City of
FRESNO
Yvonne Spence, CMC
City Clerk

July 15, 2016

MEMORANDUM

TO: Councilmembers

RE: Handouts received during the July 14, 2016 Council Meeting

Attached, please find a copy of two handouts received from Jeanette Grider during the public comment portion of the July 14, 2016 City Council meeting. Ms. Grider spoke about discolored water in Northeast Fresno.

If you have any questions, please contact me at x-7671.

Respectfully Submitted,

Todd Stermer,
Assistant City Clerk
City of Fresno

from Jeanette Grider on
7-14-2016

#1

Re-equilibration/Corrosion Issues in the Fresno Distribution System

Prepared for: City of Fresno Water Department August 25, 1998
Prepared by: HDR Engineering, Inc. Fresno, CA

Page vii

Again, aged pipe specimens (copper and Pb/Sn solder, and galvanized iron) were taken from the Fresno homes and placed in closed-loop recirculation systems constructed so as to control flow and water quality regimes. A specialized testing procedure using electrochemical corrosion monitoring techniques was used to track and assess corrosion rates on the respective test surfaces.

The most significant results of the combined testing program were:

- **Galvanization layers in premise plumbing are still largely intact.** Preserving the galvanization layer is the key to minimizing potential red water/aesthetic problem.
- Zinc layer corrosion is very sensitive to pH. Maintaining a high pH will substantially extend the service life of the existing galvanization layers.

The principal recommendations of this report: (1) Pre-blending (ground and surface water prior to distribution) will probably be unnecessary if rigorous pH control is practiced; (2) a finished water pH target of 9.0 is appropriate for the treated surface water; (3) a finished water minimum alkalinity target range of 25 - 30 mg/L (as $CaCO_3$) is readily achievable and would substantially improve the buffer intensity of the distributed water, and hence, help to maintain the distributed water target pH; (4) provision for polyphosphate addition will be useful to mitigate potential red water problems and stabilize existing iron-based corrosion scales.

Page 8

Although the groundwater is chemically stable relative to calcite precipitation, Lead and Copper Rule (LCR) compliance monitoring has shown the water to be somewhat corrosive to the lead-bearing surfaces in residential plumbing systems.

The raw water from the Enterprise Canal varies substantially from the chemical matrix presented by the historical Groundwater sources. Enterprise Canal water will have a much lower mineral content, including lower buffer capacity, lower overall hardness, and, with some seasonal variation, a lower chloride and sulfate content. Because of the difference in the inorganic character, the potential corrosion impacts of the Enterprise Canal water relative to premise plumbing materials (including galvanized pipe, lead and copper surfaces) and distribution mains were thought to be substantially different from the Groundwater. Hence, the recognition that introduction of a new source requires a review and evaluation of corrosion control strategies for the Fresno system as a whole, including treatment practice and assessment of metal release from existing corrosion scales.

Page 10

1.2 BLENDING ISSUES

Introduction of Enterprise Canal water to the Fresno system was thought to have the potential to generate several problems relative to corrosion, metal release, overall treatability and aesthetics (taste, odor and color). The more important of these concerns can be described as follows:

Lead and Copper Rule Requirements. Metal release rates on copper and lead bearing surfaces will likely be higher when exposed to the more poorly mineralized blends of Enterprise Canal and Groundwater. pH and alkalinity adjustments may be required to achieve the LCR required "optimal" corrosion control on lead bearing surfaces. Addition of corrosion inhibitors may be appropriate during the period of re-equilibration.

Oscillating Water Quality. As a result of weekly or diurnal variations in demand, portions of the Fresno system may see a variable water quality that oscillates between a low and high mineral content water. The oscillating water quality may be particularly problematic because of the possibility that the unstable mineral content could prevent the effective equilibration and passivation of corrosion surfaces. Hence, portions of the system may remain at risk for excessive metal release, colored water and other aesthetic concerns for an extended period of time.

Page 11

1.3 SCOPE AND OBJECTIVES

The study has two principle objectives:

- Determine the potential for serious red water/corrosion problems when the surface water (or surface water - ground water blend) are introduced to the Fresno distribution system.
- Define the water quality conditions and blend ratios that can minimize scale or corrosion related problems. Specific water quality/treatment issues to be evaluated included pH and alkalinity effects, blend ratios of Groundwater/Enterprise

Page 12:

2.1 INTRODUCTION

Concerns about structural damage caused by corrosion are common to every use of iron and steel. In drinking water systems, corrosion also causes massive waste of drinking water, accelerates the depletion of disinfectants and impairs the quality of drinking water since even small quantities of iron corrosion products (so called red water) can severely deteriorate its aesthetic properties. **Thus, water wastage, substitution of bottled water for tap water, and costs of internal corrosion to cast iron, ductile iron and galvanized pipe are reasons to optimize mitigation measures that minimize corrosion** as well as insure the stability of existing corrosion scales. It is also of note that corrosion scales may also shelter harmful bacteria and effect the microbial quality of the distributed water.

Page 14:

2.3 CORROSION SCALES OF CONCERN

The corrosion scales of greatest concern in Fresno are those in closest proximity to the consumerthe household plumbing (premise plumbing). In Fresno households, galvanized piping predominates with well over 50 percent of the installation.

