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Can Dynamic Bubble Templating Play a Role in Corrosion Product Morphology?

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ABSTRACT

Dynamic templating as a result of cathodic hydrogen gas production is suggested as a possible mechanism for the formation of tube-like corrosion products on an unlined cast iron pipe in a drinking water distribution system. Mounds of corrosion product, with protruding tubes and freestanding tubes, were observed within a single 30 cm section of piping. Internal morphologies for all shapes were texturally complex although mineralogically simple, composed of two iron oxide/oxyhydroxides minerals: α-FeOOH (goethite) and Fe₃O₄ (magnetite). Static templating by either microorganisms or minerals was rejected as a possible mechanism for tube formation in this study.

KEY WORDS: iron, μ-x-ray diffraction, μ-x-ray fluorescence mapping, morphologies, tube-shaped corrosion

INTRODUCTION

Unlined cast iron pipes (major alloyants carbon and silicon), common in drinking water distribution systems (DWDS) worldwide, are highly susceptible to general (interchangeable anodes and cathodes) and localized corrosion (fixed anodes) with accumulations of iron corrosion products.¹⁻³ The predominant corrosion product morphology is mound-shaped (often called a tubercle); however, other morphologies including flutes or cones, mounds with protruding tubes, and free-standing tubes have been observed.⁴ Research on the characteristics and mechanism(s) of corrosion product formation and growth has focused on mounds because of their prevalence. Working with iron corrosion products in cooling water systems, Herro⁵ defined the accumulations as structurally complex with distinct regions, i.e., a core (C), a hard shell layer (HSL), and a surface layer (SL). The stratification and mineralogy of these distinct regions are remarkably consistent in different water chemistries.⁶⁻⁷ Mechanisms of formation and growth are reasoned to be a result of iron release at the anode, followed by precipitation in close proximity to the anode.⁸ Some mechanisms for mound formation indicate a spatial relationship between anodic sites and mound formation, and a connection between the height of the mound and the depth of the resulting pit.⁹⁻¹⁰ That relationship is not always obvious in DWDS where mounds can accumulate at locations with little evidence of pit formation.⁷ Smith and McEnaney¹⁰ indicated corrosion product buildup as a result of both pitting and general corrosion. Investigators have demonstrated bacteria and bacterial stalks within core regions.⁷ However, they⁷ concluded that bacteria are not the only cause of corrosion product accumulation and that the presence of mounds/tubercles cannot be used to conclude the involvement of bacteria or microbiologically influenced corrosion (MIC).

It has been proposed by Baylis¹¹ that flutes or cones formed in a manner similar to mounds, but as the iron precipitated, the corrosion product was elon-
gated in the direction of water flow. However, no phys-
icochemical characterization of the flutes/cones or
tubes was presented. He proposed though that tube-
shaped corrosion product formation was linked to the
water calcium saturation index but provided no expla-
nation regarding this relationship.11

Tube-shaped features are common in natural,
quiescent environments, ranging in size from a few
millimeters (soda straws in caves) to meters (chinneys
at hydrothermal vents)12 and form as a result of static
and dynamic templating. Static templating is a com-
mon process where precipitating minerals accumulate
on artificial or natural substrata whose shape controls
the morphology of the precipitate. Static templating
requires flowing waters. Dynamic templating is less
common because tube growth requires a constant and
fairly uniform feature for precipitating material. Main
portions of a DWDS piping have steady flow, but resi-
dential portions experience daily stagnation.

In the following study, physicochemical data
were examined to evaluate the possibility of static
and dynamic templating processes for creating tube-
shaped iron corrosion products in DWDS. Samples
were examined using powder x-ray diffraction (XRD)
and x-ray fluorescence (XRF) in addition to synchro-
tron-based μ-XRD and μ-XRF mapping.

