

Anticipating effects of water quality changes on iron corrosion and red water

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ABSTRACT

This study investigated the effect of disinfectant, sulfate/chloride ratios, nitrate concentration, magnesium hardness and zinc on iron corrosion. For the waters tested, free chlorine better controlled red water and microbial activity in the bulk solution. Consistent with predictions based on Larson's ratio, sulfate/chloride ratio changes did not have an effect on overall iron corrosion rates, although higher chloride was associated with increased localization of corrosion and pitting. High levels of nitrate increased the rate of chlorine decay and caused release of more iron, but had no effect on chloramine decay rates. The concentration of nitrate in the water might therefore be an important factor in considering the relative merits of chloramine versus chlorine as secondary disinfectants in real distribution systems. Increased magnesium and zinc can decrease mobilization of iron (e.g. red water) caused by silicate.

Key words | disinfectant, iron corrosion, magnesium, nitrate, sulfate/chloride, zinc

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INTRODUCTION

The net present replacement value of all publicly and privately owned potable water pipes in the US is of the order of \$2.4 trillion dollars (Edwards 2004). Unlined iron mains, lined iron mains with coatings that have deteriorated over years of use, and galvanized pipes 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 (McNeill & Edwards 2001).

Background

Chlorine versus chloramine

Chlorine disinfectants have been widely and effectively used to protect the safety of drinking water since 1913 in the US (Madigan *et al.* 2000). Generally, increased concentrations of disinfectant (oxidants) would be expected to increase

iron corrosion rates (AWWA 1999; McNeill & Edwards 2001). But older work by Baylis (1926) and more recent work by others (Sarin *et al.* 2004a, b) suggested that increased oxidant could reduce the amount of iron released to water.

Due to concerns 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. But substantial economic losses or gains will be accrued dependent on whether chloramines increase or decrease longevity of pipes relative to free chlorine. Conflicting trends have been reported in the few studies that have examined the role of disinfectants in iron corrosion rates to date. LeChevallier *et al.* (1990) reported a beneficial effect of chloramines versus chlorine on iron corrosion rates. Treweek *et al.* (1985) reported no visual and no weight loss difference between chlorine and chloramines, but Eisnor & Gagnon (2004) 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 in water compared to no disinfectant, and the increase was more significant with chlorine.

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 synthesized water containing very high assimilable organic carbon (added as glucose), negligible ammonia, 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. Although it is well known that cupric ions can plate out on steel or zinc as metallic copper, where it acts as the cathode and accelerates corrosion, the actual role of cupric ions on iron corrosion in drinking water systems has not been studied (McNeill & Edwards 2001). The authors also purposefully used a very high molar ratio of $\text{NH}_3:\text{Cl}_2$ 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 very high errors relative to weight loss measurements (AWWARF & DVGW-TZW 1996). The Treweek and Eisnor studies were of longer duration, but used non-synthesized water, and temperature was also varied (Table 1). In terms of pipe material, the LeChevallier study used new iron pipes, whereas old tuberculated pipes were used in the Eisnor and Gagnon study and new black iron was used by Treweek (Table 1).

Sulfate reducing bacteria and Larson index

Sulfate-reducing bacteria (SRB) have been regarded as the most important contributor to anaerobic corrosion (Uhlig & Revie 1985) for over 60 years. Although the anaerobic pathway is generally considered less important than the aerobic pathway in iron corrosion (Sun & Edwards 2002; Sun *et al.* 2002), there are studies reporting at least 0.1–5% iron corrosion via the anaerobic path even when oxygen is saturated and the iron surface is new (Speller 1951; Rushing *et al.* 2003). These values are actually a lower bound to the actual percentage of anaerobic iron corrosion, because measured H_2 that is produced by the process can be consumed through a variety of reactions.

The studies of Larson & Skold (1957, 1958) and Larson (1975) found that the ratio of chloride and sulfate to bicarbonate was practically important to iron corrosion, as expressed in the Larson index:

$$\text{Larson index} = \frac{2[\text{SO}_4^{2-}] + [\text{Cl}^-]}{[\text{HCO}_3^-]} \quad (1)$$

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 (Hedberg & Johansson 1987; Veleva *et al.* 1998) and sulfate (Riddick 1944; Veleva *et al.* 1998) caused increased weight loss.

Strong base anion exchange, expected to be installed as a new treatment for arsenic removal at utilities around the country, removes some bicarbonate and replaces 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 and corrosion is not to be affected. However, if HCO_3^- is replaced by Cl^- , increasing $[\text{Cl}^-]$ and decreasing $[\text{HCO}_3^-]$ would increase Larson's index and be expected to worsen iron corrosion. However, 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 (Ingvorsen *et al.* 1984). 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 & Characklis (1992), Okabe *et al.* (1992) and Weimer *et al.* (1988) 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 were unrepresentative of potable waters. Nutrient limitations for SRB in potable water have never been defined (Sun & Edwards 2002; Sun *et al.* 2002) 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 Larson's index is

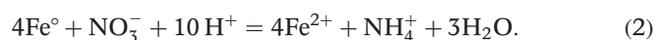
Table 1 | Test conditions used to study the effect of disinfectants on iron corrosion

	LeChevallier et al. (1990)	Treweek et al. (1985)	Elsnor & Gagnon (2004)
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 d, 0.3 m/s flow rate
Monochloramine preparation recipe	3:1 molar ratio of ammonia to chlorine	Not mentioned	1 mL 5% sodium hypochlorite and 216 mg NH ₄ Cl (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 ·H ₂ O, 0.01 mg/L (NH ₄) ₂ SO 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, > 10 mg/L CaCO ₃ alkalinity, unknown silica, magnesium, ammonia, sulfate, chloride.
pH	7	neutral to slightly acidic range	8
Temperature	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

unwittingly capturing the role of sulfate in the 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.