Page 15:

HDR and Fresno Utility people carried out sampling of pipe materials from households and public facilities in Fresno (see Figures 2-1and2-2). Both galvanized and copper pipe samples were collected.

Of most concern was the condition of the galvanized surfaces, which, surprisingly, were found to be in excellent condition. Only a small proportion of the galvanization layer had been lost, and the accumulation of iron-based corrosion scales was minimal on the galvanized surfaces. Figures 2-3 and 2-4 show the exceptionally internal condition of a typical galvanized pipe sample, these samples having been in service for over forty years. The vast majority of galvanized pipe specimens retrieved were in equally good condition. The actual zinc corrosion scale was extremely thin (< 5 mil), somewhat friable, and easily powdered when dry.

Page 18:

To verify the actual integrity of the galvanization layer, cross-sections of several pipe specimens were polished (300 grit), etched and micrographed. Figure 2-5 shows a fresh galvanization layer with an approximate 75-micron deep layer of zinc. Figure 2-6 shows a Fresno pipe section (>20 years service) with over 40 microns of galvanization remaining. Although we cannot determine what the original depth was on the samples in question, ASTM standards call for a minimum initial galvanization layer thickness of 50 microns.

Page 19:

In only a few circumstance were specimens obtained that showed significant loss of the galvanization layer and the development of meaningful iron-based corrosion scales. Figures 2-7 and 2-8 show the nature of the relatively minimal iron-based scales found in some Fresno pipe samples. In even these circumstances, the galvanization layer below the corrosion scale was largely intact, and the iron tuberculation originated from a small holiday (surface defect) that penetrated the galvanization to the base metal.

Page 21:

There is substantial potential for extended service life of this plumbing material as long as the existing galvanization layer remains intact. The likelihood of a serious red water problem generating from premise plumbing corrosion problems is remote if the galvanization layer is preserved.

Page 24 – 25:

2.5 PIPE RETRIEVAL AND PRESERVATION

Approximately fifty feet of 1"-diameter galvanized iron pipe was extracted from three different sites in the Fresno distribution system in March 1998. Pipe sections were taken from a High School, a groundwater pumping station, and an apartment complex. In all cases the pipe had been in service for over 20 years, in some cases up to 40 years, and had conveyed only groundwater.

Figure 2-12 shows the heavy encrustation of cemented soils and corrosion by-products, which coated some of the retrieved pipe's outer surface. It was necessary to carefully remove much of this debris while preparing pipe samples.

- Pipes were examined and classified. Initially, it was thought that the pipe specimens would be grouped by the degree of inner tuberculation:
  - }- Type 1: little internal tuberculation; almost completely smooth, galvanization layer intact;
  - }- Type 2: moderate tuberculation covering most of the inner pipe wall;
  - }- Type 3: heavy inner tuberculation covering nearly all of the inner pipe wall.

Pipe cutting, rinsing and classifying continued until enough samples were acquired for all the bench testing. **Because the galvanization layer was still intact on almost all the samples examined, the majority met the type one categorization. Only a few specimens rated the type two designations. No samples were characterized as type three.** The samples classified as type two were used to evaluate iron release in the dedicated iron loops, while the type one sections were used to evaluate zinc release.

Page 30:

2.8.2 pH and Blend Effects

Interpretation of the results is straightforward. Iron release is sensitive to pH, but largely insensitive to the blend ratio of the water sources or the alkalinity of the water. At pHs substantially lower than the Groundwater baseline level of 7 .8, iron release increases significantly. At the low pH (6.0 - 6.5) iron release is increased by over 40 percent in the unblended Groundwater, and by over 60 percent in the unblended Enterprise Canal water.

Conversely, pH levels higher than the baseline level diminished iron release - a pH shift to the range of 9.0-9.5 decreased iron release by as much as 20 percent relative to baseline.

Page 31:

As in the case of iron release, the results clearly demonstrate the sensitivity of the galvanization surface to pH, as well as its relative insensitivity to blending effects and supplemental alkalinity addition. The distinction between the iron and zinc release is in the magnitude of the response. **While iron release rates increased by about 50 percent for a 1.5 pH unit decrease, zinc release rates increased by over 200 percent.**

Page 47:

However, the fact that Fresno galvanization layers are still intact after 25 years tells us that corrosion rates on zinc surfaces in Fresno groundwater are exceptionally low. The measured baseline rate of 0.075 MPY converts to a loss of approximately 2 microns of galvanization layer per year, or a total of about 50 microns over 25-years. The initial depth of the galvanization on the pipe was approximately 50 - 75 microns, and our investigation of the aged specimens showed that even after 25 years a substantial zinc layer remained. This suggests the measured laboratory corrosion rates are at least consistent with the Fresno experience.

3.4.2 pH and Blend Effects:

The sensitivity of the test specimens to pH and blending effects was assessed by evaluating corrosion rates at both reduced and elevated pH (relative to baseline conditions) and by comparing the respective source waters and a 50:50 blend of the Groundwater and Enterprise Canal water (Figure 3-7).

