Characteristics of iron corrosion scales established under blending of ground, surface, and saline waters and their impacts on iron release in the pipe distribution system

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Received 12 February 2004; accepted 3 February 2005
Available online 9 April 2005

Abstract

Interior scales on PVC, lined ductile iron (LDI), unlined cast iron (UCI) and galvanized steel (G) were analyzed by XRD, RMS, and XPS after contact with varying water quality for 1 year. FeCO₃, α-FeOOH, β-FeOOH, γ-Fe₂O₃, Fe₃O₄ were identified as primary UCI corrosion products. No FeCO₃ was found on G. The order of Fe release was UCI > G ≥ LDI > PVC. For UCI, Fe release decreased as % Fe₂O₄ increased and as % Fe₂O₃ decreased in scale. Soluble Fe and FeCO₃ transformation indicated FeCO₃ solid was controlling Fe release. FeCO₃ model and pilot data showed Fe increased as alkalinity and pH decreased.

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Keywords: Iron corrosion; Water blending; XRD; RMS; XPS; Siderite
1. Introduction

Significant population growth, in conjunction with the depletion of groundwater resources, has prompted development of alternative sources for drinking water supply. Tampa Bay Water (TBW) has developed surface water and desalination facilities to augment future drinking water supply [1,2]. The finished water quality of these alternate supplies is different from finished groundwater and will interact with the existing distribution scale and have adverse effects on distribution water quality. The disruption of existing scales on pipe surfaces is of great concerns and can lead to release of several undesirable substances to drinking water.

Various pipe materials, such as iron, galvanized steel, concrete, PVC, and copper, have been extensively used in the drinking water distribution systems. Unlined iron pipes are very prone to electrochemical corrosion and their internal surfaces can become severely corroded over time. Typical iron corrosion products formed on aged pipe surfaces can be described using three different layers: (a) a macroporous layer of black rust (magnetite, Fe₃O₄) in contact with the metal, (b) a microporous film of mixture of Fe²⁺ and Fe³⁺ species that covers the macrolayer, and (c) a top layer of red rust (mainly goethite, α-FeOOH and hematite, α-Fe₂O₃). The exact composition and structure of iron corrosion scales, however, varies significantly with water qualities as well as flow properties [3,4].

In past decades, numerous studies have been conducted to investigate iron corrosion to elucidate fundamental mechanisms responsible for iron release, which often causes red water. Alkalinity, pH, chloride and sulfate are primary water quality parameters affecting iron corrosion [2,5–10]. Kuch [11] proposed that red water was caused by reduction and dissolution of formed corrosion products (e.g. γ-FeOOH) when oxygen was lacking during stagnation. A study by Sontheimer et al. [12] suggested that the formation of siderite (FeCO₃) might play an important role in iron corrosion. Despite the extensive research efforts, adverse impacts of blending different source waters on iron release have not been investigated systematically. In particular, characteristics of chemical films established for different blended waters in the same pipe are not understood, and as a result, their impacts on iron release are largely unknown.

A pilot-scale pipe distribution study was conducted to determine the effect of blending different source waters on distribution system water quality. In this study, finished ground, surface, and saline waters, were blended in varying ratios and discharged to pilot distribution systems (PDSs). Water quality parameters and scale characteristics were monitored for 12 months and correlated to pipe material and water quality. Aged pipes taken from distribution systems were used to build the PDSs and consisted of unlined cast iron, galvanized steel, lined ductile iron and PVC pipes. Pipe coupons were placed in cradles connected to the PDS. XRD (X-ray diffraction), RMS (Raman spectroscopy), and XPS (X-ray photoelectron spectroscopy) analyses were performed on the coupon corrosion scales. A thermodynamic equilibrium model based on solid phases identified by surface characterization was developed to predict iron release as a function of blended water qualities.
2. Experimental work

2.1. Source waters

Seven pilot treatment facilities were constructed to supply finished water to the pilot distribution systems. These pilot plants were designed to simulate the existing and future TBW water treatment processes. All processes included chloramination and pH stabilization for post treatment [1].

This study focused on three principal sources: G1, S1, and RO. The G1 source is conventionally treated groundwater (i.e. aeration) that distribution systems had received for decades. The S1 represents enhanced surface water treatment consisting of ferric sulfate coagulation, flocculation, settling, filtration, ozonation, biologically activated carbon filtration. The RO source simulates desalted seawater by reverse osmosis membrane processes.

2.2. Pipe materials

Four different aged pipe materials were used in this study: PVC, lined ductile iron (LDI), unlined cast iron (UCI) and galvanized steel (G). The aged pipes were obtained from actual TBW distribution systems in Pinellas, Pasco, and St. Petersburg Counties, Florida. Based on surface morphology and chemistry studied by SEM/EDS and XRD, no significant difference was found in terms of corrosion products for the same pipe material from different locations.

