

Internal Corrosion Control in Water Distribution Systems

Second Edition



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Internal Corrosion Control in Water Distribution Systems

Second Edition



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Manual of Water Supply Practices—M58, Second Edition

Internal Corrosion Control in Water Distribution Systems

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Project Manager: Melissa Valentine
Cover Art: Melanie Yamamoto
Production: Glacier Publishing Services, Inc.
Manuals Specialist: Sue Bach

Library of Congress Cataloging-in-Publication Data has been applied for

Names: Giani, Richard E., author. | Hill, Christopher P. Internal corrosion control in water distribution systems. | American Water Works Association.

Title: M58--internal corrosion control in water distribution systems / by Richard E. Giani.

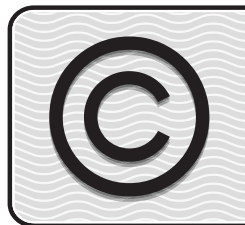
Other titles: Internal corrosion control in water distribution systems

Description: Second edition. | Denver, CO : American Water Works Association, [2017] | Earlier edition: Internal corrosion control in water distribution systems / [by Christopher P. Hill, Abigail F. Cantor]. c2011. | Includes bibliographical references and index.

Identifiers: LCCN 2017002003 | ISBN 9781625762023

Subjects: LCSH: Water-pipes--Corrosion. | Drinking water--Contamination. | Water--Distribution. | Corrosion and anti-corrosives--Testing.

Classification: LCC TD491 .G49 2017 | DDC 628.1/44--dc23 LC record available at <https://lcn.loc.gov/2017002003>



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ISBN-13 978-1-62576-202-3

eISBN-13 978-1-61300-404-3

Printed in the United States of America
American Water Works Association
6666 West Quincy Avenue
Denver, CO 80235-3098
awwa.org



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Preface



This is the second edition of AWWA Manual M58, *Internal Corrosion Control in Water Distribution Systems*, prepared by the Distribution System Water Quality Committee. It provides practical guidance to aid public water systems in designing, implementing, and maintaining an effective corrosion control program. This manual is intended to help readers understand the factors that influence corrosion, assess corrosion-related impacts, and develop a strategy to implement and maintain effective corrosion control in the water distribution system.

The increased focus surrounding corrosion-related water quality and infrastructure impacts in water distribution systems has generated new research and information in this area. As such, this update of AWWA Manual M58 is a reflection of those advancements, including changes in regulatory requirements, the addition of pertinent case studies and examples, and incorporation of other new material reflective of changes in the industry. In the future, the AWWA Distribution System Water Quality Committee will continue to update this manual as new issues and questions arise.

Editor's note: Throughout this manual, references are made to Awwa Research Foundation (AwwaRF). In 2009, the foundation changed its name to Water Research Foundation. Any publication prior to 2009 will reflect the foundation's original name.

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Acknowledgments



This second edition of AWWA Manual M58 was written through the persistent, dedicated work of the following authors:

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S. Randtke, University of Kansas, Lawrence, Kans.
R. Slabaugh, Arcadis, Indianapolis, Ind.
V. Speight, University of Sheffield, Sheffield, U.K.
E. Turner, North Texas Municipal Water District, Wylie, Texas

The authors would like to acknowledge the support of the following organizations in preparing this manual:

American Water Works Association, Denver, Colo.
Arcadis, Indianapolis, Ind., and Tampa, Fla.
CH2M, Lees Summit, Mo.
Confluence Engineering Group, LLC, Seattle, Wash.
Process Research Solutions, LLC, Madison, Wis.

The authors would also like to acknowledge the following individuals who provided editorial and technical comments:

J. Cuppett, Water Research Foundation, Denver, Colo.
L. Furatian, University of British Columbia, Vancouver, B.C.
M. Horton, United States Pipe and Foundry Company, Bessemer, Ala.
P. Kwan, HDR Engineering, Inc., Seattle, Wash.
M. Larsen, Kennedy/Jenks Consultants, Federal Way, Wash.
I. Zhu, Evoqua Water Technologies, Warrendale, Pa.

The following individuals provided peer review of this manual. Their knowledge and efforts are gratefully appreciated:

F. Lemieux, Health Canada, Ottawa, Ont.

Q. Muylwyk, CH2M, Toronto, Ont.

M. Roberts, Hazen and Sawyer, Greensboro, N.C.

M. Rodgers, Cleveland Division of Water, Cleveland, Ohio

K. Smith, City of Houston, Houston, Texas

J. Swertfeger, Greater Cincinnati Water Works, Cincinnati, Ohio

Chapter **1**

Overview of Internal Corrosion Impacts in Drinking Water Distribution Systems

Christopher P. Hill, Arcadis

INTRODUCTION

Prior to developing a corrosion control program, it is important to first gain an understanding of the factors that influence internal corrosion and metal release in drinking water distribution systems. Afterward, implementation of an effective corrosion control program can be accomplished in eight steps (Table 1-1).

Selection of an effective corrosion control strategy is not a one-time event. Changes in source water quality, treatment, distribution, operational, or regulatory changes may require a system to reevaluate, revise, optimize, or restore a corrosion control program. To assist the reader in navigating the process described in Table 1-1, this manual is organized accordingly.

PURPOSE OF THIS MANUAL

Internal corrosion of drinking water distribution and home plumbing systems has long been a recognized issue facing the drinking water industry—one that has many health, water quality, and economic implications.

Table 1-1 Eight steps to implementing an effective corrosion control program

Step	Discussed in Chapter(s)
1. Develop an understanding of the general concepts behind internal corrosion and metal release in drinking water distribution systems	1, 2
2. Determine the extent and magnitude of corrosion	3
3. Determine the possible causes of corrosion	2, 3
4. Assess corrosion control alternatives	4
5. Develop a corrosion control strategy	4, 5
6. Implement a corrosion control program	3, 6
7. Monitor the effectiveness of the corrosion control program	3, 6
8. Optimize the corrosion control program	5, 6

This manual was written with the intent to provide a practical overview of internal corrosion issues, to identify appropriate corrosion response and control methods, and to develop corrosion control monitoring programs. It is not intended to provide detailed summaries of corrosion chemistry. References to additional resources are given where the reader might find more detailed information useful.

Although this manual briefly touches on internal corrosion of nonmetallic pipe surfaces, such as asbestos–cement and cement mortar–lined ductile- or cast-iron pipe, it primarily focuses on corrosion of metal pipe surfaces, solders, and plumbing fixtures, such as those composed of lead, copper, and iron. For the purposes of this manual, the term *corrosion* refers not only to the electrochemical phenomenon that causes metal loss from pipe surfaces but also to the dissolution of existing pipe scales and corrosion by-products. Internal corrosion—that is, corrosion on the interior surface of metal pipes and fixtures—is the focus of this manual because of the potential for metal release to adversely impact distributed water quality.

CUSTOMER AND INFRASTRUCTURE IMPACTS OF INTERNAL CORROSION

Internal corrosion can cause degradation of water quality, infrastructure performance and structural failures, and scaling and reequilibration issues. It may have substantial economic impacts on water utilities and consumers alike. This section discusses the most common issues resulting from internal corrosion of drinking water distribution and home plumbing systems.

Water Quality Deterioration

Internal corrosion of distribution system piping and home plumbing may cause several water quality problems, including potential health concerns, discoloration, and taste and odor issues. These problems are primarily the result of corrosion of metal pipe surfaces, pipe solder, and plumbing fixtures or dissolution of existing pipe scales. However, some problems may be attributable to corrosion of nonmetallic system components (e.g., increases in asbestos concentrations).

Health concerns. The majority of the health concerns associated with internal corrosion are related to the release of trace metal concentrations (lead, copper, cadmium, etc.) from corroding metal surfaces (ATSDR 2007). However, corrosion can affect the ability to maintain a disinfectant residual in the distribution system, which may result in environments suitable for biofilm growth that may harvest pathogens, such as *Legionella* and various mycobacteria. The potential health concerns related to increased metal concentrations



Courtesy of DC Water

Figure 1-1 Red-water sample from a US distribution system

in drinking water are discussed further in the “Regulatory Impacts” section later in this chapter.

Color. Many of the color issues typically encountered in drinking water are attributable to internal corrosion (Kirmeyer et al. 2000a, 2000b). Corrosion of cast-iron pipe or dissolution of existing scale on cast-iron pipe may result in rust-colored water or red water as a result of the presence of ferric iron (Fe(III)). Red water can stain laundry and plumbing fixtures.

Red water (Figure 1-1) may occur as a result of “hydraulic entrainment” (i.e., the suspension and transport of loose corrosion deposits resulting from changes in flow or direction of flow) or “iron uptake” (i.e., the release of ferrous ions at the pipe surface and subsequent oxidation to ferric iron and precipitation in the bulk water) (Smith et al. 1998). Alternating periods of stagnation, anaerobic conditions, and temperature have been observed to cause red water, as have significant changes in alkalinity and chlorine residual (oxidation–reduction potential [ORP]). Maintaining consistent water quality and maintaining conditions that produce a hard iron scale are critical to minimizing the potential for red water (Smith et al. 1998, Reiber 2006).

Iron corrosion may also result in yellow or black water, which is a consequence of the presence of ferrous iron (Fe(II)). Ferrous iron may occur in waters with low dissolved oxygen concentrations (Kirmeyer et al. 2000a, 2000b). Black water may also be the result of the presence of manganese (Mn) in source waters or contribution from chemicals added during treatment, such as iron-based coagulants.

Copper corrosion may result in blue or green water, which can also stain bathroom fixtures and hair. Blue water may be a consequence of the presence of either dissolved or particulate copper corrosion by-products. Dissolved copper by-products are primarily the result of low pH and can usually be eliminated by raising the pH to above 7.5 (Edwards et al. 2000). Hard, high-alkalinity groundwaters are particularly aggressive toward copper materials (Schock and Lytle 2011). Edwards et al. (1999) found that high-alkalinity waters (>74 mg/L as calcium carbonate) produced the highest 90th-percentile copper levels at pH <7.8.

However, it is often more difficult to determine the cause of particulate copper corrosion by-products, which are found in many home plumbing systems. Particulate copper

corrosion by-products are thought to be primarily the result of microbiological, chemical, or physical factors, or some combination of factors that frequently result in pitting corrosion and/or pipe failure in addition to blue water (Edwards et al. 2000, Bremer et al. 2001).

Gray or black water may also be attributable to hot water heaters. Corrosion of zinc in galvanized piping may result in a milky appearance (Kirmeyer et al. 2000a, 2000b).

Taste and odor. Dissolved and particulate iron may cause taste and odor issues at low concentrations. The presence of iron has resulted in metallic taste (Khiari et al. 2002). In addition to metallic taste, cast-iron corrosion may also produce musty tastes and odors (Kirmeyer et al. 2000a, 2000b). Aluminum and zinc may contribute to an astringent mouthfeel, and zinc may also result in a sour taste. Reactions of disinfectants with cement–mortar linings in ductile-iron pipe may also result in astringent, oily (rancid), pine, and phenolic odors (Khiari et al. 2002). High pH may cause the release of phenols from corroding asbestos–cement pipe, which can react with chlorine to form chlorophenols (Kirmeyer et al. 2000a, 2000b).

Infrastructure Impacts

In addition to affecting water quality, internal corrosion may also impact distribution and plumbing infrastructure. Most notably, internal corrosion may result in failures of home plumbing systems, causing extensive property damage. Deterioration of distribution system piping and valves as well as other in-line devices may also result from corrosion.

Home plumbing failures. The most significant home plumbing failures that occur because of internal corrosion are copper pitting and pinhole leaks. Pitting corrosion, though not well understood, not only damages copper plumbing, but the associated leakage may also cause substantial damage to homes and result in mold growth and other issues that may pose health concerns (Edwards 2004). Table 1-2 summarizes the conditions under which potential copper corrosion has been traditionally thought to occur.

In addition to pitting corrosion, microbiologically influenced corrosion (MIC) of copper piping may also cause pitting and failure of home plumbing (Cantor et al. 2003, 2006) and MIC is often overlooked as a contributor to corrosion of plumbing systems. MIC is more likely to occur in plumbing systems with long stagnation times, in sulfide-containing waters, and in areas in which there is little to no disinfectant residual remaining (Jacobs et al. 1998, Bremer et al. 2001, Cantor et al. 2003).

Distribution system failures. Corrosion of distribution system piping may lead to pipe and valve failures resulting in increased water losses. In areas of low or negative pressure, inflow and infiltration are possible, as are bacterial and other contamination from surrounding soils and groundwaters. Failure of corroded valves may also cause operational issues, such as the inability to isolate water mains in the event of a line break, loss of pressure, reduced ability to conduct distribution flushing, and creation of stagnant sections or areas of low flow in the distribution system (e.g., if a valve stem breaks in the closed position). Failures of meters and other in-line devices may reduce system revenues because of inaccurate meter readings and may minimize the ability to accurately determine water loss or identify main breaks.

