## **CHAPTER 2**

# Phosphate Inhibitors and Red Water in Stagnant Iron Pipes

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**KEYWORDS:** corrosion, phosphate inhibitors, iron pipe, weight loss, by-product release

#### **ABSTRACT**

This four-year study evaluated the effect of phosphate inhibitors on the corrosion of iron pipes under extended stagnant water conditions. Study parameters included pH and alkalinity, age of the pipe, water stagnation time, and inhibitor type.

For iron release, addition of phosphate inhibitors had no statistically significant effect (at 95% confidence) in two-thirds of the experiments. In the remaining experiments, addition of orthophosphate or zinc orthophosphate always *increased* iron concentration. Polyphosphate addition decreased iron release at only one water quality and increased it at other conditions.

For weight loss, polyphosphate inhibitor dosing did not decrease the extent of scale buildup or overall weight loss. Orthophosphate dosing reduced overall weight loss at only one water quality condition; at all other conditions, the addition of orthophosphate had a detrimental effect.

## **INTRODUCTION**

Although iron corrosion causes a wide variety of problems, two primary concerns in drinking water distribution systems are tuberculation and "red water." Tuberculation is due to excessive scale ("rust") build-up and leads to decreased water flow, increased head loss, higher pumping costs, and potential sites for bacterial regrowth. "Red water" is the generic term for water with high particulate iron concentrations due to corrosion by-product release. Red water is often the most common water quality related customer complaint, as it leads to tap water with objectionable tastes, odors, and staining.

Phosphate inhibitors are one of the most common tools used to combat iron corrosion in distribution systems. These compounds were first introduced 60 years ago to prevent excess calcite precipitation in drinking water distribution systems. In the 1940's, hexametaphosphate gained popularity as a "wonder chemical" that supposedly offered simultaneous control of calcite precipitation, iron precipitation, and iron corrosion. The most common types of phosphate

inhibitors used today include hexametaphosphate (polyphosphate), orthophosphate, zinc orthophosphate, zinc metaphosphate, and bimetallic phosphate (sodium-zinc- or potassium-zinc-phosphate).<sup>2</sup> The exact mechanism(s) of phosphate action are unclear, and many theories abound (see reference 3 for a review).

Numerous studies have extolled the virtues of phosphates in stirred lab experiments or flowing distribution systems. <sup>4-9</sup> However, there is anecdotal evidence that phosphate inhibitors perform poorly at low flow or stagnant conditions, <sup>6, 10-13</sup> and three studies found that phosphate inhibitors either had no effect or actually increased iron corrosion under such conditions. <sup>14-16</sup> Thus, the current study was undertaken to rigorously examine long-term phosphate performance in a variety of water qualities under stagnant conditions. These conditions simulate the worst case stagnation times that might be found in "dead-end" sections of a distribution system or in home plumbing. Three different inhibitors were tested, including polyphosphate (Na<sub>22</sub>P<sub>20</sub>O<sub>61</sub>), orthophosphate (Na<sub>3</sub>PO<sub>4</sub>), and zinc orthophosphate (Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>), in five different water qualities.

After a brief review of the general experimental approach and a discussion of the quality assurance/quality control (QA/QC) procedures, results from each of the experiments will be presented. Finally, the implications of these results for understanding the role of phosphate inhibitors in corrosion control in stagnant water are described.

#### **EXPERIMENTAL METHODS**

The experimental set-up consists of 36-cm long sections of 1.4-cm diameter cast iron pipes purchased at a local hardware store. All pipes were initially rinsed three times with 0.1 N sodium hydroxide (NaOH) and then rinsed five times with reagent grade (Milli-Q) water. Boulder, CO tap water (pH = 7.8, alkalinity = 45 mg/L, silica = 5-8 mg/L, chloride = 6 mg/L, sulfate = 6 mg/L, total organic carbon = 1.3 mg/L, no phosphate inhibitor added) was used as a base water, with appropriate modifications to achieve other target pH and alkalinity conditions (Table 2-1).

For each of the above water qualities, three phosphate conditions were tested (no inhibitor, 1 mg/L orthophosphate, and 1 mg/L hexametaphosphate), making 15 water conditions total (5 water qualities x 3 inhibitor conditions). This allows direct and unambiguous

comparison of inhibitor effects in a given water. A subset of experiments also investigated the effect of zinc orthophosphate inhibitor.

An inhibitor dose of 1 mg/L as P was selected because it is in the upper range of doses used by utilities. <sup>17</sup> Initial concentrations of phosphates in the pipes were  $0.0 \pm 0.03$  mg/L (no inhibitor) or  $1.0 \pm 0.05$  mg/L (with inhibitor) in all experiments. The exception was during the 72-hour stagnation experiments in this work, for which the polyphosphate was mistakenly dosed at 0.7 mg/L as P for three weeks. Polyphosphate was dosed at 1 mg/L P for all subsequent experiments. Stock solutions of orthophosphate and polyphosphate inhibitors were prepared at concentrations of 500 mg/L and 320 mg/L as P, respectively, and were kept in the dark at  $4^{\circ}$ C. In order to make a stock solution for the zinc orthophosphate inhibitor, the solid was dissolved in a nitric acid solution (1% v/v HNO<sub>3</sub>) and heated at 91°C for 2 hours. This yielded a solution of 321 mg/L as P. Because this stock solution was very acidic, approximately 200  $\mu$ L of 1N NaOH was added to neutralize the acid in 1.3 mL of zinc orthophosphate solution dosed to each water.

The pipes were aged by regular water changes each Monday, Wednesday, and Friday for the duration of this study. To change the water, a pipe was first inverted three times to mix the water, then all of the water was poured out. The pipe was immediately refilled with fresh solution of the appropriate water quality. The pipes had a rubber stopper in each end and were laid flat, and water inside the pipes was stagnant in between these water changes. Although these conditions are not completely representative of distribution system conditions, this was the simplest way to conduct a carefully controlled stagnation experiment. Moreover, an AWWARF project run in parallel using lead and copper pipes led to substantial advances in mechanistic understanding using the exact same waters and sampling protocol. <sup>18, 19</sup>

The general approach was to intensively sample the pipes to determine the effect of various parameters on iron by-product release to the water. Because one goal was to determine the effect of pipe age on observed phosphate impacts, pipes were pre-aged for two different time periods before the experiments were conducted. As the pipes were continuously maintained, their age changed for each experiment (Table 2-2).