2.3. Pilot pipe distribution systems

A total of eighteen pilot distribution systems were assembled with aged pipe materials that had received treated groundwater similar to the G1 source. Fourteen of these lines, referred to as hybrid lines, were made of PVC, LDI, UCI and G pipes in that order. The four remaining lines were made of single pipe material. The nominal length of each line was approximately 30 m. Pipe diameters were 15 cm with the exception of galvanized which was 5.6 cm.

The pilot systems were operated with a five-day and a two-day hydraulic residence times (HRT). The flow velocities were 0.25 and 0.625 m/h. The pilot systems were operated to reflect dead zones or worst case conditions in actual distribution systems. In order to mimic the hydraulic conditions in a full-scale system, PDSs were flushed weekly with five pipe volumes at 0.3 m/s. Influent and effluent samples were monitored for dissolved and total iron, pH, alkalinity, temperature, chloride, sulfate, calcium, magnesium, sodium, silica, dissolved oxygen, and chlorine residual. Dissolved iron was measured after sample filtration using 0.45 μm filter. Total iron was determined without filtration and included particulate and dissolved iron.
2.4. Pipe coupon study

Individual cradles were developed for every pipeline for the pipe coupon study. Each cradle consisted of 10 cm PVC pipe housing and 8.8 cm PVC pipe coupon holders. The length of the cradles was approximately 3 m. Each cradle was connected in series to a pilot distribution system so that equivalent coupon, PDS water quality and flow velocity were maintained. The pipe coupon holders were easily removed from the cradle and replaced after each experimental phase for bio-film and chemical deposit analysis.

The pipe coupons of four different materials were cut into two rectangular coupons (10 × 7.5 cm): initial and final samples. The back of each pipe coupon was wrapped with Teflon tape to prevent exterior contamination. The pipe coupons were mounted and fixed on coupon holders. The coupons were removed from the cradles after a 3-month incubation period.

2.5. Pipe surface characterization

Various surface characterization techniques have been employed to identify the corrosion products on iron pipe materials [13–23]. XRD, RMS, and XPS analyses were performed in this study. XRD is a versatile, non-destructive analytical technique for identification of the various crystalline phases present in unknown powdered and solid samples. RMS provides information about molecular vibrations that can be used for sample identification and quantification. The technique allows the identification of homogeneous materials on the basis of their molecular vibrational spectra, obtained by excitation with visible laser light. Surface analysis by XPS, on the other hand, involves irradiating a solid in vacuum with monoenergetic soft X-ray and analyzing the emitted electron by energy. Because the mean free path of electron in solids is very small, the detected electrons originate from only the top few atomic layers, making XPS a unique surface-sensitive technique for chemical analysis.

The XRD analysis was carried out on powder, which had been previously scratched from the corrosion layer on the coupons and grounded in a mortar. The equipment used consisted in a 3720 X-ray diffractometer with a fine structure air-insulated X-ray tube with a copper anode (Cu Kα1 5406 Å). Full X-ray diffraction patterns were recorded for the scan angles (2θ) from 10° to 80° to identify iron oxides. Using the ICDD-PDF database, individual crystalline phases were identified from their observed XRD patterns.

RMS analysis was done by using micro-Raman system (Renishaw, Model: RM 1000 B). A 25 mW argon-ion laser (514 nm) was incident on the sample surface and the Raman scatters were collected. Raman spectrum was obtained in the range of 100–1200 cm⁻¹ as the expected corrosion products of iron and steel generally show their peaks in this range. Calibration is done with two standard samples: pure alumina silicon wafer.

For XPS analysis, 4 × 4 mm samples were cut from pipe coupons and stored in the desiccators to remove adsorbed moisture. The XPS scan was performed using a 5400 PHI ESCA. The base pressure during analysis was 10⁻⁹ Torr. Mg-Kα X-radiation
(1253.6 eV) was used at 350 W. Both survey and high-resolution narrow spectra were recorded with electron pass energy of 44.75 eV and 35.75 eV, respectively, to achieve the maximum spectral resolution. Any charging shift produced by the samples was carefully removed by using a BE scale referred to C(1s) BE of the hydrocarbon part of the adventitious carbon line at 284.6 eV. Non-linear least squares curve fitting was performed using a Gaussian/Lorentzian peak shape after background removal.

3. Results and discussion

3.1. Identification of corrosion products on aged pipe materials

Surface morphology of the test coupons of four different aged pipe materials was first examined to determine the surface features of the historical corrosion products on the pipe surface which was in practical equilibrium with conventionally treated groundwater (G1) in the distribution systems. Representative optical micrographs showing reddish brown corrosion products are presented in Fig. 1. There were no

Fig. 1. Micrograph pictures of interior corrosion products on aged (a) unlined cast iron; (b) galvanized steel; (c) lined ductile iron; (d) PVC pipes taken from distribution systems receiving conventional groundwater.
significant visual differences among coupons of the same material. The UCI coupons exhibited very thick corrosion layers, while thinner corrosion layers were found for G coupons. As expected, the corrosion deposits were significantly less on LDI and PVC coupons.

