

Corrosion Control Inside Water-filled Steel Fire Sprinkler Piping

BRUCE W. CHRIST*

Converse Consultants

*731 Pilot Road, Suite H, Las Vegas
NV 89119-4429, USA*

ABSTRACT: This article is a guide for sprinkler contractors, facilities managers, and their technical advisors who sometimes have to deal with the consequences of iron–water corrosion inside pressurized, low-carbon steel fire protection systems that contain water. The consequences include: (1) pinhole leaks and (2) build-up of insoluble corrosion residues on the interior pipe wall that increases pipe friction losses. A reference is made to sections of the National Fire Codes/NFPA 13 that address pipe materials, protection of steel piping against corrosion, and pipe friction losses. Electrochemical metal–water corrosion processes that can occur inside pressurized, low-carbon steel fire protection systems that contain water are discussed, as is microbiologically influenced corrosion. Corrosion control measures arising from the electrochemical science underlying both metal–water corrosion and microbiologically influenced corrosion are suggested.

KEY WORDS: corrosion, piping, low-carbon steel, sprinklers, electrochemical, microbiological, hydrolysis.

CORROSION – AN ONGOING CONCERN

Introduction

FIRE SPRINKLER PIPING systems made of low-carbon steel are often water-filled and pressurized. Dry and pre-action steel fire protection systems charged with compressed air usually contain residual water from various testing procedures. Corrosion has been a concern in pressurized, water-filled, low-carbon steel piping systems for many years. For example, in 1951 Speller [1a–c] addressed the role of oxygen in fueling iron–water

*E-mail: bchrist@converseconsultants.com

corrosion and concluded that minimizing exposure of water-filled, low-carbon steel pipe to dissolved oxygen reduced internal corrosion. Rittenhouse [2] reported that periodic flushing with oxygenated water accelerated corrosion degradation of a water-filled, steel fire protection system. Notarianni and Jackson [3] in 1994 discussed effects of corrosion pitting, scale build-up, and sedimentation on the life and performance of water-based, metal fire sprinkler piping systems. These authors identified four factors influencing corrosion degradation in such systems. An overriding factor is how often fresh oxygen is introduced. Oxygen dissolved in water being charged is one source of reactive oxygen, and air trapped during charging into unvented piping is another source. Moreover, dry and pre-action fire protection systems contain compressed air that is a source of oxygen. Three other factors listed by Notarianni and Jackson [3] are: (1) selection of pipe material, e.g., low-carbon steel versus copper versus plastic, (2) the corrosivity (corrosive properties) of the available water supply, and (3) ambient environmental conditions, e.g., temperature and pressure. The reliability and durability of metal fire sprinkler piping systems depend on how designers and operators address the foregoing factors, as well as the spontaneous, localized acidification of water that can occur during long detention times. Acidified water is as corrosive as dissolved oxygen. Acidification is due to hydrogen ions that are produced by hydration and hydrolysis of certain dissolved metal ions of small ionic diameter and high positive electric charge. Additionally, acidified water can be produced by the phenomenon of microbiologically influenced corrosion.

Today it is recognized that corrosion of metals is caused by electrochemical dissolving (leaching) reactions that occur at the metal–water interface [4–8]. Reactions tend to be localized in crevices [9a] and underneath aggregations of insoluble substances [9b,c,10]. Paired, mutually dependent reactions involving the metal and trace concentrations of certain chemical species dissolved in water underlie all metal–water corrosion. For example, hydrogen ions are the chemical species in acidified water that spontaneously corrode iron. Dissolved oxygen at concentrations of 8 mg/L is extremely corrosive to iron metal. Dissolved oxygen and hydrogen ions acting together are more corrosive to iron than is either species acting alone.

Low-carbon Steel Pipe

Fire sprinkler pipe is often made of low-carbon steel, which is about 98% iron. Several grades of low-carbon steel fire sprinkler pipes are specified in NFPA 13 [11a]. Such a pipe is an attractive material for

pressurized, water-filled piping systems because of its elastic stiffness, strength, and reasonable cost. However, low-carbon steel pipe is susceptible to spontaneous iron–water corrosion. Orange rust patches that grow on the inside and outside of pipe during shipping and storage illustrate this point. Rust patches are caused by electrochemical reactions between iron, moisture, and oxygen from air. The same reactions can occur when the interior pipe wall is wetted by ordinary fresh water containing dissolved oxygen at normal operating temperatures and pressures of fire sprinkler piping systems [12a]. Air that sometimes is trapped at high elevations of water-filled fire sprinkler piping systems supplies dissolved oxygen.

Corrosion Protection in NFPA 13

The need for protection of pressurized, water-based, steel fire sprinkler piping from corrosive water is recognized by the National Fire Codes [11b,c]. For example, NFPA 13 [11c] implicitly addresses internal corrosion as follows: ‘Where water supplies are known to have unusual corrosive properties and threaded or cut-groove steel pipe is to be used, wall thickness shall be in accordance with Schedule 30 [in sizes 8 in. (200 mm) or larger] or Schedule 40 [in sizes less than 8 in. (200 mm)].’ A metallurgical reason for this requirement is that plastic deformation such as that accompanying threading/cut-grooving localizes and accelerates the rate of iron–water corrosion reactions in the region of deformed metal [8].

Another reason for this requirement [11c] is that threading/cut grooving can thin the pipe wall locally. Specifying Schedule 30 or Schedule 40 pipe provides a corrosion allowance, i.e., significantly more wall thickness than is needed to contain internal pressure (usually 345–1103 kPa gage (50–160 psig)). The extra thickness can be wasted by iron–water corrosion in deformed/thinned regions without compromising the pressure-containing capability at the threaded/cut-grooved region for a much longer time than would be the case for thinner wall pipe.

Chemical composition and metallurgical structure of specified grades of low-carbon steel are not significantly different from one grade to another. All grades contain about 98 wt% iron. Consequently, it is unlikely that one grade of low-carbon steel specified in NFPA 13 [11a] is more or less susceptible to metal–water corrosion than any other specified grade. Application of a protective coating that blocks iron–water corrosion reactions at the metal–water interface can reduce susceptibility of any specified grade, provided the coating is continuous, adherent, and nonporous. Repair of coatings damaged by fabrication procedures can prevent exposure of bare iron to corrosive water.

Purpose

This article is a guide for sprinkler contractors, facilities managers, and their technical advisors who sometimes have to deal with the consequences of iron–water corrosion inside pressurized, water-filled low-carbon steel fire sprinkler piping systems. Technical information in this article also applies to dry and pre-action steel fire protection systems that contain residual water from various testing procedures. This article reviews the multiplicity of electrochemical corrosion processes that can proceed spontaneously under the ambient environmental conditions that usually prevail in pressurized, low-carbon steel fire sprinkler piping systems that contain water. State-of-the-art corrosion control measures arising from the electrochemistry that underlies both iron–water corrosion and microbiologically influenced corrosion are suggested.

ELECTROCHEMICAL ASPECTS OF IRON–WATER CORROSION

The Fundamentals of Iron–Water Corrosion

Iron–water corrosion is simply the dissolving (leaching) of iron in water. It is caused by time and temperature dependent electrochemical reactions that occur at the iron–water interface [4–8]. Reactions occur at the atomic scale of dimensions. Certain chemical species dissolved in water are essential ingredients for such reactions. Corrosion proceeds as long as ingredients are available and physical conditions are suitable. Increasing temperature usually speeds the rate of dissolving. Rates can double with each temperature increment of 8°C (15°F) [13a].

During iron leaching, negatively charged electrical particles, electrons, are extracted from iron metal (electron donor) by certain chemical species (electron acceptors) dissolved in water. For example, hydrogen ions (H^+) in acidified water can extract electrons (e^-) from iron metal (Fe_{metallic}). At the time of electron transfer, ferrous iron ions (Fe^{++}) are expelled into the water and hydrogen gas (H_2) is generated. The pair of electrochemical reactions below illustrates acid corrosion of iron.



The paired, mutually dependent reactions that extract electrons from iron and expel iron ions into water represent the fundamental act of iron–water

corrosion [14]. Hypochlorite ions, used for water disinfection, and dissolved oxygen can cause corrosion of iron by accepting electrons just as hydrogen ions do. Electrochemical corrosion reactions are spontaneous under the chemical and physical conditions that usually prevail in most water-based, steel fire sprinkler piping systems.

