

CHAPTER 3

The Importance of Temperature In Assessing Iron Pipe Corrosion in Water Distribution Systems

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KEY WORDS: iron corrosion, temperature effects

ABSTRACT

Temperature is expected to play a significant role in the corrosion of iron pipes in drinking water distribution systems. Temperature impacts many parameters that are critical to pipe corrosion including physical properties of the solution, thermodynamic and physical properties of corrosion scale, chemical rates, and biological activity. Moreover, variations in temperature and temperature gradients may give rise to new corrosion phenomena worthy of consideration by water treatment personnel.

INTRODUCTION

US water utilities will spend an estimated \$325 billion over the next 20 years to upgrade their water distribution systems,¹ with the majority of that cost associated with repairing or replacing corroded iron pipes. Contamination of drinking water by iron particles released from corroded pipe is often the most cited consumer complaint at many utilities. Iron corrosion is also an indirect human health concern, because tubercles inside of pipes may provide sites for microbial regrowth and corrosion directly consumes disinfectants, thereby lowering residuals. Finally, in one very unusual circumstance, the initiation of chlorination of a water distribution system led to the release of iron and copper particles that contained very high (up to 5 mg/L) levels of arsenic, which could have posed an acute health risk to the population.²

Corrosion of iron pipe is a complicated process that is influenced by many different factors including water quality and composition, flow conditions, biological activity, and corrosion inhibitors (see reference 3 for a review of these factors). The traditional factors evaluated when assessing iron corrosion include various water quality parameters (pH, alkalinity, buffer intensity, dissolved oxygen, etc.) and corrosion indices (Larson Index,⁴⁻⁶ Langelier Index,⁷⁻¹¹ Ryznar Index,¹² Aggressiveness Index,¹³ Momentary Excess,¹⁴ Driving Force Index,¹⁵

and Calcium Carbonate Precipitation Potential.⁸⁻¹⁰) Corrosion indices have proven to be largely ineffective for many utilities, and the use of the most famous index, the Langelier Index, is now discouraged.³ Moreover, water quality cannot always explain variations in corrosion behavior; for example, a recent study found that changes in water quality parameters such as pH and alkalinity could not fully account for observed changes in corrosion of iron pipes under stagnant conditions.¹⁶ Temperature, a potentially important factor in iron corrosion, is rarely taken into account when iron corrosion is assessed.

There are two possibilities that should be considered when investigating the influence of temperature on iron corrosion. The first is that corrosion may be significantly different at one constant temperature compared to another for a given water quality. For example, a pipe at 25°C (72°F) may experience more corrosion problems than a pipe at 5°C (40°F). The second possibility is that temperature variations might affect iron corrosion. That is, a pipe in which the temperature is varied between two temperatures (either increasing, decreasing, or cyclic) over a short period of time might corrode differently than a pipe held constant at either temperature. The following literature review examines each of these scenarios in detail, in order to alert consultants, utility managers, and regulatory personnel to phenomena that may be encountered in practice.

DIFFERENT CONSTANT TEMPERATURES

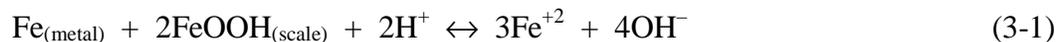
Pipes in a distribution system are almost always buried, and the temperature of the surrounding soil remains relatively constant. However, the water temperature within a pipe can change throughout the year due to seasonal variations of the water source. Thus, a pipe may exhibit different corrosion behavior in the winter versus the summer.

Only a few studies have examined the role of different temperatures in distribution system corrosion. In one study, weight loss decreased for iron samples held at 13°C versus 20°C.¹⁷ Other studies found lower iron concentrations and corrosion rates¹⁸ and fewer customer complaints of red water¹⁹ during the colder winter months. Finally, one utility reported more red water incidents during warmer summer months (M. Pearthree, personal communication). Similarly, several studies have found differences in the corrosion of lead²⁰⁻²³ and copper^{20, 23-32} at different constant temperatures.

At least five key parameters that influence corrosion can vary with temperature: dissolved oxygen (DO) solubility, solution properties (e.g. viscosity), ferrous iron oxidation rate, thermodynamic properties of iron scale, and biological activity (Figure 3-1).