For each experiment, replicate samples were collected from each pipe for three successive stagnation periods (e.g. Sunday, Wednesday, and Saturday for the 72-hour experiment) so that the mean, standard deviation, and 95<sup>th</sup> percentile confidence interval could be calculated for iron release in the same water and in the same pipe. A total and soluble (0.45-µm filtered) sample were collected from each pipe on each of the three sampling days.

It is important to note that due to the large number of samples collected, they were not filtered for 12 hours (on average) after collection. While the total iron concentration remained constant, the iron speciation (Fe<sup>+2</sup> vs. Fe<sup>+3</sup>) changed during this time. The 51-hour stagnation experiment was designed to overcome this limitation. The old pipes (aged 3.5 years) were sampled once to measure soluble iron and to collect iron particles for visual inspection. All samples were filtered immediately after collection from the pipe during this experiment.

At the conclusion of the experiments, the pipes were drained of water and dried in a nitrogen atmosphere for 24 hours. The scale was removed from the inside of each pipe using a wire brush attached to a Dremel® tool.<sup>20</sup>

## **Quality Control Measures**

A number of tests were conducted to minimize experimental error. The filters used to quantify soluble iron (0.45-µm nylon disposable, Life Science Products, Denver, CO) and sample containers (HDPE bottles, Nalgene Corp, Rochester, NY) were tested for metal leaching and sorption. No significant sorption or leaching problems were found for iron.

All samples were analyzed for iron and phosphorus with an Inductively Coupled Plasma Emission Spectrometer (ICP-ES, Liberty 150-AX, Varian, Palo Alto, CA). A blank (zero concentration) and known standard were run every ten samples during ICP-ES analysis runs for standard QA/QC procedures.

## **RESULTS**

Data from the pipe experiments are presented in two sections: effect of phosphate inhibitors on total iron by-product release (8-, 51-, and 72-hour stagnation) and weight loss measurements.

#### **Total Iron Release**

The pipes in this study released large amounts of iron by-products into the water. Typical results are shown in Figures 2-1 and 2-2, which show data from 8- and 72-hour stagnation periods for the "new" and "old" pipes (Table 2-2). The data from the 51-hour experiment had similar patterns of iron release, but are not shown here. For reference, ferric iron particles at 1–3 mg/L are sometimes visible to the human eye depending on particle size.<sup>21</sup> The secondary limit for iron in drinking water is 0.3 mg/L.

It is useful to compare iron release data from pipes with and without phosphate inhibitor at each water quality. The percent change in iron release when phosphorus was added was calculated for each condition according to Equation 2-1:

% Change = 
$$100 \frac{([Fe]_{\text{with P}} - [Fe]_{\text{without P}})}{[Fe]_{\text{without P}}}$$
 (2-1)

Thus, positive numbers indicate an increase in iron concentration (a detrimental effect), while negative numbers indicate a decrease in iron (a beneficial effect). Given all of the experimental parameters (2 inhibitor types, 5 water qualities, 2 pipe ages, and 2 stagnation times), there were 40 different combinations of conditions (Figure 2-3). For 26 of these conditions, phosphate inhibitors had no significant effect on iron release compared to pipes with no phosphorus added (the average iron concentrations were not different at 95% confidence). For another 12 conditions, addition of either orthophosphate or polyphosphate increased the iron release. There were only two conditions where the addition of polyphosphate actually reduced iron release (old pipes; pH 7.2, alkalinity 300 mg/L; 8- and 72-hour stagnation).

In sum, the addition of orthophosphate *never* had a beneficial effect on iron by-product release; it either increased iron release or had no effect compared to a pipe with no phosphorus added. Polyphosphate had a beneficial effect only at pH 7.2 alkalinity 300 mg/L; at all other conditions the addition of polyphosphate either increased iron concentration or had no effect.

## **Overall Weight Loss**

Although phosphate inhibitors did not reduce iron release, it was still possible that they lowered the iron corrosion rate. Thus, at the conclusion of the by-product release experiments, the old pipes (now aged 4-years) were drained of water and dried. The total weight loss for each

pipe was calculated as the sum of scale build-up and by-product release. Scale build-up was determined by carefully weighing the dried pipes, removing the scale, and re-weighing the pipes. This gave the weight loss due to scale build-up over the four-year life of each pipe. Weight loss due to by-product release was calculated by summing the iron concentration released during each sampling of the pipe over its lifetime. Percent change values for each parameter were calculated similar to Equation 2-1, again with positive numbers indicating a detrimental effect and negative numbers indicating a beneficial effect.

For the overall (4-year) duration of the experiment, addition of phosphate inhibitors generally had a very negative impact on all aspects of corrosion (Figure 2-4). Orthophosphate reduced scale build-up and overall weight loss compared to a pipe without phosphate inhibitor only at the high pH (9.5) condition. In the other four water qualities, addition of orthophosphate increased scale build-up, by-product release, and overall weight loss. Similarly, polyphosphate never had a beneficial effect—it had no significant effect on by-product release in two water qualities, and increased scale build-up, iron release, and overall weight loss at all other conditions.

### **DISCUSSION**

Phosphate inhibitors were rarely beneficial in controlling iron corrosion in stagnant pipes for the conditions tested in this study. If the inhibitor had a statistically significant effect, it was generally detrimental. This is in stark contrast to inhibitor action in flowing water; as mentioned earlier, many previous studies have found phosphate inhibitors useful in flow systems or in short duration laboratory experiments.

In order to understand this different behavior of inhibitors in stagnant conditions, an attempt was made to correlate the experimental results with factors previously found to influence inhibitor action (discussed below). Because this effort was largely unsuccessful, a novel "cut pipe" experiment was conducted that provided a preliminary hypothesis for polyphosphate action. Finally, a separate set of experiments using zinc ortho-phosphate will be briefly discussed.