Dissolved iron initially takes the form of positively charged electrical particles that are expelled into the water at the time of electron transfer. Chemists use the notation 'iron(II)' to indicate that these atomic size particles, ions, have an electric charge of plus two. Freshly expelled ferrous iron ions, iron(II), can transform electrochemically to ferric iron ions, iron(III), via the acid-oxygen corrosion process and also via metabolic activities of iron-oxidizing bacteria that extract an electron from iron(II). Concentrations of dissolved iron ranging from 10 to 494 mg/L have been measured in pipe water drained from operating steel fire sprinkler piping systems [15]. Comparing these concentrations with the dissolved iron concentration of 0.3 mg/L or less in water charged into fire sprinkler piping from public water supplies [16] shows that corrosion can increase dissolved iron concentrations in closed steel piping systems by about 10–1000 times. Orange/brown stains often seen where flowing water from fire sprinkler piping has splattered the surroundings of drains are due to dissolved iron. Oxygen from air spontaneously reacts with dissolved iron(II) in the splatters to produce insoluble iron(III) oxide, i.e., rust stains [17a–c,18a].

Electrical Aspects of Corrosion

Metals are electrical conductors. Dissolved chemical species make water an electrically conducting medium, i.e., an electrolyte. For example, increasing the concentration of a set of dissolved chemical species known as Total Dissolved Solids by a factor of 6 can increase the specific electrical conductance of a water sample by a factor of 10 [13b]. Corrosion reactions occur when certain electrically charged chemical species dissolved in water contact the metal surface by diffusion and electrostatic interaction. These chemical species extract electrons from the metal (oxidize the metal), thereby expelling metal ions into the water. Reactions are spontaneous if energy is released in the electron transfer process [7b]. Such electron transfer generates a voltage (electric potential) that can range from about 0.1 to perhaps 5.0 DC volts. The tendency of a metal to be corroded by specific chemical species can be estimated by reference to a table of Standard Reduction Potentials [7c]. External electrical factors are not required to cause corrosion.

Voltages at the metal–water interface depend on the specific chemical species participating in the coupled, mutually dependent electrochemical

reactions occurring at the time of electron transfer. For example, under standard state conditions, spontaneous electrostatic interaction between iron (electron donor) and dissolved oxygen (electron acceptor) generates a DC voltage of 0.81 V, whereas spontaneous electrostatic interaction between iron and dissolved oxygen plus acidity (hydrogen ions) generates 1.64 DC volts [7c]. Higher voltages indicate greater tendency for reactions to occur. Corrosion currents are localized at the metal–water interface and usually are of a few micro-amperes.

Effects of External Electrical Factors

The electrochemical voltage that drives spontaneous metal–water corrosion reactions can be altered by external electrical factors that are sometimes imposed unwittingly on the metal–water system. Positive DC voltage of sufficient magnitude applied to the metal can accelerate metal–water corrosion, whereas negative DC voltage of sufficient magnitude can slow corrosion. In fact, intentional application of negative DC voltage to a metal component is the basis for cathodic protection from metal–water corrosion [19]. External electrical factors are not likely to play a role in metal–water corrosion of metal fire sprinkler piping systems, if the piping system is electrically grounded.

CHEMICAL INGREDIENTS CAUSING IRON–WATER CORROSION

Overview

The chemical characteristic pH measures whether a water sample is acidic (pH less than 7.0 because hydrogen ions, H^+ , are present in higher concentration than hydroxyl ions, OH^-) or basic (pH greater than 7.0 because OH^- are present in higher concentration than H^+). The pH of most natural fresh waters is on the basic side of the neutral pH value of 7.0. For example, public water supplies that purvey water to fire sprinkler piping systems usually have an average pH value in the range of 7.3–8.4.

The chemical characteristic alkalinity influences the tendency of a solution to behave as if it were basic. Certain chemical species that contribute to alkalinity such as bicarbonates and carbonates release hydroxyl ions from water molecules via hydration and hydrolysis (see section on Bicarbonates, Carbonates and Alkalinity). Consequently, a solution of high alkalinity with pH in the range of 4.4–6.9 can exhibit chemical behavior that is more characteristic of a basic solution than an acidic solution [13c]. This property is useful in the control of acid corrosion.

The unusual corrosive properties of some water supplies mentioned in the National Fire Codes [11c] arise from certain reactive chemical species that usually are dissolved in ordinary fresh waters. Two ingredients responsible for most iron–water corrosion are hydrogen ions (H^+) in acids and dissolved oxygen. Furthermore, experience shows that the combination of dissolved oxygen and hydrogen ions in acidified water causes more severe corrosion of iron metal than does either alone. Additionally, the combination of dissolved sulfates and hydrogen ions in acidified water can corrode iron metal and produce sulfurous acid. Chlorine-based disinfectants, e.g., hypochlorites, added to public water supplies are another source of dissolved chemical substances that can corrode iron metal. All these chemical ingredients cause spontaneous iron–water corrosion under the usual operating conditions of temperature and pressure in water-based, steel fire sprinkler piping systems. The iron–water corrosion process caused by each of the ingredients mentioned above is listed in Table 1.

Average individual concentration of any of these corrosive chemical ingredients in a public water supply is small. In fact, average concentrations usually are so small that only an insignificant amount of interior pipe wall corrosion occurs after a steel fire sprinkler piping system is charged with such water. The consequences of such gradual corrosion accrue and become troublesome only after many months or many years of operation. Corrosion reactions halt when ingredients are used up and resume when a fresh supply of water replenishes them. Hence, long detention times put off the day when significant consequences arise. As regards dry and pre-action systems containing residual water from various testing procedures, oxygen from compressed air is continuously available for corrosion because compressed air is continuously injected to compensate for inevitable small leaks, especially in older systems.

Chemical Analysis of Public Water Supplies

Public water treatment facilities throughout the United States publish an annual report listing concentrations of numerous chemical species in finished water. Reports are in the public domain and are usually available upon request. Usually, only trace concentrations of chemical species corrosive to iron are present in finished water.

Data listed in annual reports of water treatment facilities in the southwestern United States demonstrate this point for Rocky Mountain water [20] and for Lake Mead water [21] several hundred miles downstream from its Rocky Mountain source. Individual concentrations of various

Table 1. Electron acceptor reactions of chemical species that make water corrosive to iron and low-carbon steel.

| Process | Corrosive species that corrode low-carbon steel | Electron acceptor reaction | Standard state reduction potential* (V) |
|--|---|---|--|
| Acid corrosion | Hydrogen ions (H ⁺) [9e] | 2H ⁺ + 2e ⁻ → H ₂ (gas) | 0.00 |
| Oxygen corrosion in basic (alkaline) solution | Dissolved oxygen (O ₂) [9f] | O ₂ + 4H ₂ O + 4e ⁻ → 4OH ⁻ (OH ⁻ = hydroxyl ion) | 0.41 |
| Acid solution with dissolved oxygen | Hydrogen ions (H ⁺) plus dissolved oxygen (O ₂) [28] | 4H ⁺ + O ₂ + 4e ⁻ → 2H ₂ O | 1.23 |
| Sulfate reduction in acid (non-alkaline) solution | Sulfate ions (SO ₄ ⁻²) [7c] | SO ₄ ⁻² + 4H ⁺ + 2e ⁻ → H ₂ SO ₃ + H ₂ O | 0.20 |
| Hypochlorite in basic (alkaline) solution | Hypochlorite ions (OCl ⁻) [13d] | OCl ⁻ + H ₂ O + 2e ⁻ → Cl ⁻ + 2OH ⁻ | 1.49 |
| Hypochlorite in acid (non-alkaline) solution | Hypochlorous acid molecules (HOCl) [13d] | HOCl + H ⁺ + 2e ⁻ → Cl ⁻ + H ₂ O | 0.90 |

*Relative to a standard hydrogen electrode [7c].
Note: Fe_{metallic} - 2e⁻ → Fe⁺⁺ - standard state reduction potential for dissolving iron = -0.41 V. Driving voltages for above reactions to corrode iron range from +0.41 to 1.90 V. Higher voltage indicates stronger tendency for corrosion to occur.

chemical species in water from these two sources fall between 0.5 and 220 mg/L. Specifically, average concentrations reported for chloride and sulfate ions range from 2 to 70 and 10 to 230 mg/L, respectively, depending on location of the water supply, time of year, and year of the report. Chlorides and sulfates participate in hydrolysis that acidifies water. Additionally, sulfates can participate in microbiologically influenced corrosion that acidifies water (see sections on Sulfate Reducing Bacteria and on Sulfides), and chlorides can damage certain protective surface coatings [22], thereby exposing metal to corrosion reactions.