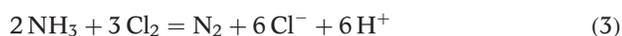
Nitrate

The corrosion reaction between iron metal and nitrate has been used to remediate nitrate contaminated water (Huang & Zhang 2005):



Nitrate is nearly stoichiometrically converted to ammonia by iron corrosion under at least some conditions (Westerhoff & James 2003). 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 via reaction with the iron, breakpoint chlorination could occur (Woolschlager *et al.* 2001):



which would remove chlorine disinfectant and increase 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.

Magnesium and silicate

Silica is an important natural component of ground and surface waters, and is sometimes added as an inhibitor to control 'red water' problems. The presence of high silica has actually been found to increase iron release and 'red water' (Rushing *et al.* 2003). Magnesium is predicted to inhibit the precipitation of calcite from CaCO_3 on pipe surfaces, and favor the deposition of the more soluble aragonite form of CaCO_3 (AWWARF & DVGW-TZW 1996), but on the other

hand, magnesium can form very insoluble compounds with silica (Harder 1972; Gill 1993; Parks & Edwards 2006), which might decrease the problem caused by silica.

Zinc

Zinc is blended into phosphate inhibitors to introduce better inhibition performance. The addition of zinc was reported to decrease corrosion compared to regular poly- or orthophosphates (Mullen & Ritter 1974, 1980; Swayze 1983), but there are also studies finding no benefit of zinc phosphates compared to regular phosphates (Swayze 1983). Zinc is also known to inhibit the formation of the calcite form of CaCO_3 (AWWARF & DVGW-TZW 1996), but no study has been conducted to demonstrate the effect of zinc alone on iron corrosion.

Study objective

The objective of this study is to investigate the relative effects of chlorine and chloramine, sulfate/chloride ratio, nitrate, magnesium, silicate and zinc on iron corrosion. These results are intended to address possible secondary impacts on water quality and iron corrosion by water treatment changes such as (1) switching from chlorine to chloramine, (2) arsenic treatment installation and nitrate removal. Two phases of research were executed to examine these issues in synthesized potable water.

MATERIALS AND METHODS

Iron corrosion with no SRB inoculation

Samples and apparatus were similar to that of Rushing *et al.* (2003). Iron samples were cylindrical cast iron coupons, each 2.5 cm in diameter and 1.9 cm in length (Grammer, Dempsey & Hudson, Inc, Newark, NJ). The iron coupons were coated with epoxy, such that only the top polished surface was exposed.

The reactors were 11 cm tall Cambro 2 L polycarbonate containers with 1.6 L solution. There were six iron coupons in each reactor. The water was continuously stirred with a 61 mm × 28 mm floating stir bar rotating at 375 rpm.

Disinfectant, magnesium and zinc effects were evaluated (Table 2). Also, a separate experiment was conducted

Table 2 | Test conditions for water with no SRB inoculation

Reactor	Alkalinity, mg/L-CaCO ₃	SO ₄ ²⁻ mg/L	Cl ⁻ mg/L	Si mg/L	NOM mg/L-C	Ca ²⁺ mg/L	Mg ²⁺ mg/L	Zn ²⁺ mg/L	Cl ₂ mg/L	Chloramine mg/L-Cl ₂
1.2	100	100	100	20	0.2	0	0	0	0	0
1.3	100	100	100	20	0.2	20	0	0	0	0
1.5	100	100	100	20	0.2	0	12	0	0	0
1.6	100	100	100	20	0.2	20	0	1	0	0
1.7	100	100	100	20	0.2	20	0	0	3	0
1.8	100	100	100	20	0.2	20	0	0	0	5

to further investigate the effect of magnesium (Table 3). The control waters were synthesized from nanopure deionized water to which the listed reagent grade salts were added.

The natural organic matter was made by systematically cleaning Aldrich humic acid (Chin & Gschwend 1991). The humic acid 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 deionized water with a final pH 4.0.

Chloramine was formed with a 1:1 molar ratio of ammonia and chlorine. Reagent grade ammonium hydroxide and commercial bleach were used. DPD testing

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.

Iron in the water was measured by collecting samples daily from each reactor. 'Soluble' iron was operationally defined by filtration through 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

Table 3 | Test conditions to examine effects of magnesium and silica, no SRB inoculation

Reactor	Alkalinity, mg/L-CaCO ₃	SO ₄ ²⁻ mg/L	Cl ⁻ mg/L	Si mg/L	NOM mg/L-C	Ca ²⁺ mg/L	Mg ²⁺ mg/L
2.1	100	100	64	20	0.2	0	0
2.2	100	100	64	20	0.2	0	3
2.3	100	100	64	20	0.2	0	12
2.4	100	100	64	20	0.2	0	25
2.5	100	100	64	20	0.2	20	25
2.6	100	100	64	40	0.2	0	25
2.7	100	100	64	20	0.2	20	0
2.8	100	100	64	0	0.2	0	25

Method 3120 B (AWWA, APHA & WEF 1998). Tests lasted 77 d and further testing with magnesium and silica lasted 35 d. 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 h, scales were removed from the coupons with a scraping tool and Dremel tool and collected. 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 solids had dissolved and the solution became clear. Digested samples were analyzed by ICP-ES.