DO Solubility

Oxygen solubility decreases at higher temperature. At a pressure of 1 atmosphere (sea level), DO saturation is 8.26 mg/L at 25°C versus 12.77 mg/L at 5°C. This difference could have three effects on iron corrosion. First, oxygen is the key electron acceptor for the corrosion of iron metal. At higher temperatures, there is less oxygen so the extent and rate of corrosion are more likely to be limited. Secondly, oxygen plays an important role in oxidizing ferrous compounds. Finally, depletion of oxygen may allow the Kuch reaction to occur, whereby existing ferric iron scale acts as the electron acceptor for the oxidation of iron metal to ferrous metal.³³



This reaction is exothermic,³⁴ so it might proceed more slowly at higher temperature. Thus, changes in DO solubility could affect corrosion rate, iron by-product speciation and concentration, and the type of scale formed.

Solution Properties

The viscosity of water decreases at higher temperature from about 1.5×10^{-2} N•sec/m² at 5°C to 9×10^{-3} N•sec/m² at 25°C. This will allow increased transport of reactants (dissolved O₂ or other electron acceptors) and products (Fe⁺² species) to and from the metal surface due to increased diffusion, thereby increasing the rate of corrosion if the process is diffusion limited. Also, the rate of Fe⁺² ion diffusion through a ferric oxide scale increases at higher temperatures.^{35, 36}

Thermodynamic Properties

Temperature can have a large effect on various thermodynamic properties of a system, including activity coefficients, solubility, and enthalpy of reaction, as described by established equations (Appendix A).

Activity coefficients increase slightly at lower temperature (Table 3-1).

Solubility of a solid phase can increase or decrease depending on the sign of the enthalpy of reaction (ΔH_r°) (Table 3-2). For representative solids shown here, decreasing the temperature from 25°C to 5°C is expected to produce a 0.07 to 1.06 log change in the solubility product.

Thus, changes in activity coefficients and solubility products may lead to very different soluble iron concentrations at various temperatures. Depending on the specific conditions, this could also cause a shift in predominance of one solid end-product to another. If another solid does form, the particulate iron concentration may change as well, due to changes in the durability, adherence, or protective properties of the new scale.

There are numerous examples in the literature which illustrate the role of temperature in the identity of compounds formed at different temperatures. In general, regions of immunity to corrosion (stability of the metal itself) and passivity (stability of the scale) decrease as the temperature is raised from 25 – 300°C.³⁷ Several studies have identified different iron scales at different temperatures in the same water quality,^{36, 38-43} although the ranges studied (20°C – 100°C) were much larger than experienced in a distribution system. Because the experimental conditions varied widely, it is not possible to draw any conclusions about the qualitative role of different oxides phases on aspects of iron corrosion in a distribution system.

Fe⁺² Oxidation.

At a given pH, the oxidation rate of ferrous iron (Fe⁺²) increases by an order of magnitude for each 15°C increase in temperature.^{44, 45} This change in iron speciation may favor formation of different compounds at different temperatures. The effect on corrosion will depend on the properties (solubility, durability, adherence, etc.) of the new scale that is formed.

Biological Activity

In this limited temperature range (5 – 25°C), biological activity can often be described by an Arrhenius-type equation, with increasing growth as the temperature rises.⁴⁶ Microbes can alter the rate of oxygen depletion and the redox conditions. In addition, the biological oxidation of ferrous iron is increased at higher temperatures.⁴⁷⁻⁵⁰

TEMPERATURE VARIATION

In addition to the differences in average temperature noted earlier, a distribution system may experience a temperature gradient over a relatively short period of time, depending on the water source. For example, a river might have a large temperature variation due to diurnal changes in solar intensity, or a reservoir may turn over from thermally stratified to well-mixed. Two studies showed that the water temperature in a distribution system (fed by a single surface water source) varied seasonally from 5°C – 21°C⁵¹ and 6°C – 28°C with a maximum change of 1.3°C per day.⁵² Also, a treatment plant might vary the mixing ratios of colder and warmer sources (i.e. groundwater versus surface water), leading to temperature changes in the distribution system.