‘Alkalinity’ and ‘hardness’ are chemical characteristics that usually appear in annual reports of public water treatment facilities. Alkalinity is determined by an acid titration technique that measures the concentration of dissolved bicarbonates, carbonates, and six other chemical species [23a], whereas hardness measures concentrations of dissolved calcium and magnesium [24a]. Both characteristics are of interest because high values of each indicate a high potential for massive build up of insoluble corrosion residues that increase pipe friction losses.

Hydrolysis of Hydrated Metal Ions Acidifies Water Locally

Fresh water in public water supplies is not acidic. Surprisingly, water that is not acidic can become acidified, and therefore extremely corrosive, via the spontaneous electrostatic processes of hydration and hydrolysis that produce hydrogen ions. Favored localities for hydration and hydrolysis are crevices [9a] and underneath aggregations [9b] such as scale, sediments, fabrication chips and filings, tubercles [9c,d], and other insoluble corrosion residues. Biofilms are another locality where acidified water can be produced, e.g., via the metabolism of acid-producing bacteria.

The electrostatic processes of hydration and hydrolysis [25–27a] act in sequence to decompose water molecules. Hydration occurs when positively charged, small diameter metal ions such as iron(III) attract and bond to as many as six water molecules via electrostatic interaction. Hydrated iron(III) ions bond strongly to the negatively charged oxygen component of a water molecule, but only weakly to the positively charged hydrogen ion. Hydrolysis of hydrated iron(III) ions occurs as positively charged, weakly bonded hydrogen ions are withdrawn from hydrated water molecules by negatively charged ions such as chlorides and sulfates. Localized concentrations of fully dissociated hydrochloric and sulfuric acid of extremely low pH [9a,b] can produce corrosive acidity within crevices and aggregations of various residues. Acidification due to hydrolysis of hydrated iron(II) ions is weaker than acidification due to hydrolysis of hydrated iron(III) ions [27a].

IRON–WATER CORROSION PROCESSES

Overview

Electrochemical dissolution of iron as described in Reaction (1A) is accompanied by an electron-acceptor reaction such as Reaction (1B) in which certain chemical species dissolved in water receive two electrons from iron. It is convenient to classify iron–water corrosion processes in terms of electron-acceptor reactions. Six such reactions are listed in Table 1. These reactions can be looked upon as essential information that guide procedures for corrosion control. Each corrosion process is discussed below.

Acid Corrosion

Acid corrosion [9e] is due to hydrogen ions extracting electrons from iron metal. It occurs in water of pH less than 7 and is most likely to occur in regions such as crevices [9a] or underneath aggregations of insoluble substances that build up on the interior pipe wall [9b,c]. These regions are localities where hydration and hydrolysis can produce hydrogen ions that acidify water. Biofilms that house acid-producing bacteria also are likely to be found in these localities. Products of acid corrosion reactions are chemically active iron(II) ions and chemically inactive hydrogen gas that migrates to high elevations in a closed piping system.

Oxygen Corrosion

Oxygen corrosion [9f,12a] is due to dissolved oxygen molecules extracting electrons from iron metal. The average concentration of dissolved oxygen is 8 mg/L in fresh water of neutral pH at 13.3°C (60°F) and atmospheric pressure [29a]. Oxygen corrosion occurs at pH greater than 7. Hydroxyl ions are a product of this reaction. They react speedily with nearby iron(II) ions to form insoluble iron(II) hydroxide.

Notarianni and Jackson [3] offered a caution as regards how often fresh oxygen is introduced into a water-based, metal piping system. This caution arises because repeated charging of new water into an entire fire sprinkler piping system that is periodically drained during stages of initial construction or renovations can set the stage for significant oxygen corrosion. Especially troublesome is air trapped at high elevations in unvented, water-based piping systems. Oxygen in trapped air spontaneously dissolves in water to fuel oxygen corrosion. Operating pressures in fire sprinkler piping systems usually range between gage pressures of 345–1103 kPa (50–160 lb/in.²). Since dissolved oxygen concentration increases with increasing pressure [1b], the

concentration of dissolved oxygen in fire sprinkler pipe water at high elevations where air is trapped is considerably higher than 8 mg/L at 13.3°C (60°F) and atmospheric pressure [29a]. Repeatedly filling a drained piping system without venting trapped air can introduce harmful volumes of dissolved oxygen.

Dry and pre-action fire protection systems pressurized with compressed air are sometimes not completely dry, because residual water from hydrostatic testing can be trapped at low elevations. Consequently, oxygen corrosion fueled by residual water that is saturated with dissolved oxygen from compressed air can occur in dry and pre-action systems.

Periodic inspector's alarm tests of operating fire sprinkler piping systems involve releasing a small volume of old water from the inspector's drain and introducing an equal volume of new water at the riser. Corrosion reactions can occur that use the fresh supply of corrosive ingredients in the small volume of new water, but the extent of corrosion that follows each test is likely to be small because the supply of new ingredients is small. It is unlikely that this test introduces air.

Acid–Oxygen Corrosion

Acid–oxygen corrosion [28] occurs in oxygenated acidic solutions when hydrogen ions and dissolved oxygen act together to extract electrons from iron metal. Although details of the electrochemistry are not fully understood [28], intensified corrosion probably occurs because dissolved oxygen reacts in combination with the hydrogen ions to transform iron(II) to electron-deficient iron(III), which promptly extracts electrons from iron metal to produce more iron(II). This cyclic corrosion of iron metal proceeds more rapidly than does the corrosive action of dissolved oxygen or hydrogen ions reacting alone with iron metal. Spontaneous corrosion that feeds upon itself cyclically is termed autocatalytic [9a]. Iron cannibalizing itself by this autocatalytic reaction is a possible explanation of the chemical drilling that produces pinhole leaks in low-carbon steel fire sprinkler piping.

Acid–Sulfate Corrosion

Acid–sulfate corrosion occurs in solutions with dissolved sulfates. Hydrogen ions and dissolved sulfates act together to extract electrons from iron metal [7c]. This electron acceptor reaction produces sulfurous acid, a mixture of two sulfur-containing molecules that is metastable and oxidizable to elemental sulfur and hydrogen sulfide [27b,30]. This version of sulfate reduction is a different process than sulfate reduction via metabolic activity of sulfate reducing bacteria.

Chlorine-based Disinfectant

Many public water systems that purvey water to fire sprinkler piping contain a chlorine residual for disinfection. Often water is treated with hypochlorite salts to produce the chlorine residual [13e]. Dissolved hypochlorite salts generate electrically neutral hypochlorous acid molecules via hydrolysis. The chlorine residual is termed 'free available chlorine' and is defined as the sum of the hypochlorous acid and hypochlorite ion concentrations [13e,29b]. Hypochlorous acid molecules are biocidal molecules that annihilate undesirable microorganisms. Hypochlorous acid and negatively charged hypochlorite ions coexist in a relationship that is extremely sensitive to pH. For example, at pH of 8.0, hypochlorite ion concentration far exceeds the concentration of hypochlorous acid molecules, whereas just the opposite is the case at pH of 6.5 [13f].

Hypochlorite ion corrosion occurs when hypochlorite ions extract electrons from iron metal. Hypochlorous acid corrosion occurs when hydrogen ions from the dissociation of hypochlorous acid molecules extract electrons from iron metal. Corrosion due to these oxidation reactions is likely to be minimal because concentrations of the chlorine residual are small, usually about 1–3 mg/L.

MICROBIOLOGICALLY INFLUENCED CORROSION

Microorganisms

Microorganisms are the agents of microbiologically influenced corrosion of metals [13g]. Some harmful microorganisms and the problems they cause are listed in the water handbook edited by Kemmer [13h]. Bacteria are a category of single-cell microorganisms that frequently participate in microbiologically influenced corrosion. They are ubiquitous and are found in all natural fresh waters, as well as in soil, and even in airborne dust particles. Bacteria in fire sprinkler pipe water have been linked to pinhole leaks [12,31,32]. Numerous species of bacteria can participate in microbiologically influenced corrosion inside fire sprinkler piping.