EXPERIMENTAL PROCEDURES

Sample Selection and Preparation
An unlined cast iron DWDS pipe section (approx-
imately 30 cm long by 15 cm inner diameter) was
obtained from a drinking water utility in the north-
eastern United States. The pipe was cut in half using
a band saw. Iron corrosion products were harvested
from one half of the pipe for powder XRD and XRF
analyses. Digital images of tubes were obtained from
one half of the pipe and the elemental composition
of the unlined iron pipe was determined using elec-
tron scanning electron microscopy (ESEM) previously
described by Ray and Little.13

Bulk Powder X-Ray Diffraction and X-Ray
Fluorescence
Approximately 0.2 g to 3.0 g of solids from areas
of interest were extracted with metal spatulas from
C, HSL, and SL of representative iron corrosion prod-
ucts. The solids were ground by hand, with an agate
mortar and pestle, until they passed through a stain-
less steel 200 (75 μm) mesh sieve. Samples were pro-
cessed for bulk powder XRD and XRF following the
protocol of Gerke, et al.14

All samples were analyzed using a Siemens
D-500° automated diffractometer system using a Cu
Ka radiation at 30 mA and 40 kV. The 2θ ranged from
5° to 70°, with a 0.02° step, and a 2 s count time at
each step. Crystalline phase identifications were made
on the basis of peak position and peak intensities
using the American Mineralogist Crystal Structure
Database15 and the Mineral Database16 (http://rruff.
geo.arizona.edu/AMS/amscd.php, http://webmin-
eral.com/).

Scanning Electron Microscopy Analysis
Iron corrosion products of sample T4 were exam-
ined using ESEM coupled with energy-dispersive
spectroscopy (EDS) as previously described by Ray,
et al.7

Synchrotron-Based μ-XRD and μ-XRF Mapping
One half of the pipe was embedded in Buehler
Epo Thin' low-viscosity epoxy. Mounds with protrud-
ing tubes and tubes were cut out of the epoxy. These
were mounted on quartz slides, cut, polished to an
average thickness of 35 μm and digitally imaged. A
mound and tube from the same sample were used for
synchrotron-based μ-XRD and μ-XRF mapping tech-
niques. Colors of the iron phases were determined
visually according to Cornell and Schwartmann.17
X-ray μ-beam studies (fluorescence and diffraction
spectroscopy) were performed at XOR/PNC 20 BM-B
of the Advanced Photon Source, Argonne National
Laboratory (Argonne, IL) under standard operating
conditions (7 GeV operation and ring current of
101 mA in top-up mode). Digital images of the repre-
sentative mound and tube were used to determine the
locations for μ-XRF elemental maps and correspond-
ing μ-XRD analyses. μ-XRF maps were recorded for
Ca, Cr, Cu, Fe, Mn, Ni, and Zn. Relative elemental
concentrations are shown using a color scale in which
dark blue represents low concentrations and red rep-
resents comparatively higher concentrations. A MAR
165' CCD (μ-XRD) studies and points of interest were
chosen based on location within the iron corrosion
product and color. The CCD detector was positioned
at approximately 200 mm from the sample and two-
dimensional μ-XRD patterns were collected for 300 s
at 15 kV with a wavelength of 0.8265 Å. Two-dimen-
sional diffractograms (2D Debye-Scherrer rings) were
converted to one-dimensional θ scans using the
Fit2D' software.18

RESULTS

Description of Pipe and Corrosion Products
Corrosion products in the form of mounds,
mounds with protruding tubes, and free-standing
tubes were observed around the circumference of the
pipe (Figure 1). The structure of tubes, their relation-
ship to mounds, and the variability of that relation-
ship is demonstrated in Figure 2. A free-standing
tube (cut parallel to long axis) was composed of verti-
cally stacked, alternating layers of C and HSL (Figure
2[a]). A tube protruding from a mound (cut parallel
to its long axis) constricted (tapered) and then broadened before closing completely (Figure 2b). In all cases a thick black HSL covered by a red SL encased the tubes and mounds (enlargement in Figure 2b). A cm-sized feature was composed of two tubes and two mounds that had grown together (Figure 3). A large black tube, dominating the upper portion of the image was growing from the filamentous-textured, yellowish red-brown material mound. The smaller micro-sized mound and tube, indicated in boxes, were examined in detail (Figures 4 and 5).