The XRD patterns of the corrosion products on cast iron, galvanized steel, and lined ductile iron is shown in Fig. 2. $\alpha$-FeOOH, $\beta$-FeOOH, $\gamma$-Fe$_2$O$_3$, Fe$_3$O$_4$, FeCO$_3$ and SiO$_2$ crystalline compounds were found on the cast iron coupons. The primary crystalline compounds on the G coupon were $\alpha$-FeOOH, $\beta$-FeOOH, $\gamma$-Fe$_2$O$_3$, Fe$_3$O$_4$, and ZnO as shown in Fig. 2(b). Major peaks for $\beta$-FeOOH and ZnO were observed in Fig. 2(b). No clear crystalline phase was found on the internal pipe surface of the LDI coupons because only small iron corrosion deposits were found on the internal pipe surfaces. These deposits probably were deposited prior to extraction and came from unlined metal surfaces in the actual distribution system.

The XPS survey spectra showed the primary UCI scale elements were C, O, Fe, Si, and N. A significant amount of Zn was found in the G scale by the XPS survey scan. High resolution scan of Zn(2p3/2) peak indicated the presence of ZnO and Zn(OH)$_2$ on the surface of the corrosion products, verifying the XRD results shown in Fig. 2(b). As expected, for LDI and PVC coupons, no significant iron signals were observed in the XPS scan spectra.

3.2. Iron release from aged pipe materials

The average water quality of G1, S1 and RO for one year (12/15/01 to 12/14/02) is summarized in Table 1. G1 had the highest alkalinity, while S1 and RO exhibited the highest sulfate and chloride, respectively. The high S1 sulfate was due to ferric sulfate coagulation. The high RO chlorides came from the addition of inorganic sea salt, which simulate Cl concentrations in RO permeate produced from sea water and match the finished water quality of the desalination plant in Tampa, Florida. The average values of total iron in the PDSs receiving G1, S1 and RO finished waters were 0.06 mg/L, 0.63 mg/L and 0.44 mg/L respectively. More than 90% of the total iron released was in the particulate form. As shown by these and other results, iron release from UCI and G pipe increased significantly with decreasing alkalinity [1,2].

Effluent PDS total iron concentration from single material lines were monitored over one year in four 3-month phases. The blend of influent PDS finished waters was changed every three months to vary PDS water quality. Table 2 shows the average water quality for each phase. The hydraulic retention time (HRT) was 5 days during Phases 1 to 3, and 2 days from the end of Phase 3 to the end of the project. The HRT was changed to maintain residual above 25 °C. The source water was a blend of G1/S1/RO, specifically 23/45/32% for Phases 1 and 3, and 60/30/10% for Phases 2 and 4. The results are presented in Fig. 3 as a function of PDS material for each phase. As shown, the order of PDS effluent total iron release by material was UCI > G > LDI > PVC, which was expected. The greater iron release from cast iron pipes in Phases 1 and 3, relative to Phases 2 and 4, was attributed to low alkalinity and was caused by a smaller G1 percentage in the PDS feed water and decreased HRT.
Fig. 2. Representative XRD patterns of corrosion products on the interior of aged (a) unlined cast iron; (b) galvanized steel; (c) lined ductile iron pipes exposed to conventionally treated groundwater.
Fig. 4 (a) shows the XRD patterns of the corrosion products on UCI coupons after a 3-month exposure to G1/S1/RO (23/45/32%). The crystalline compounds on the UCI coupons were \( \alpha \)-FeOOH, \( \beta \)-FeOOH, \( \gamma \)-Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), FeCO\(_3\), and SiO\(_2\). The \( \gamma \)-Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\) and FeCO\(_3\) on the UCI coupons increased during incubation. More background noise was noticeable in these scans, which implied more amorphous phases were in the corrosion scales following a 3-month exposure to new water. In other words, the corrosion process was ongoing.