One of the few studies to explicitly consider the effects of temperature variation on distribution system pipes is that of Smith et al⁵³ using a pilot-scale distribution system composed of unlined cast iron pipes. Because a portion of this system runs outdoors, the pipes were subject to the daily atmospheric temperature changes, causing the water temperature to cycle between 20 – 24°C diurnally. In one 70-hour stagnation test, the turbidity (monitored as a surrogate for iron concentration) showed a step increase at each low temperature inflection point. The oxygen saturation shows a similar step decrease at both high and low temperature inflections. Similarly, a pilot plant study utilizing lake water as the source saw intermittent “peaks” in metal concentrations, attributed to sloughing off of scale into the water.⁵⁴ This study makes no mention of controlling or even measuring temperature, so it is possible that these scale failures were due to temperature changes in the raw water supply. Finally, one study found increased copper release in pipes that were subject to temperature gradients (a warm pipe in a cold house during winter).⁵⁵

What might be causing these changes in corrosion as the temperature varies? First, as the temperature varies, solids may change from one phase to another as discussed previously. This might lead to formation of a heterogeneous scale, with multiple compounds on a given iron surface. Alternately, the scale may already be composed of multiple compounds due to other factors besides temperature. Either way, this heterogeneity makes the iron scale susceptible to two physical changes as the temperature varies—different density (volume) and different coefficient of thermal expansion (Figure 3-2).

Scale Density

Different scale components have different densities. This is described by the Pilling-Bedworth ratio (PBR), an expression of the volume ratio (per unit of iron) of a particular metallic compound to another (Table 3-3). Any $PBR \neq 1$ indicates that compressive or tensile stresses may be introduced into the scale, depending on the surface geometry. This aspect is important primarily when a new type of scale forms as the temperature is varied, especially if the new solid forms beneath an existing layer of scale (i.e. at the metal-scale interface).⁵⁶

Coefficient of Thermal Expansion

A particular scale component will have a different coefficient of thermal expansion (α) compared to the metal or other layers of scale (Table 3-4). For example, Fe metal will expand and contract nearly 50% more than Fe_3O_4 scale in response to the same temperature change. These differences cause mechanical stresses in the scale as the temperature changes, and can ultimately lead to scale spalling or crack formation.^{3, 57, 58} This phenomena can be important in cases where an additional solid forms, where the scale is already heterogeneous, and even where only one type of scale is formed on the iron metal.

Finally, it is important to note that the stresses due to dissimilar scale densities or coefficients of thermal expansion are generally greater for concave or convex surfaces, such as a pipe, compared to a flat surface. Likewise, such stresses become more important with decreasing diameter pipes.

In addition to causing detachment of scale fragments to the water, these stresses may cause cracks to form in the scale. In some cases, the cracks might expose unprotected metal surface to the solution, drastically increasing corrosion rates. There is some precedent for this idea in the literature. One study of iron and steel corroding in a moist atmosphere found that a scale with many cracks in it was less protective compared to an iron scale with few cracks.³⁹ Another study of steel in moist atmosphere⁴⁰ found similar results; furthermore, scratching the surface of heavily scaled specimen with a needle immediately caused a sharp decrease in the corrosion potential (indicating an increase in the corrosion reaction). In the atmospheric studies, cracking might be expected to be especially significant due to hydration and dehydration with changing humidity, however a study of cast iron studs placed in distribution system pipes also

found an increase in iron concentration in the water when deep cracks appeared in the scale on the iron studs.⁵³ There is no information regarding the role of water quality (especially the presence of phosphate inhibitor) in possibly “healing” such cracks after they are formed, or preventing their formation in the first place.

RECOMMENDATIONS

How can this information be used by water personnel when assessing iron corrosion? First, the following factors should be evaluated to see if the distribution system is subject to changes in temperature:

1. Is the source water a surface water that experiences daily or seasonal temperature variations?
2. Is the source water a reservoir or lake that stratifies and turns over seasonally?
3. Are two or more source waters of different temperature (i.e. a surface water and a groundwater) sometimes mixed at the treatment plant, or does the mixing ratio vary?
4. Is the distribution system fed by two or more treatment plants with different source waters?
5. Does any part of the distribution system run above ground, or have less ground-cover than other parts, and does water experience long stagnation times in these sections?

If the residence time of the water in the treatment plant and/or storage tanks is not long enough, any of these temperature changes may carry over to the distribution system.

The next step is to evaluate whether variations in temperature correlate with observed corrosion phenomena such as:

1. Red water episodes (increased consumer complaints)
2. Sections of the system that have to be replaced due to excessive scale build-up or corrosion failures (pipe perforation)
3. Increased loss of disinfectant residual

If a correlation is observed, the utility may want to attempt to minimize temperature changes in order to address corrosion problems.