Scaling and Reequilibration

Scaling and reequilibration are two key factors that may impact corrosion and system performance, reequilibration being the transition period following a change in distribution system water quality and lasting until equilibrium is re-established. Formation of protective metal scales is the primary corrosion control mechanism regardless of the technology employed. For example, when pH and alkalinity adjustment are used as the primary lead control strategy, the objective is to form metal solids (e.g., lead carbonate and lead oxides)

Table 1-2 Summary of potential copper corrosion issues, causes, and solutions

Characteristic of Corrosion	Type of Corrosion			
	Uniform Corrosion	Type I Pitting (Cold Water)	Type II Pitting (Hot Water)	Type III Pitting (Soft Water)
Pit shape	No pits	Deep and narrow	Narrower than Type I	Wide and shallow
Type of problem present with corrosion	Blue or green water, high by-product release	Pipe failure	Pipe failure	Blue water, voluminous by-product releases, pipe blockage
Scale morphology on attacked surface	Tarnished copper surface or loose powdery scale	Underlying Cu_2O with overlying malachite, calcite, or other basic copper salts, occasionally CuCl underlies Cu_2O	Underlying Cu_2O with overlying bronchantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$), some malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$)	Underlying Cu_2O with overlying bronchantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$), some malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$)
Water quality	Low pH (<7.2) or waters with high alkalinity (>250 mg/L)	Hard, cold well waters between pH 7.0 and 7.8, high sulfate relative to chlorides and bicarbonate, high CO_2	Hot waters, pH <7.2, high sulfate relative to bicarbonate, occasional Mn deposits	Soft waters, pH >8.0
Initiating factors	None noted	Stagnation early in pipe life, deposits within pipe such as dirt or carbon fines, high free chlorine residuals, water softeners, residual aluminum carryover from coagulation process	Higher temperatures, high free chlorine residuals, residual aluminum carryover from coagulation process	Stagnation early in pipe life, pH >8.0, residual aluminum carryover from coagulation process, low free chlorine residual
Mitigating factors and treatments	Reduce alkalinity and raise pH or use orthophosphate	Increase bicarbonate and raise pH	Raise pH and/or increase bicarbonate	Avoid stagnation early in pipe life, increase hardness and alkalinity, elevate chlorine residual to >0.5 mg/L

Source: Adapted from Edwards et al. 1994

on the pipe surface and thereby prevent corrosion, or dissolution, of lead. Similarly, the objective of orthophosphate addition is the formation of a lead phosphate layer (Vik et al. 1996).

Controlling the type of scale formed and subsequently maintaining the stability of those scales are key to an effective corrosion control program. Iron scales, for example, are present in either the ferrous (Fe^{2+}) form or ferric (Fe^{3+}) form. Ferrous iron scales are much softer than ferric iron scales and are more likely to contribute to red water (Sarin et al. 2000, Reiber 2006). Creating conditions in which harder ferric iron scales are formed and maintained is ideal to maintaining water quality.

After a protective scale is formed in distribution piping or home plumbing, maintaining scale stability is essential to effective corrosion control treatment. Changes in distribution system water quality may result in reequilibration of existing scales causing red water, increased tap lead or copper concentrations, or other issues.

For example, in 2000, the Washington Aqueduct (Washington, D.C.) switched from free chlorine to chloramine to reduce disinfection by-product concentrations in its

customer agencies' systems. As a result of this adjustment, the ORP of the finished water changed, causing a shift in the speciation of the existing lead scales and elevated lead concentrations in the District of Columbia Water (DC Water) service area (USEPA 2007). The conversion to chloramine was just one factor that contributed to the lead release. Many utilities operating chloraminated systems have not experienced similar results.

Economic Issues

Internal corrosion may have numerous economic or cost impacts. Excess corrosion can result in tuberculation or excess calcium precipitation, reducing hydraulic capacity, increasing pumping costs, and reducing fire flow capabilities. Failure of distribution system piping and home plumbing may necessitate costly repairs, not only of failed piping but also of other assets damaged because of the pipe failure.

There are also more subtle economic issues associated with corrosion. Increased lead and copper levels may not only result in negative publicity but may also have the potential to bring about litigation. The costs associated with legal action may be substantial. Water quality issues resulting from corrosion (e.g., color, taste and odor, and metals release) may also cause negative customer perceptions and not only affect (reduce) usage but also cost utilities potential future customers.

REGULATORY IMPACTS

Lead and Copper

In the United States, the Lead and Copper Rule (LCR) was promulgated in 1991 with the purpose of reducing drinking water exposures to lead and copper (56 FR 26460; *Federal Register* 1991a). The purpose of the LCR is to protect public health by minimizing lead and copper levels in drinking water, primarily by reducing water corrosivity (USEPA 2004a). Lead has been demonstrated to cause delays in physical and mental development in infants and children and has been linked to deficits in attention span and learning abilities, even at low levels (USEPA 2006a, ATSDR 2007). Short-term copper exposure may cause gastrointestinal distress; long-term exposure may cause liver or kidney damage. In individuals with Wilson's disease, which causes the body to retain copper, copper may cause severe brain damage, liver failure, and death (ATSDR 2004, NIH 2006).

The US Environmental Protection Agency (USEPA) estimates that approximately 20 percent of human lead exposure is from lead in drinking water (USEPA 2006a). The LCR established a maximum contaminant level goal (MCLG) of zero for lead and an MCLG of 1.3 mg/L for copper. The rule established a National Primary Drinking Water Regulation for lead and copper that consisted of a treatment technique requirement including corrosion control treatment, source water treatment, lead service line (LSL) replacement, and public education. The rule set an action level (AL) of 0.015 mg/L for lead and 1.3 mg/L for copper. If the 90th percentile concentration for lead or copper is above the AL, public water systems may be required to initiate water quality parameter monitoring for key corrosion control parameters, install corrosion control treatment, begin source water monitoring or treatment, replace the LSL, or undertake a public education program. USEPA issued guidance to assist utilities in complying with the corrosion control treatment requirements of the LCR in 1992 (USEPA 1992) and provided updated guidance to assist in identification and maintenance of optimal corrosion control treatment in 2016 (USEPA 2016).

Internal corrosion of LSLs, brass meters and plumbing fixtures, and copper plumbing contributes to the concentrations of lead and copper in drinking water. Pure lead pipe (LSLs), lead solder, and brass with greater than 8 percent lead were banned by the 1986 Safe Drinking

Water Act Amendments (Dudi et al. 2005). “Lead-free” brass, however, was allowed to contain as much as 2 to 8 percent lead by weight under this amendment. Greenville Utilities in Greenville, N.C., exceeded the lead AL in 2004 and 2005 even though the system does not contain any LSLs. In this case, the exceedance was attributed to leaching from lead-based solder and plumbing fixtures containing lead (Landers 2006). California banned the use of pipe solder with lead content greater than 0.2 percent in 1987. In 2010, California law defined “lead free” as less than 0.25 percent weighted average and required that all pipes, fittings, and fixtures meet this definition (California DTSC 2009). Similarly, effective January 4, 2014, the federal Reduction of Lead in Drinking Water Act redefined lead-free as containing no more than 0.25% lead as a weighted average on the wetted surface and required “any pipe or plumbing fitting or fixture, any solder, or any flux” used in the installation or repair of any public water system, or any plumbing in a residential or nonresidential facility providing water for human consumption, to be lead free (USEPA 2013a).

In Canada, the low-lead requirements are integrated into plumbing standards that are referenced in the National Plumbing Code of Canada (NPC). In November 2013, a modification of the NPC was approved whereby plumbing standards that required fittings meet the 0.25% weighted average lead limit were added to the 2010 version of NPC as an interim change. The interim change was published in late 2013 (NRCC 2013) and subsequently in the 2015 version of the NPC (NRCC 2015).

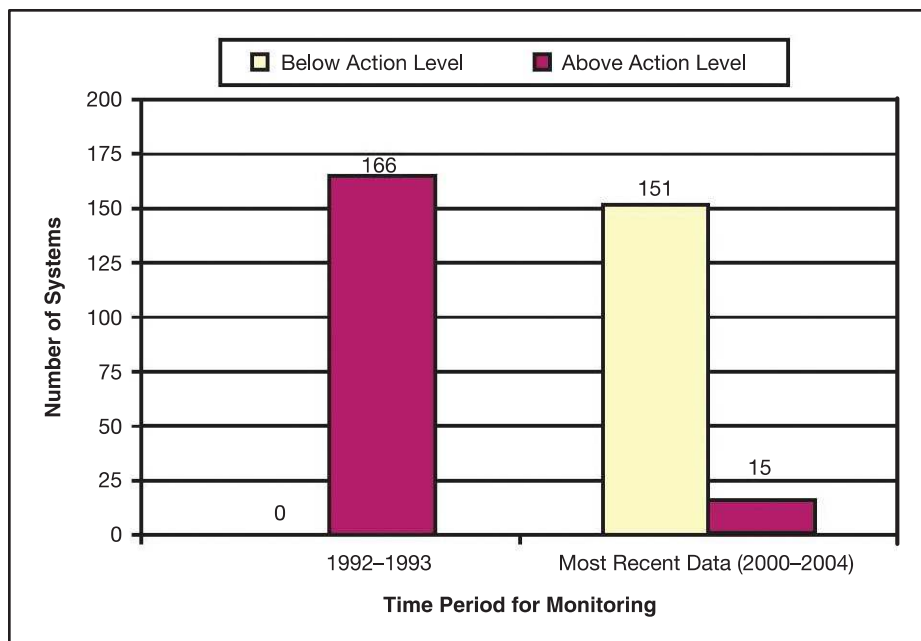
Impact of the LCR on tap-water lead concentrations. A review conducted by USEPA of LCR compliance monitoring data for public water systems serving more than 3,300 people shows that since 2000, fewer than 4 percent of those systems have exceeded the lead AL (USEPA 2004b). Prior to 2002, states were not required to report 90th percentile lead concentrations to USEPA unless those values exceeded the AL. Consequently, it is difficult to compare the tap-water lead concentrations in the years following implementation of the LCR to current levels. However, USEPA did evaluate data from 166 large public water systems that exceeded the AL following initial LCR monitoring in 1992 and 1993 (USEPA 2006d). Based on the results of subsequent monitoring conducted by these same utilities between 2000 and 2004, only 15 of those systems continued to exceed the AL (Figure 1-2).

A closer look at the data presented in Figure 1-2 reveals that tap-water lead concentrations have decreased significantly in those systems that initially exceeded the lead AL. Figure 1-3 shows that, for those 166 large systems that exceeded the AL in 1992–1993, the average 90th percentile lead concentration across all 166 systems surveyed decreased from nearly 32 µg/L to 8.2 µg/L. Over that same period, the maximum 90th percentile lead concentration decreased from 211 µg/L to 84 µg/L.

Revisions to the Lead and Copper Rule. USEPA revised the LCR in 2007 (72 FR 57781; *Federal Register* 2007) with the intent of enhancing implementation in the areas of monitoring, treatment, customer awareness, and LSL replacement. In addition, the 2007 revisions intended to improve public education by providing drinking water customers with “meaningful, timely, and useful information needed to reduce exposure to lead in drinking water.”

The most significant revisions to the LCR provided clarification regarding sample collection and reporting. Specifically, the LCR revisions required that all compliance monitoring results, including those above the required number of samples, be included in the 90th percentile determination and that all samples be taken within the same calendar year for those systems on reduced monitoring. The remainder of the revisions addressed customer notification for those residents in a utility’s sampling program and provisions to address sampling sites with known LSLs that were previously “tested out” due to sample results below the AL.

Long-term revisions to the Lead and Copper Rule. In the years since LCR implementation, a variety of noteworthy research within the drinking water community has provided new insights in lead and copper corrosion and has led to concerns that the



Source: USEPA 2006d

Figure 1-2 Number of large US water systems exceeding the lead action level

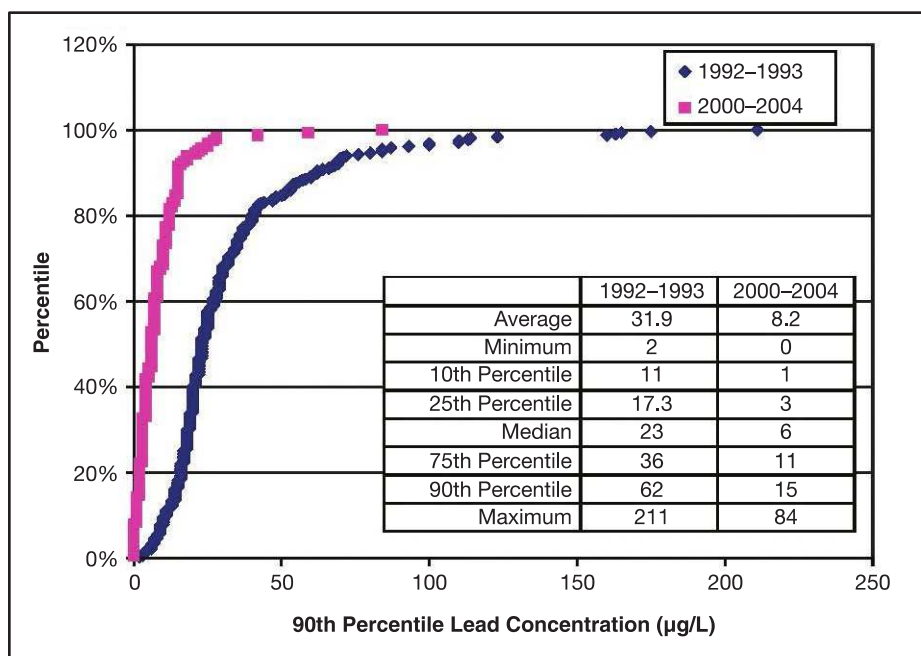


Figure 1-3 Comparison of 90th percentile LCR monitoring data for 166 large public water systems

current LCR may systematically underestimate lead and copper levels in drinking water (e.g., Del Toral et al. 2013). The Lead and Copper Rule Working Group (LCRWG) of the National Drinking Water Advisory Council (NDWAC) was formed to provide recommendations to USEPA regarding the Long-Term Revisions to the Lead and Copper Rule. The LCRWG was tasked with addressing the following issues:

- Sample site selection criteria
- Lead sampling protocols
- Public education for copper
- Measures to ensure optimal corrosion control treatment
- LSL replacement

The LCRWG met between March 2014 and June 2015 and issued its recommendations to USEPA in August 2015 (NDWAC 2015). Among its findings, the *Report of the Lead and Copper Rule Working Group to the National Drinking Water Advisory Council* concluded that the anticipated Long-Term Revisions to the Lead and Copper Rule represent a significant opportunity for “removing sources of lead in contact with drinking water and for reducing exposure to lead from drinking water.” Further, the LCRWG noted that eliminating the sources of lead in contact with drinking water would require creative funding solutions, as total replacement is expected to cost billions of dollars nationwide. It also concluded that more robust public outreach and education is necessary.