Zinc specimens were not influenced by blending, but were dramatically influenced by decreasing the pH (Figure 3-9). The shift from baseline to the 6.3-6.8 pH range more than doubled the baseline corrosion rate in all the test waters. Increasing the pH, however, did not meaningfully diminish the baseline rate. Galvanized surfaces, however, did derive benefit from the phosphate at the baseline pH, but experienced no benefit at the reduced pH.

4.1.2 Iron Surfaces

Iron-based corrosion scales on steel and galvanized pipe surfaces in Fresno homes are relatively soft, somewhat friable, and only partially comprised of iron oxides. While they cover only a minor portion of most galvanized plumbing surfaces, they represent a reservoir of oxidized metal and a potential taste and odor related organic material. While relatively small in total mass, the iron scales could be a significant source of iron oxide partrculates, and, hence, a potential cause, albeit temporarily, of red water. Destabilizing these scales would have the double impact of generating serious red water complaints, as well as causing a loss of consumer confidence that could jeopardize the long-term success of the new surface water treatment plant.

As in any project of this type, regardless of blend ratio or corrosion control efforts, some minor red water problems, as well as taste and odor complaints, are likely at the first introduction of treated surface water to the Fresno distribution system. If treated appropriately, these impacts will be temporary. The Fresno Water Department should plan on being proactive in its response to the potential complaints. In the best case, this may require a modest public relations effort. **In the worst case, the department may need to replace plumbing from some older households that are the most tuberculated.**

4.1.3 Zinc Surfaces

Galvanization layers on the majority of Fresno premise plumbing are still largely intact. The baseline groundwater conditions have generated zinc corrosion scales that have remained remarkably stable over several decades. Preserving the existing galvanization layers is the key to minimizing potential long-term red water/aesthetic problem.

4.2.2 Iron Surfaces

The conventional wisdom relative to the use of polyphosphates and iron-scale stability is flawed. The Fresno tests show that, contrary to anticipation, polyphosphates do not mobilize the metal in the iron-scale, but rather they significantly enhance its stabilization and reduce the rate of iron release. The polyphosphates apparently sorb to the surface of the corrosion scales, slowly hydrolyzing and releasing orthophosphate below the scale surface. The orthophosphate may form precipitation products with metals in the scale that serve to help stabilize the surface, or they may form a ferri-hydroxy-phosphate compound that simply immobilizes iron that might otherwise be release to the water flow. The polyphosphate effect on iron-based scales is not unique to Fresno.

Recent studies have shown similar results using corrosion scales generated in other distribution systems.The results suggests that polyphosphates offer the potential for enhanced stabilization of iron based scales, and, hence, may be of value during the initial introduction of the surface water to the Fresno system. Zinc-orthophosphate addition, however, did not prove to be meaningfully beneficial relative to iron release, even when used at high dosage levels.

4.3.2 Iron Surfaces

Like the lead and copper surfaces, distribution of treated Enterprise Canal water is not an issue for the iron surfaces. Decreased alkalinity and mineral content of the surface water will minimally impact iron release from existing iron-based scales. Of much greater importance, similar to the lead and copper surfaces, is pH, which appears to be the controlling factor for iron release. A full unit decrease in pH could increase FE releaseby as much as 50%. Conversely maintenance of high pH (> 8.5) ensures the stability of the iron-based scale. A high pH policy would, essentially, make the existing iron-based scales "bullet-proof" to water quality variations.

4.3.3 Zinc Surfaces

Because of the high proportion of Fresno homes with galvanized plumbing, it is critical to ensure the continued integrity of these plumbing systems. Loss of the galvanization layer would substantially increase the long-term possibility of red water and other aesthetic water quality issues.

The zinc-based galvanization layer is very sensitive to pH, more so than any of the other metals tested. This is true both in the sense of metal release from the corrosion scale on the galvanization layer, as well as the actual oxidation processes governing corrosion of the zinc base metal. Maintenance of a high pH in Fresno's distributed water is necessary to extend the service life of the existing galvanization layers.

Blending (TDS content) is somewhat important to corrosion on the zinc surfaces, but not as important as pH control.

Pre blending (ground and surface water prior to distribution) will probably be unnecessary if **rigorous pH control is practiced.**

5.2 RIGOROUS pH CONTROL OF TREATED SURFACE WATER IS NECESSARY

In the interest of maintaining a stable pH throughout the distribution system, HDR suggests that a permanent finished water pH target of 9 .0 be established, and that this level be maintained regardless of the treatment option selected for the Enterprise Canal water. The pH 9.0 target represents a relatively minor chemical cost, but offers the advantage of substantially increased buffering capacity (**at pH 9.0 the buffering intensity of the Enterprise Canal is approximately three fold greater than at pH 8.3** - see Figure 5-1). The enhanced buffer intensity will ensure minimal pH drift and variation across the distribution network.

5.3 ALKALINITY AUGMENTATION WOULD ENHANCE pH CONTROL

A finished water minimum alkalinity target range of 30- 35 mg/L (as $CaCO_3$) is readily achievable for Enterprise Canal water and would substantially improve the buffer intensity of the distributed water, and, hence, help to maintain the distributed water pH target.