Iron corrosion with active sulfate-reducing bacteria

The same apparatus and general procedure as above were used, but the reactors were 1 L Nalgene polycarbonate containers with an inoculation of SRB from an 80-year-old iron pipe from the distribution system of the Washington Suburban Sanitation Commission (WSSC). This utility has always used free chlorine disinfectant. The WSSC pipe had been exposed to Blacksburg tap water for 5 months at low dissolved oxygen (DO), at which time scale from the pipe was removed to isolate and culture SRB using SRB-BART test kits from Droycon Bioconcepts Inc. Postgate medium G (Okabe & Characklis 1992) was first used to cultivate SRB with the first set of six iron coupons present in each reactor. Oxygen was consumed by adding 0.375 g Na₂S to 1 L medium. After the dissolved oxygen was reduced to below 1 mg/L, SRB 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. After 35 d, 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 had occurred.

Twelve reactors remained and a second set of four new coupons were added into each reactor (making a total of 8 coupons in each reactor). The new coupons are representative of iron coupons without the 35 d 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 4). After two weeks' acclimation, sulfate/chloride ratios were varied and 4 different disinfectant types were added a week later (Table 5). The four disinfectant types were free chlorine, chloramines, free ammonia (representing water after chloramine decay) and no disinfectant (representing water after chlorine decay). Also, nitrate concentrations were changed during the experiment. Specifically, when the second set of new coupons were first added (35 d after the experiment started), the initial nitrate concentration was 20 mg/L-N; after 32 d the nitrate concentration was changed to 0.03 mg/L-N, and then 78 d later, the nitrate concentration was changed back to 8 mg/L-N until the end of the experiment. The cast iron coupons were exposed to different waters for 153 d total duration.

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. Coleman CO₂

Table 4 | Water chemistry after adding the second set of new iron coupons

Constituent	Conc. mg/L
Sulfate	14.4- SO ₄ ²⁻
Chloride	34.6- Cl ⁻
Lactate	0.3-C
NH ₄ -N	1
Phosphate	20
Nitrate-N	0.03
Other trace nutrients and vitamin solution	1/20 Postgate Medium G solution
Ca	20
Mg	20
Si	20
Alkalinity	100- CaCO ₃

Table 5 | Water chemistry conditions in different reactors for test with SRB inoculated

Reactor	Disinfectant type	Cl ₂ , mg/L	NH ₂ Cl, 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

(99.99%) gas was sparged into the stock to better dissolve the solids and keep the stock pH below 7. Then before each water change, pH was adjusted to 8 ± 0.2 by releasing the extra CO₂. This method was modified after it was clear that some precipitates were forming. In the second approach, the stock solution was made at 5 times targeted concentrations, and the sulfate, chloride and silicate were then added from separate stock solutions just before use in the experiment.

Chlorine and monochloramine residuals were monitored for decay and adjusted twice daily. Water was replaced in each reactor every 4 d. Samples were collected at each water change and iron was measured on an Inductively Coupled Plasma Mass Spectrophotometer (ICP-MS) according to Standard Method 3125-B (AWWA, APHA & WEF 1998). Microbiological activity was monitored throughout the experiment by ATP, which is the energy transfer molecule found only in living cells. A chemical reagent is used to quantify ATP, which is based on the reaction between luciferase (enzyme), luciferin and ATP. Light is emitted during this reaction and can be measured by an illuminometer (Lee & Deininger 2001). This

method has been proved to be sensitive in drinking water and correlate well with other methods like HPC and direct cell count (Lee & Deininger 2001). Half milliliter bulk water from each reactor is sampled fresh and tested by illuminometer and the reagent from AMSA, Inc. The reagent is kept in 4°C room and used within 6 months after purchase to ensure the stability.

Iron scale (corrosion products deposition) 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 molecular 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 sulfate reducing bacteria using a RapidCheck II SRB immunoassay from Strategic Diagnostics Inc. and BART test kits from Droycon Bioconcepts Inc. The RapidCheck II SRB test employs purified antibodies to detect the enzyme

adenosine-5'-phosphosulfonate (APS) reductase which is common to all strains of SRB. The BART test contains ferrous iron, which can react with H₂S produced by growing SRB by forming a black precipitate.

RESULTS AND DISCUSSION

Weight loss and iron release are the two major parameters used to measure iron corrosion. Weight loss has less error relative to other corrosion measurements (AWWARF 1996). Eisnor & Gagnon (2004) considered elevated release of iron to water to be indicative of high corrosion rates in new pipes or the release of older metal deposits into solution (Eisnor & Gagnon 2004), but McNeill & Edwards (2001) point out there is sometimes little or no relationship between iron release to water and iron corrosion rates due to the scale on the surface of the pipe that can serve as a larger reservoir of corrosion by-products. Nonetheless, the concentration of iron in water is an important water quality parameter because it can reflect potential 'red water' complaints.