In making its recommendations to USEPA,

The LCRWG took the following considerations, among others, into account in making recommendations for revisions to the current LCR.

There is no safe level of lead. Lead can pose health risks to anyone, but there are heightened risks for pregnant women, infants and young children and other vulnerable populations with both acute and chronic exposures. Effective elimination of leaded materials in contact with water and minimization of exposure to lead in drinking water is a shared responsibility; public water systems (PWSs), consumers, building owners, public health officials and others each have important roles to play. The lack of resources to reduce the sources of exposure in some communities, however, also raises important questions of disparate impact and environmental justice. Thus, creative financing mechanisms will be needed.

The LCR should remain a treatment technique rule, but it can be improved based on the scientific knowledge that has emerged since the current LCR was promulgated. Corrosion control treatment is complicated, and will vary based on specific circumstances in each public water system. Thus, regular updates to guidance by EPA based on the latest science and the creation of a national clearinghouse of information both for the public and for PWSs are needed.

The LCRWG considered but did not quantify the cost implications of its recommendations. An important factor in the group’s deliberations was the principle that PWS and state resources should be focused on actions that achieve the greatest public health protection. Recognizing that lead service line (LSL) replacement programs will be costly in some locations, the LCRWG also encouraged PWSs to incorporate anticipated costs into their capital improvement program as appropriate to their situation, and urges states to include the costs of LSL replacement in their criteria for allocation of Drinking Water State Revolving Funds.

The LCRWG specifically recommends that EPA revise the LCR to:

- Require proactive lead service line replacement programs, which set replacement goals, effectively engage customers in implementing those

goals, and provide improved access to information about LSLs, in place of current requirements in which LSLs must be replaced only after a lead action level (AL) exceedance;

- Establish more robust public education requirements for lead and LSLs, by updating the Consumer Confidence Report (CCR), adding targeted outreach to consumers with lead service lines and other vulnerable populations (pregnant women and families with infants and young children), and increasing the information available to the public;
- Strengthen corrosion control treatment (CCT), retaining the current rule requirements to re-assess CCT if changes to source water or treatment are planned, adding a requirement to review updates to EPA guidance to determine if new scientific information warrants changes;
- Modify monitoring requirements to provide for consumer requested tap samples for lead and to utilize results of tap samples for lead to inform consumer action to reduce the risks in their homes, to inform the appropriate public health agency when results are above a designated household action level, and to assess the effectiveness of CCT and/or other reasons for elevated lead results;
- Tailor water quality parameters (WQPs) to the specific CCT plan for each system, and increase the frequency of WQP monitoring for process control;
- Establish a health-based, household action level that triggers a report to the consumer and to the applicable health agency for follow up;
- Separate the requirements for copper from those for lead and focus new requirements where water is corrosive to copper; and
- Establish appropriate compliance and enforcement mechanisms. (NDWAC 2015)

USEPA is currently considering the LCRWG recommendations and is anticipated to issue a proposed rule in 2017. While not obligated to adopt the working group recommendations, USEPA is likely to include the suggestions, or some form of them, in the revised rule, most notably the recommendations for proactive LSL replacement, enhanced WQP monitoring, and more robust public education.

Health Canada guidelines. The safety of drinking water supplies in Canada is a responsibility that is shared between the provincial/territorial, federal, and municipal governments. The day-to-day responsibility of providing safe drinking water to the public generally rests with the provinces and territories while the municipalities usually oversee the day-to-day operations of the treatment facilities. Health Canada develops its *Guidelines for Canadian Drinking Water Quality* in partnership with the provinces and territories. These guidelines are used by every jurisdiction in Canada and are the basis for establishing provincial drinking water quality requirements for all Canadians (Health Canada 2015).

In Canada, the guideline for lead is a maximum acceptable concentration (MAC) of 0.01 mg/L (10 µg/L) based on a provisional tolerable weekly intake of lead established by the World Health Organization (Health Canada 1992). However, Health Canada is reviewing the lead guideline to include the most recent health information as well as sampling and monitoring strategies that address exposure from drinking water (Health Canada 2013). Treatment-based guidance for corrosion control was published in 2009 (Health Canada 2009). The recommended sampling protocol found in this guidance uses stagnation times to capture the highest levels of lead to provide the basis for a system-wide assessment of the corrosion control efficacy.

Iron and Manganese

USEPA established secondary maximum contaminant levels (SMCLs) of 0.3 mg/L for iron and 0.05 mg/L for manganese, which represent a “reasonable goal for drinking water quality” (*Federal Register* 1979, 1991b; USEPA 2013b). SMCLs control contaminants that primarily affect the aesthetic quality of drinking water and are not federally enforceable, although state primacy agencies have the authority to include them in state drinking water regulations. When present at sufficiently high levels, iron may result in rusty color, deposit of sediment, metallic taste, and reddish or orange staining. Similarly, Health Canada’s established aesthetic objective for iron in drinking water is ≤ 0.3 mg/L (≤ 300 $\mu\text{g/L}$). A MAC has not been set for iron (Health Canada 1978).

Much of the iron present in water is because of natural mineral deposits, and when present in source waters at concentrations above the SMCL, iron is frequently removed at the water treatment facility. If not removed, source-water iron may result in red water in the distribution system. However, internal corrosion of unlined cast-iron pipe, galvanized pipe, or dissolution of existing pipe scales in iron pipe may also result in aesthetic issues in drinking water distribution systems.

Iron, manganese, and aluminum scales in water distribution systems have adsorptive properties and can contain substantially higher concentrations of trace metals, such as lead, copper, cadmium, and zinc, than are present in the bulk water entering the system (Friedman et al. 2009, Deshommes et al. 2010, McFadden et al. 2011, Camara et al. 2013, Schock et al. 2014). Release of these metals can occur because of changes in pH and ORP associated with source water blending or source changeovers, treatment process changes, disinfectant residual loss, or biological reactions. These bulk water chemistry changes can cause desorption of contaminants from iron and manganese scales or can result in chemical destabilization of existing scales (Friedman et al. 2009). Physical releases of existing iron scales may trigger red-water events, which may contain elevated concentrations of trace metals. Physical release can be caused by changes in distribution system hydraulics, such as sudden changes in demand, flushing activities, fire flow events, main breaks, or other changes in flow patterns.

Cadmium

Short-term exposure to high concentrations of cadmium may result in nausea, vomiting, diarrhea, muscle cramps, salivation, sensory disturbances, liver injury, convulsions, shock, and renal failure. Long-term exposures may cause kidney, liver, bone, and blood damage (USEPA 2006b). Consequently, USEPA has established an MCLG of 0.005 mg/L for cadmium as well as a maximum contaminant level (MCL) of 0.005 mg/L. A MAC of 0.005 mg/L (5 $\mu\text{g/L}$) for cadmium in drinking water has been established on the basis of health considerations (Health Canada 1986).

Cadmium is primarily present in drinking waters as a result of erosion of natural deposits but may also be present because of leaching from cement-mortar-lined pipes (Guo et al. 1998, Berend and Trouwborst 1999) or from corrosion of galvanized piping. It has also been observed that the amount of lead and cadmium released from galvanized piping decreases with the age of the pipe as a consequence of the formation of a passivating layer on the pipe surface (Meyer 1980).

Zinc

Zinc in drinking water is primarily an aesthetic concern because it may result in a metallic taste. Consequently, USEPA has established an SMCL of 5 mg/L for zinc. An aesthetic objective has been established for zinc in drinking water of ≤ 5.0 mg/L (Health Canada 1987).

Zinc may be present in drinking water due to erosion of natural deposits or from dezincification of brass plumbing fixtures. Several studies of low-alkalinity waters have found that iron and zinc were the principal corrosion by-products of galvanized plumbing (Dangel 1975, JMM 1982).

The zinc coating on galvanized pipe may contain lead, copper, cadmium, chromium, aluminum, barium, and other impurities (AwwaRF and TZW 1996). There are a number of standards regarding galvanized pipe, most notably by ASTM International in the United States. As a result of these impurities, corrosion of galvanized pipe may result in the release of trace metal concentrations.

Asbestos

Asbestos in drinking water is most commonly present as a result of degradation of asbestos-cement piping used in drinking-water distribution systems. Though it may be present in natural soils, it does not often migrate to groundwater through soils (USEPA 2006c). Short-term exposure to asbestos in drinking water is not known to cause any health issues; long-term exposure may result in an increased risk of developing benign intestinal polyps. USEPA has established an MCLG of 7 million fibers per liter (MFL) and an MCL of 7 MFL for asbestos.

Biological Regrowth and Chlorine Demand

In the United States, the Surface Water Treatment Rule was finalized in 1989 and requires maintenance of a disinfectant residual in the distribution system, among other requirements (54 FR 27486; *Federal Register* 1989a). The Total Coliform Rule (TCR) imposed monitoring requirements for total coliform as well as for fecal coliform and *Escherichia coli* (54 FR 27544; *Federal Register* 1989b). The Revised Total Coliform Rule further established an MCL for *E. coli* and uses *E. coli* and total coliforms to initiate a “find and fix” approach to address fecal contamination that could enter into the distribution system (78 FR 10269; *Federal Register* 2013). It requires public water systems to perform assessments to identify sanitary defects and subsequently take action to correct them. Biological regrowth and chlorine demand may be affected by corrosion in many ways and vice versa. Chlorine and other oxidants impact the ORP, which is a factor in maintaining effective corrosion control. Conversely, corrosion by-products can exert an oxidant demand, diminishing distribution system disinfectant residuals and resulting in increased potential for microbiological regrowth. Microbiological regrowth not only may threaten compliance with the TCR but may also result in increased potential for MIC to occur.

Release of Trace Metals From Cementitious Coatings

Barium, cadmium, chromium, and aluminum have been found to leach from cement-mortar lining in distribution piping (Guo et al. 1998, Berend and Trouwborst 1999). While this leaching represents a potential water quality and public health concern, it is not the focus of this manual.

ADDITIONAL READING

The reader is advised to become more knowledgeable in the following areas:

- The water quality and operational factors that influence internal corrosion and metal release in drinking water distribution systems

- The potential water quality, health-related infrastructure, and regulatory concerns associated with internal corrosion
- The secondary impacts associated with changes in source-water quality, treatment, or distribution operations and the potential for those changes to affect existing corrosion control effectiveness (i.e., reequilibration of existing pipe scales)

References for this chapter give detailed information on these topics and the other topics discussed. The reader is encouraged to follow up on the referenced material that is publicly available to obtain keener insight into this discussion.