### **Factors Thought To Affect Corrosion**

A number of factors have previously been shown to influence iron corrosion in flow systems. These factors include water quality (pH, alkalinity, and buffer intensity), pipe age, inhibitor residual, and soluble iron concentration.

Initial pH and Alkalinity. Several previous studies found a relationship between the initial pH<sup>15, 22-24</sup> or alkalinity<sup>25-27</sup> and iron corrosion. This experimental design allowed examination of the effect of raising the initial pH at constant carbonate alkalinity of 45 mg/L (comparing waters 1, 3, and 5, see Table 2-1) and the effect of raising initial alkalinity at constant pH of 7.2 (comparing waters 2, 4, and 5). However, because of large variability in iron release, there were few statistically significant differences due to pH or alkalinity changes in these waters (Figures 2-1 and 2-2). This is especially true for the 8-hour stagnation in the new pipes, where iron release was approximately constant regardless of water quality or inhibitor dosing. Overall, only one pH change had a significant effect—raising the pH from 7.2 to 9.5 in the old pipes during the 8-hour stagnation produced a 38% reduction in total iron release. Two alkalinity changes had an impact on iron release, both for the old pipes during the 72-hour stagnation: raising alkalinity from 15 to 45 mg/L (108% increase in iron) and raising alkalinity to 300 mg/L (68% reduction in iron).

**Final pH.** It is not completely surprising that iron concentrations did not correlate with the initial pH of the water, because the water quality in a pipe can change dramatically over the stagnation period. Accordingly, in several experiments, the final pH after stagnation was measured.

For the new pipes, the pH changes after stagnation were generally not significant. However, for the old pipes the final pH was significantly higher in pipes with phosphate inhibitor than in pipes with no inhibitor. For example, when polyphosphate was added to a pipe with a given water quality, the final pH after stagnation was as much as two units higher than the pipe with no phosphate. However, there is no statistically significant trend when total iron release is plotted against final pH for all waters qualities ( $R^2 = 0.0005$ ). Although there is apparently no direct relationship between final pH and iron release, it is possible that these large pH changes could indirectly affect corrosion.

**Buffer Intensity.** Several previous studies indicated that iron release and corrosion rates were a function of buffer intensity.<sup>23, 28-30</sup> However, for these experiments there was no clear relationship between initial buffer intensity and iron release ( $R^2 = 0.298$ ).

**Pipe Age.** In the 72-hour stagnation experiment for the pipes with no inhibitors, the pipe age had a significant effect on iron release for all five water qualities—on average, the old pipes had 63% lower iron release than the new pipes. In contrast, pipes with phosphate inhibitor showed little difference in iron release between the two pipe ages; iron release was not statistically different in eight of ten experiments. For both types of inhibitor, only the pH 7.2, alkalinity 300 mg/L condition showed a significant difference, with an average iron reduction of 80% in the old pipes. The trends for the 8-hour stagnation experiment were not as clear as the 72-hour results, but when there was a significant difference, the old pipes always had lower release than the new pipes.

**Phosphorus Residuals.** Given that phosphorus is the active ingredient in these corrosion inhibitors, one might expect that iron concentrations would depend on the amount of P consumed in each pipe. For these experiments, there was a large variation in phosphorus consumption, ranging from zero to nearly one hundred percent. In general, longer stagnation times and older pipes led to more phosphate consumption (a lower P residual). However, there was no direct relationship between residual phosphorus (total, particulate, or filtered) and iron released (Figure 2-5), nor was there a trend in phosphorus consumption versus water quality. There was also no correlation between inhibitor type and P residual.

**Soluble Iron.** Iron released from pipes into water may be either soluble or particulate. Soluble iron is usually operationally defined as ferrous (Fe<sup>+2</sup>) species while particulate iron is considered to be ferric (Fe<sup>+3</sup>) compounds, with ferrous iron easily oxidized to ferric iron by dissolved oxygen.<sup>31, 32</sup> Ferrous iron is a key component in the "siderite model", which proposed that siderite (iron carbonate, FeCO<sub>3</sub>) is key to controlling iron corrosion .<sup>2, 33</sup> Because these experiments involved rather lengthy stagnation periods, most of the dissolved oxygen was consumed from the water, which could be conducive to ferrous iron production.

In the initial sampling protocol for this study, samples were not filtered until approximately 12 hours after collection from the pipes. Although the total iron concentration remained the same, during this period any soluble ferrous iron (Fe<sup>+2</sup>) present was quickly oxidized to ferric iron (Fe<sup>+3</sup>) which precipitated as an orange or brown solid. For example, many of the samples had either dark green particles or a greenish tint to the solution when first poured out of the pipe (possibly indicating ferrous complexes or solids), although there was no clear relationship between water quality and the sample color. After storage for 12 hours in a sealed container, every sample was orangish-brown in color, and many had orange particles settled in the bottom of the bottle. When these samples were filtered, nearly all of them had soluble (< 0.45-µm) iron concentrations of less than 0.05 mg/L (maximum soluble iron was 0.2 mg/L).

In one of the 72-hour stagnation experiments, the samples were filtered approximately four hours after being poured out of the pipe. Soluble iron concentrations ranged from zero to 2.5 mg/L, indicating that some ferrous iron had not yet been oxidized. Because this was not a triplicate sampling, it is difficult to establish any statistically significant trends in soluble iron release from this data. However, it was clear that the new pipes generally had more soluble iron than the old pipes.

To better address the issue of iron speciation, experiments were conducted in which the water samples were filtered immediately after collection from the pipe (after 51-hour stagnation). Any iron passing through a 0.45- $\mu m$  filter was operationally defined as soluble iron. These immediately-filtered samples had much higher soluble iron (as much as 4 mg/L) compared to samples that were filtered 4 or 12 hours after collection. Soluble iron ranged from zero to nearly 25% of the total iron released to the water, with the percentage of soluble iron generally increasing as pH was decreased or alkalinity was raised (Figure 2-6). However, there was no direct relationship between the amount of soluble iron and the total iron released ( $R^2 = 0.009$ ) or overall weight loss ( $R^2 = 0.087$ ) in each pipe.