**Characteristics of a Mound**

The internal structure of a 5 cm mound consisted of C dominated by yellowish-red brown material, primarily α-FeOOH (goethite) with moderate amounts of metallic luster Fe$_3$O$_4$ (magnetite), and trace amounts of CaCO$_3$ (calcite). In addition, the core was marbled with black non-metallic luster Fe$_3$O$_4$, minor amounts of α-FeOOH, and trace amounts of CaCO$_3$. The uppermost portion of C consisted of a thick layer of black non-metallic luster Fe$_3$O$_4$, covered by a discontinuous hard shell layer of black Fe$_3$O$_4$ with a metallic luster and moderate amounts of CaCO$_3$ and trace amounts of α-FeOOH. A discontinuous yellowish red SL consisted of moderate amounts of γ-FeOOH (lepidocrocite), Fe$_3$O$_4$, CaCO$_3$, and trace amounts of α-FeOOH, SiO$_2$ (quartz) and S. Iron concentrations were highest
and Mn and Ca were lowest in the core and associated veinlets. The HSL had the highest Ca concentrations, and the SL has the highest Pb, Mn, and Zn but the lowest Cu concentrations. Ni and Cr concentrations were below detection for all regions.

The internal structure of a 0.25 cm mound was similar. C1 (Figure 4, points 2 and 3) was composed of reddish brown α-FeOOH. The HSL of black metallic and non-metallic luster material was composed of Fe₂O₃ with moderate amounts of α-FeOOH at point 4. Covering the HSL was a thin surface layer of filamentous-textured, reddish brown material. The fine scale distributions of Ca, Cr, Cu, Fe, Mn, Ni, and Zn indicated that the concentrations of Cr, Cu, and Zn were very low (data not presented) for all regions of the corrosion product. The lower (C1) and upper (C2) core regions of the mound were composed primarily of Fe and trace amounts of Ni. The lower-most shell (HSL1) contained the highest concentration of Fe and moderate amounts of Ni. The outer shell (HSL2) had the same elemental distribution as HSL1. SL material was composed predominantly of Ca with lesser amounts of Fe and Ni.

**Characteristics of Tubes**

The micro-sized tube, oriented with its long axis perpendicular to the image, had an internal morphology C1 of filamentous-textured black material with a non-metallic luster, encircled by filamentous-textured reddish to yellowish brown material (C2) (Figure 5). C1 of the tube was composed primarily of Fe₂O₃ with minor to trace amounts of α-FeOOH (Figure 5, points 3 through 5) and C2 of α-FeOOH with minor to trace amounts of Fe₂O₃ (Figure 5, points 2 and 6). All parts of this corrosion product were encircled by a thin layer of metallic luster black Fe₂O₃ with minor to trace amounts of α-FeOOH (points 1 and 7, Figure 5, HSL). This is all overlain by a filamentous-textured reddish brown SL with some locations having black material with a non-metallic luster located at the outer edges. The in situ synchrotron μ-XRF mapping of C1 showed that it was composed of Fe, Ni, and minor amounts of Mn (Figure 5). C2 and HSL were also composed of Fe and lesser amounts of Ni and Mn. The SL was composed primarily of Ca with some Ni and Mn.

**DISCUSSION**

A relationship between the calcite saturation index of water and the formation of tube-shaped corrosion products was proposed by Baylis. In that work, calcite was the main accessory phase associated with cm-sized mounds, and a discrete layer of a calcium was associated with the smaller 0.25 cm-sized mound and 0.50 cm-sized tube-shaped corrosion products, indicating that the corrosion products formed in water near or exceeding the calcite saturation index. In the present study, there was no relationship between corrosion products and calcium.

In DWDS, the most likely static templates are minerals and microorganisms. Typical mineral phases associated with iron corrosion products include α- or γ-FeOOH and Fe₂O₃ and accessory phases such as FeCO₃ (siderite) and CaCO₃. In addition, as metal ions from the pipe wall are released into the drinking water, they may form atypical, elongate mineral phases. Based on the pipe wall composition and the chemical analyses of the tube-shaped corrosion products, no unique mineral phases were identified in this study. The general size of a single iron oxide/oxyhydroxide or calcite crystal in corrosion products is microns, and none have an elongate cylindrical morphology required for templating surfaces producing cm-sized features.

Microorganisms, present in all DWDS, can have rod-shaped morphologies or could produce filaments, sheaths, or stalks, which could produce static templates for tube-shaped features. For example, Leptothrix ochracea produces hollow sheaths (microtubes) that range in length from 10 µm to 200 µm and have an outer diameter of 1.4 µm. ESEM analysis of corrosion products in this study, though, did not detect microorganisms or microbial features that could serve as templates. More importantly, static templating from the presence of microorganisms produces structures that are orders of magnitude smaller than any of the tubes observed in the unlined cast iron pipe.