The XRD pattern of corrosion products on G coupons is presented in Fig. 4 (b) and shows \( \alpha \)-FeOOH, \( \beta \)-FeOOH, Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), ZnO and Zn\(_5\)(CO\(_3\))\(_2\)(OH)\(_6\) were the primary corrosion products. As seen in Fig. 4 (b), \( \alpha \)-FeOOH and \( \beta \)-FeOOH decreased, and Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\) became the major corrosion products after a 3-month exposure to G1/S1/RO water. Unlike UCI, FeCO\(_3\) was not found in the XRD analysis of G, and ZnO and Zn\(_5\)(CO\(_3\))\(_2\)(OH)\(_6\) were observed. The XRD analyses of LDI and PVC coupons showed no obvious crystalline compounds, with exception of small amounts of Ca and Fe precipitates such as CaCO\(_3\) and \( \gamma \)-Fe\(_2\)O\(_3\). Amorphous

### Table 1
Average water quality of primary water sources

<table>
<thead>
<tr>
<th>Water quality parameter</th>
<th>G1</th>
<th>S1</th>
<th>RO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity (mg/L as CaCO(_3))</td>
<td>207</td>
<td>60</td>
<td>69</td>
</tr>
<tr>
<td>pH</td>
<td>7.87</td>
<td>7.92</td>
<td>8.06</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>28.9</td>
<td>37.1</td>
<td>91.7</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>26.1</td>
<td>190.2</td>
<td>5.8</td>
</tr>
<tr>
<td>Sodium (mg/L)</td>
<td>18.0</td>
<td>48.7</td>
<td>52.3</td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
<td>84.8</td>
<td>56.5</td>
<td>28.7</td>
</tr>
<tr>
<td>SiO(_2) (mg/L)</td>
<td>13.7</td>
<td>10.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Total dissolved solids (mg/L)</td>
<td>421</td>
<td>423</td>
<td>267</td>
</tr>
<tr>
<td>Dissolved oxygen (mg/L)</td>
<td>6.53</td>
<td>6.31</td>
<td>5.15</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>24.2</td>
<td>24.0</td>
<td>24.1</td>
</tr>
<tr>
<td>UV-254 (cm(^{-1}))</td>
<td>0.060</td>
<td>0.024</td>
<td>0.028</td>
</tr>
</tbody>
</table>

G1 is conventional groundwater treated by aeration, S1 is surface water treated by enhance ferric sulfate coagulation, and RO is saline water desalted by RO membrane. Water quality data were collected from 12/15/01 to 12/14/02.

### Table 2
Operating conditions and water quality for single material PDSs

<table>
<thead>
<tr>
<th>Phase</th>
<th>Blending (G1/S1/RO%)</th>
<th>HRT (days)</th>
<th>pH</th>
<th>Alkalinity (mg/L as CaCO(_3))</th>
<th>Chloride (mg/L)</th>
<th>Sulfate (mg/L)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase 1</td>
<td>23/45/32</td>
<td>5</td>
<td>8.06</td>
<td>110</td>
<td>56</td>
<td>109</td>
<td>18.8</td>
</tr>
<tr>
<td>Phase 2</td>
<td>60/30/10</td>
<td>5</td>
<td>7.94</td>
<td>158</td>
<td>42</td>
<td>76</td>
<td>26.1</td>
</tr>
<tr>
<td>Phase 3</td>
<td>23/45/32</td>
<td>5</td>
<td>7.82</td>
<td>96</td>
<td>59</td>
<td>77</td>
<td>26.7</td>
</tr>
<tr>
<td>Phase 4</td>
<td>60/30/10</td>
<td>2</td>
<td>7.89</td>
<td>125</td>
<td>39</td>
<td>56</td>
<td>18.5</td>
</tr>
</tbody>
</table>

The pilot study was conducted in four three-month phases (12/15/01–12/14/02). Note that water quality varied slightly under the identical blending ratios (e.g. Phases 1 and 3 or Phases 2 and 4) because of the seasonal changes in raw source water qualities.

Phase 1: 12/15/01–03/14/02, Phase 2: 03/15/02–06/14/02, Phase 3: 06/15/02–09/14/02, Phase 4: 09/15/02–12/14/02.
phases were present in the samples. Consequently, background noises in the XRD spectra were high and covered minor iron phase peaks.

The existence of these iron phases was confirmed by Raman spectroscopy (RMS). A representative Raman spectrum of a UCI coupon is presented in Fig. 5. The band 285/740/1083 revealed the existence of significant amounts of FeCO$_3$. The $\alpha$-FeOOH, $\beta$-FeOOH, $\gamma$-Fe$_2$O$_3$ and Fe$_3$O$_4$ were identified by the band of 208/250/290/394 cm$^{-1}$, 310/390/705 cm$^{-1}$, 250/390/692 cm$^{-1}$ and 224/550/670 cm$^{-1}$, respectively. It is clear that RMS spectra verified the results of XRD analysis.

Lastly, the XPS analysis performed on four different pipe coupons of single material lines showed the results similar to those of XRD analysis except that no FeCO$_3$ was detected, which is due to FeCO$_3$ instability.

3.3. Correlation between surface characteristics and iron release

Blended finished waters were also fed to the hybrid PDSs which consisted of PVC, LDI, UCI and G pipes in series, and coupons cradles identical to the single material PDSs. The coupons were incubated for three months, harvested before phase changes and analyzed by XRD and XPS. Ninety percent of the iron found in the coupon scales came from the UCI pipes. The remaining 10% of the iron came from
the G pipes [2]. Thus, iron release from UCI and G pipes was investigated using PDS influent water quality created by blends of G1 (100%), S1 (100%), RO (100%), G1/S1 (55/45%), G1/RO (68/32%) and G1/S1/RO (62/27/11%).