Biofilms

The habitat of bacteria is a gelatinous, watery environment called a biofilm [33a]. Several kinds of bacteria might live communally in a biofilm. An interesting characteristic of such a community is that anaerobic bacteria can thrive in regions deep within the biofilm where oxygen is lacking, whereas aerobic bacteria can thrive in regions near the surface where water

is saturated with dissolved oxygen. Bacteria are minuscule. The maximum size of any species usually does not exceed 10 μm (400 micro-inches). Several species and many millions of bacteria might live in a single tiny biofilm. Numerous biofilms can grow on or within corrosion residues, as well as deep within pits or crevices. Viscous, gelatinous, polymeric substances produced by bacteria [34a] make up much of the mass of biofilms. These substances trap nutrients for life sustaining processes.

Bacterial Metabolism, Corrosive Waste Products and Biocide

Bacterial metabolism is explained in terms of aqueous electrochemistry [34a], just as is metal–water corrosion [4–8]. Metabolic processes proceed when the necessary chemical ingredients come together in favorable physical conditions. Bacterial metabolism occurs at appreciable rates only in certain ranges of temperature, pH, and oxygen concentration that are distinctive for each species. Outside the critical ranges of these conditions, a bacterial species is likely to experience diminished metabolic activity while awaiting favorable conditions for more vigorous growth.

Bacteria obtain energy for maintenance and growth via a sequence of electrochemical reactions [33,34b,35a,36a,37a,b] that occur in the cell envelope, i.e., in the cell wall and plasma membrane [34c–e,35b,c]. Such reactions involve electron and hydrogen ion transfer between bacteria and nutrients. Catabolism is the name microbiologists apply to a spontaneous metabolic process in which nutrients are electrochemically transformed and energy is released [37c].

Nutrients are energy-rich chemical substances with physical characteristics of size and electrical charge that facilitate interaction with the cell envelope. For example, metal ions such as positively charged iron(II) are nutrients for iron oxidizing bacteria [36b,c,38a,b]. The carbon and hydrogen of organic matter nourish acid-producing bacteria [9g,39] and sulfate-reducing bacteria [33,36d,e,38c,40]. Other bacteria utilize the sulfur and nitrogen of organic or inorganic matter as nutrients. Oxygen is essential for aerobic bacteria and is distressing to anaerobic bacteria. Pipe water wetting biofilms can be significantly more corrosive than a sample of water taken from a piping system drain due to diffusion of various waste products of bacterial metabolism, e.g., acid, into pipe water close to the biofilm.

Biocides that annihilate bacteria [12b,13e,37d] must penetrate biofilms and diffuse into the cell envelope. Chemical species of small molecular size that are electrically neutral, such as hypochlorous acid molecules, can enter the cell membrane, react with the enzyme system of the cell, and eventually annihilate it [13i,19f]. Other chemical agents for controlling bacteria include phenol and phenolic compounds, formaldehyde, gluteraldehyde, soaps, and

detergents [37d]. Corrosion control strategies that address microbiologically influenced corrosion are discussed below.

Bacteria Living inside Water-filled Piping

Iron-oxidizing bacteria (aerobic) such as *Thiobacillus ferrooxidans* and *Gallionella ferruginea* [36b,c,38a,b] can transform iron(II) to iron(III) during metabolism. *T. ferrooxidans* is active in extremely acidic water, whereas *G. ferruginea* is active in nearly neutral water. Interestingly, iron oxidizing bacteria react with iron(II) ions and do not react directly with iron metal. However, iron(III) produced by their metabolic activity can acidify water locally via hydration and hydrolysis, and the acidified water can corrode iron metal. Additionally, electron-deficient iron(III) can extract electrons directly from iron metal to produce more iron(II) [28]. Furthermore, in alkaline water, iron(III) reacts with hydroxyl ions and produces insoluble red-brown gelatinous residues.

Acid-producing bacteria such as certain species of *Clostridia* (anaerobic) produce energy by fermentation of organic matter [9g,33,39]. Organic matter is unlikely to be present in public water supplies charged into fire sprinkler piping systems. However, organic matter in the form of lubricants used during construction of piping systems or as corrosion control coatings for pipe during transit and storage might serve as nutrients for *Clostridia*. Waste products are hydrogen, carbon dioxide, and organic acids that can cause acid corrosion. Hence, *Clostridia* do not corrode iron metal directly, but rather produce acidity that causes acid corrosion.

Sulfate-reducing bacteria (anaerobic) use organic matter as nutrients [23b,c]. During dissimilatory sulfate reduction, they discard electrons as waste to sulfate ions that serve as terminal electron acceptors [36d]. Sulfate concentrations in ordinary fresh waters range from 10 to 220 mg/L. Discarded electrons can change the oxidation number of sulfur in sulfate ions from +6 to -2. Electron-deficient sulfur species other than sulfate also can serve as electron acceptors. Sulfur-containing terminal electron acceptors can become electron-rich sulfur in the form of negatively charged bisulfide ions if pH is greater than 7 or negatively charged sulfide ions if pH is less than 7 [23c]. Both of these ions can acidify water locally via hydrolysis. In this roundabout way, sulfate-reducing bacteria can be looked upon as producers of acidity that causes acid corrosion.

Sulfate-reducing bacteria are described in the book by Stanier et al. [36d]. Electron microscopic images of six species including *Desulfovibrio vulgaris* and *Desulfococcus multivorans* are shown in [36e, p. 461]. Sulfate-reducing bacteria are metabolically active in the pH range, 5.0–9.0, and they are especially active in the pH range 6.5–7.3 [40]. Explanations that attribute

microbiologically influenced corrosion to metabolism of sulfate-reducing bacteria can be reinforced by electron microscopic images of carcasses of such bacteria in the corrosion residues.

CORROSION RESIDUES

Liquids and Gases

Liquid corrosion residues include pipe water with dissolved iron in the form of iron(II) and iron(III) ions. Iron(II) is the initial corrosion residue from iron–water corrosion processes. Localities where iron(II) ions are likely to be concentrated are within crevices and underneath aggregations of insoluble substances. Freshly expelled iron(II) ions are extremely active chemically. For example, some iron(II) ions transform to iron(III) ions by giving up an electron to the oxygen–acid corrosion reaction or to iron oxidizing bacteria. Interestingly, water acidified by hydrated and hydrolyzed iron(III) ions is yellow, whereas water acidified by hydrated and hydrolyzed iron(II) ions is pale green [41].

Gases such as hydrogen, hydrogen sulfide, and carbon dioxide are produced by iron–water corrosion processes and also by the metabolic activity of certain microorganisms. These gases can accumulate at high elevations. Dissolved hydrogen sulfide and carbon dioxide can acidify water and cause acid corrosion in such localities.

Insoluble Corrosion Residues of Iron(II) and Iron(III)

Hydroxides and Oxides

Iron(II) reacts with hydroxyl ions to produce chemically active gray-green iron(II) hydroxide [8,17a]. Hydroxyl ions for this reaction are produced via oxygen corrosion, and also via hypochlorite ion corrosion. Additionally, hydroxyl ions can be produced via hydrolysis due to bicarbonate and carbonate ions [24b,25]. Iron(II) hydroxide reacts with dissolved oxygen and produces: (1) chemically stable, rusty-colored iron(III) oxide if dissolved oxygen is abundant [8,17a–c], and (2) acid-soluble black magnetic iron oxide (magnetite) if the availability of dissolved oxygen is limited [8].

Iron(III) ions are stable in acidified water. However, when hydroxyl ions appear, iron(III) forms a chemically stable, voluminous, gelatinous red residue called iron(III) hydrous oxide [42]. This residue becomes granular and powdery as it loses water [17c,42a].

Numerous colloidal particles of black magnetite sometimes flow out with draining water when an inspector's valve in a steel fire sprinkler piping system is opened for an alarm test. These particles represent a stage in

corrosion residue formation that precedes the sedimentation and agglomeration that increases pipe friction losses. Suspended particles of magnetite in an as-drawn, cloudy water sample might take a day or two to settle. Exposure to air causes a wet sample of these particles to form an extremely thin, surface layer of rust colored iron(III) oxide [18a] that can deceive an inspector into believing the particle is not black magnetite. However, these magnetite particles are attracted to a magnet despite the coating. Magnetite dissolves rapidly in weak acid solutions, making it possible to dissolve magnetite aggregations adhering to the interior pipe wall.

