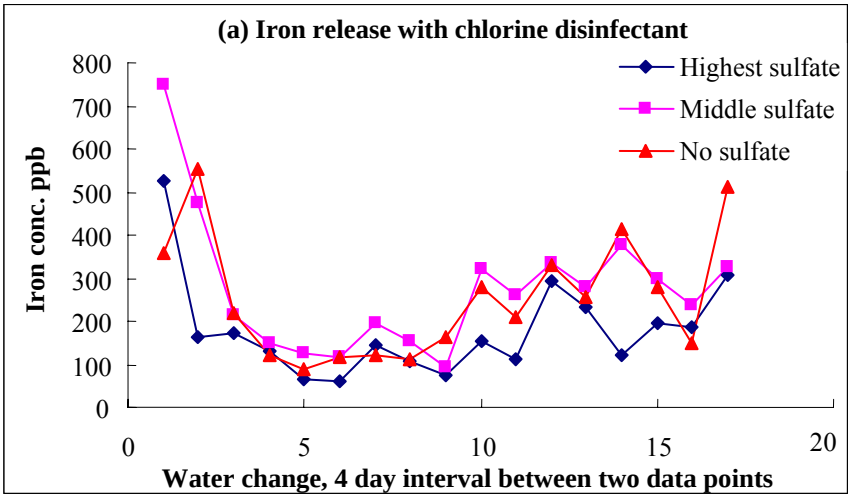
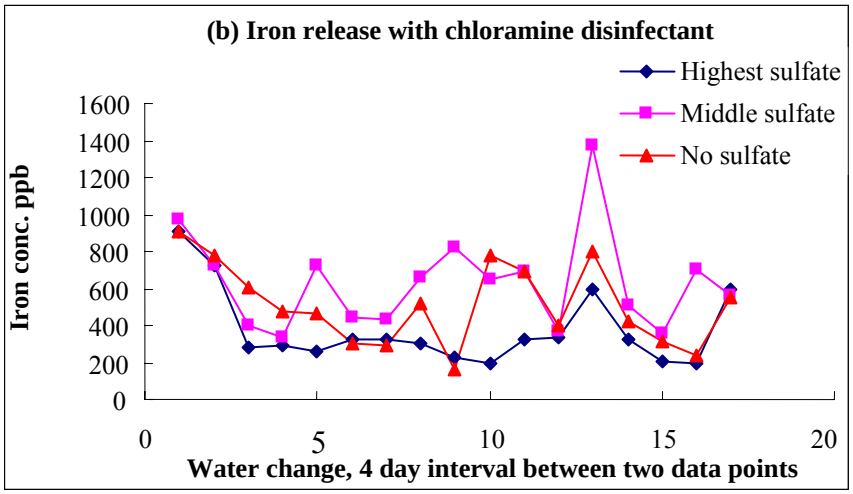


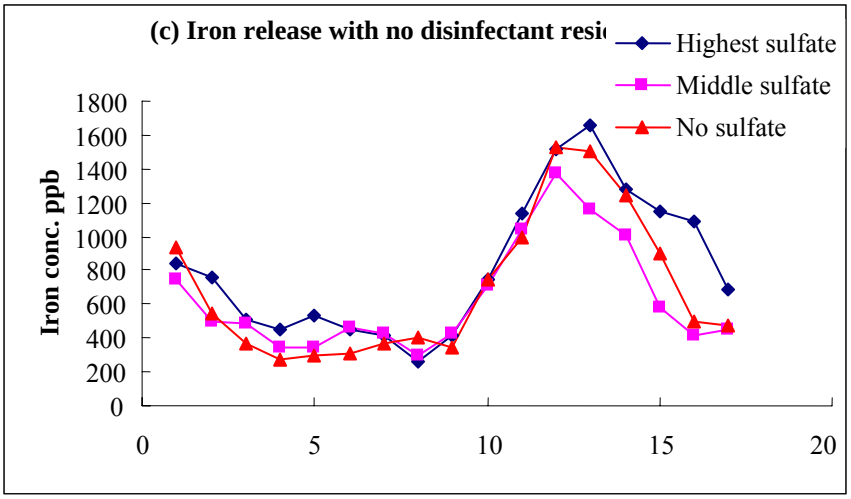
Figure A-1-6: Effect of disinfectant.

Total iron release at low nitrate concentration (0.03 mg/L-N nitrate), SRB inoculated.

(a) middle sulfate (b) no sulfate


(a) Iron release with chlorine disinfectant
Highest sulfate
Middle sulfate
No sulfate
Iron conc. ppb
800
700
600
500
400
300
200
100
0
0
5
10
15
20
Water change, 4 day interval between two data points


(b) Iron release with chloramine disinfectant
Highest sulfate
Middle sulfate
No sulfate
Iron conc. ppb
1600
1400
1200
1000
800
600
400
200
0
0
5
10
15
20
Water change, 4 day interval between two data points



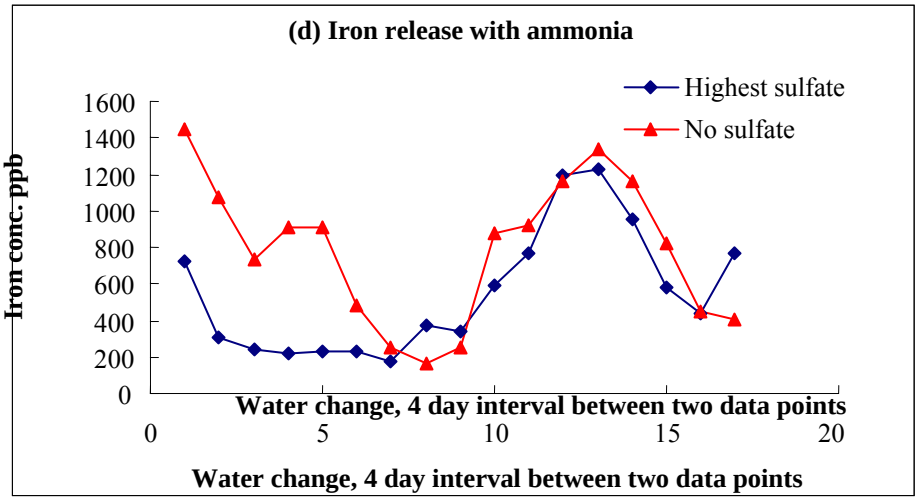


Figure A-1-7: Effect of sulfate/chloride on total iron release at low nitrate concentration (0.03 mg/L-N nitrate), SRB inoculated. (a) chlorine (b) chloramine (c) no residual (d) ammonia. Note: The stock solution making method change at 10th water change had a big effect on the relative trend of the three ratios with no residual and free ammonia situations.

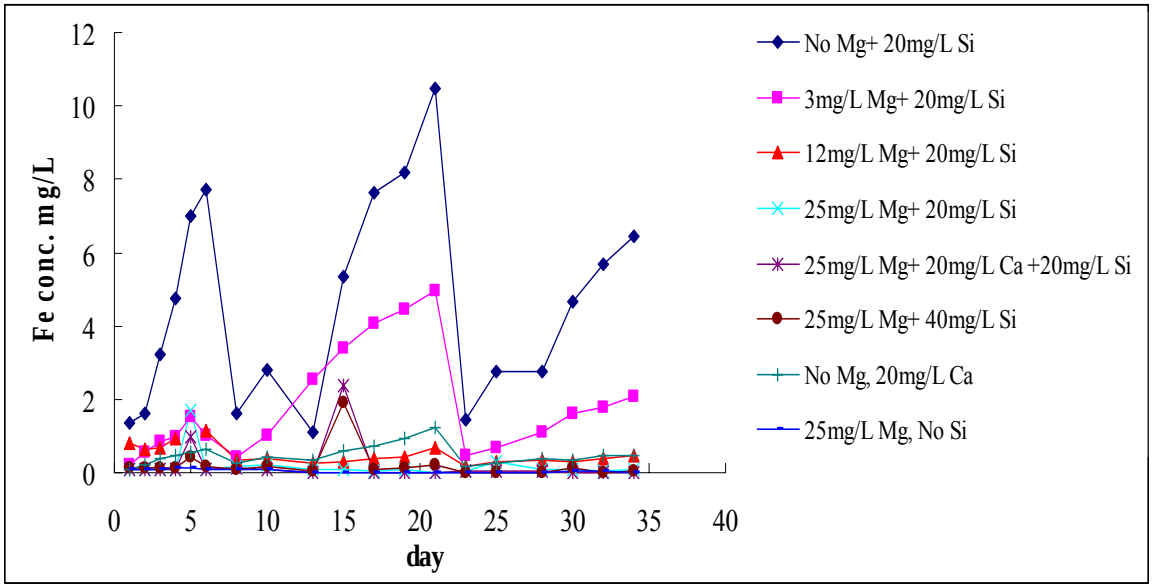
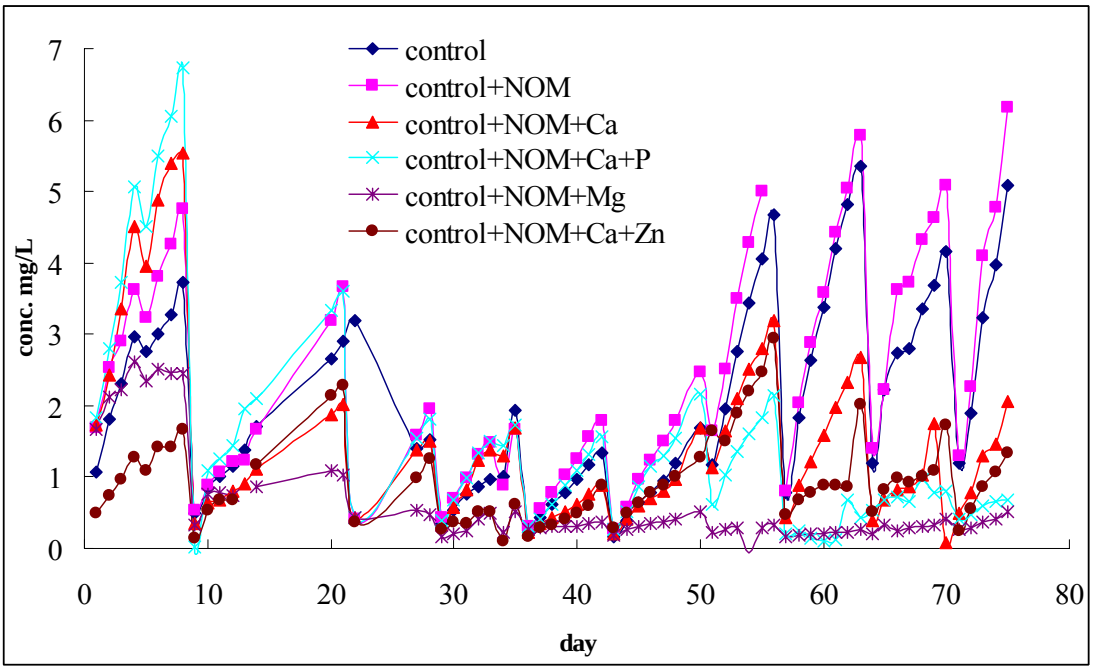
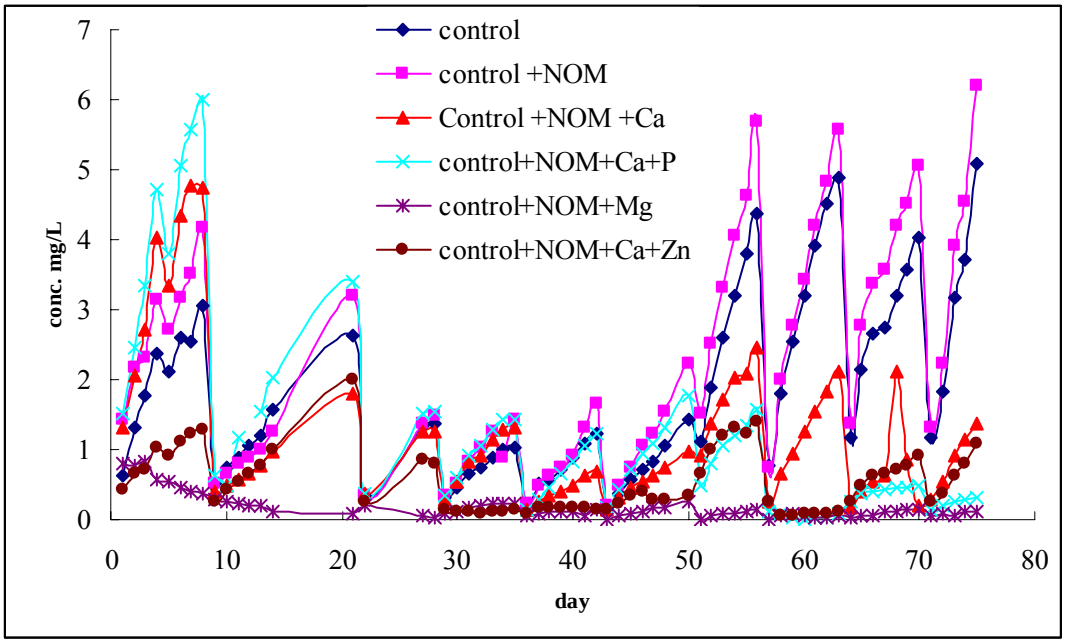