REFERENCES

- ATSDR (Agency for Toxic Substances and Disease Registry). 2004. *Toxicological Profile for Copper*. Atlanta, Ga.: ATSDR, Public Health Service, US Department of Health and Human Services. Available at: www.atsdr.cdc.gov/toxprofiles/tp132.pdf
- ATSDR. 2007. *Toxicological Profile for Lead*. Atlanta, Ga.: ATSDR, Public Health Service, US Department of Health and Human Services. Available at: www.atsdr.cdc.gov/toxprofiles/tp13.pdf
- AwwaRF and TZW (Awwa Research Foundation and DVGW-Technologiezentrum Wasser). 1996. *Internal Corrosion of Water Distribution Systems*, 2nd ed. Denver, Colo.: AwwaRF.
- Berend, K., and T. Trouwborst. 1999. Cement–mortar pipes as a source of aluminum. *Journal AWWA*, 91(7):91–100.
- Bremer, P.J., B.J. Webster, and D.B. Wells. 2001. Biocorrosion of copper in potable water. *Journal AWWA*, 93(8):82–91.
- California DTSC (Department of Toxic Substance Control). 2009. Requirements for Low Lead Plumbing Products in California. Available at: <https://dtsc.ca.gov/PollutionPrevention/upload/lead-in-plumbing-fact-sheet.pdf>
- Camara, E., K.R. Montreuil, A.K. Knowles, and G.A. Gagnon. 2013. Role of the water main in lead service line replacement: A utility case study. *Journal AWWA*, 105(8):E423–E431.
- Cantor, A.F., J.B. Bushman, and M.S. Glodoski. 2003. A new awareness of copper pipe failures in water distribution systems. In *Proceedings of the AWWA Water Quality Technology Conference*. Denver, Colo.: AWWA.
- Cantor, A.F., J.B. Bushman, M.S. Glodoski, E. Kiefer, R. Bersch, and H. Wallenkamp. 2006. Copper pipe failure by microbiologically influenced corrosion. *Materials Performance*, 45(6):38.
- Dangel, R.A. 1975. *Study of Corrosion Products in the Seattle Water Department Distribution System*. Report 670/2-75-036. Cincinnati, Ohio: USEPA.
- Del Toral, M.A., A. Porter, and M.R. Schock. 2013. Detection and evaluation of elevated lead release from service lines: A field study. *Environmental Science and Technology*, 47:9300.
- Deshommes, E., L. Laroche, S. Nour, C. Cartier, and M. Prévost. 2010. Source and occurrence of particulate lead in tap water. *Water Research*, 44(12):3734–3744.

- Dudi, A., M. Schock, N. Murray, and M. Edwards. 2005. Lead leaching from inline brass devices: A critical evaluation of the existing standard. *Journal AWWA*, 97(8):66–78.
- Edwards, M. 2004. Written testimony to Chairman Tom Davis and US House of Representatives. Committee on Government Reform, May 5.
- Edwards, M., J.F. Ferguson, and S.H. Reiber. 1994. The pitting corrosion of copper. *Journal AWWA*, 86(7):74–90.
- Edwards, M., S. Jacobs, and D.M. Dodrill. 1999. Desktop guidance for mitigating Pb and Cu corrosion by-products. *Journal AWWA*, 91(5):66–77.
- Edwards, M., S. Jacobs, and R.J. Taylor. 2000. The blue water phenomenon. *Journal AWWA*, 92(7):72–82.
- Federal Register*. 1979. National Secondary Drinking Water Regulations; Final Rule. *Federal Register*, 44(140):42195.
- Federal Register*. 1989a. National Primary Drinking Water Regulations; Filtration, Disinfection; Turbidity, Giardia lamblia, Viruses, Legionella, and Heterotrophic Bacteria, Final Rule. *Federal Register*, 54(124):27486–27567.
- Federal Register*. 1989b. National Primary Drinking Water Regulations; Total Coliforms (Including Fecal Coliform and *E. coli*); Final Rule. *Federal Register*, 54(124):27544–27568.
- Federal Register*. 1991a. National Primary Drinking Water Regulations; Lead and Copper; Final Rule. *Federal Register*, 56(110):26460.
- Federal Register*. 1991b. National Secondary Drinking Water Regulations; Final Rule. *Federal Register*, 56(20):3526.
- Federal Register*. 2007. National Primary Drinking Water Regulations for Lead and Copper: Short-Term Regulatory Revisions and Clarifications. *Federal Register*, 72(195):57781–57820.
- Federal Register*. 2013. National Primary Drinking Water Regulations: Revisions to the Total Coliform Rule; Final Rule. *Federal Register*, 78(30):10270–10365.
- Friedman, M.J., A.S. Hill, S.H. Reiber, R.L. Valentine, and G.V. Korshin. 2009. *Assessment of Inorganics Accumulation in Drinking Water System Scales and Sediments*. Project 3118. Denver, Colo.: Water Research Foundation.
- Guo, Q., P.J. Toomuluri, and J.O. Eckert Jr. 1998. Leachability of regulated metals from cement–mortar linings. *Journal AWWA*, 90(3):62–73.
- Health Canada. 1978. Iron. In *Guidelines for Canadian Drinking Water Quality* (supporting documentation). Ottawa, Ont.: Health Canada, Bureau of Chemical Hazards, Environmental Health Directorate.
- Health Canada. 1986. Cadmium. In *Guidelines for Canadian Drinking Water Quality* (supporting documentation). Ottawa, Ont.: Health Canada, Bureau of Chemical Hazards, Environmental Health Directorate.

- Health Canada. 1987. Zinc. In *Guidelines for Canadian Drinking Water Quality* (supporting documentation). Ottawa, Ont.: Health Canada, Bureau of Chemical Hazards, Environmental Health Directorate.
- Health Canada. 1992. *Guidelines for Canadian Drinking Water Quality: Guideline Technical Document—Copper*. Ottawa, Ont.: Health Canada, Water Quality and Health Bureau, Healthy Environments and Consumer Safety Branch.
- Health Canada. 2009. *Guidance on Controlling Corrosion in Drinking Water Distribution Systems*. Ottawa, Ont.: Health Canada, Water, Air and Climate Change Bureau, Healthy Environments and Consumer Safety Branch.
- Health Canada. 2013. *Risk Management Strategy for Lead*. Ottawa, Ont.: Health Canada. Available at: www.hc-sc.gc.ca/ewh-semt/pubs/contaminants/prms_lead-psgr_plomb/index-eng.php
- Health Canada. 2015. *Guidelines for Canadian Drinking Water Quality—Summary Table*. Available at: www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/sum_guide-res_recom/index-eng.php#t
- Jacobs, S., S. Reiber, and M. Edwards. 1998. Sulfide-induced copper corrosion. *Journal AWWA*, 90(7):62–73.
- JMM (J.M. Montgomery Consulting Engineering Inc.). 1982. *Internal Corrosion Mitigation Study*. Final Report. Prepared for the Portland, Ore., Water Bureau.
- Khiari, D., S. Barrett, R. Chinn, A. Bruchet, P. Piriou, L. Matia, F. Ventura, I. Suffet, T. Gittelman, and P. Leutweiler. 2002. *Distribution Generated Taste and Odor Phenomena*. Denver, Colo.: AwwaRF and AWWA.
- Kirmeyer, G.J., M. Friedman, and J. Clement. 2000a. *Guidance Manual for Maintaining Distribution System Water Quality*. Denver, Colo.: AwwaRF and AWWA.
- Kirmeyer, G.J., G. Pierson, J. Clement, A. Sandvig, V. Snoeyink, W. Kriven, and A. Camper. 2000b. *Distribution System Water Quality Changes Following Corrosion Control Strategies*. Denver, Colo.: AwwaRF and AWWA.
- Landers, J. 2006. Getting the lead out. *Public Works*, 137(4):30–32.
- McFadden, M., R. Giani, P. Kwan, and S.H. Reiber. 2011. Contributions to drinking water lead from galvanized iron corrosion scales. *Journal AWWA*, 103(4):76.
- Meyer, E. 1980. Beeinträchtigung der Trinkwassergüte durch Anlagenteile der Hausinstallation—Bestimmung des Schwermetalleintrags in das Trinkwasser durch Korrosionsvorgänge in metallischen Rohren. *DVGW-Schriftenreihe Wasser Nr.*, 23:113–131.
- NDWAC (National Drinking Water Advisory Council). 2015. *Report of the Lead and Copper Rule Working Group to the National Drinking Water Advisory Council*. Final, National Drinking Water Advisory Council. Available at: www.awwa.org/Portals/0/files/legreg/documents/NDWACRecommendations.pdf

- NIH (National Institutes of Health). 2006. *Wilson Disease*. National Digestive Diseases Information Clearinghouse, National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health. Available at: <http://digestive.niddk.nih.gov/ddiseases/pubs/wilson/index.htm>
- NRCC (National Research Council Canada). 2013. *National Plumbing Code of Canada*. Ottawa, Ont.: National Research Council Canada.
- NRCC. 2015. *National Plumbing Code of Canada*. Ottawa, Ont.: National Research Council Canada.
- Reiber, S. 2006. Corrosion, red water, and distribution system water quality. In *Proceedings of the AWWA Annual Conference and Exposition*. Denver, Colo.: AWWA.
- Sarin, P., J. Bebee, M.A. Becket, K.K. Jim, D.A. Lytle, J.A. Clement, W.M. Kriven, and V.L. Snoeyink. 2000. Mechanism of release of iron from corroded iron/steel pipes in water distribution systems. In *Proceedings of the AWWA Annual Conference and Exposition*. Denver, Colo.: AWWA.
- Schock, M., and D. Lytle. 2011. Internal corrosion and deposition control. In *Water Quality and Treatment: A Handbook on Drinking Water*, 6th ed. Edited by J.K. Edzwald. Denver, Colo.: McGraw-Hill and American Water Works Association.
- Schock, M.R., A. Cantor, S. Triantafyllidou, M.K. Desantis, and K.G. Sheckel. 2014. Importance of pipe deposits to Lead and Copper Rule compliance. *Journal AWWA*, 106(7):E336–E349.
- Smith, S.E., T. Ta, D.M. Holt, A. Delanoue, and J. Colbourne. 1998. Minimizing red water in drinking water distribution systems. In *Proceedings of the AWWA Water Quality Technology Conference*. Denver, Colo.: AWWA.
- USEPA (US Environmental Protection Agency). 1992. *Lead and Copper Rule Guidance Manual, Volume II: Corrosion Control Treatment*. EPA 811-B-92-002. Washington, D.C.: USEPA, Office of Water.
- USEPA. 2004a. *Lead and Copper Rule: Quick Reference Guide*. EPA 816-F-04-009. Washington, D.C.: USEPA, Office of Water.
- USEPA. 2004b. Summary of Lead Action Level Exceedances for Medium (3,300–50,000) and Large (>50,000) Public Water Systems. Available at: www.epa.gov/safewater/lcrr/pdfs/data_lcmr_leadsummary_0522041.pdf
- USEPA. 2006a. Lead in Drinking Water: Basic Information. Available at: www.epa.gov/safewater/lead/basicinformation.html
- USEPA. 2006b. Consumer Fact Sheet: Cadmium. Available at: www.epa.gov/OGWDW/contaminants/dw_contamfs/cadmium.html
- USEPA. 2006c. Consumer Fact Sheet: Asbestos. Available at: www.epa.gov/OGWDW/contaminants/dw_contamfs/asbestos.html

- USEPA. 2006d. Lead 90th Percentile Levels for 166 Large Water Utilities—Then and Now. Available at: www.epa.gov/safewater/lcrmr/reductionplan_comparrison.html
- USEPA. 2007. *Elevated Lead in DC Drinking Water*. EPA 815-R-07-021. Washington, D.C.: USEPA, Office of Water.
- USEPA. 2013a. Reduction of Lead in Drinking Water Act. Available at: <https://www.epa.gov/dwstandardsregulations/section-1417-safe-drinking-water-act-prohibition-use-lead-pipes-solder-and>
- USEPA. 2013b. Secondary Drinking Water Regulations: Guidance for Nuisance Chemicals. Available at: <http://water.epa.gov/drink/contaminants/secondarystandards.cfm>
- USEPA. 2016. *Optimal Corrosion Control Treatment Evaluation Technical Recommendations for Primacy Agencies and Public Water Systems*. EPA 816-B-16-003. Washington, D.C.: USEPA, Office of Water.
- Vik, E.A., R.A. Ryder, I. Wagner, and J.F. Ferguson. 1996. Mitigation of corrosion effects. In *Internal Corrosion of Water Distribution Systems*, 2nd ed. Denver, Colo.: AwwaRF and AWWA.

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Chapter **2**

Fundamentals of Internal Corrosion and Metal Release

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INTRODUCTION

There are many misunderstandings about corrosion in water distribution systems. Just using the word *corrosion* gives an incomplete picture of what is occurring. The concern is actually the transfer of metal from pipe walls into the bulk water that results in elevated metal concentrations in drinking water. Corrosion, especially uniform corrosion that is typically the focus of corrosion control studies, is only one of several mechanisms that can transfer metal from pipes (Table 2-1).

This chapter describes the common mechanisms that may cause metal release into water. Understanding and managing these mechanisms are the keys to achieving what is commonly called *corrosion control*.

Table 2-1 Chapter 2 key points

Uniform corrosion, which is typically the focus of corrosion control studies, is only one of many mechanisms that can cause the release of lead, copper, and other metals into water.

Uniform Corrosion

- In uniform corrosion, the anodic and cathodic sites move around dynamically on the pipe wall, resulting in uniform loss of metal.
 - Calcium carbonate is inadequate as a protective barrier against uniform corrosion.
 - Naturally occurring constituents such as dissolved inorganic carbon, hydroxides, and oxygen can form compounds with dissolved metals. Those compounds create protective barriers against uniform corrosion to varying degrees, as they are mostly influenced by pH and alkalinity of the water. The adequacy of the pipe films as protective barriers depends on the solubility of the compounds formed as well as the uniformity and porosity of the barrier and its ability to adhere to the pipe wall.
 - The solubility of corrosion by-products involving chloride and sulfate needs to be considered for uniform corrosion.
 - Chemicals, such as orthophosphate, can be added to produce adequate barriers against uniform corrosion on the pipe wall.
-

Microbiologically Influenced Corrosion

The extent that microorganisms are involved in the chemical and physical phenomena that influence the water quality in a distribution system has not been adequately studied. Nevertheless, there is enough knowledge about microbial growth that microorganisms can be prevented from growing excessively in water systems. Preventing excessive growth of microorganisms in water systems lowers the possibility of microbiologically influenced corrosion of metals.

