CORROSION CONTROL TREATMENT TRAINING

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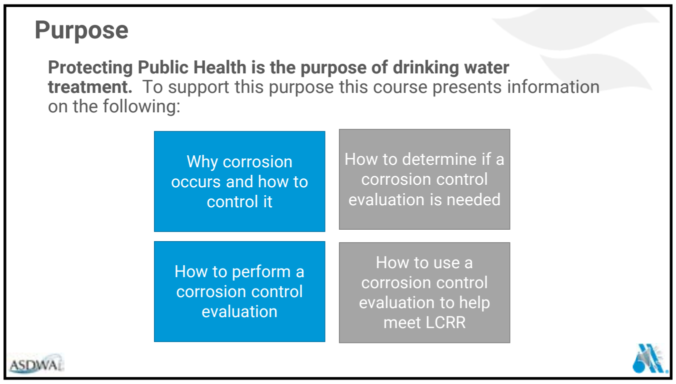

Purpose

Protecting Public Health is the purpose of drinking water treatment. To support this purpose this course presents information on the following:

- Why corrosion occurs and how to control it
- How to determine if a corrosion control evaluation is needed
- How to perform a corrosion control evaluation
- How to use a corrosion control evaluation to help meet LCRR

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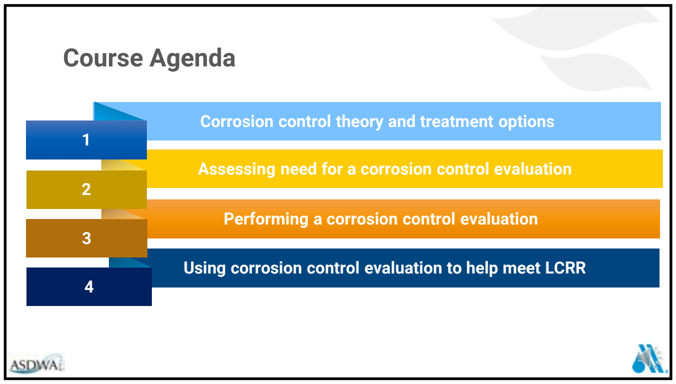

Course Agenda

1. Corrosion control theory and treatment options
2. Assessing need for a corrosion control evaluation
3. Performing a corrosion control evaluation
4. Using corrosion control evaluation to help meet LCRR

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MODULE 1
CORROSION CONTROL THEORY AND TREATMENT OPTIONS

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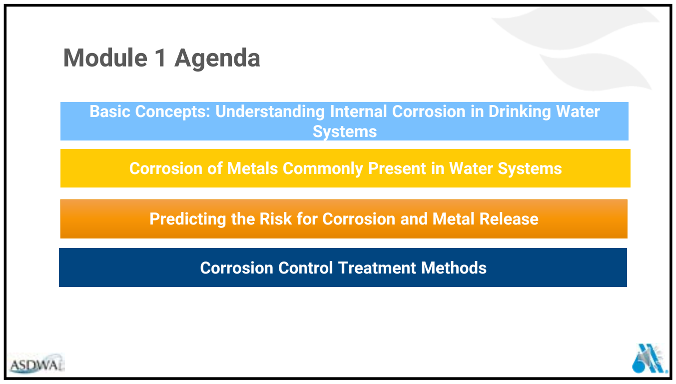

Module 1 Agenda

- Basic Concepts: Understanding Internal Corrosion in Drinking Water Systems
- Corrosion of Metals Commonly Present in Water Systems
- Predicting the Risk for Corrosion and Metal Release
- Corrosion Control Treatment Methods

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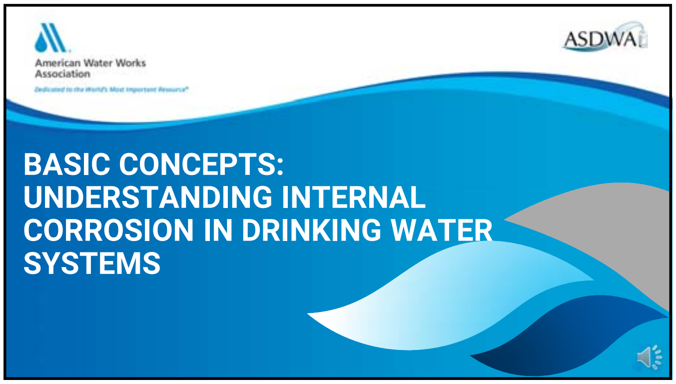