Sulfides

Some suspended black particles in a water sample as-drawn from a fire sprinkler piping system might be iron(II) sulfide. It can form when iron(II) reacts with sulfides generated by sulfate reduction. Treating a sample of iron(II) sulfide with drops of weak acid immediately produces an intense sulfurous odor from hydrogen sulfide gas that forms as hydrogen ions react with iron(II) sulfide. The same sulfurous odor sometimes accompanies water draining from piping, indicating the presence of hydrogen sulfide gas in the fire sprinkler piping system. The sulfurous odor has been termed bacterial halitosis [38c] when it results from sulfides produced by sulfate-reducing bacteria. Reaction of iron(II) sulfide with a weak acid makes it possible to dissolve iron(II) sulfide aggregations from the interior pipe wall during pipe cleaning operations.

Bicarbonates, Carbonates, and Alkalinity

Sometimes water introduced into fire sprinkler piping systems contains appreciable concentrations of dissolved bicarbonates and carbonates. Bicarbonates and carbonate concentrations are expressed as bicarbonate alkalinity (pH less than 8.3) and carbonate alkalinity (pH greater than 8.3) [13c]. Both can generate reactive hydroxyl ions via hydration and hydrolysis [24b,25]. Iron(II) reacts with bicarbonate ions to produce insoluble iron(II) carbonate if dissolved oxygen is scarce [9c,17d]. Iron(II) also can react with bicarbonate ions and abundant dissolved oxygen to produce insoluble iron(III) oxide and carbon dioxide gas [18a]. Moreover, iron(II) carbonate can react spontaneously with any dissolved oxygen in alkaline water and chemically transform to insoluble iron(III) oxide [17d].

Besides chemically combining with iron(II) and iron(III) ions, carbonates combine with dissolved calcium with increases in temperature to form insoluble scale, calcium carbonate. Consequently, hard waters of high alkalinity and/or abundant dissolved oxygen have the potential to generate massive aggregations of iron(II) and iron(III) corrosion residues, as well as calcium carbonate scale. Treating carbonate-containing residues with drops

of weak acid produces bubbles and foam as the carbonates decompose and release carbon dioxide gas. Such decomposition of carbonates makes it possible to dissolve carbonate residues from the interior pipe wall during pipe cleaning operations.

Some Characteristics of Insoluble Corrosion Residues

Massive aggregations of the insoluble corrosion residues discussed above can build up on the interior pipe wall [31,43]. Residues also show up in the fragile dome structure of tubercles [9c]. Gelatinous biofilms can grow amidst such aggregations. The largest aggregations in horizontal piping usually are in the five to seven o'clock zone, where twelve o'clock is at the top. Most of these residues are considered 'unpromising' as regards shielding steel piping from ongoing corrosion [17b].

Regions where aggregations of solid substances have built up on the interior pipe wall can be located and measured using nondestructive evaluation techniques [44,45]. Measurements can determine pipe wall thickness and thereby locate regions where corrosion has developed pits and craters that have reduced thickness to unacceptable values. Measurements also can be made on the exterior pipe surface to determine the thickness of aggregations built up on the interior pipe wall [45]. Photographic techniques can be used on drained and opened piping systems to make video images that facilitate evaluation of suspect regions by direct observation. Sometimes entire fire sprinkler piping systems are flushed with chemical substances, including weak acids and detergents, in an attempt to disrupt and remove aggregations of insoluble corrosion residues [46–48].

All of the insoluble corrosion residues described above are undesirable because they facilitate ongoing underdeposit corrosion [9b], and they increase pipe friction losses.

Pipe Friction Losses

Designers determine pipe friction losses using a Friction Loss Formula specified in NFPA 13 [11d]. This formula indicates that the frictional resistance increases exponentially with a linear decrease in the actual internal diameter of pipe. Consequently, the gradual build-up of insoluble corrosion residues and other aggregations on the interior pipe wall can increase pipe friction losses. For example, if internal diameter decreases from 50.8 to 44.5 mm (2–1.75 in.), calculation with the formula shows that pipe friction loss doubles. If internal diameter decreases from 25.4 to 19.1 mm (1–0.75 in.), pipe friction loss quadruples. Further analysis with the Friction Loss Formula demonstrates that the effect of corrosion residue

build-up on pipe friction loss is greater for small diameter pipe (25.4–50.8 mm (1–2 in.)) than for larger pipe.

Experience shows that corrosion residues and other aggregations do not build up uniformly around the interior pipe wall [31,43]. Although the Friction Loss Formula does not apply accurately to a nonuniform build-up, it is clear that the gradual build-up of uneven aggregations on the interior pipe wall reduces the actual internal diameter of the pipe and increases the pipe friction loss to a value greater than that calculated by designers from the actual internal diameter of uncorroded pipe.

An extreme case of pipe friction loss due to corrosion residues was reported in 1998 by the Iowa State Fire Marshal [49]. Investigators found that every sprinkler head in one wing of a building was plugged with ‘hardened, rust-colored granular material.’ The plugging material was interpreted to be residues from microbiologically influenced corrosion. A further interpretation is that these plugging residues contain insoluble oxides, hydroxides, and carbonates that resulted from the nonbiological precipitation processes described above.

As regards pinhole leaks, corrosion residues provide the temporary benefit of partially plugging the leaks. These corrosion residues also have the undesirable effect of promoting underdeposit corrosion processes [9b] that can grow a pinhole gradually, so that it eventually becomes a spraying leak.

CORROSION CONTROL MEASURES

Corrosion control measures intended to mitigate electrochemical corrosion inside pressurized, water-containing low-carbon steel fire sprinkler piping systems are listed below. These measures arise from the foregoing discussions of electrochemical science that underlie metal–water corrosion and microbiologically influenced corrosion as discussed earlier.

Minimize Dissolved Oxygen

Dissolved oxygen is an ingredient for oxygen corrosion and for acid–oxygen corrosion. Corrosion control with respect to dissolved oxygen involves: (1) minimizing the frequency of completely draining and recharging a piping system, (2) venting trapped air from high elevations in water-filled piping systems, (3) removing water from low elevations after hydrostatic testing and/or after trip-testing a dry piping system that is pressurized with compressed air. Water treatment engineers can inject into water being charged into a piping system a suitable oxygen scavenger that minimizes the concentration of dissolved oxygen. Limitations on corrosion inhibition measures such as introduction of a chemical oxygen scavenger

and those chemical methods discussed under the following three sub-sections are usually piping-system-specific. Such limitations should be brought to light in discussions among facilities managers, sprinkler contractors, and their technical advisors.

Elevate pH of Piping System Water

Public water supplies have pH in the range, 7.3–8.4. Acid corrosion of iron metal is not possible in water with pH of 8.3–8.5 because the hydrogen ions that cause acid corrosion are not present in this pH range [1c,17e]. Consequently, chemically treating water as it is being charged into a steel fire sprinkler piping system with chemicals that elevate and maintain pH between 8.3 and 8.5 should have the effect of blocking most acid corrosion. As regards safety of water so treated, pH of 8.3–8.5 falls in the drinking water pH range of 6.5–8.5 that is specified in the National Secondary Drinking Water Regulations [16]. Another benefit of maintaining pH in the range 8.3–8.5 is that sulfate-reducing bacteria are likely to be nearly inactive in this pH range [40]. Whatever diminished metabolic activity of sulfate-reducing bacteria occurs in this pH range generates bisulfide ions as a waste product [23c], which are likely to be less harmful as regards acid corrosion than sulfide ions that are generated at pH less than 7. Lastly, pH in this range tends to hinder the corrosive action of dissolved oxygen [6].

Remove Aggregations that Build up on Interior Pipe Wall

Aggregations include fabrication chips and filings, scale, sediments, and insoluble corrosion residues. Biofilms are aggregations of gelatinous substances in which communities of several types of microorganisms live. Regions where aggregations of insoluble inorganic material and biofilms build up on the interior pipe wall can be located and measured using nondestructive evaluation techniques such as ultrasound [44,45]. Ultrasonic measurements also can determine pipe wall thickness, thereby locating regions where corrosion has reduced thickness to unacceptable values.