CONCLUSIONS

Temperature influences many parameters, including dissolved oxygen solubility, solution viscosity, diffusion rates, activity coefficients, enthalpies of reaction, compound solubility, oxidation rates, and biological activity. Each of these factors can affect the rate of iron corrosion, the composition and properties of scale built up inside pipes, and aspects of corrosion by-product release. While the role of temperature is speculative at this time, unless utilities are alerted to its possible importance and at least consider its effects, improved understanding of corrosion phenomena may be limited.

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Table 3-1: Activity coefficient (γ) variation with temperature.

| Ion | γ at 5°C | γ at 25°C |
|-------------------------------|-----------------|------------------|
| H ⁺ | 0.916 | 0.914 |
| OH ⁻ | 0.902 | 0.900 |
| Fe ⁺² | 0.686 | 0.678 |
| Ca ⁺² | 0.686 | 0.678 |
| CO ₃ ⁻² | 0.679 | 0.671 |
| Fe ⁺³ | 0.456 | 0.446 |
| PO ₄ ⁻³ | 0.408 | 0.397 |

Table 3-2: Change in solubility product (K) with temperature.

| Compound | ΔH_r° (25°C) [kJ/mole] | log K (25°C) | log K (5°C) | Reference |
|--|--|-----------------|----------------|-----------|
| Fe(OH) ₂ (s) | 19.91 | -14.74 | -15.00 | 59 |
| | | -15.10 | -15.35 | 60 |
| | | -14.70 | -14.95 | 44 |
| FeCO ₃ (s) | -25.67 | -10.24 | -9.92 | 61 |
| | | -10.70 | -10.38 | 44 |
| | | -10.68 | -10.36 | 60 |
| Fe(OH) ₃ (s) | 84.52 | -37.22 | -38.29 | 59 |
| | | -38.70 | -39.76 | 44 |
| FeOOH (s) | -61.16 | -1.00 | -0.23 | 44 |
| FePO ₄ (s) | -28.40 | -17.82 | -17.47 | 59 |
| FePO ₄ •2H ₂ O (s) | -9.36 | -26.00 | -25.88 | 44 |
| CaCO ₃ | -- | -8.42 | -8.35 | 44 |
| H ₂ O | -- | -14.0 | -14.73 | 44 |

Table 3-3: Selected Pilling-Bedworth Ratio (PBR) values ⁵⁷

| Compounds | PBR |
|---|------|
| FeO : Fe | 1.68 |
| Fe ₂ O ₃ : Fe | 2.14 |
| Fe ₃ O ₄ : Fe | 2.1 |
| Fe ₃ O ₄ : FeO | 1.2 |
| Fe ₂ O ₃ : Fe ₃ O ₄ | 1.02 |

Table 3-4: Selected coefficients of thermal expansion (α) values ⁵⁷

| Compound | α ($^{\circ}\text{C}^{-1}$) |
|--------------------------------|--------------------------------------|
| Fe | 15.3×10^{-6} |
| FeO | 12.2×10^{-6} |
| Fe ₂ O ₃ | 10.96×10^{-6} |
| Fe ₃ O ₄ | 10.5×10^{-6} |