The UCI XRD patterns of coupons exposed to these six different blended waters showed little difference, except that G1 exhibited the lowest FeCO$_3$ content as indicated by the relative FeCO$_3$ peak intensity. The XRD spectra of the G coupons also showed no significant variation. Since the XRD was done on powdered samples, the change following three-months of incubation might have occurred only in the first 1–3 μm of the surface scale and was masked by sample preparation.

Fig. 4. Representative XRD patterns of corrosion products on (a) unlined cast iron; (b) galvanized steel pipe coupons following three months of exposure to G1/S1/RO (23/45/32%) water in single material lines.
The XPS technique is very surface sensitive and provided information on chemical changes that occurred at the interface between water and inorganic film on pipe surface due to dissolution and precipitation of corrosion products caused by changes in water quality. Standard peak positions (i.e., 710.4 eV for Fe$_3$O$_4$, 710.8 eV for Fe$_2$O$_3$, and 711.8 eV for FeOOH) and FWHM (i.e., 3.6 eV for Fe$_3$O$_4$, 3.8 eV for Fe$_2$O$_3$ and FeOOH) of iron species were determined by scanning pure samples and comparison to the NIST XPS Database. The differences of binding energy of various iron phases are significant (>0.3 eV) and can be differentiated. Any samples charging shifts were carefully removed by using a BE scale referred to as C(1s) BE of the hydrocarbon part of the adventitious carbon line at 284.6 eV. Non-linear regression based on minimization of least squares of the error was used to correlate the iron content in the solid phases of the iron corrosion products to a Gaussian/Lorentzian curve for peak shape. Following this procedure, the content accuracy was within a ±0.1 $a$ (a is the peak area percentage given by Fe peak deconvolution). Fig. 6(a) presents the detailed scan and the deconvolution of Fe2p3/2 peak of unlined cast iron aged coupon exposed to G1(100%). The deconvolution of Fe(2p3/2) peak revealed four separate peaks, which corresponded to Fe$_3$O$_4$, Fe$_2$O$_3$, FeOOH and the minor peak. Minor peaks shown here were in the range from 713 eV to 715.5 eV. It might have two sources: (1) the minor Fe$^{2+}$(2p3/2) peaks from FeSO$_4$ and/or the Fe$^{3+}$ portion of Fe$_3$O$_4$; and (2) the Fe$^{3+}$(2p3/2) peak of Fe$_2$(SO$_4$)$_3$. FeSO$_4$ and Fe$_2$(SO$_4$)$_3$ came from the deposition of soluble iron sulfate species after the UCI coupons were taken from the high sulfate finished waters produced by Fe$_2$(SO$_4$)$_3$ coagulation. The deconvolution of Fe(2p3/2) peak of G coupons is presented in Fig. 6(b) and also shows the presence of Fe$_2$O$_3$, Fe$_3$O$_4$, and FeOOH. The curve fit summary of the deconvolution of Fe(2p3/2) peak is listed in Table 3 for UCI and G coupons exposed to these six
water environments. As shown, the peak area percentage, which stands for the relative amount of corrosion products in the scale, varied with water quality.

The correlation ($R^2$) between Fe(2p3/2) peak area percentage of UCI coupons and the total and dissolved iron levels from the hybrid lines are schematically presented in Fig. 7. A linear relationship between Fe$_3$O$_4$ and total and dissolved iron release from the hybrid PDS is shown in Fig. 7(a). The slopes are negative, which means iron release decreased as Fe$_3$O$_4$ in the corrosion scale increased. Stability of Fe$_3$O$_4$ in the scale reduces iron release. Another correlation was found between peak area percentages of Fe$_2$O$_3$ and pilot iron release data. Fig. 7(b) showed that dissolved and total iron release increased with increasing Fe$_2$O$_3$. Fe$_2$O$_3$ plays an important role on iron release in water. But Fe$_2$O$_3$ solubility is very low and actual dissolved iron concentration was much higher than predicted by Fe$_2$O$_3$ equilibrium, which indicates that Fe$_2$O$_3$ should not be the controlling solid phase of iron release.

Fig. 6. Representative high-resolution XPS scan and the deconvolution of Fe(2p3/2) peak of corrosion products formed on (a) cast iron; (b) galvanized steel pipe coupons following 3-month exposure to conventionally treated groundwater.
In this study, FeCO₃ was detected by XRD and RMS, but not by XPS. Heuer’s study [17] showed that FeCO₃ transformed to Fe₂O₃ completely after exposure to air at room temperature for 4 h. In our study, iron coupons were taken from pilot distribution systems, stored in dessicators for 2 weeks, prepared for analysis and analyzed. In the long storage period, FeCO₃ transformation to Fe₂O₃ occurred in the surface layer prior to XPS analysis as shown by the Fe₂O₃ peak area found by XPS. The positive linear correlation between FeCO₃ in the surface layer and iron concentration indicates FeCO₃ is the controlling solid phase for iron release in UCI in drinking water distribution systems.