5.4 POLYPHOSPHATE ADDITION CAPABILITY IS CHEAP INSURANCE

In order to mitigate potential red water problems and help stabilize iron-based corrosion, we recommend that the provision for polyphosphate chemical addition be a part of the new surface water treatment plant. We do not anticipate that polyphosphate will be required as a permanent treatment measure, but the results of this study show it can be effective, even as a short-term measure, at enhancing iron-based scale stability and minimizing the potential for red water. In effect, the polyphosphates are an inexpensive form of insurance against potential consumer complaints during the introduction period for the treated surface water.

In the event of a red water episode, the anticipated polyphosphate dosage level could be as high as 5 mg/L (as PO_4). We do not believe that the selection of the polyphosphate formulation is critical - most polyphosphates are created equal. This leaves the selection open to a bidding process that would minimize cost.

#2

emphasis on ensuring surface water does not generate a compliance issue relative to the Lead and Copper Rule. Again, aged pipe specimens (copper and Pb/Sn solder, and galvanized iron) were taken from the Fresno homes and placed in closed-loop recirculation systems constructed so as to control flow and water quality regimes. A specialized testing procedure using electrochemical corrosion monitoring techniques was used to track and assess corrosion rates on the respective test surfaces.

The most significant results of the combined testing program were:

- Galvanization layers in premise plumbing are still largely intact. Preserving the galvanization layer is the key to minimizing potential red water/aesthetic problem.
- There is a minimal reservoir of iron-based corrosion scales in the Fresno system. Even so, minor red water problems are likely at introduction of treated surface water – regardless of blend ratio or corrosion control efforts.
- Zinc layer corrosion is very sensitive to pH. Maintaining a high pH will substantially extend the service life of the existing galvanization layers.
- Blending (TDS content) is important to corrosion on the zinc surfaces, but not as important as pH control.
- Iron release rates from existing scales are not seriously impacted by decreases in mineral content.
- pH is the controlling factor for iron release – a full unit decrease can substantially increase Fe release.
- Zinc-orthophosphate addition is not beneficial relative to iron release and red water problems.
- Contrary to Zinc-orthophosphates, polyphosphates offer the potential for enhanced stabilization of iron based scales, and, hence, may be of value during the initial introduction of the surface water.
- TDS variability will not significantly alter metal release ratio on either lead or copper surfaces if pH/alkalinity stability is achieved.
- Lead-bearing solders are sensitive to change in mineral content (blending). However, base corrosion rates are low and the absolute rate remains low even in the face of a large change in mineral content.
- Copper is relatively insensitive to blended waters – pH and alkalinity remain important.

The principal recommendations of this report: (1) Pre-blending (ground and surface water prior to distribution) will probably be unnecessary if rigorous pH control is practiced; (2) a finished water pH target of 9.0 is appropriate for the treated surface water; (3) a finished water minimum alkalinity target range of 25 – 30 mg/L (as $CaCO_3$) is readily achievable and would substantially improve the buffer intensity of the distributed water, and hence, help to maintain the distributed water target pH; (4) provision for polyphosphate addition will be useful to mitigate potential red water problems and stabilize existing iron-based corrosion scales.

SECTION 2: CORROSION SCALES AND RED WATER

2.1 INTRODUCTION

Concerns about structural damage caused by corrosion are common to every use of iron and steel. In drinking water systems, corrosion also causes massive waste of drinking water, accelerates the depletion of disinfectants and impairs the quality of drinking water since even small quantities of iron corrosion products (so called red water) can severely deteriorate its aesthetic properties. Thus, water wastage, substitution of bottled water for tap water, and costs of internal corrosion to cast iron, ductile iron and galvanized pipe are reasons to optimize mitigation measures that minimize corrosion as well as insure the stability of existing corrosion scales. It is also of note that corrosion scales may also shelter harmful bacteria and effect the microbial quality of the distributed water.

Although the species of Fe(II) and Fe(III) are not toxic *per se* and considered as a secondary, non-health related contaminants under the Safe Drinking Water Act, their importance relative to the operation of a water distribution systems and the satisfaction of the customers the systems serves is enormous.

2.2 THEORIES OF IRON CORROSION

Electrochemical oxidation of iron proceeds in two steps, namely Fe(0)→Fe(II)→Fe(III). An electron acceptor is required for each step. In drinking water, oxygen is the typical electron acceptor while chlorine and chloramines are also highly reactive due to their high electrochemical potential ($E^0_{HClO/Cl^-} = 1.07$ V, compared with $E^0_{O_2/OH^-} = 0.27$ at pH 7.0). Halogenated compounds such as CCl_4 and $CHCl_3$ have also been found to be active as electron receptors in the oxidation of Fe(0) and Fe(II). The absolute concentrations of these species are much less than those of oxygen or chlorine species, but their electrochemical reactions may significantly affect their fate in potable water distribution networks.