BASIC CONCEPTS: UNDERSTANDING INTERNAL CORROSION IN DRINKING WATER SYSTEMS

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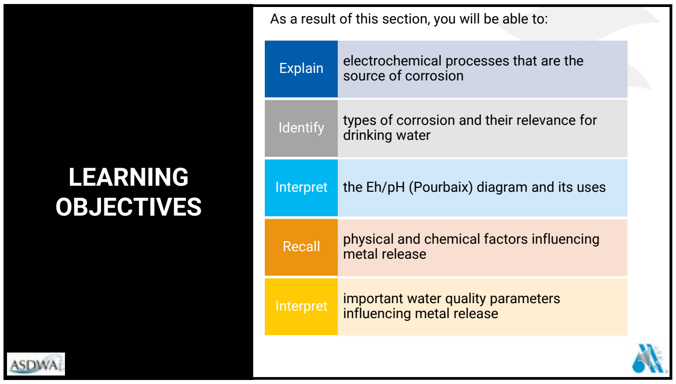


LEARNING OBJECTIVES

As a result of this section, you will be able to:

Explain	electrochemical processes that are the source of corrosion
Identify	types of corrosion and their relevance for drinking water
Interpret	the Eh/pH (Pourbaix) diagram and its uses
Recall	physical and chemical factors influencing metal release
Interpret	important water quality parameters influencing metal release

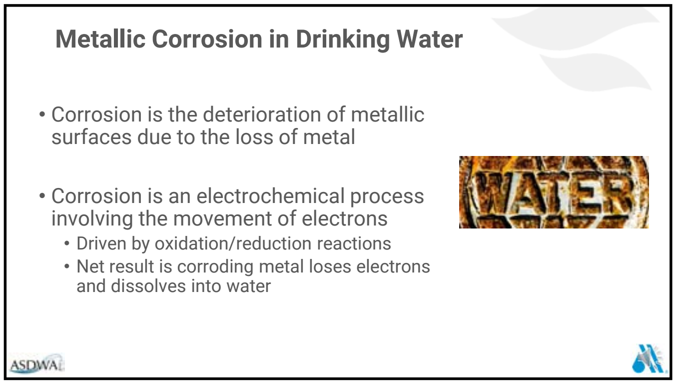
Materials and Corrosion Issues Discussed

Lead, Copper and Galvanized Steel

Iron and Steel

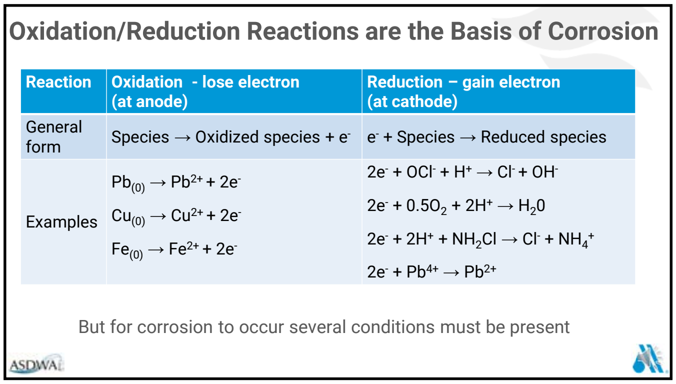
Brass

Leaded Solder



Metallic Corrosion in Drinking Water

- Corrosion is the deterioration of metallic surfaces due to the loss of metal
- Corrosion is an electrochemical process involving the movement of electrons
  - Driven by oxidation/reduction reactions
  - Net result is corroding metal loses electrons and dissolves into water