Correlations between surface characteristics of aged G pipes and iron release were also examined. Table 4 summarizes the coefficients of determination ($R^2$) for regression XPS and pilot iron data. No clear relationship was found between different iron species and iron release levels. All $R^2$ values were less than 0.4. This is not surprising since elevated iron levels were primarily due to the disruption and releases of chemical films formed on cast iron pipes.
3.4. Kinetic effects on iron release and surface characterization

The change of scale formation and iron release with respect to time was investigated in this work. Mutoti et al. [26] found that iron release from UCI pipe came from the interior wall of the pipe and hence, could be accurately described by a zero order kinetic model. Imran et al. [26] found that iron release from UCI and G pipe over a five day HRT was accurately predicted by a steady state water quality model.

![Graph showing Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{3} versus actual total and dissolved iron released from hybrid pilot distribution lines receiving various blended waters (Phase 3).](image)

**Table 4**

Correlation ($R^2$) between total and dissolved iron release from hybrids lines and relative peak areas of different iron corrosion products on galvanized steel pipe internal surfaces determined by XPS iron peak analysis.

<table>
<thead>
<tr>
<th></th>
<th>Total iron</th>
<th>Dissolved iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{4}</td>
<td>-0.002</td>
<td>-0.318</td>
</tr>
<tr>
<td>Fe\textsubscript{3}O\textsubscript{3}</td>
<td>+0.005</td>
<td>-0.001</td>
</tr>
<tr>
<td>FeOOH</td>
<td>-0.001</td>
<td>+0.353</td>
</tr>
<tr>
<td>Minor peak</td>
<td>+0.002</td>
<td>+0.328</td>
</tr>
</tbody>
</table>

Note that + and − signs stand for positive and negative correlations, respectively.

![Graph showing Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{3} versus actual total and dissolved iron released from hybrid pilot distribution lines receiving various blended waters (Phase 3).](image)
The models developed by Mutoti and Imran were published in the AwwaRF Final Report “Effects of Blending on Distribution System Water Quality”, Taylor et al. [26] and showed total iron release was dependent on pipe material, water quality, geometry, and velocity. Dietz [27] found that the time to reach steady state total iron in the bulk water following a change in water quality was approximately one month and was accurately described by a first order model, which was dependent on pipe material, water quality and time. These results found total iron release came from the interior pipe wall and steady state total iron release was dependent on pipe material, geometry and water quality; however the concentration of total iron released in the bulk water decreased with velocity.

The change in surface characterization over time was investigated by exposing coupons to G1, S1, RO and a G1/S1/RO blend for one, three and six month periods and analyzing the coupons by XPS. As shown in Fig. 6, the results indicate FeOOH, Fe₂O₃, and Fe₃O₄, were the major corrosion products in the top surface layer. Previously, Fe₂O₃ was shown to correlate well with total and dissolved iron. Because the detected Fe₂O₃ might have been transformed from FeCO₃, and the observed dissolved iron concentrations were much higher than Fe₂O₃ solubility, the correlation of Fe₂O₃ with iron release might imply the correlation of FeCO₃ with iron release. Fig. 8 shows that Fe₂O₃ peak area percentage does not significantly change for a one, three, or six months incubation time, which implies the Fe₂O₃ (FeCO₃) content in the surface layer reached equilibrium in one month, which was consistent with Dietz [27]. The results also show that even though the Fe₂O₃ peak area % changed to some degree with time and source waters, all of them follow the trend: S1 > RO > G1/S1/RO > G1. Higher percentages of Fe₂O₃ (FeCO₃) area corresponded to higher iron release.

3.5. Thermodynamic equilibrium iron release model

The soluble iron release from aged pipe surfaces may be predicted using thermodynamic calculations based on equilibrium constants associated with solid phases in
corrosion scales. Such models are inherently flawed as particle release is not considered; however these models may provide insight into release mechanisms. Based on XRD and XPS analyses of UCI coupons following incubation, siderite (FeCO₃) was assumed to be the controlling solid phase for soluble iron. Pourbaix (potential–pH) diagrams were created and also suggested that FeCO₃, Fe(OH)₂ or Fe(OH)₃ existed within the free energy and pH conditions of our pilot study.