Sulfate/chloride ratio

There was no significant weight loss and iron release trend for the different sulfate/chloride ratios. SRB were detected on almost all coupons. The cell density only ranged from 10⁵ to 10⁴ cells/mL, indicating SRB activity is relatively low. The ubiquitous presence of SRB even in reactors with no sulfate source added was quite surprising, which would indicate that SRB activity was not strongly affected by sulfate/chloride ratios. It is possible that the sulfur for the SRB came from the iron metal itself; since SEM results confirmed that 1.8 ± 1.0% (average mass percentage ± standard deviation) sulfur was detected on iron surfaces with no sulfate added, while the typical sulfur content in cast iron is 0.12% by mass (AWWARF & DVGW-TZW 1996). The higher sulfur content present in this experiment could be the result of sulfur accumulation onto iron coupons during the inoculation period. Another possibility not tested in this study is that the SRB strain used was a facultative sulfate/nitrate reducer, which is capable of

utilizing nitrate to support growth when sulfate is not available (Saraiva *et al.* 2001).

In terms of disinfectant decay, chloramine is often more stable and longer lasting than free chlorine (USEPA 2005). However, practical utility experience indicated that chloramines can, on rare occasions, decay faster than chlorine (Powell 2004), although it should be noted that high temperature at this utility might play a major role. In this study, when the nitrate concentration was low (0.03 or at 8 mg/L-N), chlorine had nearly the same decay rate as chloramine at the highest sulfate condition, while chlorine decayed faster than chloramine in the conditions with middle and no sulfate (Figure 1). So it is very likely that under certain water chemistry conditions, chloramine is not always a more stable disinfectant than chlorine as generally assumed.

The morphology of the scale (iron corrosion products deposition) 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 contributing to red water problems. Previous research commonly agrees that chloride initiates pits and sufficient sulfate and nitrate inhibit pit initiation (Cragolino & Tuovinen 1983), and other authors found chloride caused more pitting than sulfate in steel (Brown *et al.* 2005). These studies have always been conducted with thousands of mg/L chloride and sulfate concentration (Cragolino & Tuovinen 1983) and are not necessarily applicable to drinking water systems. In our study, because of the relatively low sulfate and chloride concentration, no obvious pits were observed, but one interesting finding is that for most older coupons

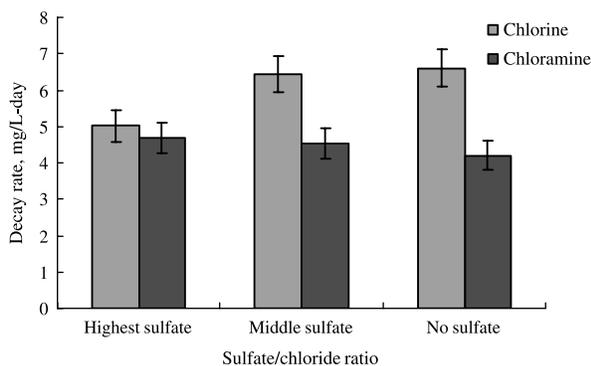


Figure 1 | Disinfectant decay rate with 0.03 mg/L-N nitrate, SRB inoculated. Error bars represent 90% confidence intervals.

(153 d exposure), in the reactors with high sulfate, low chloride, the coupons had more uniform scale than those with low sulfate, high chloride (Figure 2).

Effect of disinfectant

There was no significant difference in overall weight loss or iron mass in scale between different disinfectant types, either with or without the inoculation of SRB (Figure 3 and Table 1).

Chlorine disinfectant always had less iron leaching compared to the reactors with no disinfectant and with chloramines without the inoculation of SRB (Figure 4). With the inoculation of SRB, reactors with chlorine also had the lowest iron release compared to other disinfectant types, and this result only applied to low nitrate conditions (Figure 5). A paired *t*-test was conducted to compare the head to head results for total iron leaching giving a final ranking chlorine < chloramines < no disinfectant ($p < 0.05$). The only exceptional case was with the 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 a *p* value of 0.05.

Many microbes are involved in corrosion processes and they are generally considered to increase corrosion rates (McNeill & Edwards 2001). 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 and would therefore decrease iron release according to Sarin *et al.* (2004a). Addition of ammonia alone increased microbial activity relative to the condition with no disinfectant, consistent with a higher level of nutrients for microbial growth. A paired *t*-test demonstrated microbial activity with chlorine < chloramines < no



Highest sulfate, low chloride No sulfate, highest chloride

Figure 2 | Iron coupon top surface scale comparison (with chloramines), SRB inoculated.

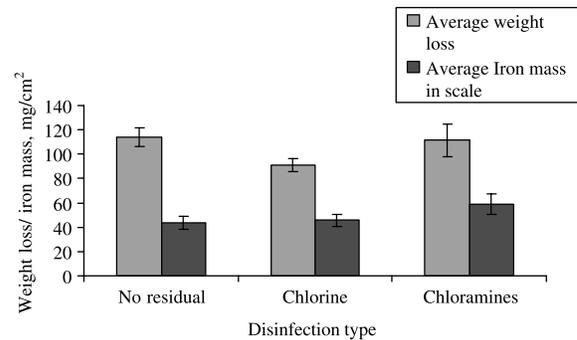


Figure 3 | Weight loss and iron mass in scale with different disinfectant, no SRB.

residual < ammonia ($p < 0.05$) (Figure 6). The high microbial activity in reactors with ammonia might be expected to increase iron release; but on the contrary, there was less iron released in the reactors with ammonia than those with no disinfectant residual (Figure 5).