Corrosion causes the formation of exceedingly complex surface scales that include ferrous, ferric and mixed oxyhydroxides, carbonates, phosphates and sulfides [*Sontheimer, Kölle and Snoeyink 1981*]. Localized electrochemical processes and spatial variations of the composition of iron corrosion products are also notable. The cumulative rate of conversion of O_2 to H_2O/OH^-, HClO to Cl^- and RX to RH (RX denotes a halogenated organic species) is coupled with the rate of metal oxidation. These processes are expected to balance only at a unique value of the corrosion potential, E_{corr} [*Internal Corrosion 1996*], which is amenable to experimental measurements. However, an assumption that E_{corr} unambiguously describes the state of the iron surface and scales is an over-simplification. The presence of iron minerals that are not good conductors of electricity indicates that reactions of the scales are not governed solely by the E_{corr} of the metal proper and the corroding surface is subject to both electrochemical and chemical controls. There

Many fundamental and practical questions regarding iron corrosion mechanisms and red water formation remain unclear. Some important aspects of the overall iron corrosion process for which we have no satisfactory explanation include:

- *Electrochemical Control of Corrosion Reactions*: If a thick layer of iron corrosion products is present on an iron surface, is the rate of iron release controlled by changes in the electrical potential of the iron surface (and therefore by water quality factors such as oxidant level (chlorine) that control that potential)?
- *Relationship of Scale Properties to Water Quality and Flow Conditions*: How rapidly and in what way do the surface properties of the scale change during periods of stagnation, or in response to changes of water quality (e.g., depletion of dissolved oxygen)?
- *Mechanisms of Iron Release*: Is disaggregation of the accumulated surface scales an important source of red water, or is red water primarily or exclusively caused by dissolution reactions at the surface, followed by precipitation in solution? What role do specific corrosion products play in determining the predominance and rates of the processes? Does NOM affect the mechanism of red water?
- *Speciation of Released Iron*: What iron species are released from the surface? Are they soluble or colloidal? Are they in the +II or +III oxidation state?

By its nature, the study conducted for the City of Fresno cannot answer these fundamental questions. It does, however, give empirical evidence of how some of these factors can impact release of iron from well-acclimated corrosion scales when a major shift in water quality is introduced.

2.3 CORROSION SCALES OF CONCERN

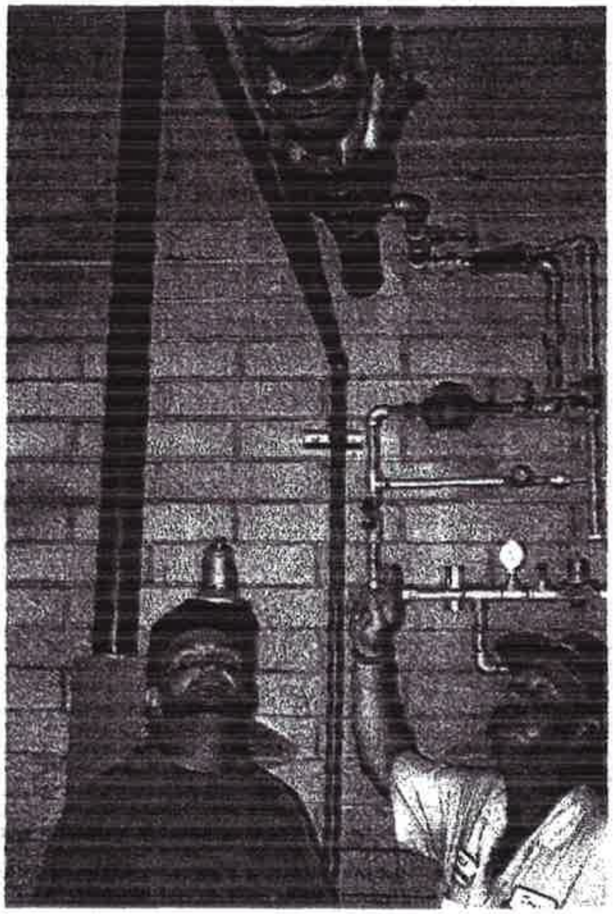
The vast majority of Fresno's distribution system consists of mortar lined ductile iron, PVC, and a limited amount of asbestos cement pipe. Only a small portion of Fresno's distribution system is unlined cast or ductile iron pipe. In short, serious re-equilibration problems related to Fresno's distribution system piping are unlikely.

The corrosion scales of greatest concern in Fresno are those in closest proximity to the consumer-the household plumbing (premise plumbing). In Fresno households, galvanized piping predominates with well over 50 percent of the installation. The next most common premise plumbing material is copper tubing, and although the exact proportion is unknown, local plumbers feel that galvanized plumbing is two to three times more common than copper in older homes. Copper, however, may be more prevalent in some new developments.

HDR and Fresno Utility people carried out sampling of pipe materials from households and public facilities in Fresno (see Figures 2-1 and 2-2). Both galvanized and copper pipe samples were collected.

Of most concern was the condition of the galvanized surfaces, which, surprisingly, were found to be in excellent condition. Only a small proportion of the galvanization layer had been lost, and the accumulation of iron-based corrosion scales was minimal on the galvanized surfaces. Figures 2-3 and 2-4 show the exceptionally internal condition of a typical galvanized pipe sample, these samples having been in service for over forty years. The vast majority of galvanized pipe specimens retrieved were in equally good condition. The actual zinc corrosion scale was extremely thin (< 5 mil), somewhat friable, and easily powdered when dry.