Accumulation and Transport

- Metals and other inorganic material can accumulate on pipe walls by both gravitational and biofilm-mediated processes.
 - Lead, copper, and other metals such as arsenic and radium can be sorbed and coprecipitated with the inorganic material and become ingrained in the pipe wall scale.
 - Accumulated materials, including lead and copper, can be released by both chemical and physical means back into the water at higher concentrations than seen at entry points to the distribution system.
-

Other Metal Release

There are other mechanisms of metal release that should not be overlooked: galvanic corrosion, concentration cells, erosion corrosion, pipe manufacturing quality, pipe installation, and system maintenance.

Summary

Understanding and addressing all of the mechanisms of metal release is critical to lowering lead, copper, iron, and other metals concentrations in drinking water.

MECHANISMS OF METAL RELEASE BY UNIFORM CORROSION

Importance of a Protective Barrier

The correct way to apply the term *corrosion* to drinking water systems is in reference to an electrochemical interaction between a metal surface, such as a pipe wall, and the water with which it is in contact. The electrochemical interaction is similar to that of a battery (Figure 2-1) (Peabody 2001).

The components of a battery are (Peabody 2001)

- negative terminal called the *anode*,
- positive terminal called the *cathode*,
- medium to carry electrons from the anode to the cathode,
- chemical that can accept the electrons at the cathode, and
- chemical that can pair with the metal ion released at the anode.

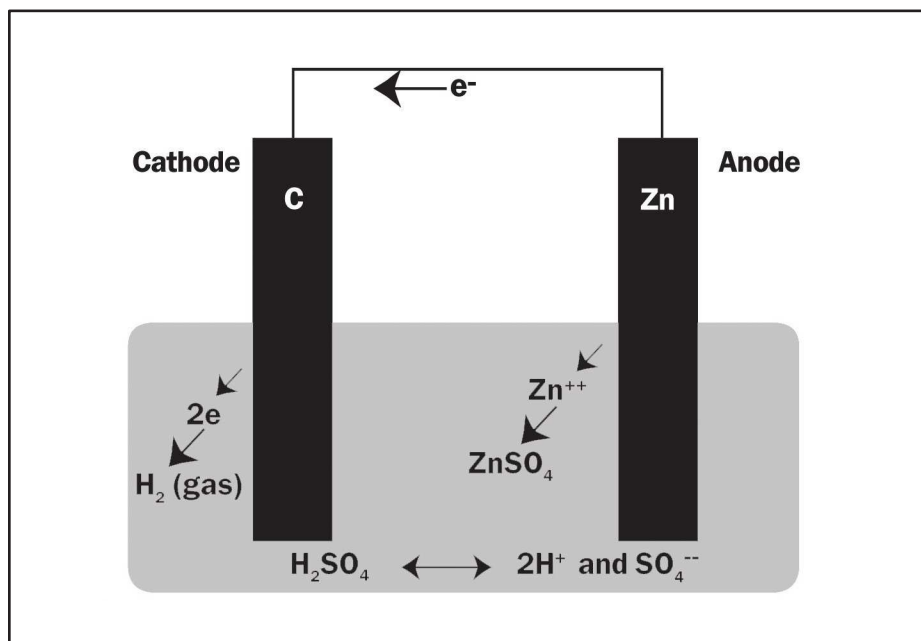
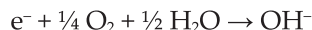


Figure 2-1 Typical battery

In uniform corrosion taking place inside the piping of water distribution systems, the anode and cathode occur dynamically at random sites on the pipe wall (Figure 2-2). These “negative and positive terminals” are microscopic in surface area. They are thought to occur because of natural microscopic imperfections and variations on the metal surface (AwwaRF and TZW 1996).

The electrons flow from the microscopic anodes to the microscopic cathodes through the pipe wall, which is similar to the role that wiring plays in an electrical circuit (AwwaRF and TZW 1996).

The water solution in contact with the cathode provides the chemicals to accept the electrons (AwwaRF and TZW 1996). For instance, oxygen in the water solution can accept an electron, and the reduction reaction occurs:



In the meantime, metal atoms from the solid metal at the anode, having given up electrons, undergo an oxidation reaction. The oxidized metal is now soluble in the adjacent water solution. That is, solid metal has been lost, transferred to water as a metal ion. It is this oxidation of the metal that is termed *corrosion*. Because of the dynamically changing anodes, there is equal probability that metal will be lost at any site along the pipe wall. Therefore, the term *uniform corrosion* is used (AwwaRF and TZW 1996).

The water solution now contains positively charged metal ions from the anode and negatively charged ions from the cathode as well as various ions from the water source and added water treatment chemicals. New compounds are formed as oppositely charged ion pairs (AwwaRF and TZW 1996).

Figure 2-2 suggests, in a simplified manner, methods to stop uniform corrosion from occurring. There is no wire with an on/off switch to break the flow of electrons. Only two components in the water/pipe system can be manipulated. First, electron acceptors in the water solution, such as oxygen, can be eliminated. This approach is sometimes, but not always, practical in water treatment. A second approach is to create a barrier, or protective (passivating) film, between the metal surface and the water solution (Figure 2-3). However,

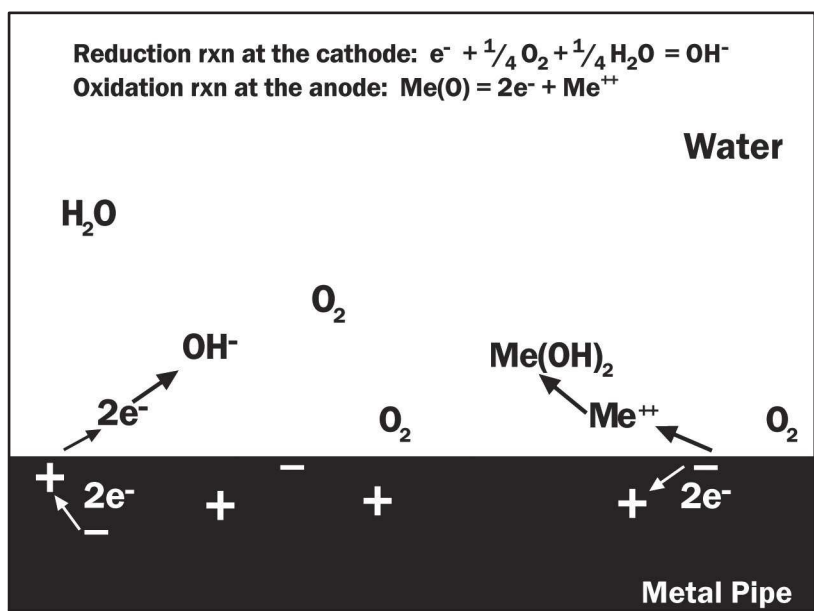


Figure 2-2 Typical electrochemical interaction between water and metal pipe

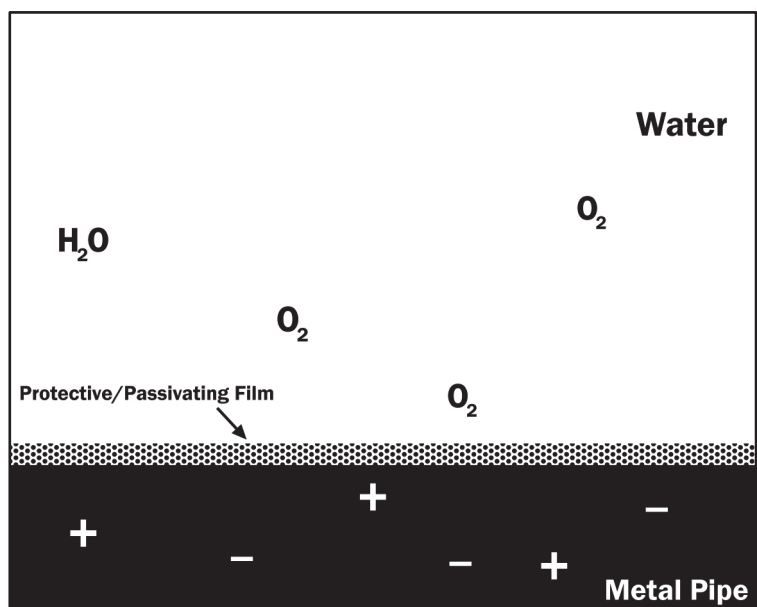


Figure 2-3 Barrier between water and metal pipe

the film must be an insoluble, uniform, nonporous layer that is well adhered to the pipe wall, preventing electron acceptors from contacting the electrons at the cathodic sites on the pipe wall (AwwaRF and TZW 1996). Further details related to forming a passivating film are described later in this chapter in context with various metals commonly used in water piping.

The Failure of Calcium Carbonate Scales as Protection Against Uniform Corrosion

If a barrier can be created between the metal surface and the water, then uniform corrosion can be stopped. However, the barrier must be uniform, nonporous, insoluble, and

well adhered to the pipe wall to prevent contact between the metal and the water and prevent the flow of electrons and molecules. As stated previously, a barrier with these characteristics is called a *passivating film*. Many decades ago, it was thought that calcium carbonate could create such a barrier.

Calcium carbonate (CaCO_3) naturally occurs in water and is easy to add to water and manipulate in water. It is known that changes to pH, temperature, calcium hardness, and alkalinity can force calcium carbonate to precipitate out of solution. A number of simple methods have been developed to calculate relative quantities of calcium carbonate that will precipitate as a scale. The most common of these methods are the Langelier index, the calcium carbonate precipitation potential, the Aggressiveness index, and the Ryznar index. In the past, the goal has been to achieve a certain quantity of calcium carbonate scale that will stop uniform corrosion but not so much scale that pipes will become significantly reduced in diameter or plugged.

It would be convenient if corrosion control and control of metal release were as simple as calculating the Langelier index. However, an important corrosion reference book, *Internal Corrosion of Water Distribution Systems* (AwwaRF and TZW 1996), emphasizes the inadequacies of calcium carbonate scale. These arguments are based on microscopic studies of this scale's physical properties on lead, copper, and iron pipe walls (AwwaRF and TZW 1996). It has been confirmed that this coarse scale cannot stop the electron receptor molecules from migrating to the pipe wall. Studies cited in the book also show the lack of correlation of Langelier index with concentration of metals in the water (AwwaRF and TZW 1996).

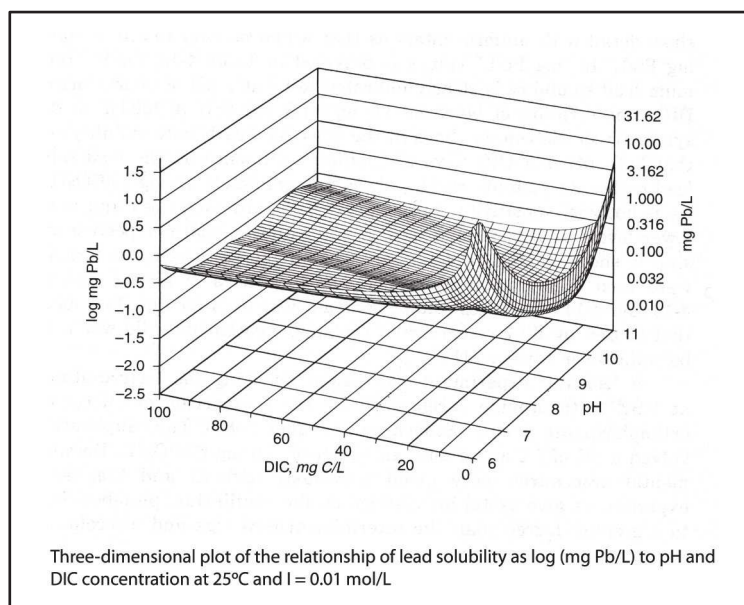
Because calcium carbonate is inadequate as a passivating film, other pipe wall barriers must be considered.

Other Pipe Films and Scales

An attempt to create the perfect physical barrier to uniform corrosion of a metal surface can be made by considering the metal ions that are released into the water from the anodes. It is the physical and chemical characteristics of the new compounds formed with the released metal ions that determine whether or not uniform corrosion will continue, slow down, or stop.

An important characteristic of the new compounds is their solubility in water. If a new compound formed with the metal ions is highly insoluble, the compound will stay in a solid form that will possibly accumulate on the metal surface. If the solid forms a uniform, nonporous film that adheres to the pipe wall, a physical barrier to uniform corrosion can be created. If the new compound formed by metal ions is highly soluble, very little to none of the compound will be found, because solids on the metal surface and the dissolved metal will be carried away by the water. Uniform corrosion will persist at a high rate as long as the components of the soluble compound are provided in the water to interact with the released metal ions (AwwaRF and TZW 1996).