Oxidation/Reduction Reactions are the Basis of Corrosion

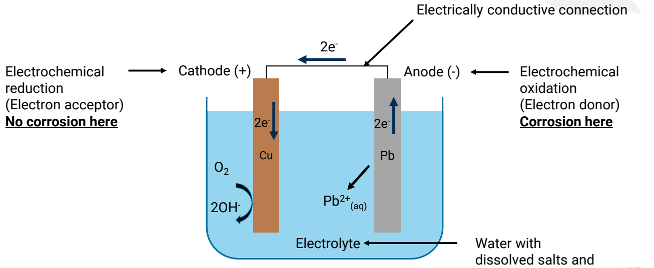
Reaction	Oxidation - lose electron (at anode)	Reduction – gain electron (at cathode)
General form	Species → Oxidized species + e^-	e^- + Species → Reduced species
Examples	$Pb_{(0)} \rightarrow Pb^{2+} + 2e^-$ $Cu_{(0)} \rightarrow Cu^{2+} + 2e^-$ $Fe_{(0)} \rightarrow Fe^{2+} + 2e^-$	$2e^- + OCl^- + H^+ \rightarrow Cl^- + OH^-$ $2e^- + 0.5O_2 + 2H^+ \rightarrow H_20$ $2e^- + 2H^+ + NH_2Cl \rightarrow Cl^- + NH_4^+$ $2e^- + Pb^{4+} \rightarrow Pb^{2+}$

But for corrosion to occur several conditions must be present

Corrosion Requires 4 Components to Occur

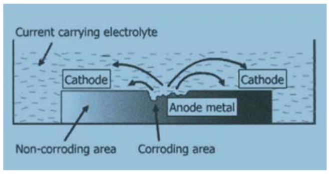
1. Anode – place electrons are provided and metal is lost (i.e. corrodes)
2. Cathode – place electrons are accepted and corrosion scales may deposit
3. Metallic pathway between anode and cathode
4. Electrolytic solution (water containing ions) in contact with anode and cathode

Four Components of Galvanic Cell - Example Involving Cu and Pb

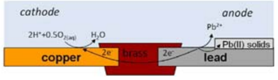


Common Types of Internal Corrosion

Uniform Corrosion



Galvanic Corrosion



Chemical equation for Pb corrosion

At the anode: $Pb_{(s)} \rightarrow Pb^{2+} + 2e^-$
At the cathode: $0.5\ O_{2(aq)} + 2H^+ + 2e^- \rightarrow H_2O$
Net reaction: $Pb_{(s)} + 0.5\ O_{2(aq)} + 2H^+ \rightarrow Pb^{2+} + H_2O$

Uniform and Galvanic Corrosion

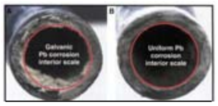
Uniform

Wasserstrom et al 2017

Galvanic

DeSantis et al. 2018

Compared



Triantafyllidou & Edwards 2011

Galvanic Series Predicts if Galvanic Corrosion can Occur

Corrodes easily

Difficult to corrode

Material	Anode reaction	Potential (volts)
Magnesium	$Mg_{(s)} \rightarrow Mg^{2+} + 2e^-$	+2.37
Zinc	$Zn_{(s)} \rightarrow Zn^{2+} + 2e^-$	+0.76
Steel, iron	$Fe_{(s)} \rightarrow Fe^{2+} + 2e^-$	+0.44
Cast iron	$Fe_{(s)} \rightarrow Fe^{2+} + 2e^-$	+0.44
Tin	$Sn_{(s)} \rightarrow Sn^{2+} + 2e^-$	+0.14
Lead	$Pb_{(s)} \rightarrow Pb^{2+} + 2e^-$	+0.13
Brass	-	≈ -0.34
Bronze	-	≈ -0.31
Copper	$Cu_{(s)} \rightarrow Cu^{2+} + 2e^-$	-0.35
Gold	$Au_{(s)} \rightarrow Au^{3+} + 3e^-$	-1.5

- Material with greater potential (volts) corrodes when in contact with material of lower potential
- Greater difference in potentials, greater tendency for corrosion to occur

KNOWLEDGE CHECK

Can the tendency for a metal to corrode can be predicted?
(True/False)

Types of Corrosion Resulting in Metal Release

Type	Description	Becomes relevant when
Uniform	Uniform thinning of metal	Fresh lead or copper surface present
Galvanic	Metals of different electrochemical potential in contact within electrolyte	Lead contacts more noble (cathodic) metal.
Microbially influenced	Microbes moderate or catalyze corrosion	Microbial action releases metals or destabilizes scales
Selective leaching	Zinc selectively leached from galvanized pipe	Loss of zinc allows galvanized pipe to corrode; these corrosion products retain/release lead or other metals