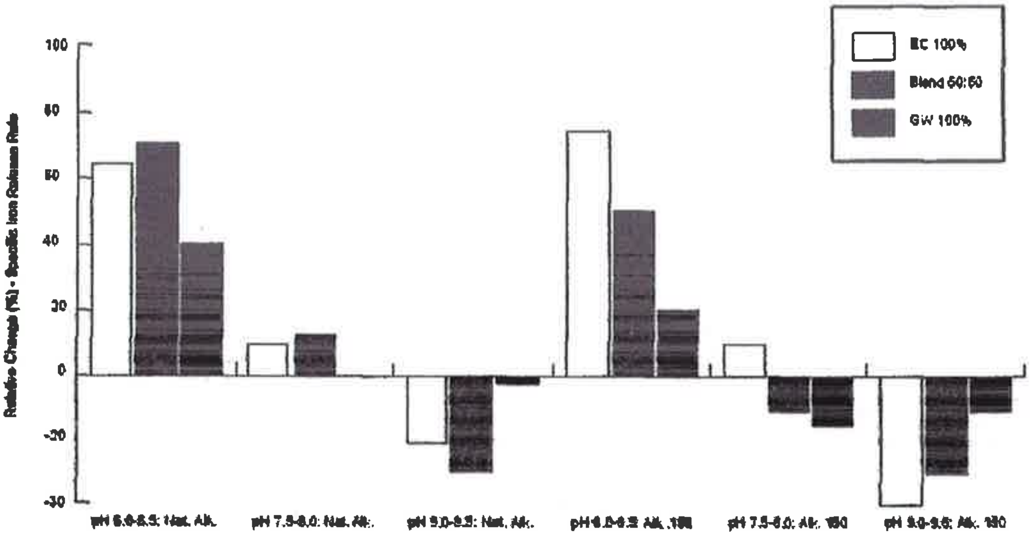
Figure 2-1. Fresno water department personnel retrieving pipe samples.



In only a few circumstance were specimens obtained that showed significant loss of the galvanization layer and the development of meaningful iron-based corrosion scales. Figures 2-7 and 2-8 show the nature of the relatively minimal iron-based scales found in some Fresno pipe samples. In even these circumstances, the galvanization layer below the corrosion scale was largely intact, and the iron tuberculation originated from a small holiday (surface defect) that penetrated the galvanization to the base metal.

Figure 2-7. Iron-oxide accumulation on Fresno galvanized pipe.

Figure 2-14. Iron loop data summary – pH effects.



The Enterprise Canal and blended water exposures produce changes in iron release that are similar to those observed in undiluted Groundwater. While the blend ratio does not appear to generate a major adverse effect on iron release, it must be recognized that the testing protocol is not sensitive enough to determine more subtle effects. The results do, however, clearly show the sensitivity of iron release to pH, and the importance of maintaining a high pH to minimize iron release.

Similar to Figure 2-14, Figure 2-15 displays the change in specific zinc release (relative to baseline levels) brought about by exposure to different blends of the Enterprise Canal and Fresno Groundwater for various pH ranges at both native alkalinity levels, and with supplemental alkalinity addition. As in the case of iron release, the results clearly demonstrate the sensitivity of the galvanization surface to pH, as well as its relative insensitivity to blending effects and supplemental alkalinity addition. The distinction between the iron and zinc release is in the magnitude of the response. While iron release rates increased by about 50 percent for a 1.5 pH unit decrease, zinc release rates increased by over 200 percent. Zinc release showed little decrease associated with increased pH, but the ability to detect a change is likely hampered by the relatively low baseline zinc release rates and the general imprecision of the measurement technique.

1.5 unit pH decrease =
zINC release over 200%

on an unpassivated surface. Even so, the baseline corrosion rate of the lead-tin solder specimens were exceptionally low under almost all conditions - generally less than 0.01 MPY. A moderate corrosion rate for a lead-tin solder surface is less than 0.02 MPY. No evidence was visible that the solder surfaces were shedding lead oxide particulates. Baseline corrosion in the Enterprise Canal water was somewhat higher than the Groundwater, but still low enough as not to be problematic relative to lead release.

Baseline corrosion rates measured on the Fresno zinc samples (aged galvanized pipe) were somewhat less than that measured on the aged copper tubing (0.075 - 0.1 MPY). Unfortunately, the literature provides few references on physical measures of corrosion rates of galvanized surfaces in drinking water environments, hence, it is difficult to verify how the Fresno experience compares to other utilities. However, the fact that Fresno galvanization layers are still intact after 25 years tells us that corrosion rates on zinc surfaces in Fresno groundwater are exceptionally low. The measured baseline rate of 0.075 MPY converts to a loss of approximately 2 microns of galvanization layer per year, or a total of about 50 microns over 25-years. The initial depth of the galvanization on the pipe was approximately 50 – 75 microns, and our investigation of the aged specimens showed that even after 25 years a substantial zinc layer remained. This suggests the measured laboratory corrosion rates are at least consistent with the Fresno experience.

3.4.2 pH and Blend Effects

The sensitivity of the test specimens to pH and blending effects was assessed by evaluating corrosion rates at both reduced and elevated pH (relative to baseline conditions) and by comparing the respective source waters and a 50:50 blend of the Groundwater and Enterprise Canal water (Figure 3-7). For copper, the blending studies show that at the nominal baseline pH, the combination of the two waters had little impact on the test specimen corrosion rate. However, a reduction in the pH (6.3 – 6.8) did elevate corrosion rates in all the test waters by as much as 50 percent, while raising the pH of the test waters to about 9.0 had a distinct beneficial impact. Overall, copper corrosion on the Fresno samples was relatively insensitive to changes in alkalinity levels and mineral content produced by the blending. The copper is moderately sensitive to reduced pH, and slightly sensitive to increased pH.