Nitrate

Nitrate has not been considered to be a key factor in iron corrosion (LeChevallier *et al.* 1993; McNeill & Edwards 2001). There are studies indicating nitrate can inhibit iron pitting corrosion (Cragolino & Tuovinen 1983; Ma *et al.* 2003), but the short term nature of these tests and high concentration (hundreds to thousands mg/L nitrate) used in those studies may not apply to drinking water systems (Ma *et al.* 2003). In this study, three different nitrate concentrations (20, 0.3 and 8 mg/L) were used to investigate the effect of nitrate on iron corrosion.

The switch from 20 mg/L-N nitrate to 0.03 mg/L-N nitrate caused a drastic drop of total iron release in the

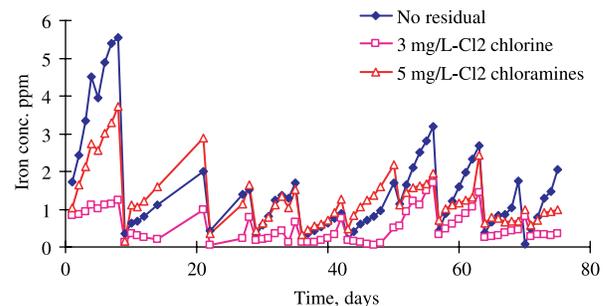


Figure 4 | Total iron released to water under O₂-saturated condition, no SRB inoculation. The gradual increase of iron represents iron accumulation during the test and the sudden drops represent a water change (reactor 1.3, 1.7, 1.8).

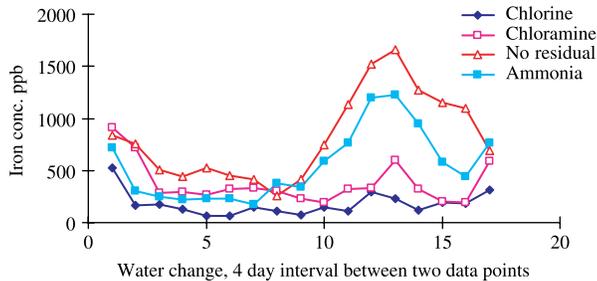


Figure 5 | Total iron release with highest sulfate/chloride ratio and at low nitrate concentration (0.03 mg/L-N nitrate), SRB inoculated (reactors 3.1, 3.4, 3.8, 3.11). Note: the iron data change at 10th water change was due to different stock solution preparation.

reactors with chlorine, but total iron concentration in the reactors with chloramines did not decrease immediately after the switch (Figure 7). Later increase in nitrate concentration up to 8 mg/L-N did not increase iron concentrations in reactors with chlorine as expected. This might be because iron corrosion was low after 5 months' exposure, or 8 mg/L-N nitrate was not high enough to cause an effect.

The monitored ammonia production rates and disinfectant decay rates provide some mechanistic insights into the effect of nitrate. In the reactors with no disinfectant residual, 0.3 mg-N/L-d bulk water ammonia was produced on average at 20 mg/L-N nitrate, and about 0.05 mg/L-d ammonia was produced with 8 mg/L nitrate; but there was no detectable ammonia increase in bulk water when chlorine is present (Figure 8). For chloramine, the disinfectant decay rate was not a function of nitrate concentration; but chlorine decayed faster at 20 mg/L-N nitrate compared to 0.03 mg/L-N nitrate concentration, while 8 mg/L-N nitrate didn't cause this increase (Figure 9).

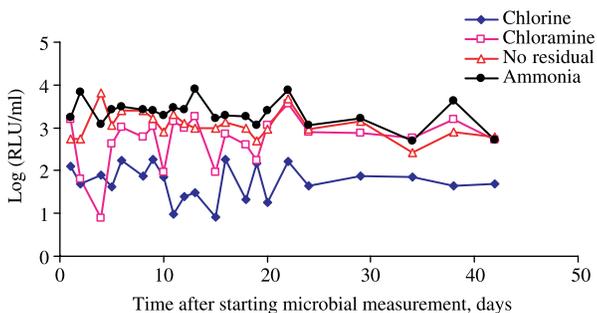


Figure 6 | Microbiological activity in bulk water based on ATP test at highest sulfate, SRB inoculated. Note: unit for ATP is RLU/ml, which has a correlation with HPC measurement of $\log(\text{CFU/ml}) = 0.35 + 1.47\log(\text{RLU/ml})$ in one drinking water study according to Lee & Deininger (2001).

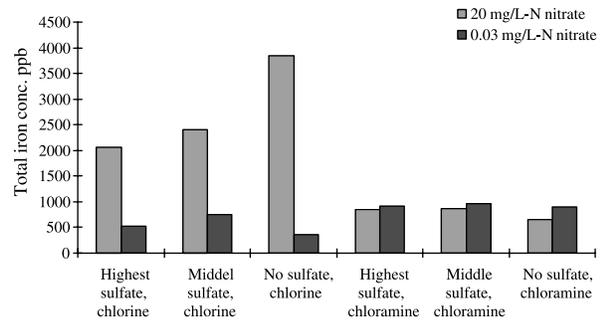


Figure 7 | Immediate change in total iron caused by reducing the nitrate concentration from 20 mg/L to 0.03 mg/L, SRB inoculated.