Figure A-1-8: Effect of Magnesium and Silica.

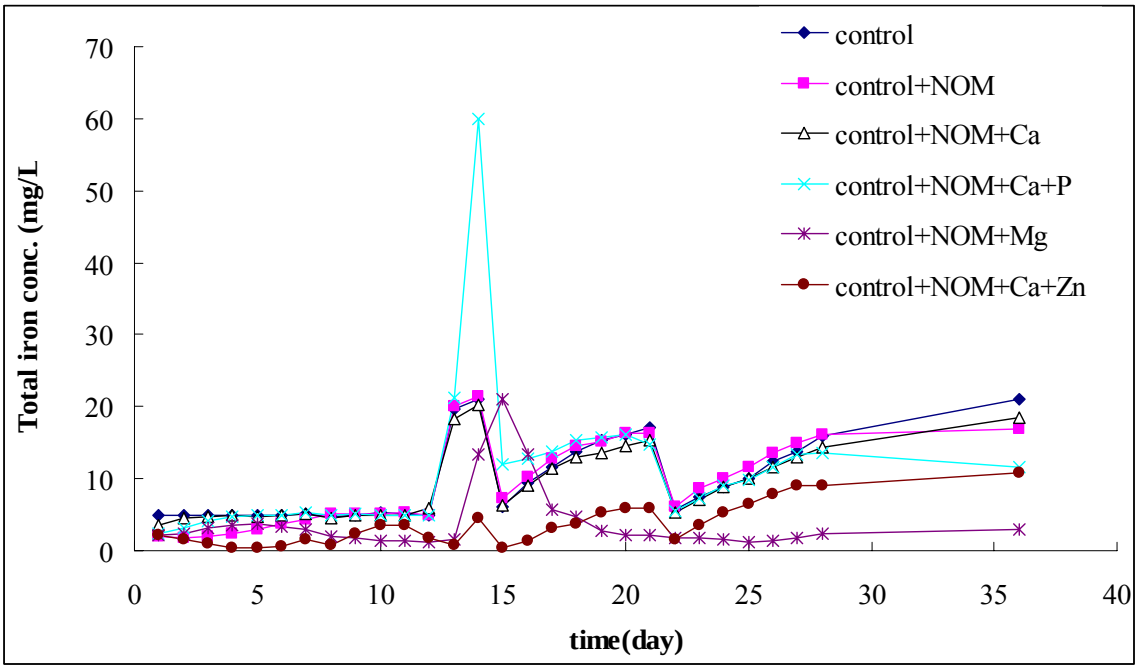
Soluble iron release under O_2-saturated condition, no SRB inoculation.



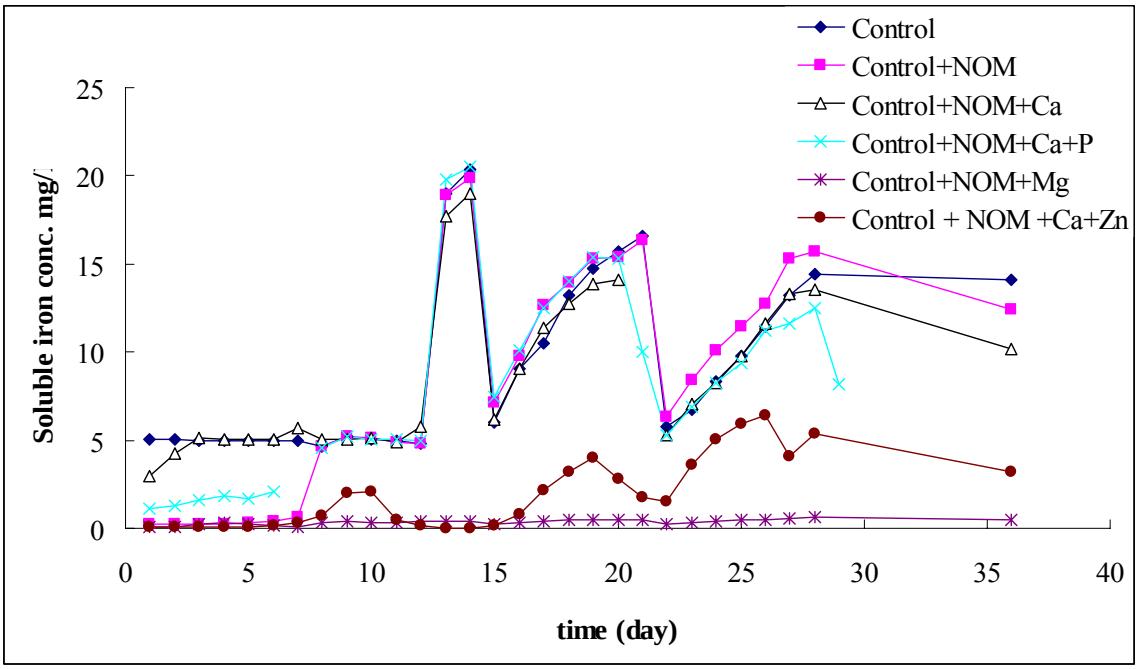
(a) Total iron released to water under O_2-saturated condition, no SRB inoculation. The gradual increase of iron represented the accumulation through each water change and the sudden drops represent a new water change



(b) Soluble iron released to water under O_2-saturated condition, no SRB inoculation. The gradual increase of iron represented the accumulation through each water change and the sudden drops represent a new water change



(c) Total iron released to water under low-O_2 condition, no SRB inoculation. The gradual increase of iron represented the accumulation through each water change and the sudden drops represent a new water change



(d) Soluble iron released to water under low-O_2 condition, no SRB inoculation. The gradual increase of iron represented the accumulation through each water change and the sudden drops represent a new water change

Figure A-1-9: Effect of NOM, Calcium, phosphorus, magnesium, and zinc.