Corrosion deposits (particularly in Fe pipe) can create unacceptable head loss

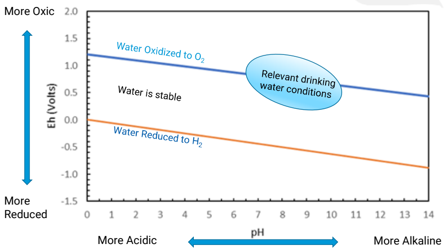
Types of Corrosion Resulting in Pipe Failure

Type	Description	Becomes relevant when
Pitting	Localized formation of pits	Problem for copper pipe
Crevice	Corrosion at voids between surfaces	• Limited concern with respect to lead and copper • Possible in Fe pipe when associated with external corrosion • Corrosion deposits in Fe pipe create unacceptable head loss
Stress	Corrosion worsened by high levels of mechanical stress	
Fatigue	Corrosion worsened by mechanical fatigue	

Overview of Eh/pH Diagram

Plots condition of water by oxidation/reduction state and pH

- Note water is not stable at all conditions
- Drinking water conditions occupy small part of diagram



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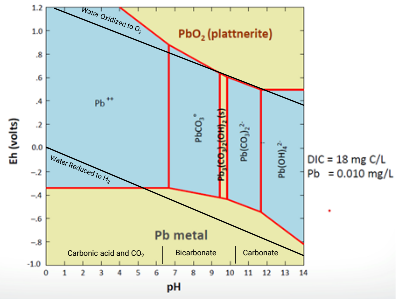
Example Eh/pH Diagram for Pb/Carbonate System



Adapted from Triantafyllidou & Schock 2019

- Called Pourbaix Diagram
- Predicts equilibrium state of a metal as a function of oxidation/reduction potential (measured as Eh) and pH

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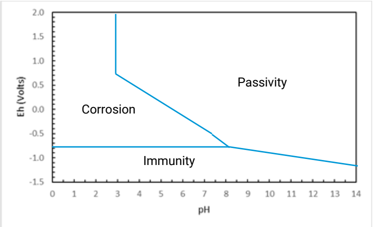
Regions in Pourbaix Diagram

- **Corrosion**: susceptible to corrosion (sufficient chemical potential to initiate corrosion)
- **Immunity**: not susceptible to corrosion (insufficient chemical potential to initiate corrosion)
- **Passivity**: stable surface coating forms interrupting corrosion



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KNOWLEDGE CHECK

What water quality parameters are used when plotting a Pourbaix Diagram?

a) Alkalinity and pH
b) Oxidation reduction potential and pH
c) Metal concentration and pH
d) Oxidation reduction potential and temperature

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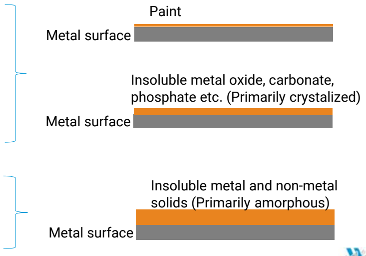
Passivation vs. Diffusion Barrier

- Passivation
  - Formation of insoluble barrier on metal surface interrupting oxidation/reduction reaction causing corrosion
  - Can be very effective
    - Aluminum, stainless steel
- Diffusion Barrier
  - Formation of amorphous barrier which slows/hinders diffusion of metals to bulk water



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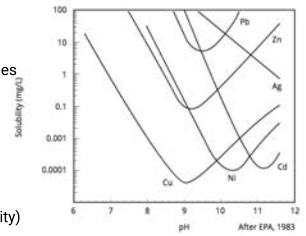
Metal Release from Corrosion Scales and Deposits – Solubility and Kinetics

- *Solubility* is the maximum amount of the substance that can dissolve into water
- Metal corrosion scales have different solubilities
  - Solubility is strongly influenced by pH
- Rate substance dissolves is measured by its *dissolution kinetics*
- Actual amount of metal which dissolves is controlled by
  - Amount of metal that can dissolve (solubility)
  - Speed at which it can dissolve (kinetics)



Solubility diagram for some common metal hydroxides

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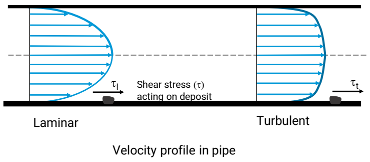
KNOWLEDGE CHECK