The new compounds formed using the metal ions from the metal surface can be called, "corrosion by-products" or "by-products of uniform corrosion." The reality is that many corrosion by-products form with naturally occurring ions in the water, such as carbonates (CO_3^{2-}), hydroxides (OH^-), and oxygen (O_2). The new compounds are only partially insoluble, so a natural balance occurs between the metal compound in the solid form that accumulates on the metal surface, the metal compound in the solid form that remains entrained in the water, and the dissolved metal compound. Multiple compounds can remain in these various states at the same time. Attempts can be made to push one or more of the compounds into a more insoluble, barrier-forming state by adjusting pH and/or alkalinity or adding a corrosion inhibitor (such as orthophosphate or silicate).



Source: AwwaRF and TZW 1996

Figure 2-4 Graphical representation of lead carbonate solubility model

The manipulation of corrosion by-products can be illustrated by considering the control of lead, copper, and iron uniform corrosion as discussed below.

Lead

Carbonate. Researchers began their exploration for adequate protective barriers on lead pipe by examining the structure and composition of scales that had built up naturally on pipe walls. A classic example of this type of exploration was described in a 1987 article by Colling and colleagues. The researchers examined the composition of lead pipe wall deposits using X-ray diffraction and infrared spectroscopy. The deposits' structure was viewed with scanning electron microscopy. Other similar studies were performed in Europe and in the United States in the 1970s and 1980s (AwwaRF and TZW 1996).

The most common compounds found on a lead pipe wall are cerussite (PbCO_3) and hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$). Researchers' early observations found that "the concentrations of lead [in the water] are controlled by the solubility of lead salts in the pipe deposits" (Colling et al. 1987).

Given that lead pipe deposits were found to have carbonate (CO_3^{2-}) compounds as a major component, dissolved inorganic carbon (DIC) became the focus of subsequent studies. Controlled experiments with lead pipes were devised. DIC and pH were varied in the water, and the resultant lead concentration was studied (Colling et al. 1987, AwwaRF and TZW 1996).

Taking this relationship a step further, a theoretical lead carbonate solubility model was developed. Thermodynamic solubility constants were used to calculate the lead concentration in water based on DIC and pH (Schock 1980). Figure 2-4 is a graphical representation of the lead carbonate solubility model, where soluble lead concentration in water is predicted by DIC and pH. This lead carbonate solubility model became the basis for directives to water utilities for lead control in the Lead and Copper Rule (LCR), part of the federal primary drinking water regulations in the United States when the rule was published in 1991 (*Federal Register* 1991).

Oxide. As more experience was gained by water quality personnel working to comply with the LCR, it became obvious that the lead carbonate model did not predict all

releases of lead into drinking water. First, the model did not consider compounds formed when lead was in the +4 oxidation state. In this state, lead has lost four electrons in the corrosion process instead of two, as was only considered for the model shown in Figure 2-4. In the higher oxidation state, lead can form an oxide called plattnerite ($\beta\text{-PbO}_2$) or its polymorph, scrutinyite ($\alpha\text{-PbO}_2$) (Lytle and Schock 2005). These compounds are highly insoluble in water and can form the desired passivating barrier of solids on metal surfaces. The phenomenon has been seen to greatly slow the uniform corrosion of lead with resultant low-lead concentrations in drinking water (Lytle and Schock 2005, Wang et al. 2012).

The effects of lead in the +4 oxidation state came into focus around 2004 when observations were made during a change in disinfection chemicals from chlorine to chloramine at one water utility. Water utilities can choose to use chloramine to maintain disinfection throughout a water distribution system rather than chlorine to lower the possibility of creating carcinogenic disinfection by-products. Because chloramine is not as strong an oxidant as chlorine, the oxidation–reduction potential (ORP) of the water is lowered after this chemical change. This means that lead released in the corrosion process can no longer achieve the highly oxidized state needed to form the relatively insoluble plattnerite/scrutinyite film. The existing protective film is lost, and the lead concentration in the water can increase greatly (Lytle and Schock 2005). Because of this finding, it is now recognized that keeping a high ORP in water systems to form plattnerite/scrutinyite on lead surfaces can help control lead.

Hydroxide. Under certain conditions that are not common for drinking water characteristics, lead hydroxides can play a significant role as a corrosion by-product. One utility's water historically has had a very low alkalinity with a very high pH of over 10. The water utility was encouraged to lower the pH of the water to below 10 based on the predictions of the lead solubility model represented in Figure 2-4. However, the lead concentration increased. Further investigation determined that the water system had a significant presence of a compound on its pipe walls not predicted by the model. It was a type of lead hydroxide called plumbonacrite, where its solubility decreases as the pH is increased and approaches 13. When the pH was lowered to match the lead solubility model's predictions of Figure 2-4, the plumbonacrite re-solubilized and increased the lead concentration in the water (Rego and Schock 2007). This emphasizes the need to understand the type of lead compounds actually present in the system and not just those predicted by the lead solubility model of Figure 2-4.

Chloride and sulfate. Chloride and sulfate can be present naturally in drinking water or from contamination of water sources, such as with the influence of road salt on well water. The source of chloride and sulfate in drinking water can also be from treatment chemicals and operational changes. For example, chloride and sulfate concentrations are affected by switching from chlorine gas to hypochlorite generation using brine solutions—changing from a sulfate-containing coagulant such as alum to chloride-containing coagulant such as ferric chloride—anion exchange for arsenic treatment, and desalination.

In terms of lead corrosion, the solubilities of lead chloride and lead sulfate are many orders of magnitude greater than that of lead carbonate. Table 2-2 shows a comparison. That is, if high levels of chloride or sulfate are found in water, high dissolved lead chloride or sulfate compound concentrations would be expected.

It is important to keep in mind that the effects of chloride and sulfate will vary based on the ratio of chloride-to-sulfate concentrations in the water *and* the ratio of alkalinity to the sum of the chloride and sulfate concentrations (Nguyen et al. 2011). The carbonate ions, as expressed by the measurement of alkalinity, compete with the chloride and sulfate. A high concentration of carbonate ions (a high alkalinity) can passivate lead when the chloride and sulfate concentrations are relatively lower (Larson and Skold 1958, Nguyen et al. 2011). However, a higher chloride-to-sulfate mass ratio can increase galvanic corrosion (corrosion at the interface of adjacent dissimilar metals) and subsequently increase lead

Table 2-2 Solubility of various lead compounds found in drinking water

Compound	Chemical Formula	Solubility in Grams of Compound per 100 g Water at 20°C
Lead carbonate	PbCO ₃	0.00011
Lead sulfate	PbSO ₄	0.0041
Lead chloride	PbCl ₂	0.99

Source: Perry and Green 1984

release from leaded components (Edwards and Triantafyllidou 2007, Nguyen et al. 2011). Therefore, the relationship among alkalinity, chloride concentration, and sulfate concentration should be investigated in each water system under study.

Orthophosphate. So far, this discussion has described scales and films formed by compounds of naturally occurring ions such as CO₃⁻², O⁻², and OH⁻. There are also chemicals that can be added to water to intentionally form passivating films on metal surfaces to minimize uniform corrosion of lead.

One common chemical is orthophosphate (PO₄⁻³). Its ability to form passivating films on lead surfaces in contact with water uses the very same mechanisms previously discussed. That is, metal ions are released into the water from the anodic sites on the metal surface. The metal ions form compounds (corrosion by-products) with the phosphate ions that have been added to the water. The lead-phosphate compound theoretically precipitates out of the water as a solid and forms a film on metal surfaces to prevent contact of the pipe with the water to minimize uniform corrosion of lead (AwwaRF and TZW 1996).

Several lead and phosphate compounds are possible, but research has concluded that a compound called hydroxypyromorphite (Pb₅(PO₄)₆ or Pb₃(PO₄)₂) is most likely the solid that controls the solubility of lead in the water when orthophosphate has been added (AwwaRF and TZW 1996). Many technical articles demonstrate the effectiveness of orthophosphate in offline pipe test rigs for lowering lead released to water. It has also been concluded that the solubility of the lead and orthophosphate compounds that form is dependent on pH and DIC in addition to the concentration of orthophosphate (AwwaRF and TZW 1996).

The USEPA recommends the use of orthophosphate as phosphoric acid or a potassium or sodium salt and not other products such as zinc orthophosphate or blends with polyphosphate as described below (USEPA 2016).

In another consideration, despite the LCR's dependence on the use of orthophosphate for lead and copper corrosion control in drinking water systems, the regulation of phosphorus discharged by wastewater treatment plants around the country is increasing for nutrient control in receiving waters. In 2016, twelve states have wastewater phosphorus limits in place as regulated by US National Pollutant Discharge Elimination System permits (Rodgers 2014). These Clean Water Act regulations along with the requirements of the Safe Drinking Water Act's LCR must be considered for each drinking water system in the United States and similar environmental balances considered elsewhere.

Zinc orthophosphate. The use of zinc orthophosphate to minimize lead in drinking water has caused much confusion. It is theorized that zinc forms carbonates that block cathodic sites on the pipe wall while phosphate forms compounds blocking anodic sites (AwwaRF and TZW 1996). There may be advantages for use of this chemical for galvanized iron, where the zinc lining is replenished thereby inhibiting release of accumulated lead (Grasha et al. 1981), and for cement mortar-lined piping, where calcium leaching is inhibited (AwwaRF and TZW 1996). However, there is no evidence that zinc orthophosphate offers more benefit for lead control with other piping materials than other orthophosphate compounds (Schneider et al. 2011).

Also, zinc can cause environmental problems for wastewater treatment plants in terms of finished water discharge and sludge disposal. These environmental factors should be considered when weighing chemical options for corrosion control.

The use of this chemical is discouraged by USEPA guidance (USEPA 2016).

Polyphosphate and blends. Polyphosphate–orthophosphate blends have been used with the intent to create corrosion control barriers on pipe walls. Polyphosphates are polymers composed of repeated linked units of orthophosphate ions in various molecular structures. They have completely different properties than simple non-polymeric orthophosphate compounds such as phosphoric acid (H_3PO_4) or potassium orthophosphate (K_3PO_4). How the phosphate ions in orthophosphate compounds can form new compounds with lead ions that have low solubility in water was previously discussed. The new compounds theoretically precipitate out of the water and form a protective barrier on the pipe wall.

In contrast, polyphosphate compounds are known to bond with metal ions, bringing them into their molecular structure and holding these metal ions in solution. That bonding feature is the very reason that polyphosphates have traditionally been used in water distribution systems to “sequester” calcium, iron, and manganese. That is, calcium, iron, and manganese ions in the water are taken up by the added polyphosphates and not allowed to form other compounds where they might precipitate as solids on water customers’ sinks and laundry. Although it was known many years ago that calcium, iron, and manganese kept in solution were sequestered, it was not realized that other metal ions in the water, such as lead and copper, were also captured. Even if the polyphosphate is blended in a product with orthophosphate, this polyphosphate–metal mixture can be consumed by the water utility customer and can be measurable in regulatory samples for lead and copper (Holm and Schock 1991, Cantor et al. 2000).

Since the publishing of the LCR in 1991, polyphosphates and blends of polyphosphates and orthophosphates have been marketed as a means to both sequester iron and manganese and minimize lead and copper in the system by precipitation of a fine metallic compound as a barrier on the pipe wall. Polyphosphate products and blended polyphosphate–orthophosphate (poly-orthophosphate) products can perform these two opposing functions but not necessarily at the same time (Klueh and Robinson 1988, Koudleka et al. 1982, Zinder et al. 1984). When the polyphosphate product is first introduced into the distribution system, it is in its polymeric form and sequesters metals, including iron, manganese, copper, and lead. However, a number of factors in the distribution system environment break up the polyphosphate compound into orthophosphate ions. These factors include pH, temperature, time, polyphosphate concentration, polyphosphate-to-orthophosphate ratio, type of polyphosphate species, and the presence of other various constituents in the water. When the polyphosphate has reverted to orthophosphate ions in this way, it can have the passivating effect on the pipe wall described previously (Klueh and Robinson 1988, Koudleka et al. 1982, Zinder et al. 1984).

A problem with adding polyphosphate as an agent to minimize lead and copper release is that there is no way to predict where and when the polyphosphate will revert to orthophosphate. Even if a prediction could be made, there would most likely be some locations and time frames in which water utility customers were consuming the higher metal concentrations until the reversion to orthophosphate could take place.

Past technical literature has warned against using polyphosphates (AwwaRF and TZW 1996). One study showed lead concentration increasing to four times that of untreated water with the addition of a polyphosphate–orthophosphate blend (Cantor et al. 2000). Holm and Schock (1991) concluded that “the application of polyphosphates for the specific purpose of lead corrosion control entails considerable uncertainty and risk.”

USEPA guidance discourages the use of phosphate products that contain polyphosphate compounds and recommends stringent demonstrations of such a product’s effects on lead and copper release from piping material (USEPA 2016).