SECTION 4: SUMMARY AND CONCLUSIONS

4.1 CORROSION AND SCALE CHARACTER

4.1.1 Lead and Copper Surfaces

Baseline corrosion rates measured in Groundwater water are generally low for the LCR test surfaces (aged copper and Pb/Sn solder). Baseline corrosion rates on the Pb/Sn solder surfaces are especially low, well below any level of reasonable concern relative to compliance issues with the LCR. The low baseline corrosion rates are indicative of the historically low metal release levels measured in Fresno's LCR compliance monitoring program. Aged copper corrosion scales are stable and effectively passivate the underlying base metal. The lead-tin solder surfaces did not develop voluminous scales and there was no evidence that the solder surfaces shed lead oxide particulates.

No evidence of pitting was found on any of the Fresno test specimens, nor did any of the corrosion control strategies tested appear to initiate the pitting process on either the aged or fresh specimens. The predominant form of mineral scale present on the copper surfaces was a light greenish-brown deposit, which is typical of a combination malachite and cuprite scale and common to copper surfaces exposed to a groundwater quality of this type.

4.1.2 Iron Surfaces

Iron-based corrosion scales on steel and galvanized pipe surfaces in Fresno homes are relatively soft, somewhat friable, and only partially comprised of iron oxides. While they cover only a minor portion of most galvanized plumbing surfaces, they represent a reservoir of oxidized metal and a source of potential taste and odor related organic material. While relatively small in total mass, the iron scales could be a significant source of iron oxide particulates, and, hence, a potential cause, albeit temporarily, of red water. Destabilizing these scales would have the double impact of generating serious red water complaints, as well as causing a loss of consumer confidence that could jeopardize the long-term success of the new surface water treatment plant.

As in any project of this type, regardless of blend ratio or corrosion control efforts, some minor red water problems, as well as taste and odor complaints, are likely at the first introduction of treated surface water to the Fresno distribution system. If treated appropriately, these impacts will be temporary. The Fresno Water Department should plan on being proactive in its response to the potential complaints. In the best case, this may require a modest public relations effort. In the worst case, the department may need to replace plumbing from some older households that are the most tuberculated.

4.1.3 Zinc Surfaces

Galvanization layers on the majority of Fresno premise plumbing are still largely intact. The baseline groundwater conditions have generated zinc corrosion scales that have remained remarkably stable over several decades. Preserving the existing galvanization layers is the key to minimizing potential long-term red water/aesthetic problem.

4.2 ORTHO AND POLYPHOSPHATE EFFECTS

4.2.1 Lead and Copper Surfaces

Zinc-orthophosphate was, at best, marginally effective at reducing the corrosion rates on copper and Pb/Sn solder surfaces. The benefits of orthophosphate addition was somewhat apparent at the lower pHs tested (< 7.5), but was not clear at the baseline pH levels assessed. The results of the zinc-orthophosphate testing do not suggest that it would be beneficial to initiate an orthophosphate addition program, nor is there an indication of a need to further control corrosion on these surfaces.

4.2.2 Iron Surfaces

The conventional wisdom relative to the use of polyphosphates and iron-scale stability is flawed. The Fresno tests show that, contrary to anticipation, polyphosphates do not mobilize the metal in the iron-scale, but rather they significantly enhance its stabilization and reduce the rate of iron release. The polyphosphates apparently sorb to the surface of the corrosion scales, slowly hydrolyzing and releasing orthophosphate below the scale surface. The orthophosphate may form precipitation products with metals in the scale that serve to help stabilize the surface, or they may form a ferri-hydroxy-phosphate compound that simply immobilizes iron that might otherwise be release to the water flow. The polyphosphate effect on iron-based scales is not unique to Fresno. Recent studies have shown similar results using corrosion scales generated in other distribution systems.

The results suggests that polyphosphates offer the potential for enhanced stabilization of iron based scales, and, hence, may be of value during the initial introduction of the surface water to the Fresno system. Zinc-orthophosphate addition, however, did not prove to be meaningfully beneficial relative to iron release, even when used at high dosage levels.

4.2.3 Zinc Surfaces

Galvanized surfaces derived modest benefit from orthophosphate addition at the baseline pH, but experienced no benefit at reduced pH.

4.3 pH AND BLEND ISSUES

4.3.1 Lead and Copper Surfaces

Introduction of appropriately treated Enterprise Canal water, or a blend of treated Groundwater and Enterprise Canal water, is not a threat to the integrity of the existing lead and copper corrosion surfaces, and will generate few, if any, LCR compliance problems. Pb/Sn solder surfaces are the most sensitive to any change in mineral content (surface water addition). However, baseline corrosion rates on these surfaces are so low that the absolute rate remains low even in the face of a large percentage increase.