The thermodynamic model assumes all soluble iron is in equilibrium with all solid phases considered for model development. Concentrations of dissolved complexes (e.g. carbonate, chloride and sulfate) were estimated after consideration of related reactions. The summation of all dissolved iron species is total bulk water iron and is shown in following equation.

\[
\text{Fe}_T = [\text{Fe}^{2+}] + [\text{FeOH}^+] + [\text{Fe(OH)}_2^0] + [\text{Fe(OH)}_3^-] \\
+ [\text{FeHCO}_3^-] + [\text{FeCO}_3^0] + [\text{FeSO}_4^0] + [\text{FeCl}^+] \\
= \frac{10^{-10.89} \times [\text{H}^+]}{\text{Alka}} \times 10^{-10.3} \left( 1 + \frac{10^{-9.5}}{[\text{H}^+]^2} + \frac{10^{-20.6}}{[\text{H}^+]^3} + 10^{32} \text{Alka} \\
+ 10^{4.38} \text{Alka} \times 10^{-10.3} \times \left( \frac{10^{-10.3}}{[\text{H}^+]^2} + 10^{2.25} [\text{SO}_4^{2-}] + 10^{0.9} [\text{Cl}^-] \right) \right)
\]

Table 5
Chemical reactions used for thermodynamic modeling [24,25]

<table>
<thead>
<tr>
<th>Reactions</th>
<th>pK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe²⁺ + H₂O ↔ FeOH⁺ + H⁺</td>
<td>9.50</td>
</tr>
<tr>
<td>Fe²⁺ + 2H₂O ↔ Fe₂(OH)₂^0 + 2H⁺</td>
<td>20.60</td>
</tr>
<tr>
<td>Fe²⁺ + 3H₂O ↔ Fe(OH)₃^– + 3H⁺</td>
<td>32.00</td>
</tr>
<tr>
<td>Fe²⁺ + HCO₃⁻ ↔ FeHCO₃⁻</td>
<td>-2.00</td>
</tr>
<tr>
<td>Fe²⁺ + CO₃²⁻ ↔ FeCO₃^0</td>
<td>-4.38</td>
</tr>
<tr>
<td>Fe²⁺ + CO₃²⁻ ↔ FeCO₃(S)</td>
<td>-10.89</td>
</tr>
<tr>
<td>Fe²⁺ + 2H₂O ↔ Fe(OH)₂(S) + 2H⁺</td>
<td>12.90</td>
</tr>
<tr>
<td>FeCO₃(S) + 2H₂O ↔ Fe(OH)₂(S) + 2H⁺ + CO₃²⁻</td>
<td>23.79</td>
</tr>
<tr>
<td>Fe²⁺ + SO₄²⁻ ↔ FeSO₄⁰</td>
<td>-2.25</td>
</tr>
<tr>
<td>Fe²⁺ + Cl⁻ ↔ FeCl⁺</td>
<td>-0.90</td>
</tr>
<tr>
<td>Fe³⁺ + H₂O ↔ Fe(OH)₂³⁻ + H⁺</td>
<td>3.05</td>
</tr>
<tr>
<td>Fe³⁺ + 2H₂O ↔ Fe₂(OH)₃^4⁺ + 2H⁺</td>
<td>6.31</td>
</tr>
<tr>
<td>2Fe³⁺ + 2H₂O ↔ Fe₂₂(OH)₄⁺ + 2H⁺</td>
<td>2.91</td>
</tr>
<tr>
<td>Fe³⁺ + 3H₂O ↔ Fe₃(OH)₃^4⁻ + 3H⁺</td>
<td>13.80</td>
</tr>
<tr>
<td>Fe³⁺ + 4H₂O ↔ Fe₄(OH)₄⁺ + 4H⁺</td>
<td>22.7</td>
</tr>
<tr>
<td>3Fe³⁺ + 4H₂O ↔ Fe₃(OH)₄⁺ + 4H⁺</td>
<td>5.77</td>
</tr>
<tr>
<td>Fe³⁺ + 3H₂O ↔ (am) Fe₃(OH)₂(S) + 3H⁺</td>
<td>3.20</td>
</tr>
<tr>
<td>Fe³⁺ + SO₄²⁻ ↔ FeSO₄⁻</td>
<td>-4.04</td>
</tr>
<tr>
<td>Fe³⁺ + 2SO₄²⁻ ↔ Fe₂(SO₄)₂⁺</td>
<td>-5.38</td>
</tr>
<tr>
<td>Fe³⁺ + Cl⁻ ↔ FeCl²⁺</td>
<td>-1.48</td>
</tr>
<tr>
<td>Fe³⁺ + 2Cl⁻ ↔ FeCl⁵⁻</td>
<td>-2.13</td>
</tr>
<tr>
<td>Fe³⁺ + 3Cl⁻ ↔ FeCl⁷⁻</td>
<td>-1.13</td>
</tr>
</tbody>
</table>
Alka is an abbreviation for alkalinity, which is in mol/L. Note that the model is developed based on 0.38 V and 25°C. These are reference conditions for waters in the pilot study. The chemical reactions involved in the model development are summarized in Table 5. According to the ORP values measured in field, Fe²⁺ exceeded Fe³⁺. Thus ferric species were ignored in the model development.