Sodium silicate. Sodium silicate is sometimes used as an agent to minimize lead concentrations in water; however, little research and field information are available to prove its effectiveness. The limited work that has been done has shown that a relatively high concentration of silicate is needed (around 20 mg silicon dioxide (SiO_2)/L) and that it may take months to see any reduction in lead concentrations (AwwaRF and TZW 1996). In addition, sodium silicate is successfully used to sequester iron and manganese—just like the dual use of polyphosphates. It is not known by what mechanism sodium silicate works both to prevent lead from entering the water and to sequester iron and manganese. It may form a passivating compound on the pipe wall or it may adsorb lead, iron, and manganese ions to the surface of a silicate film on the pipe wall (AwwaRF and TZW 1996). It may also act to increase the pH of low-alkalinity water that, in turn, would lower the uniform corrosion potential for lead and copper (AwwaRF and TZW 1996). Sodium silicate has been mostly eliminated from many utilities' plans of action because of this lack of information, the increased operating cost associated with the cost of the chemical and increased dose, and the time it takes to see results. A 2005 article brought the possibilities of sodium silicate use back to life by describing both successful reduction of lead and copper and increased aesthetic qualities in terms of iron and manganese in a water system (Schock et al. 2005).

Free chlorine. Free chlorine, used as a disinfectant in water distribution systems, is a strong oxidant. One would expect that a strong oxidant would readily accept electrons at the cathodic sites on the pipe, and corrosion would increase at the anodic sites (AwwaRF and TZW 1996). However, that assumption is not always correct. As was discussed previously, when the presence of free chlorine pushes the ORP of the water high enough, lead is able to lose four electrons instead of two (AwwaRF and TZW 1996). When lead loses four electrons, it can form a highly insoluble and protective lead dioxide (PbO_2) in either of two forms: plattnerite or scrutinyite. Lead concentration in the water is, by consequence, lowered. Refer to the "Oxide" section previously.

Conclusion. This discussion on the uniform corrosion of lead demonstrates that the release of a metal, such as lead, into water is a complex combination of competing chemical interactions, microbiological interactions (see the "Mechanisms of Metal Release by Microbiological Activity" section later in this chapter), and transport by accumulated pipe wall scales (see the "Mechanisms of Metal Release by Accumulation and Transport" section later in this chapter). Every situation of elevated lead has its own nuances that must be understood. The lead solubility model of Figure 2-4 does not and cannot express these multiple factors and predict the lead concentration in water. Instead, an attempt at uncovering the significant multiple factors of lead release must be made. This Manual of Water Supply Practices provides the knowledge base necessary to perform such an exploration.

Copper. In considering the uniform corrosion of copper, the identification of mechanisms that encourage the metal's release to water is just as complex as that for lead. There are many in the field of internal corrosion control that see uniform corrosion based on copper carbonate and oxide compound solubility as the primary cause of observed copper concentrations in excess of the LCR's action level of 1,300 $\mu\text{g/L}$. In addition, others have observed many situations where uniform corrosion based on copper chloride and sulfate compound solubility predominates and where microbiologically influenced corrosion predominates (Cantor 2014).

Carbonate, oxide, hydroxide, and free chlorine. Copper release is high when new copper pipe first comes in contact with water, and the young scales are predominately cupric hydroxide (CuOH_2) (Schock et al. 1995, Edwards et al. 1996). Over time, the least soluble copper compounds, such as malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$, a copper carbonate) and tenorite (CuO , a copper oxide) build up on the metal surface and a more protective barrier develops. Copper release to the water slows and copper concentration in the water drops. The rate and degree to which this will occur is dependent on pH, alkalinity, and chemicals in the water that may interfere with scale development. Some situations where only chemical

factors were measured were observed to reach passivation in four days and others over 10 years (Hidmi and Edwards 1999, Turek et al. 2011). A 2014 presentation (Schock and Lytle 2014) explained the chemistry behind uniform corrosion of copper based on carbonate compound solubility. In this case, alkalinity and pH were described and represented graphically as the major factors affecting the uniform corrosion of copper.

The copper solubility graph (Schock and Lytle 2014) from the 2014 presentation describes that the following conditions are prone to copper release greater than the LCR action level of 1,300 µg/L by uniform corrosion:

- pH <7
- pH 7 to 7.2 and alkalinity >35 mg/L as CaCO₃
- pH 7.2 to 7.5 and alkalinity >100 mg/L as CaCO₃
- pH 7.5 to 8 and alkalinity >150 mg/L as CaCO₃
- pH 8 to 8.3 and alkalinity >250 mg/L as CaCO₃

In addition, ORP is a major factor in shifting young copper hydroxide scales into a soluble phase (Schock and Lytle 2014). ORP is influenced by the concentration of chlorine disinfectant in the water because it is an oxidant. With this information, the researchers concluded that any chlorinated water system is prone to excessive copper release by uniform corrosion.

Alternatively, others have found that the pH, alkalinity, and ORP relationships to high copper release may not always predominate and that other factors such as microbologically influenced corrosion (MIC), chloride, and sulfate may be more important in many situations (Cantor 2014).

Chloride and sulfate. The technical literature regarding chloride and sulfate and copper corrosion is contradictory. In some technical literature, the presence of chloride formed a passivating scale (Edwards et al. 1994) and lowered the copper corrosion current (Edwards et al. 1996) while in other literature, the presence of chloride increased the soluble copper concentrations over the predicted amount (Schock et al. 1995). Others found that chloride initiated copper pitting (Ives and Rawson 1962, Edwards et al. 1994).

Natural organic matter. Natural organic matter (NOM) has been reported to increase copper solubility by forming soluble complexes with copper and interfering with protective scale formation (Schock et al. 1995, Korshin et al. 1996, Edwards and Sprague 2001). Others found that NOM prevented copper pitting (Edwards et al. 1994, Edwards and Sprague 2001, Sarver and Edwards 2012). As discussed later in this chapter in the “Mechanisms of Metal Release by Microbiological Activity” section and in chapter 3, the presence of NOM can also act as a food source for microorganisms with higher levels of NOM, increasing microbial activity and the occurrence of MIC.

Orthophosphate. Orthophosphate is effective in lowering copper release into water from uniform corrosion where the pH is above 7.0. At acidic pH values, orthophosphate is ineffective in lowering copper release (AwwaRF and TZW 1996). At higher pH values around 8.0 where copper release is diminished because of the pH increase, orthophosphate addition shows no additional benefit (AwwaRF and TZW 1996, Schock and Sandvig 2006). Orthophosphate prevents high copper release in alkalinities greater than 200 mg/L as CaCO₃ on new pipe in test apparatuses, if dosed with at least 3.3 mg/L as orthophosphate (Schock and Lytle 2014).

Polyphosphate and blends. The previous discussion concerning lead pointed out how the use of polyphosphate and some polyphosphate–orthophosphate blends to mitigate uniform corrosion often has the opposite effect. It is the polyphosphates’ reversion to orthophosphate that gives it the ability to minimize metal release if conditions are favorable. Many studies reported in the literature have shown that copper levels can increase

dramatically with the addition of polyphosphate and blends (AwwaRF and TZW 1996). Studies carried out on polyphosphate-blend addition in hot water showed a benefit in reduction of copper release, but it was also acknowledged that the higher temperatures push the polyphosphate to revert to orthophosphate (AwwaRF and TZW 1996).

One case study by Knobeloch et al. (1998) exemplifies the point that the use of polyphosphate–orthophosphate blends can be unpredictable. Some water customers in one city experienced staining of sinks and hair and fell ill with gastrointestinal upsets. Their malaise was traced to high copper levels ($>5,000 \mu\text{g/L}$) in the drinking water (Knobeloch et al. 1998). A polyphosphate–orthophosphate blend had recently been added to sequester dissolved iron in the groundwater source. An investigation proved that by removing the polyphosphate blend from the drinking water, copper levels in new homes were dramatically lowered (Cantor et al. 2000). This case study is related here to demonstrate what can happen when polyphosphate, either alone or as a polyphosphate–orthophosphate blend, is added to a drinking water system and is not properly monitored. The literature is clear that metals will increase in concentration in the presence of polyphosphate until the polyphosphate reverts to orthophosphate.

Sodium silicate. As previously discussed with lead, there is not enough literature to assess the effectiveness of sodium silicate as a means to provide a protective barrier between metal and water. Studies have not determined whether the silicate decreases the release of copper into the water or if the increase in pH as a result of sodium silicate addition gives the benefit of copper control (AwwaRF and TZW 1996).

Conclusion. As in the case of lead release from metal surfaces, copper release is a complex interaction of multiple chemical and microbiological factors and transport by pipe wall scales. The copper solubility model, which describes a simplified view of uniform corrosion based solely on carbonate chemistry, cannot predict, by itself, the copper concentration in water.

Iron. Iron concentration in drinking water has not historically been a concern from the perspective of regulatory compliance because it has typically been identified as an aesthetic concern in water. However, as will be discussed later in the “Mechanisms of Metal Release by Accumulation and Transport” section of this chapter, iron can sorb lead and other metals, accumulate them in scales, and transport them to the consumers’ taps. Therefore, the production of iron particulates as a result of the corrosion of iron plumbing materials can eventually lead to a major mechanism of lead release into the drinking water (Schock et al. 2014). Therefore, iron corrosion in a water system must be controlled with the same chemical and microbiological concerns as with lead and copper.

Alkalinity/DIC and pH. As with lead and copper exposed to water, iron exposed to water is affected by oxygen and other oxidants as electron acceptors in the electrochemical battery of metal corrosion. And once again, alkalinity and pH play a major role in forming compounds with the metal ions that are released into the water (AwwaRF and TZW 1996).

The corrosion scale for iron pipe is quite complex and can follow several pathways as to which compounds are formed, whether or not they increase or decrease the corrosion of the iron piping, and whether or not they remain soluble in the water or form solids (rusty water). If there is a slow oxidation of the metallic iron, then the resultant corrosion by-product formation moves toward the production of FeCO_3 (siderite)—for example, a relatively nonporous scale that can hinder the migration of oxidants to the cathodic sites on the pipe wall. But if there is rapid oxidation of the metallic iron, a less dense and more porous iron scale is formed. In this case, oxygen and ions can migrate to the pipe wall through the scale as well as react with compounds in the scale itself. Other factors, such as chloride and sulfate concentrations, can play a role in further transformation to other iron compounds (AwwaRF and TZW 1996).

Summaries of the physical and chemical characteristics of the layers and factors that influence iron release are described elsewhere, as in an article by Burlingame et al. 2006 and in chapter 2 of AwwaRF and TZW 1996.

Orthophosphate. Orthophosphates have been shown to reduce the corrosion rates of iron and also to stabilize the iron scale that forms on the pipe surface (AwwaRF and TZW 1996).

Polyphosphate and blends. Polyphosphates and blends have been shown to increase iron uniform corrosion rates and destabilize the iron scale on the pipe surface (AwwaRF and TZW 1996). That is to say, the same chemical mechanism that allows polyphosphate to be used as a sequestering agent for iron actively pulls iron scale from pipe surfaces and holds the iron in solution, thereby increasing iron concentration in the water.

Free chlorine. Observations where only chemical parameters were measured have been made that free chlorine increases the release of iron into the water (Cantor et al. 2003). In addition, the physical characteristics of the iron scale depend on the rate of reaction between the iron and the oxidant. Free chlorine reacts rapidly, with soluble iron forming more-porous and less-dense solids than those formed in a slower reaction with oxygen or chloramine (Burlingame et al. 2006).

Conclusion. In terms of lead and copper control, iron corrosion is important to track in a water system because iron corrosion by-products can facilitate lead and copper transport to consumers' taps. This is discussed later in the "Mechanisms of Metal Release by Accumulation and Transport" section. Iron is also susceptible to MIC, discussed in the next section. Like lead and copper, iron undergoes complex chemical and microbiological interactions in water systems.

MECHANISMS OF METAL RELEASE BY MICROBIOLOGICAL ACTIVITY

Microbiologically influenced corrosion (MIC) is a type of nonuniform corrosion. However, it should not be necessarily considered as a localized phenomenon because the conditions that cause this type of corrosion to occur can be pervasive throughout a water system.

MIC has been greatly overlooked as a cause of lead and copper (and iron) release into drinking water in the literature, which is likely related to the difficulty in quantifying the presence of microorganisms in the past. With improvement in analytical techniques, investigators who measure microbiological populations along with chemical interactions in water systems observe that MIC can not only elevate metals concentrations in the adjacent water but can also cause pitting and pinhole leaks starting from the interior surface of a metal pipe or plumbing component (Little et al. 1992, Bremer et al. 2001, Fallowfield et al. 2011, Cantor 2014).

Also with the advance of technology, a new perspective of water systems is emerging with the realization that water distribution systems have a microbiome, a community of microorganisms that thrives in the system (Raskin et al. 2014, Gomez et al. 2014, Ji et al. 2014, Douterelo et al. 2014). At this time, little is known about the extent that microorganisms become intertwined in the chemical and physical phenomena that shape the water quality in a distribution system.

Nevertheless, some straightforward measurements can aid in tracking and controlling excessive growth of microorganisms in water systems. These simple concepts alone can lower the possibility that MIC and its associated water quality and pipe integrity problems will occur.