Corrosion reactions occur promptly at fresh metal surfaces created during fabrication processes such as sawing and drilling. Consequently, removing metal chips and filings that accumulate inside the pipe during fabrication minimizes such accelerated corrosion. Removing chips and filings before pipe sections are installed also minimizes underdeposit corrosion [9b] that localizes corrosion to regions underneath or within aggregations. Lastly, removal of chips and filings that are oil-coated from lubricants used during sawing and drilling minimizes microbiologically influenced corrosion by bacteria that use hydrocarbon compounds for nutrition.

Circulating a solution of acidified, chlorine-based disinfectant or other kinds of disinfectants [12b,44,45] through a drained fire sprinkler piping system tends to disrupt and flush out aggregations on the interior pipe wall. Hypochlorite disinfectant provides hypochlorous acid molecules that can penetrate biofilms and annihilate bacteria that cause microbiologically influenced corrosion. Weak acidification of the flushing solution in the pH range of 5–6 promotes effective cleansing of most insoluble corrosion residues and also promotes disinfection without causing severe acid corrosion. Rinsing a cleansed piping system using a solution having pH around 8.3–8.5 with detergent added can counteract corrosive action of acid residue from the flushing solution and promote removal of any organic matter such as fabrication lubricants.

Minimize Hardness, Bicarbonate and Carbonate Alkalinity, Sulfate and Chloride Ion Concentrations

Chemically treating water as it is being charged into a fire sprinkler piping system so as to minimize hardness, bicarbonate and carbonate alkalinity, and sulfate and chloride ion concentrations can reduce the massive aggregations of corrosion residues that accrue inside piping filled with water containing substantial concentrations of these chemical species. Cost-effective chemical or physical processes that minimize troublesome concentrations of hardness, bicarbonate and carbonate alkalinity, and sulfate and chloride ions can be developed using present day knowledge of water treatment chemistry.

Protect Surfaces with Coatings

Continuous, adherent, non-porous surface coatings can prevent corrosive chemical species in water from contacting iron metal of the interior pipe wall [1d,17e]. For example, the zinc metal surface coating produced in ‘galvanizing’ processes, e.g., hot dipping, serves as a sacrificial material that corrodes preferentially to the underlying iron metal. A chemically stable iron oxide called ‘mill scale’ that forms at the elevated temperatures of heat treatment following pipe fabrication operations sometimes serves as a protective surface coating. These and other surface coatings are likely to be scraped away during piping system fabrication processes such as threading and cut grooving, and sawing and drilling. Corrosive waters can attack bare iron exposed in any region where surface coatings have deteriorated. Recoating a damaged region, perhaps with a nonreactive polymeric paint, minimizes exposure of iron metal to corrosive water.

Specify a Corrosion Allowance

Designers can contend with metal loss due to a water supply with unusual corrosive properties by specifying a corrosion allowance, i.e., by specifying ample pipe wall thickness that can be sacrificed to corrosion. A corrosion allowance does not stop corrosion, but it does increase the service time before corrosion causes undesirable consequences.

Heat Treat Cold Worked Metal

An undesirable consequence of threading and cut-grooving during piping system fabrication is localized cold working (plastic deformation) of iron metal. Iron–water corrosion reactions are localized and speeded up in deformed regions, as compared to reaction rates in undeformed regions [8]. Annealing or stress relief heat treatment of the cold worked region can minimize such corrosion reactions.

Use a Maintenance Log

A maintenance log establishes a useful month-to-month record of: (1) periodic repairs and construction modifications to a fire sprinkler piping system, (2) changes in the chemical composition of the water supply to a piping system, (3) periodic injections of water treatment chemicals such as oxygen scavengers, other corrosion inhibitors, and biocides, (4) results of nondestructive inspections that measure pipe wall thickness and locate regions of massive aggregations built up on the interior pipe wall, and (5) any other factors known to sprinkler contractors and facilities managers that influence the corrosion durability of pressurized, water-filled, dry, and pre-action fire protection systems.

Apply Biocides

Disinfected waters are likely to contain small concentrations of bacteria that can participate in corrosion processes. The Standard Plate Count of all the different kinds of microorganisms that are in a sample of disinfected water is likely to be in the range of 10–1000 colony-forming units. Given time, nutrients, and favorable chemical and physical conditions, bacteria of the types discussed in the section on Microbiologically Influenced Corrosion can multiply to concentrations 10–100 times higher than their original concentrations. Replacing nutrients such as hydrocarbon cutting oils and gasket lubricants with nonhydrocarbon substances is a strategy to starve sulfate-reducing bacteria of nutrients that facilitate such multiplication.

Water treatment engineers inject biocides into piping system water to destroy colonies of bacteria that aggregate in biofilms. Expertise [12b,37] is required to identify biocides that are lethal to suspect types of bacteria. Still further expertise [46–48] is required to ensure that the injected biocide reaches and penetrates all the biofilms inside the piping system.

ACKNOWLEDGMENTS

Piping system installers, managers at fire sprinkler contractors, and facilities managers provided perspective on many of the practical aspects of fire sprinkler piping system fabrication and operation mentioned in this article. Ms Brenda Little provided tutorial information about biofilms and bacteria that participate in microbiologically influenced corrosion. Mr Myron Shenkiryk provided several technical discussions and references to the literature about corrosion of fire sprinkler piping. Mr Jan Kilduff provided illuminating technical discussions about hydration and hydrolysis. Mr Roland Huggins assisted with references to NFPA 13 and to the literature about corrosion of fire sprinkler piping. Mr Mike Gorman provided information about state-of-the-art ultrasonic testing. Mr Robert Lauber provided discussions about practical aspects of plumbing systems and reviews of early drafts of the manuscript. The management of Converse Consultants/Las Vegas, Nevada provided essential office facilities for manuscript preparation.

REFERENCES

1. Speller, F.N., *Corrosion – Causes and Prevention*, Third Edition, McGraw-Hill Book Company, Inc., New York, 1951.
 - a. “Prevention of Corrosion in Closed Water Systems by Removal of Dissolved Gases,” Vol. 99, No. 10, Chapter 9, pp. 414–415.
 - b. “Influence of Factors External to the Metal – Classification of Corrosion,” Chapter 5, Figure 39 – “Solubility of Oxygen in Water at Various Temperatures and Pressures,” p. 167.
 - c. “Influence of Factors External to the Metal – Classification of Corrosion,” Chapter 5, Section 2 – Electrolytes in Solution/Alkalies, pp. 194–199.
 - d. “Prevention of Corrosion Under-Water,” Chapter 8, Sub-section on “Protective Coatings Resulting from Water Treatment,” pp. 382–389.
2. Rittenhouse, R.C., “Program Reduces Fire Protection System Corrosion,” *Power Engineering*, Vol. 99, No. 10, October 1995, pp. 21–23.
3. Notarianni, K. and Jackson, M.A., “Material Degradation – Corrosion, Scale Build-Up, and Sedimentation/Steel,” In: Parts 3.1 and 3.3 in *Comparison of Fire Sprinkler Piping Materials: Steel, Copper, Chlorinated Polyvinyl Chloride and Polybutylene*, in Residential and Light Hazard Installations, NISTR 5339, National Institute of Standards and Technology, Gaithersburg, MD, June 1994, pp. 8–10.