(a) Total iron, O_2-saturated condition (b) Soluble iron, O_2-saturated condition

(c) Total iron, low-O_2 condition (b) Soluble iron, low-O_2 condition

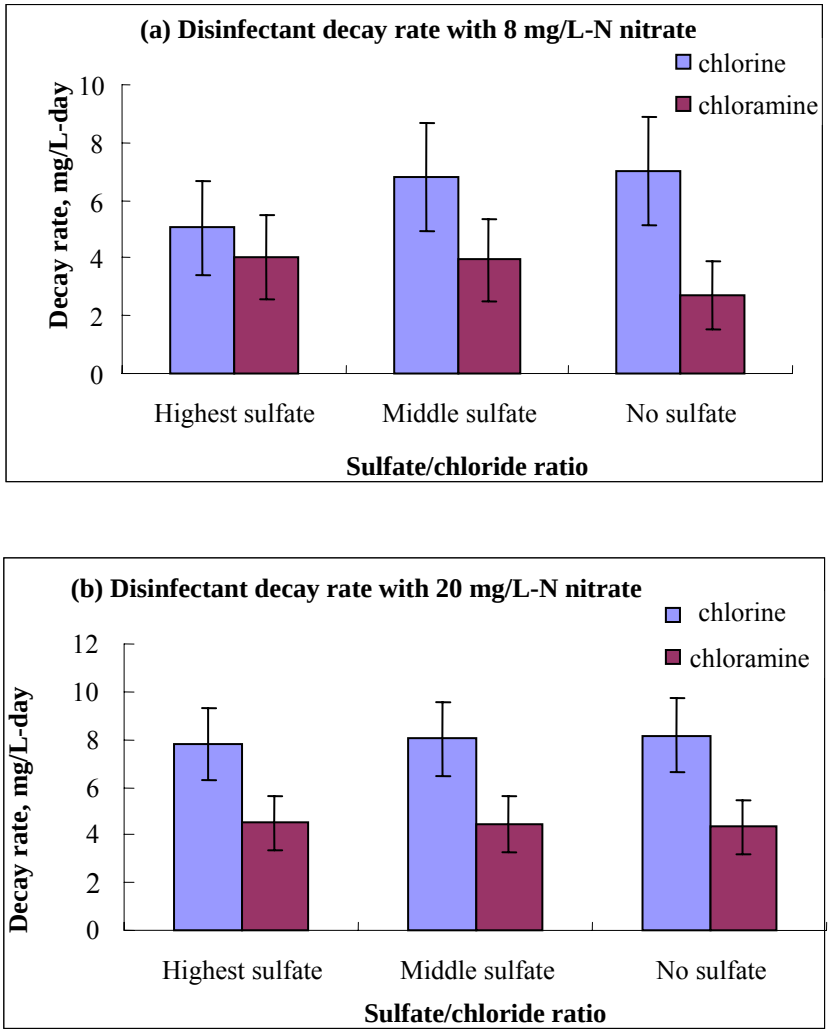
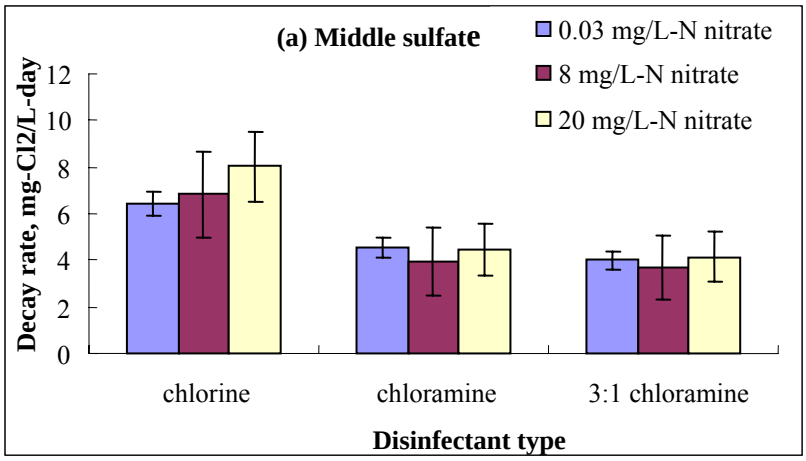


Figure A-1-10: Effect of sulfate/chloride ratios.

Disinfectant decay rate, SRB inoculated. (a) 8 mg/L-N nitrate (b) 20 mg/L-N nitrate Error bars represent 90% confidence intervals.



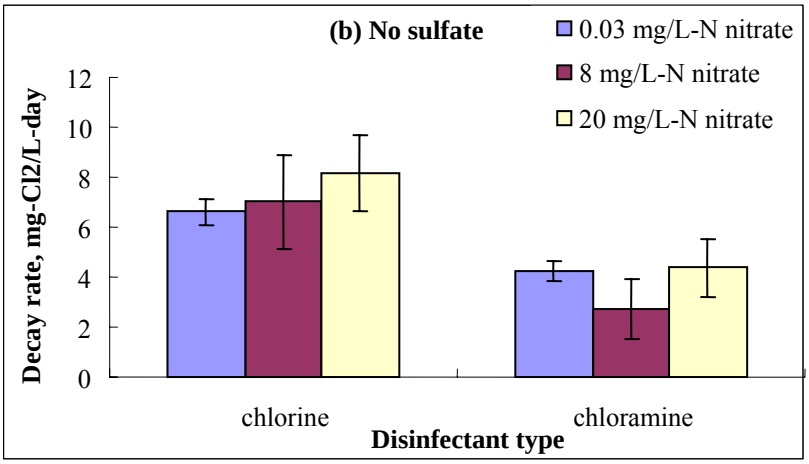
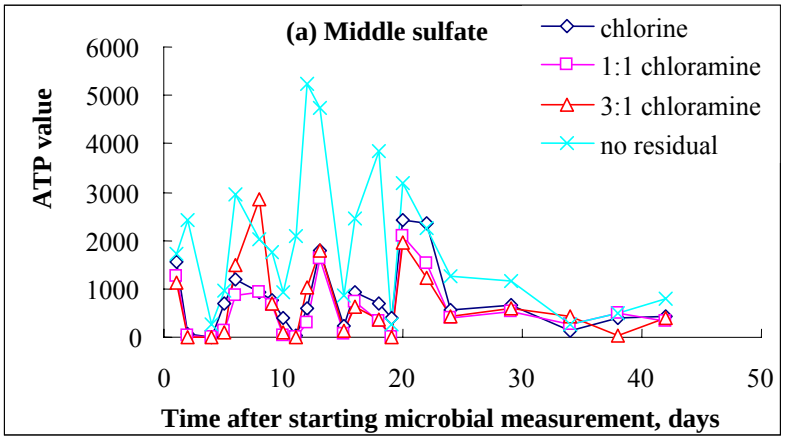


Figure A-1-11: Effect of nitrate. Disinfectant decay rate, SRB inoculated. (a) Middle sulfate (b) No sulfate. Error bars represent 90% confidence intervals.



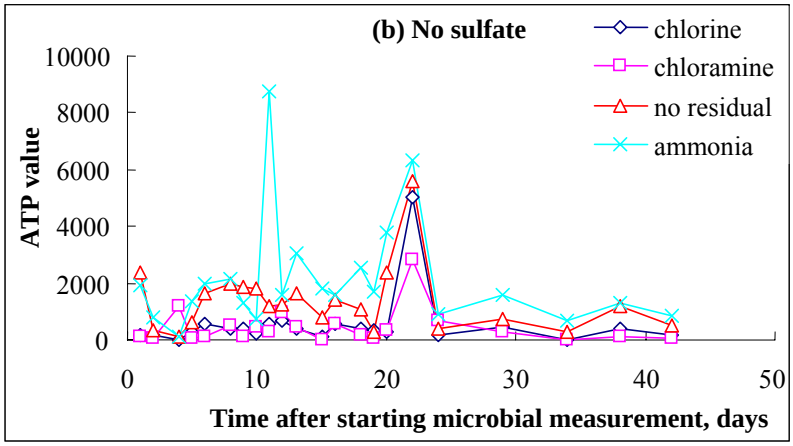


Figure A-1-12: Microbiological activity in bulk water based on ATP test, SRB inoculated. (a) Middle sulfate (b) No sulfate

Chloramine

Highest sulfate Middle sulfate No sulfate

Old coupons

New coupons

Chlorine

Highest sulfate Middle sulfate No sulfate

Old coupons

New coupons

No residual

Highest sulfate Middle sulfate No sulfate

Old coupons

New coupons

Ammonia

Highest sulfate No sulfate

Old coupons

New coupons

Figure A-1-13: Scale morphology after 153 days exposure (old coupons) and 118 days exposure (new coupons), SRB inoculated.

Control control + 12 mg/L-Mg control + 1 mg/L-Zn

Figure A-1-14: Scale morphology after 46 days exposure, no SRB added.

No Mg + 20 mg/L-Si

3 mg/L-Mg + 20 mg/L-Si

12 mg/L-Mg + 20 mg/L-Si

25 mg/L-Mg + 20 mg/L-Si

25 mg/L-Mg+20 mg/L-Ca +20 mg/L-Si

25 mg/L-Mg+ 40 mg/L-Si

No Mg, 20 mg/L-Ca + 20 mg/L-Si

25 mg/L-Mg, No Si

Figure A-1-15: Scale morphology after 37 days exposure, no SRB added.

Table A-1-1: Different iron corrosion measurement methods under low-O_2 condition.

Parameters	Iron release	Weight loss	H_2 evolution and confidence
NOM	---	---	↓, 95%
Ca^{2+}	---	---	---
Phosphate	---	---	↑, 97%
Mg^{2+}	↓	↓	↑, 99%
Zn^{2+}	↓	↓	---
Free Cl_2	↓	---	↑, 93%
Chloramines	↓	---	---
Free chlorine vs. chloramine	free chlorine < chloramine	No difference	96% confident, free chlorine > chloramine
Mg vs. Ca	Mg < Ca	No difference	98% confident, Mg > Ca

Note: ↑: increase, ↓: decrease, --- no significant effect

CHAPTER II: IMPLICATIONS OF NUTRIENT RELEASE FROM IRON METAL FOR MICROBIAL REGROWTH IN WATER DISTRIBUTION SYSTEMS

Siyuan C. Morton[#], Yan Zhang[&] and Marc A. Edwards[*]

ABSTRACT — Control of microbial regrowth in iron pipes is a major challenge for water utilities. This work examines the inter-relationship between iron corrosion and bacterial regrowth, with a special focus on the potential of iron pipe to serve as a source of phosphorus. Under some circumstances corroding iron and steel may serve as a source for all macronutrients necessary for bacterial regrowth including fixed carbon, fixed nitrogen and phosphorus. Conceptual models and experimental data illustrate that levels of phosphorus released from corroding iron are significant relative to that necessary to sustain high levels of biofilm bacteria. Consequently, it may not be possible to control regrowth on iron surfaces by limiting phosphorus in the bulk water.