Microbial Growth

The term *microbial growth* is a general descriptor of the process used by microorganisms to replicate, which generally involves bulking up in size and then dividing to make additional

microbial copies. For microbial growth to occur in water, certain macronutrients, chemical components, and micronutrients must be present for use by microbes. These chemicals provide the raw materials and energy for tearing down and reassembling cellular materials.

Macronutrients. Macronutrients are the chemical compounds consumed in the largest quantities by microorganisms that contribute the most energy to power their life cycles. The generic chemical formula for microorganisms is roughly $C_5H_7O_2NP_{0.05}$. Therefore, required macronutrients for microbial growth include carbon (C), phosphorus (P), nitrogen (N), hydrogen (H), and oxygen (O) (Rittmann and McCarty 2001).

Organic carbon is the preferred form of C for microbial growth because it allows for the fastest growth rate. The type of organic carbon present provides the potential for particular types of microbial growth. Typical forms of organic carbon utilized by microbes include

- organic acids (e.g., acetic, citric, and formic);
- alcohols (e.g., ethanol, glycerol, and methanol);
- sugars, also referred to as carbohydrates (e.g., glucose, pyruvate, and succinate);
- amino acids (e.g., alanine and glutamate); and
- complex organic decay products (e.g., lignin, tannin, and cellulose) (Rittmann and McCarty 2001).

Organic carbon in surface water is typically the result of decaying vegetation and/or aquatic organisms in the water, which is often defined as natural organic matter, or NOM. This can be augmented by organic contaminants (e.g., animal feces, fertilizers, and petroleum products) that are transported by stormwater runoff or from sewage system inputs (e.g., leaky pipes, outfall, overflows, or failed septic systems) (Ehrlich and Newman 2009, Edzwald 2011). Decay of NOM or organic contaminants can release C, N, and P to the environment and thus stimulate microbial growth (Ehrlich and Newman 2009). However, as discussed later in chapter 3, not all NOM is available for microbial use.

Groundwater recharge traveling through the soil zone will pick up and transport organic carbon toward the aquifer, with organic carbon concentration typically decreasing with depth in the aquifer because of continued microbial degradation (Ehrlich and Newman 2009). Most organic carbon in groundwater is the result of decaying vegetation. In deep aquifers, organic carbon is typically either in a complex form and unavailable for microbial use or the remnant of fossil matter (Goldscheider et al. 2006). Surface water that, for various reasons, can short-circuit the flow into deeper aquifers has the potential for increasing the organic carbon content of groundwater.

However, lack of a suitable organic carbon source does not stop microbiological growth. Certain microbes (autotrophs) can utilize DIC as their source of C instead of organic carbon (Goldscheider et al. 2006, Rittmann and McCarty 2001).

Requirements for P are typically satisfied by dissolved inorganic phosphate. Various microbes appear to have the ability to acquire inorganic phosphate that is either bound to an oxidized metal or within a crystalline matrix (mineral weathering). Organically bound phosphorus can also be a source of P (Jaisi et al. 2011, Rogers and Bennett 2004).

Ammonia is the preferred form of N. However, certain microbes have the ability to utilize nitrate, nitrite, and nitrogen gas for their growth needs (Rittmann and McCarty 2001).

Requirements for H and O are typically satisfied by acidity (lower pH water has a higher concentration of hydrogen ions) and carbon dioxide or dissolved oxygen, respectively (Rittmann and McCarty 2001).

Chemical components. Nearly every living cell uses adenosine triphosphate (ATP) as its basic energy carrier (Wolfe-Simon et al. 2011), which is used to support processes

needed for the assimilation of nutrients into new cellular materials. The ATP energy cycle requires chemical components for microbial growth that include an electron donor and an electron acceptor for energy generation (Rittmann and McCarty 2001).

The use of organic carbon as the electron donor classifies a microbe as a *heterotroph*, whereas the use of an inorganic compound or element as the electron donor (e.g., dissolved metal, sulfide, ammonia, methane, or hydrogen) classifies a microbe as an *autotroph* (Rittmann and McCarty 2001).

The use of oxygen as the electron acceptor classifies a microbe as an *aerobe*, whereas the use of an inorganic compound or element as the electron acceptor (e.g., nitrate, sulfate, oxidized metal, or carbon dioxide) classifies a microbe as an *anaerobe* (Rittmann and McCarty 2001).

The use of organic carbon as both the electron donor and electron acceptor classifies a microbe as a *fermenter* (Rittmann and McCarty 2001).

Facultative microbes can use multiple forms of electron donors or electron acceptors, whereas *obligate microbes* can only use one form (Rittmann and McCarty 2001).

As an example of the complexity of microbial growth, for growth of autotrophic microorganisms to occur, dissolved carbon dioxide or carbonate and bicarbonate (DICs) satisfies the macronutrient C requirement, and a dissolved metal (such as a reduced form of iron, manganese, sulfide, and/or arsenic), ammonia, nitrogen gas, or methane satisfies the electron donor requirement. The electron acceptor requirement can be satisfied by dissolved oxygen for aerobic conditions or an oxidized metal, nitrate, sulfate, carbon dioxide, or organic matter for anaerobic conditions (Goldscheider et al. 2006).

In summary, there is adaptability and synergy of microbiological communities in obtaining the chemical components and compounds to support growth.

Micronutrients. Micronutrients are chemical compounds required in small quantities to support various cells functions. Examples of micronutrients or trace elements are sodium, potassium, magnesium, calcium, iron, sulfur, manganese, cobalt, zinc, copper, and molybdenum (Rittmann and McCarty 2001, Madigan and Martinko 2006). These chemicals are typically found in sufficient quantities in drinking water.

Microbial growth and energy. As indicated previously, macronutrients (C, N, P, H, and O), chemical components (electron donor and electron acceptor for energy production), and micronutrients are required for microbial growth to occur. The greater the energy difference there is between the electron donor and the electron acceptor, the greater the potential there is for microbial growth and the faster the rate of growth will be (Rittmann and McCarty 2001, Madigan and Martinko 2006).

Under aerobic conditions in the presence of organic carbon, about 30 percent of the biochemically available carbon would be used to provide energy for microbiological growth, with 70 percent of the carbon incorporated into new cellular material. Under these same nutrient conditions, but lacking oxygen (anaerobic), about 50 percent of the organic carbon would be used for energy production. This leaves less carbon available for incorporation into new cellular materials. Therefore, a slower growth rate occurs under anaerobic conditions than aerobic conditions (Rittmann and McCarty 2001).

Lacking the presence of organic carbon, less energetic forms of electron donors are utilized (ammonia, H₂, or sulfide) by autotrophic bacteria, with a large portion of the energy in these compounds used to make organic carbon from carbon dioxide (carbon source) for assimilating into new cellular materials, and thus a slower growth rate (Rittmann and McCarty 2001).

The presence of biofilm, the carbohydrates excreted by some microorganisms to adhere to surfaces and for colony protection, creates the potential for a diverse microbial population in proximity to one another. This could enhance the microbial growth because niche bacteria supplement organic carbon and ammonia, respectively, through processes of carbon fixation and nitrogen fixation (Rittmann and McCarty 2001).

Corrosion Pathways

There are various pathways by which MIC can occur.

MIC via transport of nutrients into cells. For microbial growth to occur, nutrients and required chemical components must cross the microbial cell membrane and enter the cell to satisfy cellular needs. Otherwise, they must be accessible to the outer cell membrane for surface-related reactions (Madigan and Martinko 2006).

Transport of nutrients across the cell membrane is highly regulated by biochemical sensors in the membrane to prevent the unwanted transport of harmful compounds into the cell, and to maintain charge balance, salinity, and pH within the cell.

Under nutrient-rich conditions, nutrients are typically able to freely flow in the direction of the concentration gradient and into the cell through *gated porins* (ion-selective channels) in the cell membrane (Madigan and Martinko 2006).

Under nutrient-poor conditions, nutrients must be actively transported into the cell against the concentration gradient. This requires the microbe to produce proteins bound to the outer membrane of its cell that can capture and transport specific nutrients. The energy used to power the transport is in the form of ATP, which also provides other energy needs of the cell (Madigan and Martinko 2006).

The ABC transport system is the most common form of active transport across the cell membrane. ABC stands for ATP-binding cassette, where a *cassette* is a mobile genetic component. Proteins used for nutrient transport generally have a lock and key arrangement, and they protrude from the exterior surface of a microbe in search of a specific nutrient or compound. Once a protein locks on to a target compound, it is transported across the cell membrane (Madigan and Martinko 2006).

The target nutrient compound could be free floating, loosely sorbed to other compounds, or bound to solid minerals. Studies of mineral weathering in groundwater have shown the ability of microbes to selectively remove iron or phosphorus from solid quartz minerals to satisfy cellular needs (Rogers and Bennett 2004). This suggests that the active transport of nutrients across the cell membrane could cause MIC in water systems if the target nutrient is part of a surface on engineered materials in the water system. That is, the transport mechanism of supplying microbiological cells with nutrients may play a role in MIC of plumbing materials.

MIC via biofilm material. *Biofilm* is the term used to describe the mass (community) of microorganisms and the enzymes and other extracellular material that the microorganisms excrete that allow them to stay attached to a surface. Biofilms are generally described by their makeup of polysaccharides, which can change in response to environmental conditions. Biofilms can be corrosive to pipe surfaces if organic acids are present in the polysaccharides that are excreted by the microorganisms. That is, localized low-pH environments created by the biofilm on the pipe wall can corrode the metal (Bremer et al. 2001).

In addition, chemical reduction and oxidation cycles could occur within the biofilm as symbiotic types of bacteria are brought into proximity. These chemical cycles would affect the state of adjacent metals. For example, the anaerobic heterotrophs in the oxygen-starved interior of the biofilm would convert iron pipe to soluble ferrous iron. Then the aerobic autotrophs on the exterior of the biofilm would convert soluble ferrous iron to solid iron precipitates.

MIC via microbiological products. Biofilms can also be corrosive to pipe surfaces if biological processes occurring in the biofilm result in corrosive environmental conditions (e.g., as with the production of a high-sulfide concentration).

Potential for Occurrence of Microbiologically Influenced Corrosion

Regarding MIC, there are many types of microorganisms to be concerned about in a water distribution system, including but not limited to those that cause nitrification. Potential sources of microbiological nutrients, such as nitrogen, phosphorus, sulfate, and carbon, cannot be ignored (Srinivasan and Harrington 2007, Fleming et al. 2005, AWWA 2006).

Several aspects of a water system environment can be investigated to determine whether MIC is occurring.

Biostability. Biostability of water is a balance of factors that encourage the growth of microorganisms versus factors that discourage their growth. Literature on biostability is available (Van der Kooij 1992, Volk and LeChevallier 2000, Escobar and Randall 2002, Zhang et al. 2002). Factors include macronutrient concentrations (carbon, phosphorus, and nitrogen) in the water, disinfection concentration in the water, and resultant microbiological populations. A simple, but effective method of assessing biostability is to track trends of these factors.

Especially important in that exercise is measuring and tracking the population of all microorganisms in the water at various locations in the water system. A relatively new technology to measure the concentration of ATP in the water produces results that can be translated into the population of microorganisms at the sampling location. As discussed previously, ATP is the energy molecule used by living organisms. The analysis protocol ensures that only ATP from living microorganisms is captured in the sample fraction that is analyzed. If ATP is found in a drinking water sample by this analysis, then there are living microorganisms in the water. The ATP test is a better investigative tool for biostability than older analytical methods, such as heterotrophic plate count. This is because the ATP concentration quantifies all microorganisms in the water (except viruses), not just particular types of bacteria, and is not limited only to bacteria. The specifics of water analyses are explained in chapter 3, as there are several interesting new microbiological analytical techniques. With the ATP test, trends of microbiological populations can be compared with nutrient and disinfection trends. As disinfection is increased or nutrients decreased in water system operations, the effect on the microbiological population can be measured and operations that appear to lower the populations repeated.

A more theoretical but quantitative assessment can be made by comparing the molal concentrations of nutrients to calculate the potential microbiological population. That is, the required ratio of C:N:P changes slightly with each type of microorganism and the nutrient environment they require (Rittmann and McCarty 2001). Microorganisms using organic carbon for growth in an aerobic environment generally require the ratio C144:N16:P1 (Letscher et al. 2015). Lacking organic carbon, the required ratio becomes C88:N16:P1 for autotrophic growth (Rittmann and McCarty 2001).

A ratio of C100:N10:P has been used to generally analyze the potential for microbial growth in water, with C based on carbon that is accessible to microorganisms as a nutrient (Edzwald 2011). See chapter 3 for further discussion.

These ratios can be used to determine which required components are limiting and predict whether excessive microbiological growth could occur. When the concentrations of nutrients in the water approach the nutrient ratios required for various microorganisms' growth, a higher disinfection concentration is needed in the water to counteract the growth.

There should also be awareness that some disinfectants are more powerful than others. Although chloramine disinfection has advantages over free chlorine as a disinfectant in some water systems, a higher dose of chloramine is required to equal the protective level of free chlorine at a lower dose. For instance, it would not be uncommon for a water system using chloramine to use a dose of 2.0 to 2.5 mg/L total chlorine (Zhang et al. 2002)