4. Evans, U.R., "Electrochemical Corrosion," In: Chapter IV in *The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications*, Edward Arnold Ltd., London, 1960, pp. 87–132.
5. Pourbaix, M., "Introduction to Corrosion," In: Chapter 1 in *Lectures on Electrochemical Corrosion*, Plenum Press, New York, 1973, pp. 15–19.
6. Scully, J.C., "Aqueous Corrosion," In: Chapter 2 in *The Fundamentals of Corrosion*, Third Edition, Pergamon Press, New York, 1990, pp. 54–129.
7. Oxtoby, D.W., Gillis, H.P. and Nachtrieb, N.H., *Principles of Modern Chemistry*, Fourth Edition, Saunders College Publishing-Harcourt Brace College Publishers, New York, 1999.
 - a. Sub-chap. 12.6, "Corrosion and its Prevention," pp. 430–432.
 - b. Sub-chap. 12.3, "The Gibbs Free Energy and Cell Voltage," pp. 411–418.
 - c. "Standard Reduction Potentials At 25°C," Appendix E, pp. A-38 to A-39.
8. Kotz, J.C. and Purcell, K.F., "Corrosion: An Example of Electron Transfer," In: Sub-chapter 19.8 in *Chemistry & Chemical Reactivity*, Sanders College Publishing-Holt, Rinehart and Winston, Orlando, Florida, 1987, pp. 734–735.
9. Herro, H.M. and Port, R.D., *The NALCO Guide to Cooling Water Systems Failure Analysis*, McGraw-Hill, Inc., New York, 1993.
 - a. "Crevice Corrosion/Chloride and Sulfate Assisted Hydrolysis," Chapter 2, pp. 15–16.
 - b. "Underdeposit Corrosion," Chapter 4, pp. 67–96.
 - c. "Tuberculation/Structure and Chemical Composition of Tubercles," Chapter 3, pp. 37–41 and Figure 3.4, p. 40.
 - d. "Tuberculation/Chloride-assisted Hydrolysis and Acidity Underneath Tubercles," Chapter 3, pp. 41–42.
 - e. "Acid Corrosion," Chapter 7, pp. 159–183.
 - f. "Oxygen Corrosion," Chapter 5, pp. 97–118.
 - g. "Biologically Influenced Corrosion/Acid Producers," Chapter 6, p. 122.
10. Davis, J.R., ed., "Forms of Corrosion: Recognition and Prevention," In: Chapter 4 in *Corrosion – Understanding The Basics*, ASM International, Materials Park, Ohio, 2000, pp. 114–120.
11. National Fire Codes, NFPA 13, *Standard for the Installation of Sprinkler Systems*, 1996 Edition, National Fire Protection Association, Batterymarch Park, Quincy, MA 02269.
 - a. Sub-paragraph 13:2-3, Table 2-3.1, "Pipe or Tube Materials and Dimensions," pp. 13–12.
 - b. Paragraph 13:4–14.4.2, "Protection of Piping against Corrosion," pp. 13–55.
 - c. Sub-paragraph 13:4–14.4.2.2, "Protection of Piping against Corrosion," pp. 13–55.
 - d. Sub-paragraph 13:6–4.2.1, "Friction Loss Formula."
12. Bsharat, T.K., "Detection, Treatment and Prevention of Microbiologically Influenced Corrosion in Water-Based Fire Protection Systems," Technical Report of the National Fire Sprinkler Association, Inc, 4 Robin Hill Corporate Park, Patterson, New York, June 1998, 16 pp.
 - a. Basic Corrosion, Figure 1 illustrates carbon steel being oxidized into its ionic state, p. 4.
 - b. Appendix A – Examples of Biocides: Chlorine, Iodine, Hydrogen Peroxide, Ozone, p. 12.
13. Kremmer, F.N., ed., *The NALCO Water Handbook*, Second Edition, McGraw-Hill Book Company, New York, 1988.
 - a. "Corrosion Control"/Sub-section "Temperature," Chapter 20, p. 20.8.
 - b. "The Water Molecule," Chapter 1, Figure 1.5, p. 1.6.
 - c. "Water Chemistry and Interpretation of Water Analyses," Chapter 4, pp. 4.5–4.12.
 - d. "Oxidation-Reduction," Chapter 19, Table 19.2, p. 19.9.
 - e. "Control of Microbial Activity/Oxidizing Biocides – Nonoxidizing Biocides," Chapter 22, pp. 22.8–22.16.
 - f. "Control of Microbial Activity/Oxidizing Biocides," Chapter 22, Figure 22.6, p. 22.9.
 - g. "Control of Microbial Activity," Chapter 22, pp. 22.1–22.22.
 - h. "Control of Microbial Activity," Chapter 22, Table 22.1, p. 22.2.
 - i. "Oxidizing Biocides," Chapter 22, p. 22.11.

14. Bockris, J. and Reddy, A.K.N., "Electrochemistry"/Sub-section "Some Characteristics of Electrodes," In: Chapter 1 in *Modern Electrochemistry-Ionics*, Second Edition, Plenum Press, New York, 1998, p. 5.
15. Duranceau, S.J., Poole, J. and Foster, J.V., "Wet-pipe Fire Sprinklers and Water Quality," *Journal AWWA*, Vol. 91, No. 7, pp. 78–90.
16. National Secondary Drinking Water Regulations, In: *Non-Enforceable Guidelines Regulating Contaminants That May Cause Cosmetic Effects*, U.S. Environmental Protection Agency, Office of Water, <http://www.epa.gov/safewater/mcl.html>, 04/17/2002, p. 8.
17. Talbot, D. and Talbot, J., "Corrosion of Iron and Steels/Rusting," In: Chapter 7 in *Corrosion Science and Technology*, CRC Press LLC, Boca Raton, Florida, 1998, pp. 234–239.
 - a. Sub-chap. 7.2.1.2: "Iron(II) Oxides, Hydroxides, and Derivatives," pp. 235–236.
 - b. Sub-chap. 7.2.2.1: "Fresh Waters," pp. 236–237.
 - c. Sub-chap. 7.2.1.1: "Iron (III) Oxides, Hydroxides, and Derivatives," pp. 234–235.
 - d. Sub-chap. 7.2.1.2: "Formation and Transformation of Iron(II) Carbonate in Hard Water," p. 236.
 - e. Sub-chap. 7.2.2.3: "Alkaline Waters," p. 238.
18. Brown, T.L., Lemay, Jr., H.E. and Bursten, B.E., *Chemistry – The Central Science*, Sixth Edition, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1994.
 - a. "Metals and Metallurgy/Formation of Iron(III) Oxide," Chapter 24, p. 914.
 - b. "Acid-Base Equilibria/Hydrolysis of Metal Ions," Chapter 16, pp. 606–607.
19. Basalo, C., ed., "Principles of Cathodic Protection," In: Chapter 1 in *Water and Gas Mains Corrosion, Degradation and Protection*, Ellis Horwood LTD., London, 1992, pp. 299–308.
20. Rose, M., *Denver Water's 2003 Treated Water Quality Summary Report*, Denver Water's Water Quality Laboratory, 6100 W. Quincy Avenue, Denver, Co 80235, 25 pp.
21. Van Wagenen, S., *2003 Raw & Finished Water Summary – SNWS Raw Water Inorganics, and SNWS Finished Water Inorganics*, Southern Nevada Water System, 243 Lakeshore Road, Boulder City, Nevada 89005.
22. Sedricks, A.J., "Electrochemistry," In: Chapter 3 in *Corrosion of Stainless Steels*, Wiley-Interscience, John Wiley & Sons, Inc., New York, 1996, p. 90.
23. Drever, J.I., *The Geochemistry of Natural Waters – Surface and Groundwater Environments*, Third Edition, Prentice Hall, Upper Saddle River, NJ, 1997.
 - a. "The Carbonate System and pH Control/Alkalinity and Titration Curves," Chapter 3, p. 46.
 - b. "The Carbonate System and pH Control"/Sub-section "Calcium Carbonate Solubility," Chapter 8, p. 55.
 - c. "Redox Conditions in Natural Waters"/Sub-section "Respiration and Decay"/Part 3 – "Sulfate Reduction," Chapter 8, pp. 161–162.
24. Frey, P.R., *College Chemistry*, Sixth Printing, Prentice Hall, Inc., New York, 1954, pp. 404–405.
 - a. "Water; Hydrogen Peroxide" – Chapter 21/"Softening Water by Precipitation of Calcium and Magnesium Ions" – Sub-chapter 21.13," pp. 331–333.
 - b. "The IVA Group" – Chapter 25/"Carbonic Acid and its Salts" – Sub-section 25.13, pp. 404–405.
25. Vogel, A.I., "The Theoretical Basis of Quantitative Inorganic Analysis – The Hydrolysis of Salts," In: Chapter 1 in *A Text-Book of Quantitative Inorganic Analysis*, Third Edition, Longmans, Green & Co Ltd., Bungay, Suffolk, Great Britain, 1961, pp. 27–33.
26. Pauling, L., "Acids and Bases/The Titration of Weak Acids and Bases/The Hydrolysis of Salts of Metals Other than the Alkalies and Alkaline Earths," In: Chapter 21, Sub-chapter 21-4 in *General Chemistry – An Introduction to Descriptive Chemistry and Modern Chemical Theory*, W.H. Freeman and Company, San Francisco, 1950, pp. 446–447.