## **Cut Pipe Experiments**

Because none of the traditional factors such as water quality or phosphorus residual could completely explain the observed trends in iron release or weight loss, additional ideas were investigated. One potential hypothesis for the detrimental effect of polyphosphate inhibitor is its

effect on scale formation. The interaction between polyphosphate and iron scale is unclear; some studies indicate that polyphosphate disperses ferric iron particles in the water<sup>15, 34, 35</sup> while others suggest it only complexes ferrous iron.<sup>12, 15, 36</sup> Regardless, polyphosphate has been reported to reduce scale build-up in pipes.<sup>5, 13, 34, 35, 37-41</sup> However, for the stagnant conditions of these experiments, polyphosphate appeared to actually increase the amount of scale on the pipe walls.

To examine this possibility in greater detail, a "cut pipe" study was conducted. In these experiments, the pipes with water qualities #1-#4 (Table 2-1) that had been dosed with phosphate for 3.5 years were cut in half with a band saw. The pipes were kept on the regular water change schedule, but in one of the pipe halves, dosing of 1 mg/L polyphosphate or orthophosphate was continued, similar to the original condition. In the other half, phosphate dosing was completely stopped. Iron concentrations were monitored in each pipe, and at the end of the experiment, scale build-up and total weight loss were determined as discussed in the previous section. This procedure allowed direct comparison of the effect of stopping the inhibitor dose in pipes with the same scale already built up on the surface.

Results for the pipes dosed with orthophosphate were inconclusive. However, a clear trend was observed for the pipes dosed with polyphosphate: there was a dramatic increase in iron by-product release in pipes where the polyphosphate dosing was stopped. For example, for pipes with water quality pH 7.2, alkalinity 15 mg/L, the iron concentration was initially four times higher in the pipe where polyphosphate dosing was stopped (Figure 2-7). Similar results were obtained in three of the four other water qualities. However, this effect was relatively short-lived; when the pipes were sampled three months after the dosing change, the iron concentrations were the same in the two pipe sections.

One possible reason for this large increase in iron concentration is that stopping the phosphate dosing caused the iron scale to be released into the water. In fact, at each of the four water qualities tested, the pipe section where polyphosphate dosing was ceased had less scale build-up than the corresponding pipe where phosphate was dosed (Table 2-3). This trend is consistent with the data presented on overall scale build-up (Figure 2-4); pipes dosed for four years with polyphosphate always had more scale build-up than similar pipes never dosed with

phosphate. Moreover, visual inspection of the pipes showed large tubercles present in the pipes dosed with inhibitor (especially polyphosphate), whereas tubercles were not found in pipes where phosphorus was not added.

These cut pipe experiments were relatively short term, so further confirmation is necessary. However, it seems clear that there is a difference in scale formation in stagnant waters compared to previous research with flow conditions when polyphosphate is present. This phenomenon may be related to the low levels of dissolved oxygen induced by the stagnant conditions of these experiments.<sup>42</sup>

## **Zinc Orthophosphate**

Having established that the traditional phosphate inhibitors (orthophosphate and polyphosphate) were generally detrimental to iron corrosion under stagnant conditions, the issue of zinc addition was investigated. Many studies have touted the benefits of including zinc in a phosphate inhibitor, <sup>7, 8, 39, 41, 43-47</sup> while others found that zinc orthophosphate offered no additional benefit over regular orthophosphate. <sup>41, 48-52</sup> A separate experiment was conducted to compare the effectiveness of zinc orthophosphate versus regular orthophosphate under stagnant conditions. New pipes were started in June 1997 and dosed with either no phosphorus, orthophosphate (1 mg/L as P from Na<sub>3</sub>PO<sub>4</sub>), or zinc orthophosphate (1 mg/L as P from Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>). These pipes were maintained for 4.5 months and then sampled in triplicate with an 8-hour stagnation period. Because this experiment was a much shorter duration than the other inhibitor experiments discussed previously, no overall weight loss determinations were made.

The zinc orthophosphate had a statistically significant effect at only two conditions, increasing the iron by-product release in both cases (Figure 2-8). For the pH 7.2, alkalinity 45 mg/L pipe the zinc orthophosphate increased total iron release, whereas the regular orthophosphate was no different from the pipe with no phosphorus added. In the pH 7.2, alkalinity 300 mg/L pipe, the zinc orthophosphate also increased total iron release, but this was the same effect as regular orthophosphate. These two water conditions also had the highest soluble iron release, but the amount of soluble iron was indistinguishable between the three pipes (no P, ortho-P, or zinc ortho-P).

During this experiment, less than 30% of the phosphorus was consumed in any of the pipes. The majority of the remaining phosphorus residual was particulate; in fact, only the pH 9.5 water had significant soluble phosphorus (25% of the total). There was no relationship between the phosphorus residual and the iron released. For the cases where there was a difference in iron release (pH 7.2, alkalinity 45 mg/L and pH 7.2, alkalinity 300 mg/L), there was identical phosphorus residual in the orthophosphate versus zinc orthophosphate pipes. In contrast, for the pipes where there was a difference in phosphorus residual, there was no difference in total iron released.

It is interesting to note that there was a linear relationship between the total residual zinc and total residual phosphorus ( $R^2 = 0.935$ ), giving a relationship of 2.4 moles of zinc per mole of phosphorus. This is greater than the 1.5 moles of zinc per mole of phosphorus initially added. Most of the zinc and phosphorus was particulate, and the ratio of particulate zinc to particulate phosphorus is the same (2.5), but the relationship is not as linear ( $R^2 = 0.523$ ).

In summary, these experiments showed no benefit from adding zinc orthophosphate compared to regular orthophosphate. In fact, addition of zinc orthophosphate actually increased the iron concentration in two of the five water qualities tested. These results, combined with other potential negative impacts (such as increased zinc loading to the receiving wastewater treatment plant), suggest that zinc orthophosphate should not be used to mitigate iron corrosion by-product release from stagnant pipes.