Key words — phosphorus, microbial regrowth, nutrient, iron pipe, corrosion

INTRODUCTION

Microbial regrowth is a significant concern for water utilities. The inter-relationship between iron corrosion and bacterial regrowth has long been known (Larson, 1939) and it

was recently suggested that the distribution system can somehow contribute to waterborne disease (Payment et al., 1997). There is widespread controversy as to how microbial regrowth of heterotrophic bacteria is best controlled. To oversimplify the current argument, the following equation is useful:

Organic Matter + Nitrogen + Phosphate + Trace Nutrients → Regrowth (Equation 1)

If a key nutrient such as phosphorus was present at levels low enough to slow or stop further bacterial growth, problematic regrowth would not occur. If high levels of chlorine disinfectants are present, bacterial regrowth can be repressed even if adequate nutrients are present. However, bacterial regrowth can become problematic if all key nutrients are available and disinfectants are not present.

Research has established that higher iron corrosion rates could increase the number of biofilm bacteria, possibly due to protection of bacteria by consumption of disinfectant at the pipe surface via corrosion reactions (LeChevallier et al., 1990, 1993). Near the pipe wall where biofilms are attached, chlorine disinfectant concentrations are too low to control bacteria since it is consumed by corrosion and reactions with other constituents such as dissolved natural organic matter. From this perspective, even though monochloramine is a less effective disinfectant than free chlorine, it can be more effective in controlling bacteria on iron since free chlorine is rapidly destroyed by the corroding pipe wall (LeChevallier et al., 1990, 1993). It has also been suggested that biofilm growth on pipes is high because the scale (rust) can absorb, concentrate and alter the organic matter in the water, rendering it more bioavailable (Camper et al., 2003). Some bacteria can also directly utilize ferrous iron or hydrogen produced from iron corrosion for growth (e.g., Videla, 1996).

Recent studies in Japan and Finland have argued that in finished drinking water or in certain samples collected from the distribution system, phosphorus is an important limiting factor for bacterial regrowth (Sathasivan et al., 1997, 1999; Lehtola et al., 2001, 2002; Miettinen, et al, 1997; Keinanen et al., 2002, Lehtola et al., 2002, Lehtola et al., 2004). Each µg P added to drinking water is reported to support the growth of 1.2×10^8 cells (Sathasivan et al., 1997, 1999). This is in marked contrast to results from the US and elsewhere, where studies suggested that orthophosphate dosing to distributed water did not increase biofilm growth on iron in actual or simulated distribution systems (Camper et al., 2003; LeChevallier et al., 1993). Instead, in the US and elsewhere it is believed that organic matter limits regrowth (van der Kooij, 1992; Camper et al., 2003). A key assumption by proponents of the phosphate limitation theory is that "phosphorus can not be introduced into the system unless it is introduced with the water entering the system (Sathasivan et al., 1997, 1999)." That is, the water itself is the only possible source of phosphorus for bacteria. If phosphate is limiting and disinfectant concentrations is low, dosing of a phosphate corrosion inhibitor could create problems with re-growth (Miettinen, et al, 1997).

Iron Pipe as a Possible Source of Phosphorus

A recent literature review (Morton, et al., 2004) noted that iron and steel-making processes begin with iron ore which can contain from 0.02-1% by weight phosphorus. When the ore is heated up to >1300-1600° C in furnaces the phosphate is reduced to lower oxidation states (Friel et al., 1976). Phosphorus is present in iron and steel in its reduced form as iron phosphide [Fe-Fe_3P eutectic] and other species. In some cases, ferrophosphorus (iron phosphides) is also added during iron and steel making process to

reduce energy costs by lowering the casting temperature, enhance abrasion resistance, and improve corrosion resistance (Corbridge, 1978; Epstein, 1936; Stoughton, 1923). Iron/steel used in water distribution systems typically contains 0.03-0.2% phosphorus by weight (AWWARF and DVGW-TZW, 1996).

This phosphorus is released when the iron or steel is corroded. We term phosphorus species with an oxidation state lower than +5 "reduced phosphorus" (Morton, 2003a, 2004, 2005). Recent exploratory testing detected reduced phosphorus release to water during iron corrosion as phosphite and hypophosphite. For instance, in preliminary tests cast iron filings (0.2% P) were immersed in 10^{-3} M NaOH, and more than 0.5 mg/L-P of phosphite was present in water after 21 days (Morton et al., 2005). This is of interest in the context of regrowth since many bacteria can utilize phosphite directly as a P source (Casida, 1960; Malacinski et al., 1966; Morton, 2004). Reduced phosphorus may not be detected by standard environmental analysis (Morton et al, 2003a, 2005)

The average corrosion rate of iron in typical distribution systems range from a low of about 0.9 milli-inches-per year (mpy) to above 10 mpy (Volk et al., 2000; LeChevallier et al, 1993; AWWARF and DVGW-TZW, 1996). Since anodes and cathodes are often separated on iron pipe, anodic areas actually experience corrosion rates per unit area much higher than these values, whereas cathodic areas corrode at a slower rate. Nonetheless, for purposes of illustration uniform corrosion rates of 1-10 mpy are assumed. If iron with 0.2% P (AWWARF and DVGW-TZW, 1996) was corroding at 10 mpy and all phosphorus was released, the average concentration of phosphorus in the fully mixed bulk water would increase 1 μg/L after seven days in a 1 foot diameter pipe. Thus, the iron pipe is a potentially significant source of phosphorus. Since the

importance of this source would increase as pipe diameter decreased, small diameter galvanized pipes in homes might be a more significant source of phosphorus for bacteria.

It is also instructive to consider that biofilms on a pipe wall would have access to any released phosphorus from the iron before it was diluted by flow within the pipe. For a pipe with 0.2% phosphorus content corroding at 10 mpy, 1.1×10^{-3} µg P is available for release per cm^2 of pipe each day. Using the Sathasivan et al., (1999) finding of 1.2×10^8 cells grown/µg P, this level of phosphorus release could support 1.32×10^5 cells each day. This would be very significant relative to actual bacterial biofilm counts on the order of 10^4 to 10^7 colony forming units (CFU) or heterotrophic plate count per cm^2 of iron pipe, especially considering that these bacterial densities build up over a period of weeks (e.g., Volk et al., 2000; LeChevallier et al., 1993). Clearly, the level of phosphorus released from the pipe is sufficient to support biofilm growth at significant levels, even if phosphorus was not present in the distributed water.

Re-examining past literature on phosphorus limitation. A close examination of previous research findings of phosphate limitation in water supplies reveals that most experiments were conducted using water as it left the treatment plant and before it had contacted iron pipes. In such circumstances the iron pipe cannot serve as a source for bacteria. Only one study used water samples collected from within the distribution system (Sathasivan et al., 1999), and it is uncertain whether those samples were collected from water that had contacted iron pipes. Cementitious, copper or stainless steel pipe materials are not likely to leach significant concentrations of phosphorus to water. In water distribution systems that did not contain materials that leach phosphorus, it is more

likely that phosphorus could be the limiting nutrient, and adding it to the water could stimulate regrowth

In contrast, previous work studying regrowth in the presence of iron pipe or in real water distribution systems did not find that phosphate addition increased biofilm densities (Camper et al., 2003; Abernathy, et al., 1998; Butterfield, et al., 2002; Volk et al., 2000). The conclusion was that phosphate was not a limiting factor to growth in these waters. This is also the expected trend if sufficient phosphorus were coming from the corroding iron metal itself.

Anticipated fate and transport of P released from pipe

It is anticipated that the oxidation state of phosphorus released from corroding iron could play a role in P bioavailability within the scale or on the pipe wall. To illustrate, consider the disposition of iron corrosion products and redox zones on a corroding iron pipe (Figure 2-1). For purposes of this discussion, it is assumed that bacteria are distributed throughout these zones in a mixture of biofilm and inorganic scale layers. In the outermost regions of scale (Figure 2-1) significant concentrations of disinfectant or high levels of oxygen might be present. Although free chlorine and other strong oxidants are rapidly removed, it is instructive to determine whether free chlorine quickly reacts with hypophosphite (PO_2–P) and phosphite (PO_3–P) to produce phosphate which is thermodynamically stable (Pourbaix, et al., 1966). In the outer zone of scale (zone c in Figure 2-1) that contacts O_2 and disinfectants, ferric iron (Fe^{3+}) species are dominant. Phosphite and hypophosphite may be more bioavailabile in this region, because phosphate would be precipitated as ferric phosphate or $FePO_4$ in the high oxidizing zone or sorbed to $Fe(OH)_3$ solids. Ferric phosphite, ferric hypophosphite and sorption of these

reduced phosphorus species to $Fe(OH)_3$ solids has not been reported. Underneath the oxidizing zone, there is a region in which ferrous iron (Fe^{2+}) species are likely dominant in green-rust type materials. Since vivianite or $Fe_3(PO_4)_2$ solids are quite insoluble while phosphite and hypophosphite solids are not known, it is possible that reduced phosphorus species might be more mobile in this zone.

In summary, the idea that significant levels of phosphorus can originate from corroding iron could reconcile many seemingly conflicting results in previous research. Experiments in this work were designed to examine the release of phosphorus species from iron, and qualitatively define key aspects of reduced phosphorus chemistry in relation to fate and bioavailability within iron pipe scale.

MATERIALS AND METHODS

To evaluate the release of phosphorus species from iron during aerobic corrosion and their stability at room temperature under different pH conditions, four different types of 20 mL samples were set up including pure distilled and deionized H_2O (DI H_2O), 10^{-3} M NaCl, 10^{-3} M HCl, and 10^{-3} M NaOH. Four grams of cast iron filings were added to each of these background solutions. A parallel set of tests was run under identical conditions but with an initial 100 µg/L P spike of hypophosphite or phosphite. Samples were collected and filtered and analyzed with IC-ICP for PO_2, PO_3, and PO_4 (Morton, et al., 2005). The detection limit of the IC-ICP method was 10 µg/L-P (Morton et al., 2005).