A hypothesis was developed to explain these results, based on the reaction between iron corrosion and nitrate: Thermodynamically, nitrate is expected to be completely converted to ammonia by iron corrosion through Equation (2), but this reaction is more rapid at lower pH, so only 0.3 mg-N/L-d bulk water ammonia was produced at 20 mg/L-N nitrate at pH 8 in this study.

Based on breakpoint chlorination reaction (Equation (3)), if 0.3 mg/L ammonia was formed each day, 1.8 mg/L

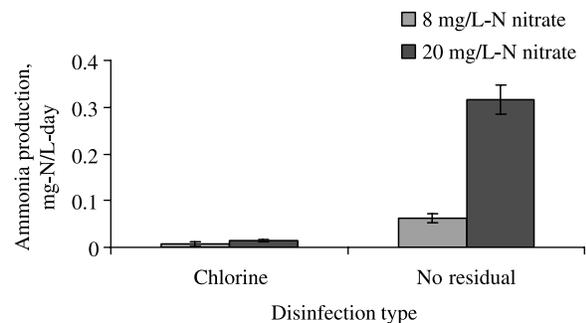


Figure 8 | Average ammonia production, SRB inoculated. Error bars represent standard deviation.

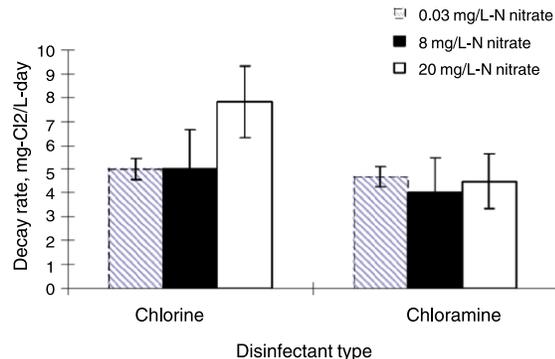


Figure 9 | Disinfectant decay rate with highest sulfate, SRB inoculated. Error bars represent 90% confidence intervals.

Table 6 | Comparing possibility for ammonia formation from nitrate

Factors	Accelerate nitrate conversion to ammonia (48)	Distribution system	This study	Predicted worst case for chlorine decay
Pipe surface/Volume ratio	High	0–12" pipe	Similar to 1" pipe	Small pipe in homes
Flow rate	low	0–2 m/s	Relatively fast and constant	Stagnant
pH	Low	6–9	8	Low pH
Nitrate concentration	High	0–10 mg/L	20 mg/L	High nitrate

chlorine would be consumed, which can explain the higher rate of chlorine decay at high nitrate (Figure 9). In contrast, formation of ammonia from nitrate in the presence of chloramine would tend to increase the stability of chloramine. The amount of ammonia formed from 8 mg/L nitrate at pH 8 was not high enough to cause a detectable increase in chlorine decay rate at this pH.

At 20 mg/L-N nitrate, chlorine decayed quickly, and the reactors with chlorine had low or no residual most of the time before the scheduled chlorine residual boosting up to 4 mg/L. At low nitrate concentration, the reactors with chlorine had high chlorine residual most of the time due to slower decay. Since the reactor with no disinfectant residual released more iron than the reactor with chlorine (Figure 5), it would be expected that high nitrate would cause more iron release than low nitrate.

Possible implications of nitrate effect in drinking water systems

High surface to volume ratio, high nitrate concentrations, low pH and low flow rate would tend to increase the rate of chlorine decay in the presence of nitrate (Table 6). In this experiment the initial pH was relatively high, the iron surface/water volume ratio was relatively small (similar to that found in a 10 inch pipe) and water movement in these reactors (375 rpm) was relatively fast compared to that in distribution systems. Despite these unfavorable conditions for conversion of nitrate to ammonia, the ammonia that was produced could still consume 1.8 mg/L free chlorine each day. If this happens, at least 50% of the target chlorine residual in most distribution systems would be removed quickly from this reaction alone, resulting in excess

microbial growth. One AWWA survey indicated that 457 water utilities (out of 799 survey respondents) had 1% or greater cast iron, galvanized or steel for their service lines (AWWA 1996). These pipes have small diameter and stagnant conditions are common, so ammonia production from nitrate might be significant.

Magnesium and silica

In this study, generally, the presence of magnesium (versus no magnesium) and higher silica (40 mg/L versus 20 mg/L) slightly decreased weight loss. We speculate that this slight benefit from magnesium and silica to iron corrosion rates might be due to formation of magnesium silicates.

High levels of silica (20 mg/L) without magnesium released the highest level of iron. When 25 mg/L magnesium was present, total iron release increased as silica level increased, consistent with the finding of Rushing *et al.* (2003). For a student paired *t*-test at 95% confidence, the average total iron level in the reactor with 40 mg/L-Si was 300% higher than that with no silica, and the reactor with 20 mg/L-Si was 100% higher than that with no silica. Total and soluble iron concentration decreased as magnesium

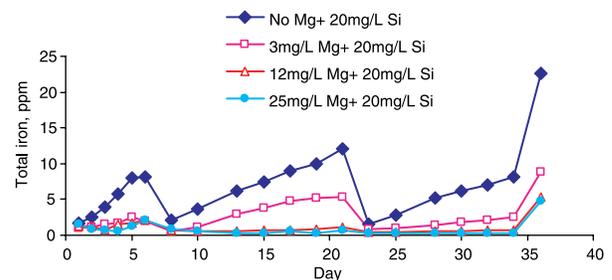
**Figure 10** | Effect of magnesium on total iron release, no SRB inoculation.