#### **CONCLUSIONS**

Iron release from pipes into stagnant water is highly variable during stagnant conditions. For this study, factors that had no simple direct relationship to total iron release include pH and alkalinity of the water, buffer intensity, pH after stagnation, and phosphorus residual. One factor that was important is the age of the pipes; old pipes (aged 3 years) had lower iron release than new pipes (aged 2-4 weeks). Although most of the iron released to the water was particulate, significant soluble (< 0.45- $\mu$ m) iron was present. Most of this soluble iron was oxidized within four hours of leaving the pipe.

Addition of polyphosphate or orthophosphate inhibitor was rarely beneficial for controlling iron corrosion during long stagnation conditions. Where there was a statistically significant effect, these inhibitors tended to increase iron concentration, scale thickness, and overall weight loss compared to similar pipes not dosed with phosphate.

A preliminary hypothesis for the negative action of polyphosphate is that polyphosphate leads to increased scale build-up in stagnant waters. This is supported by observations of increased tuberculation and scale thickness in pipes dosed with polyphosphate, as well as evidence of scale sloughing from pipes where the polyphosphate dosing was stopped.

Zinc orthophosphate did not have a beneficial effect compared to regular orthophosphate or pipes with no phosphorus dosed. When it had a statistically significant effect, zinc orthophosphate increased iron concentrations.

In general, phosphate inhibitors are not recommended for iron corrosion control under chronically stagnant water conditions.

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#### **REFERENCES**

- 1. Hoover, C.P. & Rice, O. Threshold Treatment. Water Works and Sewerage, 86:10 (1939).
- 2. American Water Works Association Research Foundation & DVGW-Technologiezentrum Wasser. *Internal Corrosion of Water Distribution Systems, Second Edition*. American Water Works Association, Denver, CO (1996).
- 3. McNeill, L.S. & Edwards, M. Review of Iron Pipe Corrosion in Drinking Water Distribution Systems. submitted to *Journal AWWA* (2000).
- 4. Rice, O. & Hatch, G.B. Threshold Treatment of Municipal Water Supplies. *Journal AWWA*, 31:7:1171 (1939).
- 5. Gidley, H.T. & Weston, R.S. Corrosion Control by Sodium Hexametaphosphate. *Journal AWWA*, 32:9:1484 (1940).
- 6. Hatch, G.B. & Rice, O. Threshold Treatment of Water Systems--Corrosion Control and Scale Prevention with Glassy Phosphate. *Ind. and Eng. Chem.*, 37:8:710 (1945).
- 7. Kleber, J.P. Use of Bimetallic Glassy Phosphates for Corrosion Control. *Journal AWWA*, 57:6:783 (1965).
- 8. Mullen, E.D. & Ritter, J.A. Monitoring and Controlling Corrosion by Potable Water. *Journal AWWA*, 72:5:286 (1980).
- 9. Benjamin, M.M.; Reiber, S.H.; Ferguson, J.F.; Vanderwerff, E.A. & Miller, M.W. Chemistry of Corrosion Inhibitors in Potable Water. AWWARF Report, Denver, CO (1990).
- 10. Hatch, G.B. & Rice, O. Corrosion Control with Threshold Treatment--Inhibition of the Corrosion of Iron and Steel with Hexametaphosphate. *Ind. and Eng. Chem.*, 32:12:1572 (1940).
- 11. Cohen, M. Sodium Hexametaphosphate as a Corrosion Inhibitor for Ottawa Tap Water. *Transactions of the Electrochemical Society*, 89:105 (1946).
- 12. Larson, T.E. Evaluation of the Use of Polyphosphates in the Water Industry. *Journal AWWA*, 49:12:1581 (1957).
- 13. Rompre, A.; Allard, D.; Niquette, P.; Mercier, C.; Prevost, M. & Lavoie, J. Implementing The Best Corrosion Control For Your Needs. Proc. AWWA Water Quality Technology Conference, Paper M14-6. Tampa, FL (1999).

- 14. Pallo, P.E. A Study of Corrosion Control with Sodium Hexametaphosphate. *Journal AWWA*, 38:4:499 (1946).
- 15. Rice, O. Corrosion Control with Calgon. *Journal AWWA*, 39:6:552 (1947).
- 16. Maddison, L.A. & Gagnon, G.A. Evaluating Corrosion Control Strategies For A Pilot-Scale Distribution System. Proc. AWWA Water Quality Technology Conference, Paper M14-5. Tampa, FL (1999).
- 17. Edwards, M.; Jacobs, S. & Dodrill, D. Desktop Guidance for Mitigating Pb and Cu Corrosion By-products. *Journal AWWA*, 91:6:66 (1999).
- 18. Edwards, M.; McNeill, L.S. & Gladwell, D. Complexation of Lead by Polyphosphate and Implications for Corrosion Control. submitted to *Journal AWWA* (2000).
- 19. Edwards, M.; McNeill, L.S. & Holm, T.R. Role of Phosphate Inhibitors in Mitigating Pb and Cu Corrosion. AWWARF Final Report, Denver, CO (2000).
- 20. Reiber, S.; Ferguson, J.F. & Benjamin, M.M. An Improved Method for Corrosion-Rate Measurement by Weight Loss. *Journal AWWA*, 80:11:41 (1988).
- 21. Edwards, M.; Jacobs, S. & Taylor, R. The Blue Water Phenomenon: What We Know and Don't Know. *Journal AWWA*, in press (2000).
- 22. Larson, T.E. & Skold, R.V. Current Research on Corrosion and Tuberculation of Cast Iron. *Journal AWWA*, 50:11:1429 (1958).
- 23. Stumm, W. Investigation of the Corrosive Behavior of Waters. *Journal of the ASCE Sanitary Engineering Division*, 86:SA6:27 (1960).
- 24. Hidmi, L.; Gladwell, D. & Edwards, M. Water Quality and Lead, Copper, and Iron Corrosion in Boulder Water. Report to the City of Boulder, CO (1994).
- 25. Hedberg, T. & Johansson, E. Protection of Pipes Against Corrosion. *Water Supply*, 5:3/4:SS 20 (1987).
- 26. Raad, R.; Rompre, A.; Prevost, M.; Morissette, C. & Lafrance, P. Selecting the Best Corrosion Control Strategy Using a New Rapid Corrosion Monitoring Tool. Proc. AWWA Water Quality Technology Conference, Paper 5C-1. San Diego, CA (1998).
- 27. Horsley, M.B.; Northrup, B.W.; O'Brien, W.J. & Harms, L.L. Minimizing Iron Corrosion in Lime Softened Water. Proc. AWWA Water Quality Technology Conference, Paper 5C-3. San Diego, CA (1998).
- 28. Pisigan Jr., R.A. & Singley, J.E. Influence of Buffer Capacity, Chlorine Residual, and Flow Rate on Corrosion of Mild Steel and Copper. *Journal AWWA*, 79:2:62 (1987).