In order to examine the influence of strong oxidants, such as free chlorine on released phosphorus species, 5 mg/L chlorine was dosed into samples containing 200 ppb PO_2 and

PO_3. A small volume of solution was withdrawn, filtered and analyzed by IC-ICP over time.

To test the stability of these three phosphorus species (PO_2, PO_3 and PO_4) in the presence of ferric iron (and oxygen), 100 mL solutions with 37.5 mg/L-P of sodium hypophosphite monohydrate (99%, Acros), phosphorous acid (98%, Acros), and sodium phosphate dibasic anhydrous (100.1%, Fisher Scientific) solutions were added with $FeCl_3$ (solid) to a final concentration of 200 mg/L-Fe. For each P species, there were three samples, and three respective controls without iron but with Cl^- added as KCl to the same final Cl^- concentration. Samples and controls were then adjusted to three pH conditions (pH 4, 7, 8.5) with HCl or NaOH. Over the experiment period, 5 mL samples of solution were collected after filtration through a 0.2 uM pore size filter after stirring, and analyzed with IC-ICP method for PO_2 and PO_3 (Morton, et al., 2005) and ascorbic acid method for PO_4.

To illustrate the influence of ferrous iron on stability of phosphorus species, the above experiment was repeated but after purging with 99.9998% N_2 for 20 minutes in a glove box. 200 mg/L-Fe of $FeSO_4$ solid was added to each container, and a corresponding amount of K_2SO_4 was added to control bottles. Filtered samples were collected as mentioned above.

Unless specified, soluble phosphorus species were operationally quantified after filtration through 0.45 μm pore size filters.

EXPERIMENTAL RESULTS AND DISCUSSION

Tests were conducted on samples in the presence of cast iron and with or without hypophosphite or phosphite spikes. The test solutions included pure water, 1 mM NaCl, 1 mM HCl or 1 mM NaOH.. No detectable phosphate appeared in any of the samples at any point in the experiment. If it was formed via corrosion it was therefore removed by scale.

100 μg/L phosphite spikes disappeared from samples in a few days except for the solution of 10^{-3} M NaOH, for which about 500 μg/L PO_3-P was produced after three weeks as a result of cast iron corrosion (Figure 2-2). On the basis of the observed loss of phosphite spikes, even if phosphite was released from metal during corrosion at neutral or acidic pH, it would be removed from water. These losses are possibly attributable to oxidation of the phosphite to phosphate and then precipitation/sorption to iron hydroxides. Thus, cumulative phosphite release to the solution from corrosion may be much higher than the concentrations measured at neutral or acidic pH.

At higher pH, there was minimal loss of phosphite from the spiked solution and its final concentration was much higher than at neutral or acidic pH. Slight variations in corrosion rates between samples is the likely reason that PO_3-P ended slightly higher in the control than in the sample with the 100 ppb spike of PO_3-P.

Only traces of hypophosphite near the detection limit were present after the experiment depicted in Figure 2-2 and this data is not shown. Spiked hypophosphite was more slowly lost than phosphite in all samples, and the rate of hypophosphite removal was also lower at higher pH (Figure 2-3).

Control samples containing 100 μg/L PO_2 and PO_3 but no iron were stable in the presence of oxygen for a period of weeks (stored at 4 ºC or at room temperature). After 2 hours in the presence of 5 mg/L free Cl_2, greater than 85% of PO_2 and 60% of PO_3 remained in the solution (Figure 2-4). Therefore, in the absence of iron the oxidation of PO_2 and PO_3 is relatively slow even in the presence of free chlorine.

After addition of 200 mg/L Fe^{3+}, at least 90% of the PO_2 remained in the solutions after 4 hours and about 50% of the PO_3 remained in solution after 6 hours at pH = 7 or 8.5. In marked contrast, 85-100% of the PO_4 was removed from solution by Fe^{3+} at pH 4, 7 and 8.5 after only 1 hour (Figure 2-5). Clearly, PO_2 and PO_3 are not removed from solution as readily as phosphate.

If 200 mg/L Fe^{2+} was spiked to water and O_2 was absent, after 24 hours there was no detectable removal of PO_2 (Figure 2-6) and PO_3 was only removed at pH 8.5 (<40% removal). On the other hand, after one hour, 100% of the PO_4 was removed at pH 7 and more than 90% of PO_4 was removed at pH 8.5 (result not shown). Phosphate is very readily immobilized by both ferrous and ferric iron (Snoeyink, 1980). The expectation is that phosphate will be scavenged in the redox zone dominated by Fe^{+2} much more effectively than phosphite or hypophosphite at pH at or above 7.0.

Deep within biofilm scale, bacteria which could utilize phosphite or hypophosphite could have a major competitive advantage versus bacteria that could use only phosphate, since phosphate might be relatively scarce.

Conceptual analysis of phosphorus release from iron corrosion

Rough estimates were made of phosphorus mass transport from the water versus phosphorus from corrosion. Assuming uniform corrosion at 8 mpy and metal with a

0.2% phosphorus content, total phosphorus release from corrosion is on the order of 10^{-10} $g/m^2/sec$ (Table 2-1). Comparable P flux to the pipe surface from the water is expected even at a very low level of 0.01 μg P/L in water flowing at 0.4 m/sec (Table 2-2). In general, these results indicate that P released from iron pipe during corrosion will typically be at least 10 times less than the P supplied to the pipe surface.

However, in several situations, P from iron corrosion could be of similar magnitude or even dominant relative to P supplied from the water. For example, when water is stagnant or at flow rate < 0.01 m/s, if the water contained 0.01-1 μg P/L, P from corrosion could be comparable or greater than the 10^{-11} - 10^{-13} $g/m^2/sec$ from the water. Or, deep under scale layers, the reduced P from iron corrosion could be much more significant to bacteria than PO_4 from the bulk water, since PO_4 is readily removed by corrosion products (e.g. Fe^{2+}, Fe^{3+}) and will be less likely to be transported through scale. In such situations, the reduced P released from iron corrosion could accumulate and support biofilm growth. Finally, considering non-uniform corrosion, much higher fluxes of reduced phosphorus would occur in small anodic areas deep under scale that is isolated from bulk water. The main conclusion is that reduced phosphorus from corrosion can serve as a significant P source even if phosphate was completely removed from the source water or completely removed by scale.

The ready availability of phosphorus from iron might partly explain why corroding iron usually has much higher biofilm densities than cement, polyvinyl chloride (PVC), polycarbonate, glass and stainless steel whenever such comparisons are made for the same water. In one study (Camper et al., 1996), coliform numbers and heterotrophic plate counts (HPC) on polycarbonate coupons were much (10-fold) lower than for mild-

steel coupons when they were in separate reactors. However, if polycarbonate was in the same reactor as mild steel, it had comparable coliform and HPC. The strong implication was that the steel was somehow promoting growth on the nearby polycarbonate. Release of nutrients such as phosphorus from the steel to the polycarbonate is a possible explanation for this result.

The role of disinfectants might also be much more complicated than first believed. It is possible that free chlorine (and chloramine) could limit phosphorus availability in the outermost scale layers (Figure 2-1), since they would tend to precipitate or absorb orthophosphate to solids forming via corrosion. In other words, dosing of an oxidant might induce a phosphorus limitation when it did not exist previously. We speculate that this might help explain the perplexing finding that dosing of chlorine sometimes dramatically decreases overall iron corrosion rates, as it might trigger phosphorus limitations within the scale.

Other possible nutrients from iron corrosion

Although the results were preliminary and we cannot quantify the magnitude of the effect, our experiments also demonstrated that NH_3 could be formed from N_2 gas via anaerobic iron corrosion (Morton, 2003b). This is consistent with findings published by other researchers (Schrauzer et al., 1976; DÖrr et al, 2003). If confirmed, this might help explain how biocorrosion can proceed readily even in environments where fixed nitrogen would otherwise be limiting, even though fixed nitrogen species such as nitrate are readily available in drinking water distribution systems. Finally, although the experimental results are not presented, we also measured production of methane from bicarbonate in water after contact with iron, and we took steps to eliminate this reaction

in all experiments presented herein by conducting tests in the absence of inorganic carbon. Others have observed similar effects (Hardy et al., 1996). The ability of iron to abiotically fix carbon is clear.

A comparison of organic carbon formed from iron corrosion by autotrophic bacteria relative to bulk drinking water was conducted using calculations similar to the comparison on phosphorus as discussed earlier. Fixed organic carbon can be produced by autotrophic iron oxidizing bacteria and hydrogen bacteria, and the yield factors for these two bacteria are: 0.007-0.117 molC/mol Fe^{2+} (Neubauer et al., 2002) and 0.119 molC/mol H_2 (Tanaka et al., 2001). Assuming that iron corrosion proceeds exclusively through an anaerobic pathway via H_2 and Fe^{+2} production, followed by efficient utilization of these substrates by these autotrophs, allows estimation of fixed carbon created per unit area of surface at a given corrosion rate. For water containing 10 μg/L fixed carbon, potential fixed carbon produced per unit area from autotrophic activities during corrosion is much less than would be supplied from the water (Table 2-1). However, during stagnant conditions, or certainly deep under anodic areas, corrosion might be a significant source of carbon for bacterial regrowth. Indeed, autotrophic bacteria capable of utilizing H_2 have been isolated from pipe scale in tests using simulated water distribution systems (LeChevallier et al., 1993).

A final overall implication is that in some cases, limiting regrowth might sometimes be directly dependent on reducing the iron corrosion rate, since corrosion can serve as the source of many potentially limiting nutrients. The link between higher regrowth and higher iron corrosion is, in fact, the experimental finding of LeChevallier et al (1990, 1993) and others, but the cause was believed to be protection of the biofilm from

disinfectants. It is also possible that this result is at least partly attributable to lower production of essential nutrients.

CONCLUSIONS

Significant phosphorus can be derived from corroding iron relative to the levels required to support bacterial regrowth.

Phosphite and hypophosphite are relatively resistant to oxidation and are less likely to be removed by ferrous and ferric iron than phosphate.