Figure 11 | Iron scale at different magnesium levels with/without silica.

concentration increased from 0 to 12 mg/L-Mg, but further addition of magnesium up to 25 mg/L did not have additional benefits (Figure 10). So the role of magnesium is 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 (Hakkarainen 1998; Wang & Qu 2003), thereby reducing the electrostatic repulsion force and the likelihood iron particles would disperse into the water (Magnuson *et al.* 2001; Rushing *et al.* 2003).

Further study of the magnesium effect revealed that the scale became more uniform with higher magnesium levels, and the co-occurrence of silica was necessary for the formation of a uniform scale (Figure 11).

Zinc

The addition of zinc decreased both weight loss and iron release. Weight loss was decreased by about 20% and iron release was decreased by about 40% on average; more details on these effects are presented elsewhere (Zhang 2005).

CONCLUSIONS

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

- Chlorine was a better disinfectant than chloramine in the aspect of controlling red water (less iron release) and microbial activity (less heterotrophic bacterial growth) in the bulk water.
- When nitrate concentrations were increased, chlorine decayed faster and more iron was released. Nitrate reduction to ammonia by iron and resulting breakpoint chlorination reactions are the likely cause for this effect.

Changes in nitrate from 0.03 mg/L to 20 mg/L had no effect on chloramine decay.

- Sulfate-reducing bacteria can maintain their activity on iron pipes, even after three months' exposure to disinfectant and without any detectable sulfate in the water.
- Sulfate/chloride ratio changes did not have an effect on iron corrosion as expected based on Larson's ratio, possibly because SRB activity in this study was very low and the iron samples used contained enough sulfur to support SRB growth.
- Increased magnesium and zinc can decrease red water problems caused by silicate.

It should be noted that these results are only applicable to cast iron surfaces that have not been exposed to water before. For old iron pipes in drinking water distribution systems that are covered with corrosion scales, some of these trends might be different.

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REFERENCES

- AWWA 1996 *WATER: \STATS, The Water Utility Database, Electronic format.*
- AWWA 1999 *Water Quality and Treatment*, 5th edn. McGraw-Hill, New York.
- AWWA, APHA, WEF 1998 *Standard Methods*, 20th edn. American Public Health Association, Washington, DC.