- 29. Van Der Merwe, S.W. The Effect of Water Quality Variables on the Corrosive Behaviour of Water Coagulated with a Cationic Polyelectrolyte and with Lime/Activated Silica. *Water Supply*, 6:4:SS 2 (1988).
- 30. Clement, J.A. & Schock, M.R. Buffer Intensity: What Is It and Why It's Critical for Controlling Distribution System Water Quality. Proc. AWWA Water Quality Technology Conference, Paper 4B-6. San Diego, CA (1998).
- 31. Singer, P.C. & Stumm, W. The Solubility of Ferrous Iron in Carbonate-Bearing Waters. *Journal AWWA*, 62:3:198 (1970).
- 32. Stumm, W. & Morgan, J.J. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, Third Edition. John Wiley & Sons, Inc, New York, NY (1996).
- 33. Sontheimer, H.; Kolle, W. & Snoeyink, V.L. The Siderite Model of the Formation of Corrosion-Resistant Scales. *Journal AWWA*, 73:11:572 (1981).
- 34. Illig Jr., G.L. Glassy Phosphates in Water Treatment. *Journal AWWA*, 49:6:805 (1957).
- 35. Boffardi, B.P. Potable Water Treatment and Monitoring for Corrosion and Scale Control. *Journal of NEWWA*, 102:June:111 (1988).
- 36. Bailey, T.L. Corrosion Control Experiences at Durham, North Carolina. Proc. New England Water Works Association Seminar on Corrosion Control in Drinking Water Systems. (1980).
- 37. Hatch, G.B. & Rice, O. Surface-Active Properties of Hexametaphosphate. *Ind. and Eng. Chem.*, 31:1:51 (1939).
- 38. Lamb III, J.C. & Eliassen, R. Mechanism of Corrosion Inhibition by Sodium Metaphosphate Glass. *Journal AWWA*, 46:5:445 (1954).
- 39. Reese, W.J. Corrosion Defeated by Improved Control Method. *Water and Sewage Works*, 109:4:160 (1962).
- 40. Arceneaux, W. Operation and Maintenance of Wells. *Journal AWWA*, 66:3:199 (1974).
- 41. Swayze, J. Corrosion Study at Carbondale, Illinois. *Journal AWWA*, 75:2:101 (1983).
- 42. Uhlig, H.H.; Triadis, D.N. & Stern, M. Effect of Oxygen, Chlorides, and Calcium Ion on Corrosion Inhibition of Iron by Polyphosphates. *Journal Electrochem. Soc.*, 102:2:59 (1955).
- 43. Murray, W.B. A Corrosion Inhibitor Process for Domestic Water. *Journal AWWA*, 62:10:659 (1970).

- 44. Mullen, E.D. & Ritter, J.A. Potable-Water Corrosion Control. *Journal AWWA*, 66:8:473 (1974).
- 45. Shull, K.E. An Experimental Approach to Corrosion Control. *Journal AWWA*, 72:5:280 (1980).
- 46. Bancroft, D.A. Corrosion Control Program in Danvers, Massachusetts. *Journal of the New England Water Works Association*, 102:163 (1988).
- 47. Horn, B.P. & McGiffney, G.J. Mitigating Water Distribution Corrosion Problems at Edwards Air Force Base, California. Proc. AWWA Annual Conference. Chicago, IL (1999).
- 48. Huang, D.J.-S. Polyphosphate For Corrosion Control in Water Distribution System. Dissertation, University of Missouri, Columbia, MO (1980).
- 49. Wagner, I. & Kuch, A. The Influence of Water Parameters on Corrosion Rate, Scale Deposition and Iron (III) Uptake in Unprotected Iron Pipes. *Water Supply*, 2:3/4:SS 11 (1984).
- 50. Williams, S.M. The Use of Sodium Silicate and Sodium Polyphosphate to Control Water Problems. *Water Supply*, 8:195 (1990).
- 51. Malcolm Pirnie. Central Avra Valley Storage & Recovery Project, Task 6: Water Quality Management Program, Iron Release Testing Results. (1998).
- 52. Volk, C.; Dundore, E.; Schiermann, J. & LeChevallier, M. Practical Evaluation of Iron Corrosion Control in a Drinking Water Distribution System. *Water Res.*, 34:6:1967 (2000).

Table 2-1: Water Qualities for Pipe Experiments

Water #	рН	Carbonate Alkalinity (mg/L as CaCO <sub>3</sub> )	Typical Adjustment
1	7.8	45	not adjusted
			(Boulder tap water conditions)
2	7.2	300	add 0.006 moles NaHCO <sub>3</sub> to 20 L water,
			bubble with CO <sub>2</sub> for 20 seconds
3	9.5	45	add 0.005 moles NaOH to 20 L water
		(60 mg/L total alkalinity)	
4	7.2	15	add 0.005 moles HClO <sub>4</sub> to 20 L water,
			bubble with CO <sub>2</sub> -free air for 10 min
5	7.2	45	bubble with CO <sub>2</sub> for 5 seconds

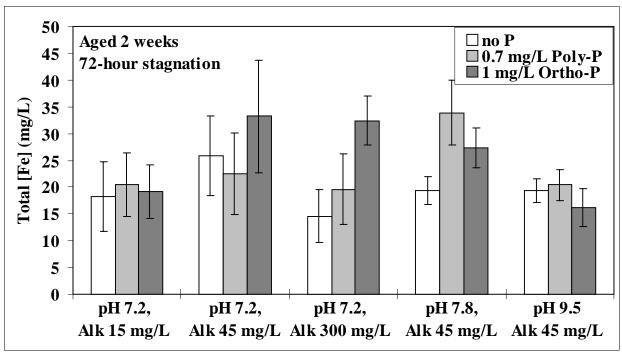
Table 2-2: Pipe ages during experiments.