Corroding iron and steel can abiotically produce all main macronutrients necessary for heterotrophic bacterial regrowth including fixed carbon, fixed nitrogen, and phosphorus (see equation 1). However, it is uncertain whether the levels of macronutrients produced by iron corrosion are sufficient to support heterotrophic bacterial growth at problematic levels.

ACKNOWLEDGEMENT

This work was supported by the National Science Foundation (NSF) under grant BES-0201849. The opinions, findings, conclusions or recommendations are those of the authors and do not necessarily reflect the views of NSF.

APPENDIX 2. COMPARISON BETWEEN NUTRIENT FROM BULK WATER AND FROM IRON CORROSION

Nutrient flux from corrosion

Simplified anaerobic iron corrosion process:

$$Fe + H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$$

C comes from autotrophic bacteria grown on corrosion by-products, specifically: Hydrogen-oxidizing bacteria can produce 0.19 molC/mol H_2 (Ishizaki, et al., 2001) Iron-oxidizing bacteria can produce 0.12 molC/mol Fe^{2+} (Neubaeuer, et al., 2002), Autotrophic sulfate reducing bacteria can produce 0.13 molC/mol H_2 (Cypionka and Pfennig, 1986; Van Houten, et al., 1994). Autotrophic denitrifiers can produce 0.16 molC/mol H_2 (Wang and Qu, 2003).

100% of P is released when iron pipe is corroded; P content in iron pipes is 0.03% to 0.2% (AWWARF and DVGW-TZW, 1996), and 0.2% P content is used for the highest phosphorus release from pipe.

Nutrient flux from bulk water

Diffusion Equation:

$$J = -D/\delta \cdot (C_1 - C_2) = -K(C_1 - C_2) \text{ (Bennett and Momentum, 1982)}$$

J: bulk diffusion flux, g/m^2•s

D : Diffusion coefficient, m^2/s;

δ : Diffusion constant, m;

C_1, C_2 : Concentration of P in the water and on the pipe surface, g/m^3.

K: mass transfer coefficient, m/s $K = 0.023\text{Re}^{0.80} \cdot \text{Sc}^{0.33} \cdot \text{D/d}$, $Sc = \mu/(\rho \cdot D)$

For turbulent flow (Reynolds's number Re> 4000, $\mathrm{Re} = d \cdot v \cdot \rho / \mu$, where d is pipe diameter (a 12 inch pipe diameter used to get the lowest flux), v is water velocity (0-2 m/s), μ is water viscosity (1.66×10^{-3} Pa•s), ρ is water density($1.036 \times 10^{3} kg / m^{3}$). Assume:

1). Concentration on pipe surface equal zero (C_2 = 0), the diffusion equation is simplified to $J = -KC$.

2) Organic carbon content in water is 1 ppb to 1ppm (use 1 ppb in the table for the lowest carbon flux from water), phosphorus in water is 0.01 ppb to 1 ppm (use 0.01ppb in the table for the lowest phosphorus flux from water).

To simplify the calculation, assume diffusion coefficient for phosphate and carbon is $1.64*10^{-9} m^2/s$ (Greankolis, 1983); For laminar flow, $K = 3.8 \cdot D / d$; $J = -3.8 \cdot (D / d) \cdot C$.

REFERENCES

Abernathy, C. and Camper. A. (1998) The Effect of Corrosion Control Treatments and Biofilm Disinfection on Unlined Ferrous Pipes. Final Project Report. National Water Research Institute.

AWWARF and DVGW-TZW (1996) *Internal Corrosion of Water Distribution Systems*, Second Edition. American Water Works Association, Denver, CO, pp 29-70.

Bennett, C. O. and Myers, J. E. (1982*) Momentum, Heat and Mass Transfer*, 3rd edition. Mcgraw-Hill, OH.

Butterfield, P. W., Camper, A. K., Biederman, J. A., and Bargmeyer, A.M. (2002) Minimizing biofilm in the presence of iron oxides and humic substances. *Water Res.* 36, 3893-3910.

Camper, A., Jones, W. L., and Hayes, J. T. (1996) Effect of growth conditions and substratum composition on the persistence of coliforms in mixed population biofilms. *Appl. Environ. Microbiol.* 62, 4014-4018.

Camper, A. K., Brastrup, K., Sandvig, A., Clement, J., Spencer, C., and Capuzzi., A. J. (2003) Impact of distribution system materials on bacterial regrowth. *JAWWA* 95(7), 107-121.

Casida, L. E. (1960) Microbial oxidation and utilization of orthophosphite during growth. *J. Bacteriol.* 80, 237-241.

Corbridge, D.E.C. (1978) *Phosphorus: An Outline of its Chemistry, Biochemistry and Technology*, 1st edition. Elsevier Scientific Publishing Co., Amsterdam.

Cypionka, H., Pfennig, N. (1986) Growth yields of desulfotomaculum orients with hydrogen in chemostat culture. *Arch Microbiol* 143, 396.

Dörr, M., Käβbohrer, J.; Grunert, R. (2003) A possible prebiotic formation of ammonia from dinitrogen on iron sulfide surfaces. *Angew. Chem. Int. Ed.*42, 1540-1543.

Epstein, S. (1936) *The alloys of iron and carbon*. Vol.1, McGraw-Hill Book Company, Inc., New York.

Friel, J. J., and Goldstein, J. I. (1976) An experimental study of phosphate reduction and phosphorus-bearing lunar metal particles. *Proc. Lunar Sci. Conf.* 7th. pp 791-806.

Greankolis, C. J. (1983) *Transport Process and Unit Operations*, 2nd edition. Allyn and Bacon Inc, Boston, MA.

Hardy, L.I. and Gillham, R.W. (1996) Formation of hydrocarbons from the reduction of aqueous CO_2 by zero-valent iron. *Environmental Science and Technology* 30(1), 57-65.

Ishizaki, A., Tanaka, K., and Taga, N. (2001) Microbial production of poly-d-3-hydroxybutyrate from CO_2. *Appl. Microbiol. Biotechnol.* 57, 6.

Keinanen, M.M., Korhonen, L.K., Lehtola, M.J., Miettinen, I.T., Martikainen, P.J., Vartianen, T., and M.H. Suutari. (2002). The microbial community structure of drinking water biofilms can be affected by phosphorus availability. Applied and Env. Microbiology, 68(1), 434-439.

Larson, T.E. (1939) Bacteria, corrosion and red water. *JAWWA*. 31(7), 1186-1196.

LeChevallier, M. W., Lowry, C. D., and Lee, R. G. (1990) Disinfecting biofilms in a model distribution system. *JAWWA* 82(7), 87-99.

LeChevallier, M. W., Lowry, C. D., Lee, R. G., and Gibbon, D. L. (1993) Examining the relationship between iron corrosion and the disinfection of biofilm bacteria. *JAWWA* 85 (7), 111-123.

Lehtola, M. J., and Miettinen, I. T. (2001) Microbially available organic carbon, phosphorus, and microbial growth in ozonated drinking water. *Wat. Res.* 35(7), 1635-1640.

Lehtola, M. J., Miettinen, I. T., Keinanen, M.M., Kekki, T.K., Laine, O., Hirvonen, A., Vartianen, T., and Martikainen, P. J. (2004). Microbiology, chemistry and biofilm development in a drinking water distribution system with copper and plastic pipes. Water Res. 38, 3769-3779.

Lehtola, M. J., Miettinen, I. T., and Martikainen, P. J. (2002). Biofilm formation in drinking water affected by low concentrations of phosphorus. Can. J. Microbiol. 48, 494-499.

Lehtola, M. J., Miettinen, I. T., Vartianen, T., and Martikainen, P. J. (2002) Changes in content of microbially available phosphorus, assimilable organic carbon and microbial growth potential during drinking water treatment processes. Wat Res. 36, 3681-3690.

Malacinski, G., and Konetzka, W. A. (1966) Bacterial oxidation of orthophosphite. *J. Bacteriol.* 91, 578-582.

Miettinen L. T., Vartiainen, T., and Martikainen, P. J. (1997) Phosphorus and bacterial growth in drinking water. *Applied and Environmental Microbiology* 63(8), 3242-3245.

Morton, S. C., Glindemann, D. and Edwards M. A. (2003a) Phosphates, phosphites, and phosphides in environmental samples. *Environ. Sci. Tech.* 37(6), 1169-74.

Morton, S. C. (2003b) Phosphorus in the environmental and its role in anaerobic iron corrosion. Ph.D. dissertation, Virginia Polytechnic Institute and State University.

Morton, S. C., Edwards, M. (2004) Reduced phosphorus compounds in the environment. Accepted by *Critical Reviews in Environmental Science and Technology*.

Morton, S. C., Glindemann, D., and Edwards, M. A. (2005) Analysis of reduced phosphorus in samples of environmental interest. Accepted by *Environ. Sci. Tech.*.

Neubauer, S. C., Emerson, D., and Megonigal, J. P. (Aug., 2002) Life at the energetic edge: kinetics of circumneutral iron oxidation by lithotrophic iron-oxidizing bacteria isolated from the wetland-plant rhizosphere. *Applied and Environmental Microbiology* 68(8), 3988-3995.

Payment, P., Siemiatycki, J., Richardson, L., Renaud, G., Franco, E., and Prévost, M. (1997) A prospective epidemiological study of gastrointestinal health effects due to the consumption of drinking water. *International Journal of Environmental Health Research* 7, 5-31.

Pourbaix, M. (and others), translated by Franklin J. A. (1966) *Atlas of Electrochemical Equilibria in Aqueous Solutions* (English Translation), Pergaman Press, New York.

Sathasivan, A., Ohgaki, S., Yamamoto, K., and Kamiko, N. (1997) Role of inorganic phosphorus in controlling regrowth in water distribution system. *Wat. Res. Tech.* 5(8), 37-44.

Sathasivan, A., and Ohgaki, S. (1999) Application of new bacterial regrowth potential method for water distribution system – a clear evidence of phosphorus limitation. *Wat. Res.* 33(1), 137-144.