One potential mechanism for tube formation is precipitation of anodically produced iron particulate...
FIGURE 4. μ-XRF maps of Ca, Fe, Mn, Ni, and Zn concentrations for a micro-sized classic mound-shaped iron corrosion product. The numbers indicate the locations of the representative μ-XRD traces. Core (C), hard shell layer (HSL), surface layer (SL).

It has been demonstrated that both tubes (hollow whiskers) and mound-shaped corrosion products can form in the same pipe during stagnation and high flow, respectively. Both conditions are common in residential mains, service lines, and premise plumbing. Regarding tube formation, Butler and Ison proposed, "Ferrous ions, formed at the anodic area at the root of the whisker, diffuse along the tube, and growth of the whisker proceeds at the tip, where these ions are oxidized and precipitated as iron oxide on coming in contact with the aerated water." Whiskers were up to 90 mm in length with growth rates more than 1 mm per day. Whisker diameter tapered from 0.4 mm at the base to 0.2 mm at the growing tip. The whiskers...
were made up of goethite, magnetite, and a mixture of both.

As previously demonstrated in laboratory experiments, the nature and location of the cathodic reaction can influence corrosion product morphology. Several cathodic reactions are possible in unlined cast iron pipes exposed to oxygenated, chlorinated drinking water. The most obvious potential cathodic reactions are reduction of water and $\text{O}_2$, resulting in $\text{H}_2$ and $\text{OH}^-$, respectively. In the absence of oxygen, it is possible for a previously deposited ferric scale to accept electrons from metallic iron ($\text{Fe}_{\text{metal}}$) as follows in the equation:\textsuperscript{27}

$$\text{Fe}_{\text{metal}} + 2\text{FeOOH}_{\text{scale}} + 2\text{H}^+ \rightarrow 3\text{Fe}^{2+} + 4\text{OH}^- \quad (1)$$

Under oxygen-depleted conditions, McEnaney and Smith\textsuperscript{28} suggested that FeOOH scale could be reduced to magnetite by a process of reductive dissolution as follows:

$$3\text{FeOOH}_{\text{scale}} + e^- \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2\text{O} + \text{OH}^- \quad (2)$$

Chimney features reportedly have served as vents for corrosion products (including $\text{H}_2$) on gray cast iron in water at 50°C.\textsuperscript{10} Smith and McEnaney observed\textsuperscript{10} that the chimneys formed under the crust and sur-
mised that acidic conditions developed under the crust similarly to acidic regions near pits in chloride solutions of comparable concentrations (100 ppm Cl). Mankowski and Szklarska-Smilowska established that increased acidity within pits was a consequence of significant Cl² levels above the bulk solution content. Smith and McEnaney proposed that under acidic conditions H⁺ reduction (as opposed to water reduction in neutral conditions) would become the cathodic process within the accumulated corrosion products and O₂ reduction would occur on the nodule crust. They did not relate growth of the chimneys to dynamic templating.

CONCLUSIONS

- Mounds, mounds with protruding tubes, and free-standing tubes were identified as corrosion morphologies in a single 30 cm section of unlined cast iron pipe removed from a DWDS. Regardless of form or size, the physicochemical characteristics for all corrosion products were similar. Surface-bound microorganisms and minerals were eliminated as possible static templates due to their size relative to the tubes. Dynamic templating because of cathodic hydrogen production is suggested as a possible mechanism for tube-like corrosion product formation in unlined cast iron piping.

- It is proposed that in cast iron pipes exposed to aerated, chlorinated drinking water, metallic iron is oxidized to Fe²⁺ by dissolved oxygen in the water, released into the water and further oxidized to Fe³⁺, forming Fe(OH)₃, which accumulates on the inner wall of the cast iron pipe at locations that are not necessarily associated with localized corrosion. The Fe(OH)₃ dehydrates and becomes FeOOH. Below a critical O₂ concentration, FeOOH is reduced to Fe₂O₃. Gas production at the cathode causes breaks (vents) in the crust. Growth of the vents into tubes is the result of templating on the cathodically produced gas bubbles. This proposed series of events has not been demonstrated in the laboratory under conditions that are relevant to a DWDS. However, the proposed cathodic reactions can be used to explain the consistent mineralogy among the shapes and sizes of corrosion products formed in DWDS with differing chemistries.

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