	AGE DURING SPECIFIED	
EXPERIMENT	EXPERIMENT	
	"Old" Pipes <sup>1</sup>	"New" Pipes <sup>2</sup>
72-hour stagnation	3 years	2 weeks
8-hour stagnation	3.1 years	4 weeks
51-hour stagnation	3.5 years	not used
Zinc Ortho-P (8-hour stagnation)	not used	4.5 months
Weight loss determination	4 years	not used

Table 2-3: Comparison of scale build-up over four year life of pipes.

WATER QUALITY	SCALE BUILD-UP (g)		
	Pipe With	Pipe with	
	1 mg/L Poly-P	Poly-P stopped	
pH 7.2, Alk 15 mg/L	0.200	0.150	
pH 7.2, Alk 300 mg/L	0.040	0.030	
pH 7.8, Alk 45 mg/L	0.140	0.060	
pH 9.5, Alk 45 mg/L	0.310	0.120	

<sup>&</sup>lt;sup>1</sup>Exposure started June 1994 <sup>2</sup>Exposure started June 1997



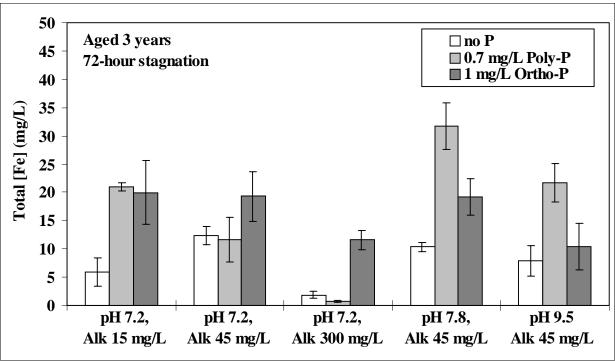
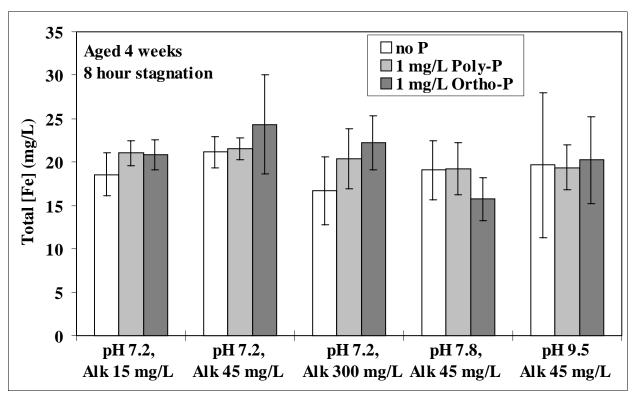


Figure 2-1: Total iron released during 72-hour stagnation experiments. Error bars represent 95%ile confidence intervals from triplicate sampling.



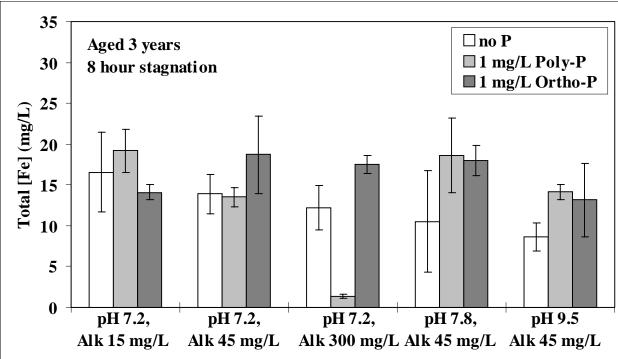


Figure 2-2: Total iron released during 8-hour stagnation experiments. Error bars represent 95%ile confidence intervals from triplicate sampling.

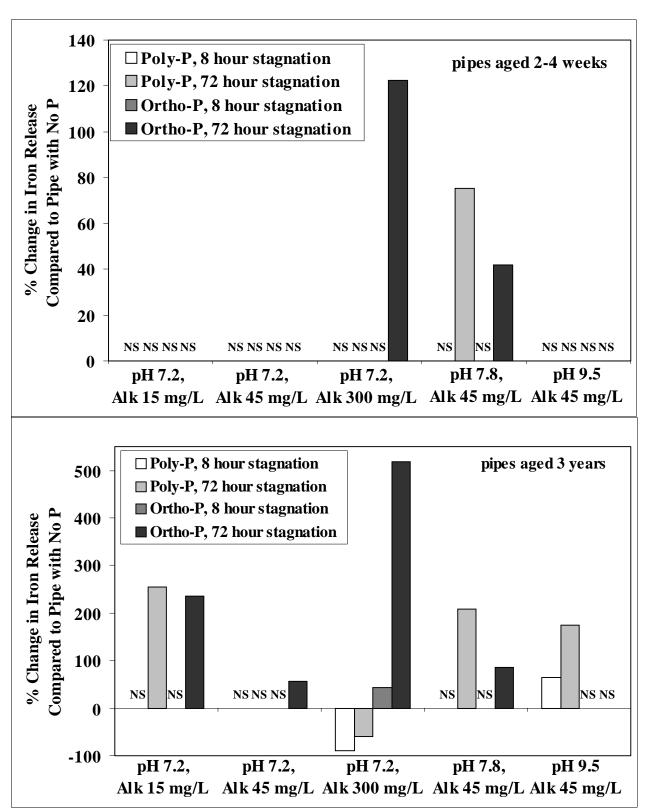
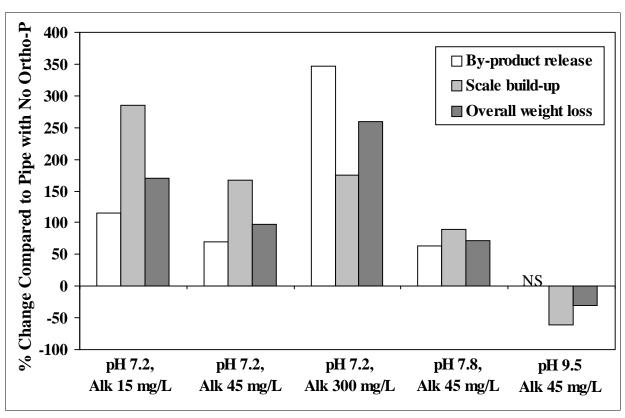