Schrauzer, G. N. and Guth, T. D. (1976) Hydrogen evolving systems. 1. the formation of H_2 from aqueous suspensions of $Fe(OH)_2$ and reactions with reducible substrates, including molecular nitrogen. *J. American Chem. Soc.* 98(12), 3508-3513.

Snoeyink, V. L. and Jenkins, D. (1980) *Water Chemistry*. John Wiley & Sons, New York.

Stoughton, B. (1923) *The metallurgy of iron and steel*. McGraw-hill Book Company, Inc. New York.

Tanaka, A. K., Taga, N. (2001) Microbial production of poly-3-hydroxybutyrate from CO2. *Applied Microbiol Biotechnol* 57, 6-12.

van der Kooij. (1992) Assimilable organic carbon as an indicator of bacterial regrowth. *JAWWW* 84(2), 57-65.

Van Houten, R.T.; Hulshoff Pol, L.W.; Lettinga, G. (1994) Biological sulphate reduction using gas-lift reactors fed with hydrogen and carbon dioxide as energy and carbon source. *Biotechnol. & Bioeng.* 44, 586.

Videla, H.A. (1996) *Manual of Biocorrosion*. Lewis Publishers, Boca Raton, FL.

Volk, C., Dundore, E., Schiermann, J., and LeChevallier, M. (2000) Practical evaluation of iron corrosion control in a drinking water distribution system. *Wat. Res.* 34(6), 1967-1974.

Wang, H-Y., Qu, J-H. (2003) Combined bioelectrochemical and sulfur autotrophic denitrification for drinking water treatment. *Wat. Res.* 37, 3767.

FIGURE AND TABLE

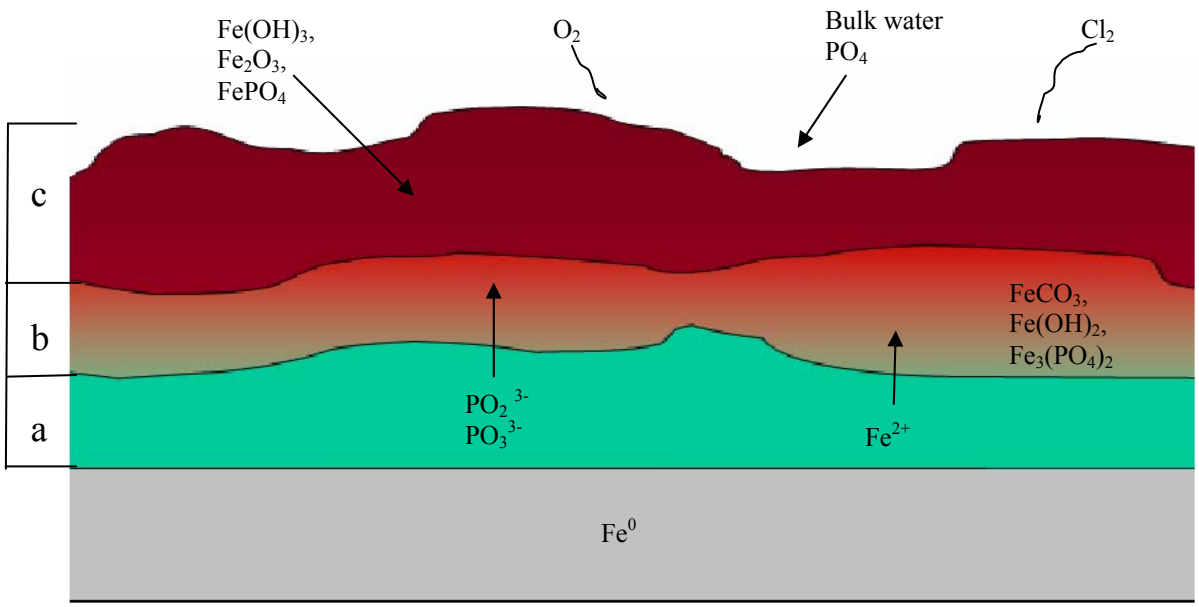


Figure 2-1. Conceptualization of iron speciation in scale on pipe in drinking water systems. The outermost scale layers are oxidized (Fe^{+3}) layers, whereas the inner layers are anoxic and Fe^{+2} dominates. a) no oxidant (O_2, disinfectants, etc.) layer; b) low oxidizing layer; c) highly oxidizing layer.

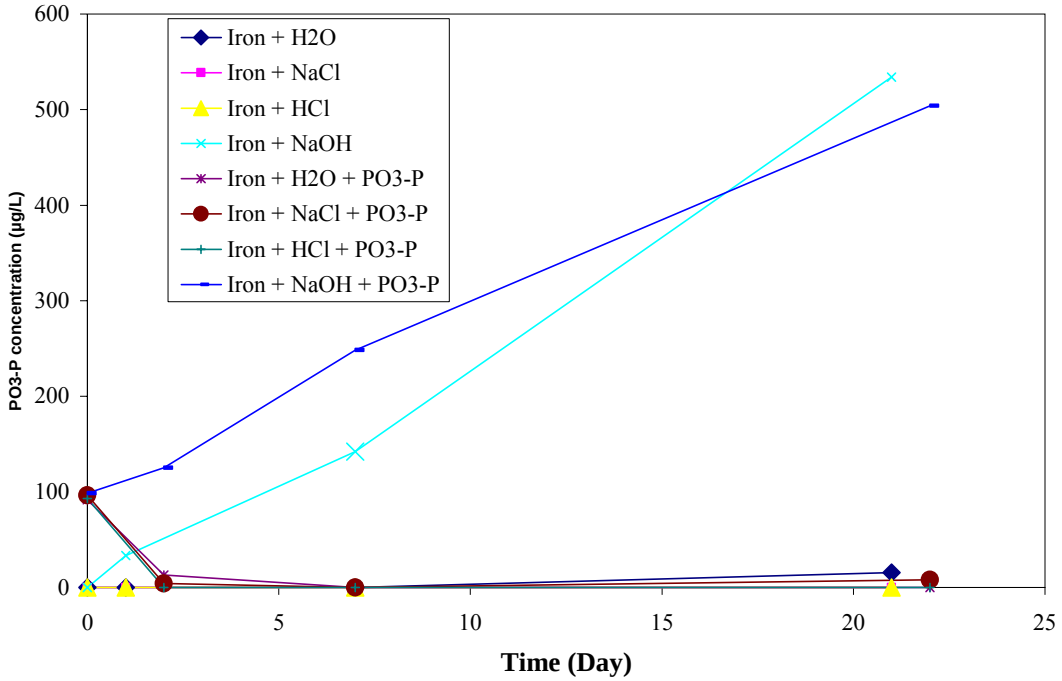


Figure 2-2. Phosphite (PO_3-P) from cast iron corrosion in different waters with and without 100 µg/L initial spikes of PO3-P.

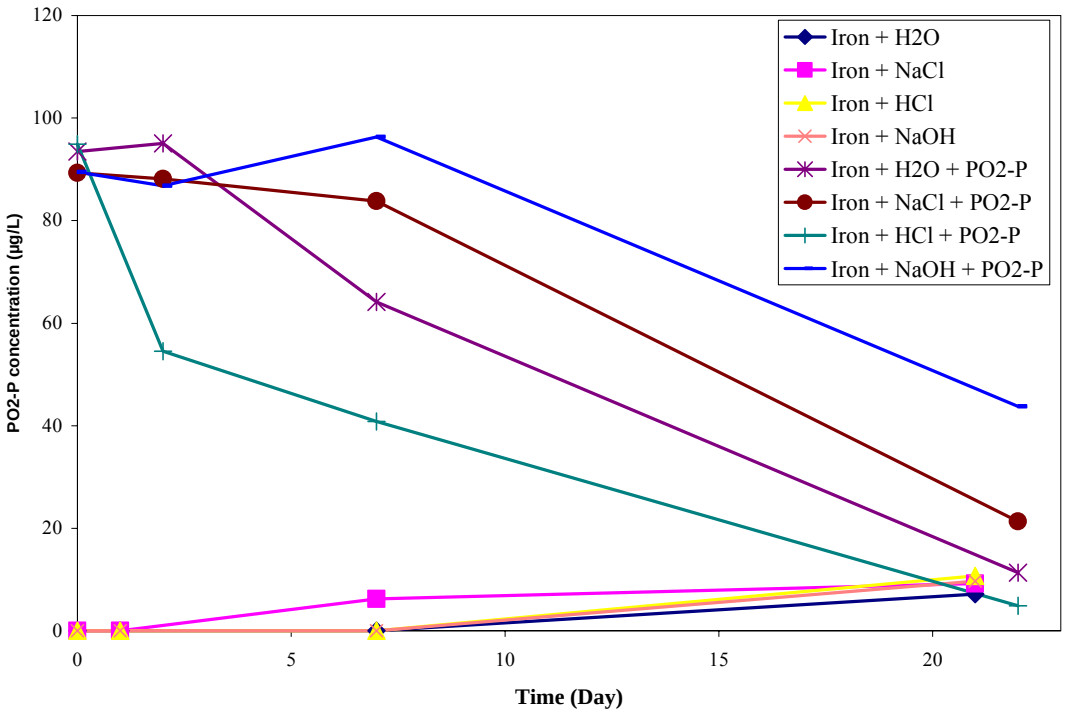


Figure 2-3. Hypophosphite (PO_2-P) in water during corrosion of cast iron with and without initial 100 µg/L spikes of hypophosphite.