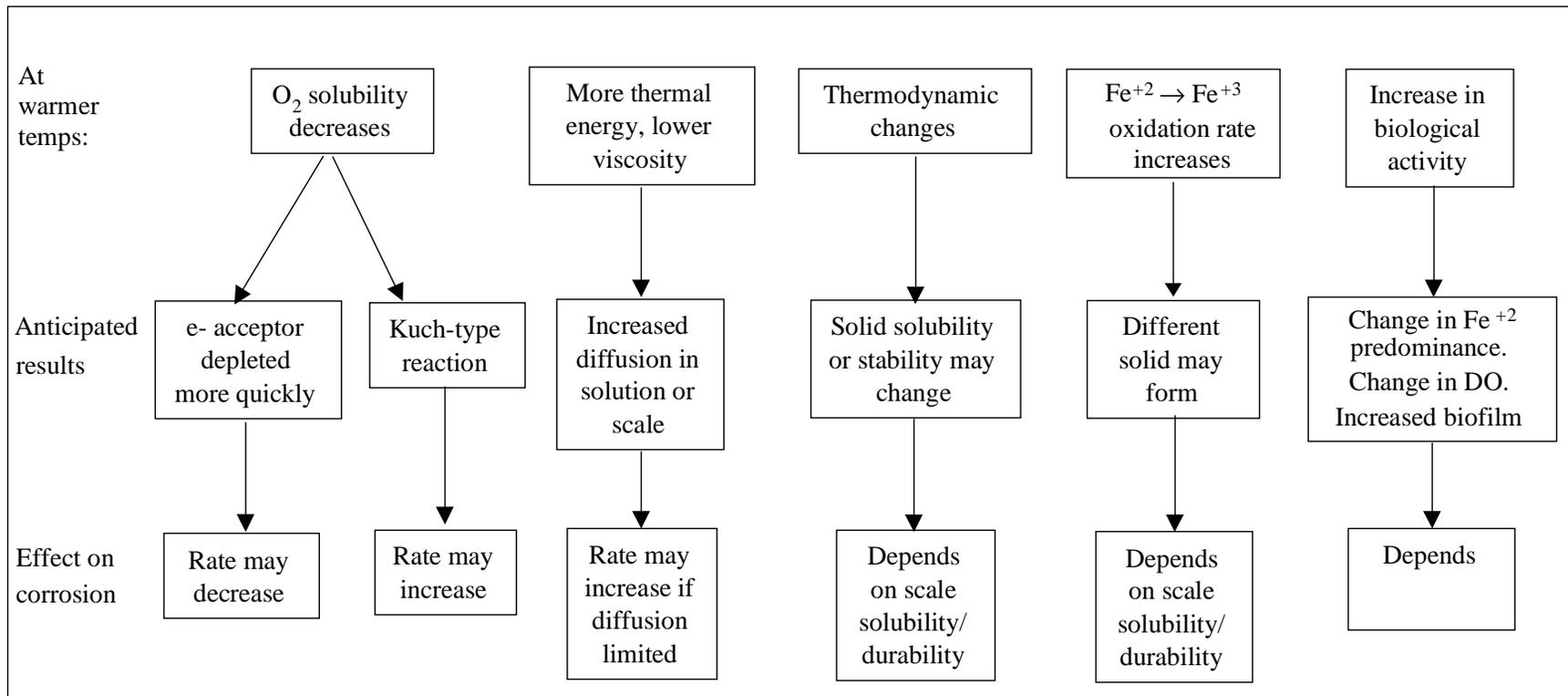


Figure 3-1: Possible effects of different constant temperature on aspects of iron corrosion.

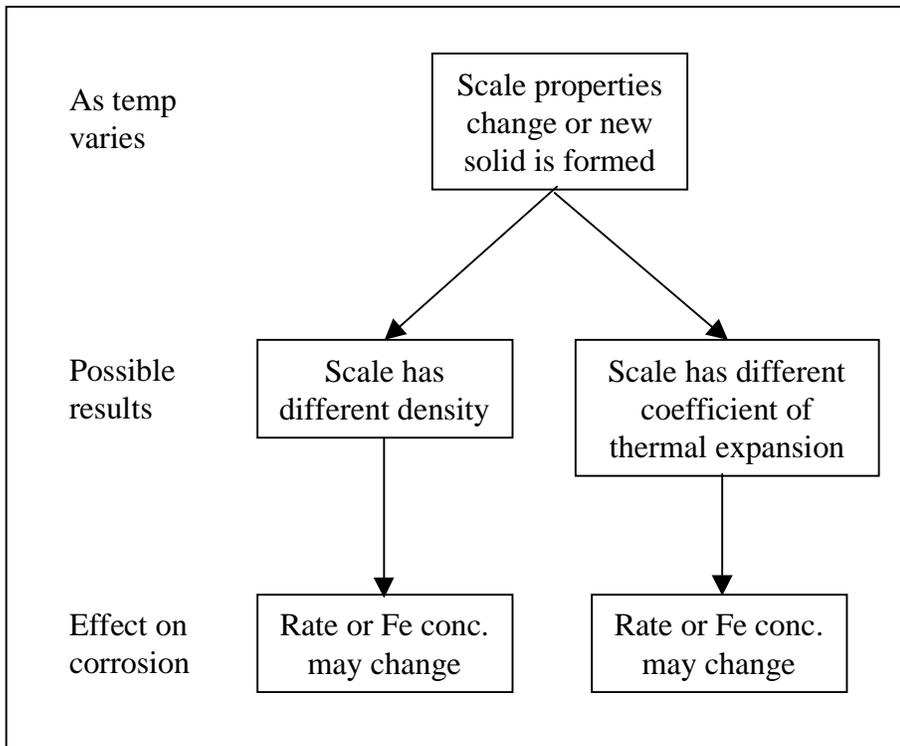


Figure 3-2: Possible effects of varying temperature on iron corrosion.