27. Jones, L. and Atkins, P.W., Chemistry – Molecules, Matter, and Change, Fourth Edition, W.H. Freeman and Company, New York, 2000.
 - a. “Aqueous Equilibria”/“Ions as Acids and Bases,” Chapter 16/Sub-chapter 16.1, pp. 700–701.
 - b. “The Elements: The Last Four Main Groups”/“Sulfur Oxides and Oxoacids,” Chapter 20/Sub-chapter 20.7, p. 898.
28. Rieger, P.H., “Corrosion – Reaction of a Metal with Air-Saturated Water,” In: Chapter 7 in Electrochemistry, Second Edition, Chapman and Hall, New York, 1994, p. 416.
29. Staff of Betz Laboratories, Inc., Betz Handbook of Industrial Water Conditioning, Ninth Edition, Betz Laboratories, Inc., Trevose, PA, 1991.
 - a. “Preboiler and Boiler Corrosion Control,” Chapter 11, p. 84.
 - b. “Analytical Methods and Equipment-Chlorine, Free,” pp. 321–322.
30. Douglas, B., McDaniel, D. and Alexander, J., “The Chemistry of Some Nonmetals”/“Redox Chemistry of Sulfur and Selenium,” In: Chapter 16/Sub-chapter 16.3.8 in Concepts and Models of Inorganic Chemistry, Third Edition, John Wiley & Sons, New York, 1994, pp. 786–787.
31. Clark, B.H., “Microbiologically Influenced Corrosion in Fire Sprinkler Systems,” Fire Protection Engineering, No. 9, Winter 2001, pp. 14–22.
 - a. Figure titled, “Obstructive Growth from MIC,” p. 15.
 - b. Figure titled, “Interior Biofilm Buildup with Clearly Seen Corrosion Cell Tubercle Shell,” p. 16.
32. Pope, D.H., “Microbiologically Influenced Corrosion in Fire Protection Sprinkler Systems,” Technical Report of Bioindustrial Technologies, Inc., 175 Clover, Suite 2, Bayfield, Colorado, May 1999, 9 pp.
33. Little, B.J., Ray, R.I. and Pope, R.K., “The Relationship between Localized Corrosion and the Biological Sulfur Cycle – A Review,” J. Corrosion, Vol. 56, No. 4, 2000, pp. 433–443.
 - a. Figure 1, “Strata within a Typical Biofilm and Possible Reactions within the Strata.”
34. Singleton, P., Bacteria in Biology, Biotechnology and Medicine, Fourth Edition, John Wiley & Sons, New York, 1997.
 - a. “The Bacterial Cell/Capsules and Slime Layers,” Chapter 2.2.11, p. 24.
 - b. “Metabolism I: Energy,” Chapter 5, pp. 62–86.
 - c. “The Bacterial Cell,” Chapter 2, pp. 6–34.
 - d. “The Bacterial Cell/Cytoplasmic Membrane,” Chapter 2.2.8, p. 15
 - e. “The Bacterial Cell/Cell wall,” Chapter 2.2.9, pp. 17–23.
35. Tortora, G.J., Funke, B.R. and Case, C.L., Microbiology – An Introduction, Fifth Edition, The Benjamin Cummings Publishing Company, Inc., Redwood City, CA, 1995.
 - a. “Microbial Metabolism,” Chapter 5 and Sub-sections titled “Energy Production” & “Oxidation-Reduction,” p. 111.
 - b. “Functional Anatomy of Prokaryotic and Eukaryotic Cells/The Bacterial Cell Wall,” Chapter 4, pp. 77–79; Fig. 4.12.
 - c. “Functional Anatomy of Prokaryotic and Eukaryotic Cells,” Chapter 4, pp. 70–102; Fig. 4.5/p. 74; Fig. 4.20/p. 91.
36. Stanier, R.Y., Ingraham, J.L., Wheelis, M.L. and Painter, P.R., The Microbial World, Fifth Edition, Prentice-Hall, Englewood Cliffs, New Jersey, 1986.
 - a. “Microbial Metabolism,” Chapter 4, pp. 78–101.
 - b. “The Chemautotrophic and Methophilic Eubacteria/The Iron Bacteria/*Thiobacillus ferrooxidans*,” Chapter 16, p. 391.
 - c. “The Chemautotrophic and Methophilic Eubacteria/The Iron Bacteria/*Gallionella*,” Chapter 16, p. 390.
 - d. “Gram-Negative Anaerobic Eubacteria/The Sulfur-Reducing Bacteria,” Chapter 20, pp. 459–463.
 - e. “Gram-Negative Anaerobic Eubacteria/The Sulfur-Reducing Bacteria,” Chapter 20, Figure 20.9, p. 461.

37. Alcamo, I.E., Fundamentals of Microbiology, Sixth Edition, Jones and Bartlett Publishers, Inc., Boston, MA, 2001.
 - a. "Bacterial Metabolism," Chapter 5, pp. 126–159.
 - b. "Oxidative Phosphorylation/Electron Transport," Chapter 5, pp. 136–137.
 - c. "A Comparison of Two Key Aspects of Cellular Metabolism," Table 5.1, p. 127.
 - d. "Chemical Control of Microorganisms," Chapter 22, pp. 698–721.
 - (1) "Important Chemical Agents – Halogens," Chapter 22.2, pp. 704–707.
 - (2) "Other Chemical Agents – Gluteraldehyde," Chapter 22.3, p. 714.
38. Postgate, J., The Outer Reaches of Life, Cambridge University Press, Cambridge, England, 1994.
 - a. "Living on Minerals/*Thiobacillus ferrooxidans*," Chapter 8, pp. 101–102.
 - b. "Living on Minerals/*Gallionella*," Chapter 8, pp. 99–101.
 - c. "Life without Oxygen/Bacterial Halitosis," Chapter 6, pp. 82–84.
39. Ryan, K.J., ed., "Clostridia, Gram-negative Anaerobes, and Anaerobic Cocci/Clostridia," In: Chapter 18 in Sherris Medical Microbiology, Third Edition, Appleton & Lange, East Norwalk, CT, 1994, pp. 295–304.
40. Starkey, R.L. and Wight, K.M., "Anaerobic Corrosion of Iron in Soil," Journal Series Paper of the New Jersey Agricultural Experimental Station, Rutgers University, New Brunswick, New Jersey, 1945, p. 8 and Figure 3, p. 10.
41. Atkins, P.W., "The Elements Scandium Through Nickel," In: Sub-chapter 21.2/Figure 21.12 in General Chemistry, Scientific American Books, W.H. Freeman and Company, New York, 1989, p. 773.
42. Weiser, H.B., The Hydrous Oxides, First Edition, McGraw-Hill, New York, 1926, pp. 34–38.
 - a. "Introduction," pp. 1–2.
 - b. "The Hydrous Oxides of Iron/Hydrous Ferric Oxide," Chapter 2, pp. 34–38.
43. Christ, B.W., "Corrosion Processes Inside Steel Fire Sprinkler Piping," Fire Protection Engineering, No. 27, Summer 2005, pp. 18–24; Hurley, M., ed., Society of Fire Protection Engineers, 7315 Wisconsin Avenue, Suite 1225 West, Bethesda, Maryland, USA.
44. Bray, D.E. and Stanley, R.K., "Pipe Inspection/Sub-section 8–9.4," In: Chapter 8 in Nondestructive Evaluation, A Tool in Design, Manufacturing and Service, CRC Press, Boca Raton, FL, 1997, p. 127.
45. Gorman, M., MICSCAN Services for FPS Inspection, Digital Wave Corporation, 11234A East Caley Avenue, Englewood, Colorado 80111, USA (info@digitalwavecorp.com).
46. Mitigating MIC, Sprinkler Age, Vol. 17, Sept. 1998, pp. 26–27
47. Ratlof, J., The Bugs of Rust. Science News, Vol. 128, July 1985, pp. 42–44.
48. Farmerie, J., "Treating Closed Water Loops," Plumbing Engineer, Vol. 32, No. 5, May 2004, pp. 32–34.
49. Marshall, R., "Iowa Authorities Suspect MIC," Sprinkler Age, Vol. 17, September 1998.