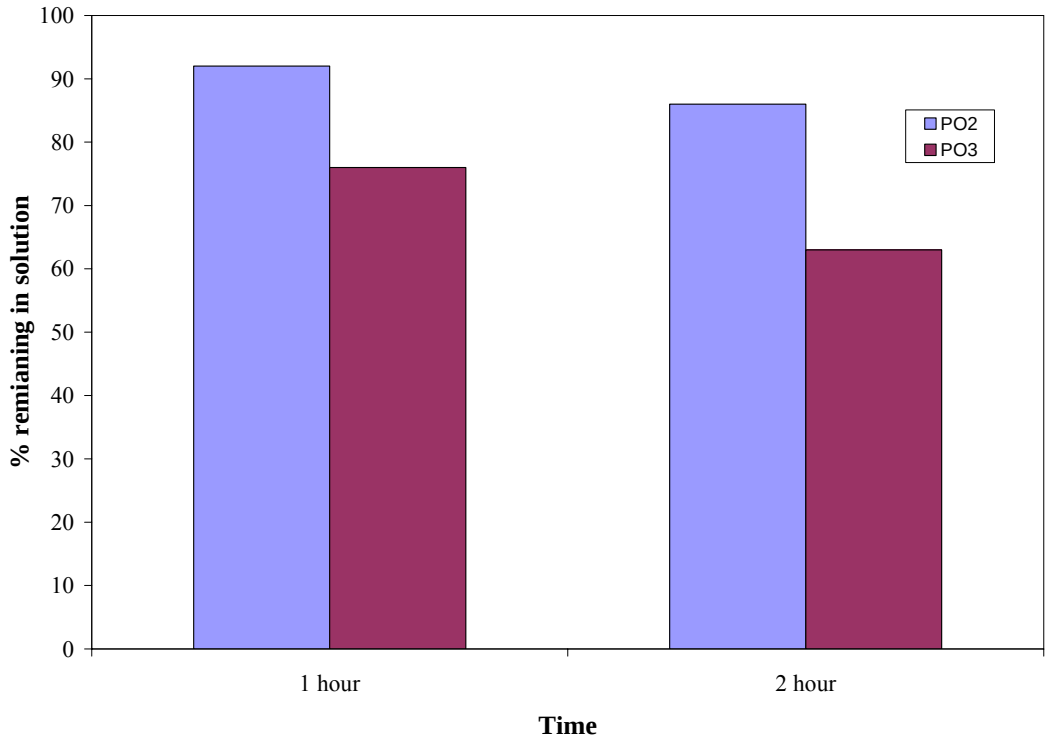


Figure 2-4. Stability of PO_2 and PO_3 in the presence of free chlorine

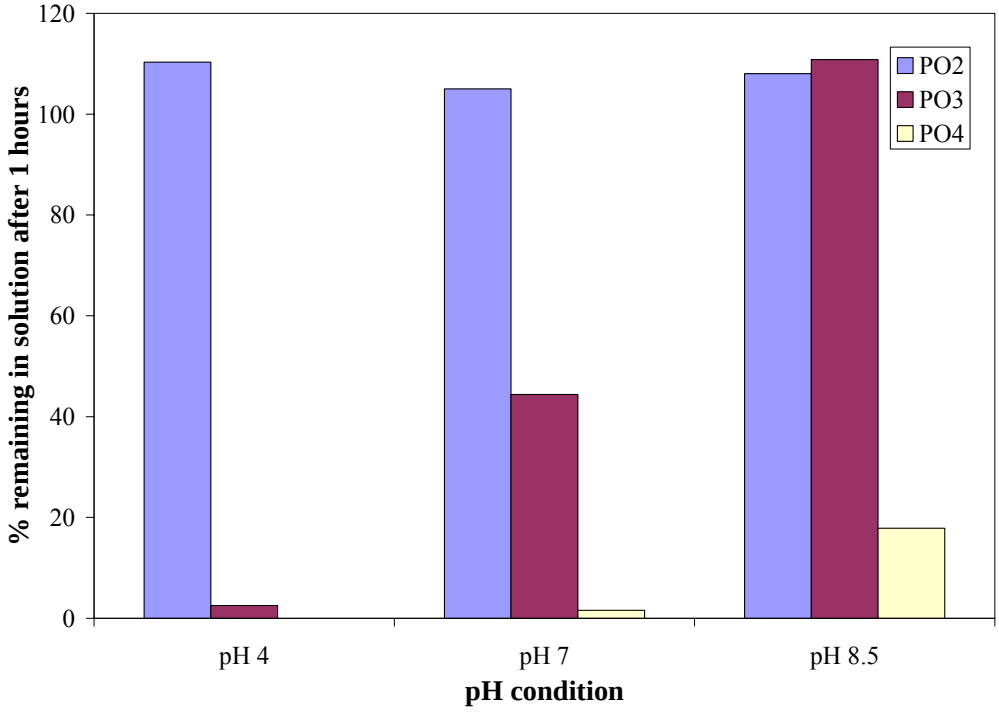


Figure 2-5. The stability of different phosphorus species in the presence of ferric iron and oxygen.

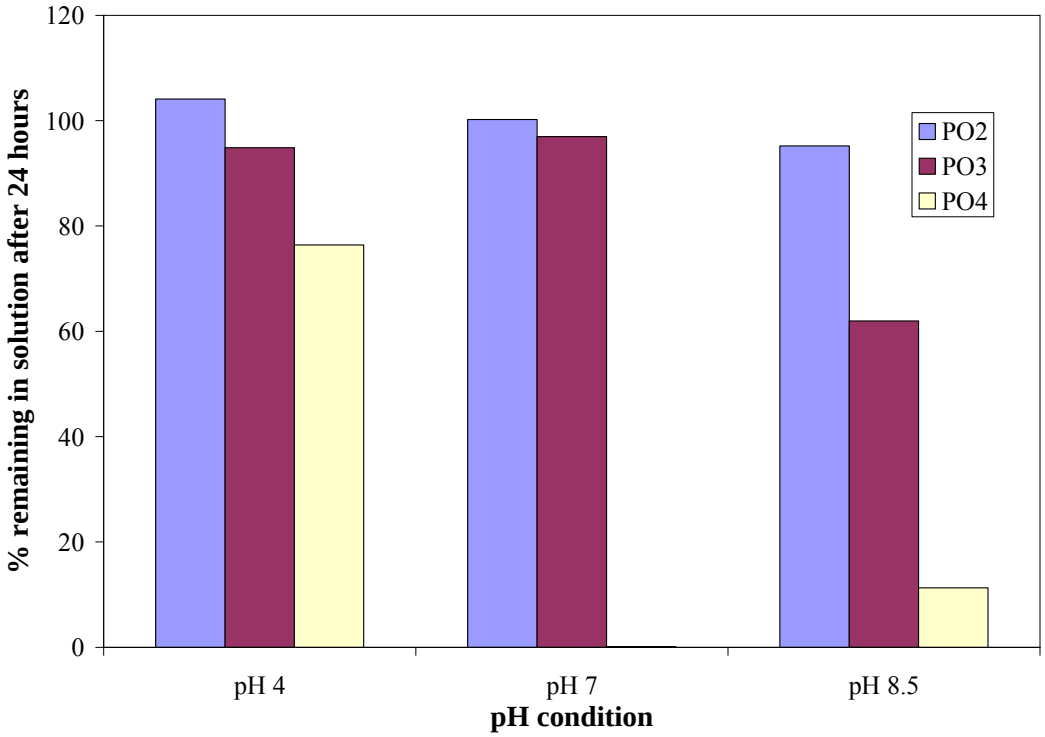


Figure 2-6. The stability of different phosphorus species in the presence of ferrous iron.

Table 2-1. Calculated Nutrient Originated From Iron Corrosion

Corrosion rate, mpy	Iron corroded, $g/m^2 \bullet s$	C produced by iron bacteria, $g/m^2 \bullet s$	C produced by hydrogen bacteria, $g/m^2 \bullet s$	C produced by Autotrophic SRB, $g/m^2 \bullet s$	C produced by denitrifiers, $g/m^2 \bullet s$	P released from corrosion, $g/m^2 \bullet s$
1	6.36×10^{-9}	1.60×10^{-10}	2.59×10^{-10}	1.84×10^{-10}	2.18×10^{-10}	1.27×10^{-11}
2	1.27×10^{-8}	3.19×10^{-10}	5.18×10^{-10}	3.68×10^{-10}	4.37×10^{-10}	2.55×10^{-11}
3	1.91×10^{-8}	4.79×10^{-10}	7.78×10^{-10}	5.52×10^{-10}	6.55×10^{-10}	3.82×10^{-11}
4	2.55×10^{-8}	6.38×10^{-10}	1.04×10^{-9}	7.37×10^{-10}	8.73×10^{-10}	5.09×10^{-11}
5	3.18×10^{-8}	7.98×10^{-10}	1.30×10^{-9}	9.21×10^{-10}	1.09×10^{-9}	6.37×10^{-11}
6	3.82×10^{-8}	9.58×10^{-10}	1.56×10^{-9}	1.10×10^{-9}	1.31×10^{-9}	7.64×10^{-11}
7	4.46×10^{-8}	1.12×10^{-9}	1.81×10^{-9}	1.28×10^{-9}	1.53×10^{-9}	8.91×10^{-11}
8	5.09×10^{-8}	1.27×10^{-9}	2.07×10^{-9}	1.47×10^{-9}	1.75×10^{-9}	1.01×10^{-10}
9	5.73×10^{-8}	1.43×10^{-9}	2.33×10^{-9}	1.66×10^{-9}	1.96×10^{-9}	1.15×10^{-10}
10	6.37×10^{-8}	1.60×10^{-9}	2.59×10^{-9}	1.84×10^{-9}	2.18×10^{-9}	1.27×10^{-10}

Table 2-2. Calculated Nutrient Flux fom Bulk Water

Water velocity, m/s	Reynolds' number	K, m/s	C flux, $g/m^2 \cdot s$	P flux, $g/m^2 \cdot s$
0	0	2.04×10^{-8}	2.04×10^{-11}	2.04×10^{-13}
0.01	2.71×10^{3}	2.04×10^{-8}	2.04×10^{-11}	2.04×10^{-13}
0.1	2.71×10^{4}	3.91×10^{-6}	3.91×10^{-9}	3.91×10^{-11}
0.4	1.08×10^{5}	1.19×10^{-5}	1.19×10^{-8}	1.19×10^{-10}
1	2.71×10^{5}	2.47×10^{-5}	2.47×10^{-8}	2.47×10^{-10}
2	5.42×10^{5}	4.30×10^{-5}	4.30×10^{-8}	4.30×10^{-10}