Figure 2-3: Percent change in total iron release in new (aged 2-4 weeks) or old (aged 3 years) pipes compared to pipe with no inhibitor added. "NS" indicates not significant at 95% confidence.



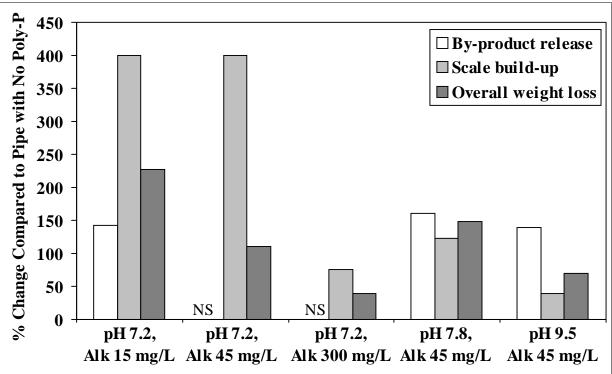


Figure 2-4: Percent change in weight loss over 4-year lifetime of a pipe with orthophosphate (top) or polyphosphate (bottom) compared to a pipe with no phosphate added. "NS" indicates not significant.

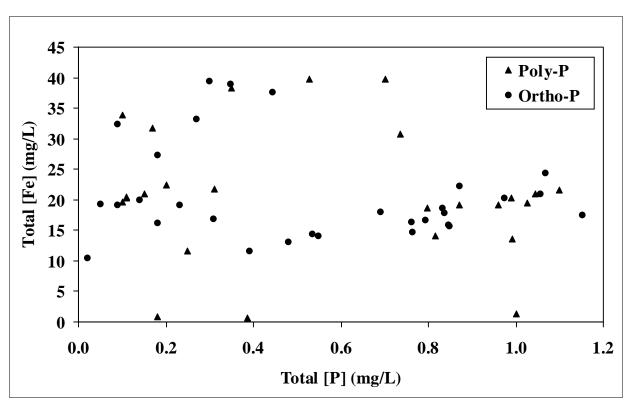


Figure 2-5: Total iron released as a function of residual phosphorus (measured after stagnation). Data include 8-, 51-, and 72-hour stagnation, all pipe ages and water qualities.

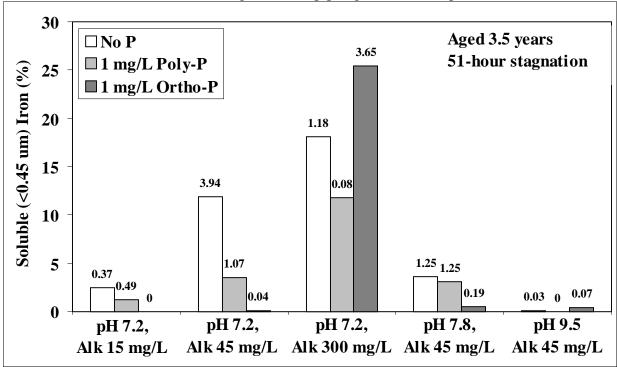


Figure 2-6: Percentage of total iron released as soluble (< 0.45- $\mu m$ ). Data labels show the absolute concentration of soluble iron in mg/L.

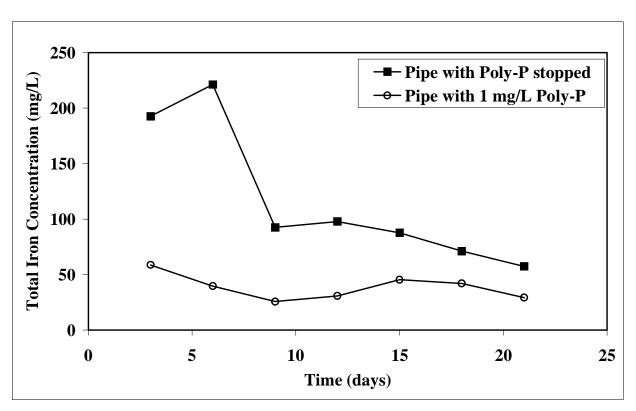


Figure 2-7: Iron released during a cut pipe experiment.

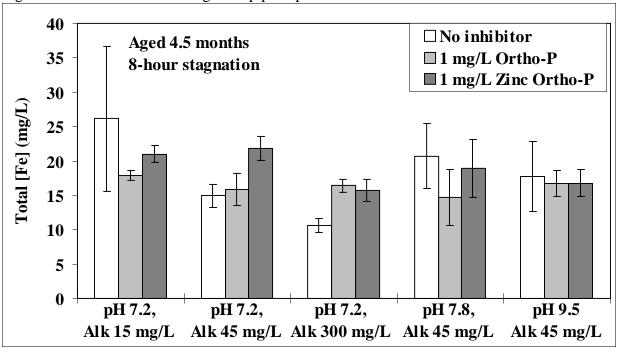


Figure 2-8: Total iron released during orthophosphate vs. zinc orthophosphate experiments, 8-hour stagnation. Error bars represent 95%ile confidence intervals from triplicate sampling.