- AWWARF, DVGW-TZW 1996 *Internal Corrosion of Water Distribution Systems*. AWWARF, Denver, CO.
- Bayliss, J. R. 1926 Prevention of corrosion and red water. *J. AWWA* **15**(6), 598–631.
- Brown, R. C., Fan, M., Cooper, A. T. 2005 Available at: http://www.netl.doe.gov/publications/proceedings/03/ucr-hbcu/posters/Brown_p.pdf Accessed on 8/18/05.
- Chin, Y. P. & Gschwend, P. M. 1991 The abundance, distribution, and configuration of porewater organic colloids in recent sediments. *Geochim. Cosmochim. Acta* **55**, 1309–1317.
- Cragolino, G. & Tuovinen, O. H. 1983 The role of sulfate-reducing and sulfur-oxidizing bacteria on localized corrosion. *Corrosion* 1983. Anaheim, California Paper 244.
- Edwards, M. 2004 Controlling corrosion in drinking water distribution systems: a grand challenge for the 21st century. *Wat. Sci. Technol.* **49**(2), 1–8.
- Eisnor, J. D. & Gagnon, G. A. 2004 Impact of secondary disinfection on corrosion in a model water distribution system. *J. Wat. Supply: Res. Tech. - AQUA* **53**(7), 441–452.
- Gill, J. S. 1993 Inhibition of silica-silicate deposit in industrial waters. *Colloids Surf. A: Phys. Engng. Aspects* **74**, 101–106.
- Hakkarainen, T. J. 1998 Conditions of growth of open corrosion pits in stainless steels-electrochemical experiments on model pits. *Corrosion* 1998, Paper 310.
- Harder, H. 1972 The role of magnesium in the formation of smectite minerals. *Chem. Geol.* **10**, 31–39.
- Hedberg, T. & Johansson, E. 1987 Protection of pipes against corrosion. *Wat. Supply* **5**(3/4), SS 20.
- 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 Fe²⁺. *Wat. Res.* **39**, 1751–1760.
- Ingvorsen, K., Zehnder, A. B. & Jorgensen, B. B. 1984 Kinetics of sulfate and acetate uptake by *Desulfobacter postgatei*. *Appl. Environ. Microbiol.* **47**(2), 403–408.
- Larson, T. E. 1975 *Corrosion by Domestic Waters*. State of Illinois Department of Registration and Education, Illinois State Water Survey, Bulletin, 59.
- Larson, T. E. & Skold, R. V. 1957 Corrosion and tuberculation of cast iron. *J. AWWA* **49**(10), 1294–1302.
- Larson, T. E. & Skold, R. V. 1958 Laboratory studies relating mineral quality of water to corrosion of steel and cast iron. *Corrosion* **14**, 285.
- LeChevallier, M. W., Lowry, C. D. & Lee, R. G. 1990 Disinfecting biofilms in a model distribution system. *J. AWWA* **82**(7), 87–99.
- 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. *J. AWWA* **85**(7), 111–123.
- Lee, J.-Y. & Deininger, R. A. 2001 Rapid quantification of viable bacteria in water using an ATP assay. *Am. Lab.* **33**(21), 24.
- Ma, H. Y., Yang, C., Li, G. Y., Guo, W. J., Chen, S. H. & Luo, J. L. 2003 Influence of nitrate and chloride ions on the corrosion of iron. *Corrosion* **59**(12), 1112–1119.
- McNeill, L. S. & Edwards, M. A. 2001 Iron pipe corrosion in distribution systems. *J. AWWA* **93**(7), 88–100.
- Madigan, M. T., Martinko, J. & Parker, J. 2000 *Brock Biology of Microorganisms*, 9th edn. Prentice-Hall, Englewood Cliffs, NJ.
- Magnuson, M. L., Lytle, D. A., Frietch, C. M. & Kelty, C. A. 2001 Characterization of submicrometer aqueous iron(III) colloids formed in the presence of phosphate by sedimentation field flow fractionation with multiangle laser light scattering detection. *Anal. Chem.* **73**, 4815–4820.
- Mullen, E. D. & Ritter, J. A. 1974 Potable-water corrosion control. *J. AWWA* **66**(8), 473.
- Mullen, E. D. & Ritter, J. A. 1980 Monitoring and controlling corrosion by potable water. *J. AWWA* **72**(5), 286.
- Okabe, S. & Characklis, W. G. 1992 Effects of temperature and phosphorus concentration on microbial sulfate reduction by *Desulfovibrio Desulfuricans*. *Biotechnol. Bioengng.* **39**, 1031–1042.
- Okabe, S., Nielsen, P. H. & Characklis, W. G. 1992 Factors affecting microbial sulfate reduction by *Desulfovibrio desulfuricans* in continuous culture: limiting nutrients and sulfide concentration. *Biotechnol. Bioengng.* **40**, 725–734.
- Parks, J. L. & Edwards, M. A. 2006 Boron removal via formation of magnesium silicate solids during precipitative softening. *ASCE J. Environ. Engng.* accepted.
- Powell, R. 2004 Implementation of chloramination by a Florida utility: the good, the bad, and the ugly. *AWWA WQTC Conf.*
- Riddick, T. M. 1944 The mechanism of corrosion of water pipes. *Water Works and Sewerage* **91**: Reference and Data: R-133-138.
- Rushing, J. C., McNeill, L. S. & Edwards, M. 2003 Some effects of aqueous silica on the corrosion of iron. *Wat. Res.* **37**, 1080–1090.
- Saraiva, L. M., da Costa, P. N., Conte, C., Xavier, A. V. & LeGall, J. 2001 In the facultative sulphate/nitrate reducer *Desulfovibrio desulfuricans* ATCC 27774, the nine-haem cytochrome c is part of a membrane-bound redox complex mainly expressed in sulphate-grown cells. *Biochim. Biophys. Acta.* **1520**(1), 63–70.
- Sarin, P., Snoeyink, V. L., Bebee, J., Jim, K. K., Beckett, M. A., Kriven, W. M. & Clement, J. A. 2004a Iron release from corroded iron pipes in drinking water distribution systems: effect of dissolved oxygen. *Wat. Res.* **38**, 1259–1269.
- Sarin, P., Snoeyink, V. L., Lytle, D. A. & Kriven, W. M. 2004b Iron corrosion scales: model for scale growth, iron release, and colored water formation. *J. Environ. Engng.* **130**(4), 364–373.
- Speller, F. N. 1951 *Corrosion Causes and Prevention*, 3rd edn. McGraw-Hill, New York.
- Sun, Y. & Edwards, M. 2002 Water chemistry and h₂ evolution during anaerobic iron corrosion, *Proc AWWA Annual Conference, New Orleans, June*. AWWA.
- Sun, Y., Morton, S. C. & Edwards, M. 2002 Equilibrium and kinetic aspects of iron corrosion in the presence of phosphate. *Proc. 2002 Water Quality Technology Conference in Seattle, WA, November*.
- Swayze, J. 1983 Corrosion study at Carbondale. *Illinois. J. AWWA* **75**(2), 101–102.

- Treweek, G. P., Glicker, J., Chow, B. & Sprinker, M. 1985 Pilot-plant simulation of corrosion in domestic pipe materials. *J. AWWA* **77**(10), 74–82.
- Uhlig, H. H. & Revie, R. W. 1985 *Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering*, 3rd edn. John Wiley, Sons, New York.
- USEPA 2005 Available at: <http://www.epa.gov/region09/water/chloramine.html> Accessed on 8/15/2005.
- 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 Rev.* **16**(3), 235–284.
- Wang, H.-Y. & Qu, J.-H. 2003 Combined bioelectrochemical and sulfur autotrophic denitrification for drinking water treatment. *Wat. Res.* **37**, 3767–3775.
- Weimer, J., Van Kavelaar, M. J., Michel, C. B. & Ng, T. K. 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. Microbiol.* **54**(2), 386–396.
- Westerhoff, P. & James, J. 2003 Nitrate removal in zero-valent iron packed columns. *Wat. Res.* **37**, 1818–1830.
- 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. *Wat. Sci. Technol.: Wat. Supply* **1**(4), 103–110.
- Zhang, Y. 2005 *Relative Effects of Water Chemistry on Aspects of Iron Corrosion*. Masters thesis, Virginia Tech.

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