The pH of the distributed water and maintenance of pH stability are the critical control parameters relative to lead and copper surfaces. The corrosion character of both copper and solder specimens was demonstrated sensitive to a pH reduction. However, as long as a suitable pH control practice is maintained (distributed pH level above 8.5) current corrosion conditions in the distribution system will likely remain unchanged, regardless of surface water addition.

4.3.2 Iron Surfaces

Like the lead and copper surfaces, distribution of treated Enterprise Canal water is not an issue for the iron surfaces. Decreased alkalinity and mineral content of the surface water will minimally impact iron release from existing iron-based scales. Of much greater importance, similar to the lead and copper surfaces, is pH, which appears to be the controlling factor for iron release. A full unit decrease in pH could increase Fe release by as much as 50 percent. Conversely, maintenance of high pH (> 8.5) ensures the stability of the iron-based scale. A high pH policy would, essentially, make the existing iron-based scales "bullet-proof" to water quality variations.

>pH

4.3.3 Zinc Surfaces

Because of the high proportion of Fresno homes with galvanized plumbing, it is critical to ensure the continued integrity of these plumbing systems. Loss of the galvanization layer would substantially increase the long-term possibility of red water and other aesthetic water quality issues.

The zinc-based galvanization layer is very sensitive to pH, more so than any of the other metals tested. This is true both in the sense of metal release from the corrosion scale on the galvanization layer, as well as the actual oxidation processes governing corrosion of the zinc base metal. Maintenance of a high pH in Fresno's distributed water is necessary to extend the service life of the existing galvanization layers.

Blending (TDS content) is somewhat important to corrosion on the zinc surfaces, but not as important as pH control.

SECTION 5: RECOMMENDATIONS

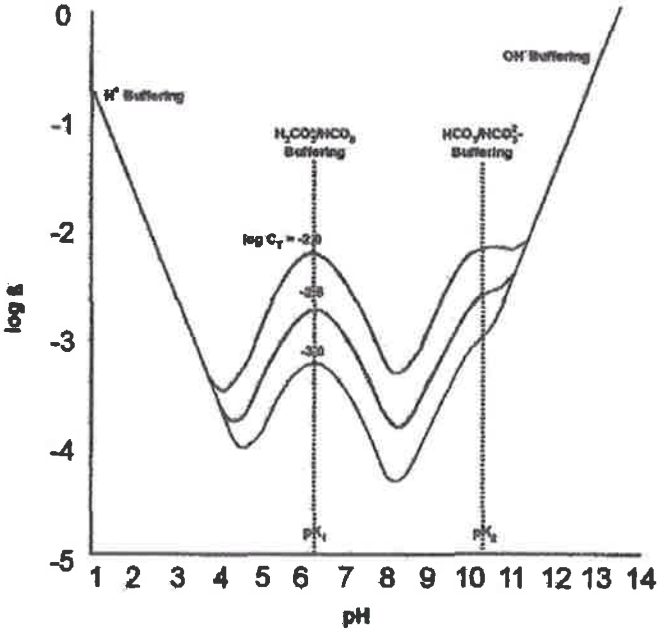
5.1 PRE-BLENDING OF SURFACE AND GROUNDWATER IS NOT A REQUIREMENT

Pre blending (ground and surface water prior to distribution) will probably be unnecessary if rigorous pH control is practiced. While not inconsequential, the potential impacts of distributing an unblended water are not so great as to merit the expense and marginal benefit associated with blending the waters prior to treatment or distribution.

5.2 RIGOROUS pH CONTROL OF TREATED SURFACE WATER IS NECESSARY

In the interest of maintaining a stable pH throughout the distribution system, HDR suggests that a permanent finished water pH target of 9.0 be established, and that this level be maintained regardless of the treatment option selected for the Enterprise Canal water. The pH 9.0 target represents a relatively minor chemical cost, but offers the advantage of substantially increased buffering capacity (*at pH 9.0 the buffering intensity of the Enterprise Canal is approximately three fold greater than at pH 8.3 – see Figure 5-1*). The enhanced buffer intensity will ensure minimal pH drift and variation across the distribution network.

Figure 5-1.



5.3 ALKALINITY AUGMENTATION WOULD ENHANCE pH CONTROL

A finished water minimum alkalinity target range of 30 – 35 mg/L (as $CaCO_3$) is readily achievable for Enterprise Canal water and would substantially improve the buffer intensity of the distributed water, and, hence, help to maintain the distributed water pH target.

5.4 POLYPHOSPHATE ADDITION CAPABILITY IS CHEAP INSURANCE

In order to mitigate potential red water problems and help stabilize iron-based corrosion, we recommend that the provision for polyphosphate chemical addition be a part of the new surface water treatment plant. We do not anticipate that polyphosphate will be required as a permanent treatment measure, but the results of this study show it can be effective, even as a short-term measure, at enhancing iron-based scale stability and minimizing the potential for red water. In effect, the polyphosphates are an inexpensive form of insurance against potential consumer complaints during the introduction period for the treated surface water.

✓ In the event of a red water episode, the anticipated polyphosphate dosage level could be as high as 5 mg/L (as PO_4). We do not believe that the selection of the polyphosphate formulation is critical – most polyphosphates are created equal. This leaves the selection open to a bidding process that would minimize cost.