The siderite model was used to predict the iron release for the expected distribution system water quality. Fig. 9 shows the predicted and actual iron concentrations as a function of pH and alkalinity for a two and five day HRT. The actual total iron release exceeds the predicted total iron release and the actual total iron release for five day HRT exceeds the total iron release for a two day HRT, as predicted by

![Image](image_url)
Mutoti et al. model [26]. As ninety percent or more of the average total released iron was in the particulate form, the equilibrium model would not be expected to accurately predict total iron release. Dissolved iron release as predicted by siderite model exceeded the actual release of dissolved iron but was less than actual total iron release. Although the siderite model did not consider particulate release, the siderite model predicts iron will decrease as pH and alkalinity increase, which was observed with the actual data and illustrates the utility of equilibrium models for identification of trends. This trend is also clearly observed with actual five day HRT data with alkalinity as shown in Fig. 10.

Other equilibrium models were developed assuming Fe(OH)\(_2\) or Fe(OH)\(_3\) as the controlling solid phase. The predicted values of Fe(OH)\(_2\) model were much higher (1000 times) than actual TBW pilot total iron data [2]. The Fe(OH)\(_3\) model grossly under-predicts iron release and the predicted values are 200,000 times lower than actual TBW pilot dissolved iron data. Thus, the FeCO\(_3\) model produced the least error was the best equilibrium model for predicting total iron, which indicates that total iron release was significantly affected by the FeCO\(_3\) solid phase as has been suggested by others [12]. However, these results and other references associated with this project [26,27] show that total iron release was primarily particulates and was most accurately described by empirical models based on pipe water quality, geometry, hydraulics and time.

4. Conclusions

Primary inferences from this study are as follows:

- A pilot pipe distribution study conducted over one year under various blended waters (i.e. blends of ground, surface and saline waters) showed that iron
release from aged pipes varied with blended water qualities as well as aged pipe materials. Specifically, total iron concentration increased significantly when aged pipes were exposed to water quality that was different from historical groundwater, such as treated surface water and desalinated seawater water quality. Aged pipe materials also affected iron release: the order of aged pipe material on total iron release was unlined cast iron > galvanized steel ≫ lined ductile iron > PVC, which demonstrated the importance of pipe surface characteristics on iron release.

- Based on XRD and RMS results, FeCO$_3$, α-FeOOH, β-FeOOH, γ-Fe$_2$O$_3$, Fe$_3$O$_4$ were identified as primary corrosion products of unlined cast iron pipes. Similar solid phases were identified for galvanized steel pipes except that no FeCO$_3$ was present. Significant amounts of zinc oxides (e.g. ZnO) were detected in corrosion scales of galvanized steel. No or very small iron corrosion deposits were found on the internal surface of aged lined ductile iron and PVC pipes.

- No significant FeCO$_3$ in the corrosion scales of unlined cast iron pipes was detected by XPS analysis because FeCO$_3$ is very unstable and would transform into Fe$_2$O$_3$ on contact with air. XPS showed iron release decreased as less soluble Fe$_3$O$_4$ increased in the corrosion scales, and that iron released increased as the percentage of the more Fe$_2$O$_3$ increased in scale. Dissolved iron concentrations were much higher than the predicted by Fe$_2$O$_3$ solubility, suggesting that iron released in distribution systems is controlled by the solubility of FeCO$_3$ which could transform into Fe$_2$O$_3$ when exposed to air.

- A thermodynamic siderite (FeCO$_3$) model was developed assuming FeCO$_3$ is the controlling solid phase for dissolved iron. The siderite model as any equilibrium model does not consider particulate iron, which accounted for more than ninety percent of total iron and did not accurately predict total iron release. However, the model did predict that total iron release decreased as alkalinity and pH decreased as observed in pilot study, which illustrated the utility of equilibrium models for identification of trends.

Acknowledgments

Support for this research was provided by Tampa Bay Water (TBW), and AWWA Research Foundation (AwwaRF). The authors specially acknowledge Roy Martinez, AwwaRF Senior Account Officer, who was the Project Officer, and Chris Owen, TBW Quality Assurance Officer. The TBW Member Governments: Pinellas County, Hillsborough County, Pasco County, Tampa, St. Petersburg, and New Port Richey; and the AwwaRF Project Advisory Committee are recognized for their review and recommendations. Pick Talley, Robert Powell, Dennis Marshall and Oz Wiesner from Pinellas County, and Dr. Luke Mulford from Hillsborough County are also specifically recognized for their contributions. UCF Environmental Engineering graduate students, especially Jorge Arevalo and faculty who worked on this project are recognized for their efforts.
References