Referring to the solubility diagram on the previous slide, which metal is the least soluble at pH 10?

a) Zinc (Zn)
b) Copper (Cu)
c) Lead (Pb)
d) Nickel (Ni)

Forces and Stresses Acting on Pipe Wall Deposits



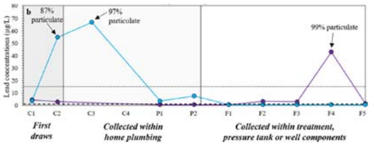
Velocity profile in pipe

- Water flow in pipe creates shear stress (τ) on deposits adhering to pipe wall
- Shear stress increases with
  - Distance from wall
  - Average velocity of water
  - Turbulent vs. laminar flow ($\tau_t > \tau_l$)
- Deposit breaks free when shear strength is exceeded
  - Deposit to wall
  - Within deposit
- Other forces release deposits
  - Flow reversal
  - Water hammer
  - Physical disturbance

Dissolved and Particulate Metal Release

- Dissolved metal released by
  - Corrosion of metal
  - Dissolution of corrosion deposits
- Particulates containing metals released by
  - Forces acting on deposits
- Dissolution weakens deposits
  - Less force needed to release particulates
- Profile sampling can capture dissolved and particulate metal release

Tap lead profile sampling



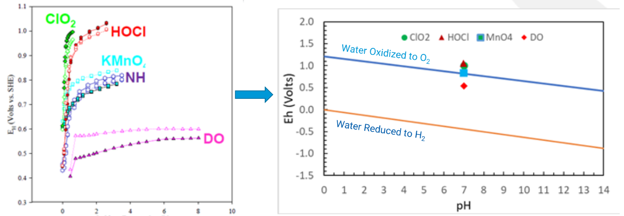
Adapted from Pipet et al. 2015

KNOWLEDGE CHECK

Why are particulates associated with Pb release so difficult to deal with?

a) Particulates release from scales is unpredictable
b) Particulates can accumulate downstream from its point of release
c) A large proportion of the particulate can consist of Pb
d) All of the above

Oxidation Reduction Potential (ORP) is Controlled by Oxidants in Water



James et al. 2004

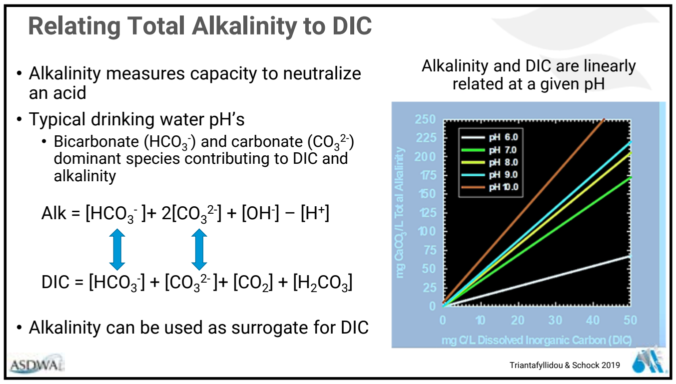
Oxidizing potential influences
- Type of corrosion
- Rate corrosion occurs
- If corrosion scales forms
- Stability of corrosion scales

Dissolved Inorganic Carbon (DIC)

- Sum of inorganic carbon in water contributed by the carbonate system:

DIC = carbon dioxide + carbonic acid + bicarbonate + carbonate
Or
DIC = $[CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

- Must be calculated
- Plays critical role in corrosion control due to its impact on the formation and stability of Pb, Cu and Fe scales
  - Carbonate species form metallic mineral scales (example $PbCO_3$)
  - Carbonate species can complex metal ions destabilizing scales



Relating Total Alkalinity to DIC

- Alkalinity measures capacity to neutralize an acid
- Typical drinking water pH's
  - Bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) dominant species contributing to DIC and alkalinity

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

$$\updownarrow \qquad \updownarrow$$

$$DIC = [HCO_3^-] + [CO_3^{2-}] + [CO_2] + [H_2CO_3]$$

- Alkalinity can be used as surrogate for DIC

Alkalinity and DIC are linearly related at a given pH

Triantafyllidou & Schock 2019

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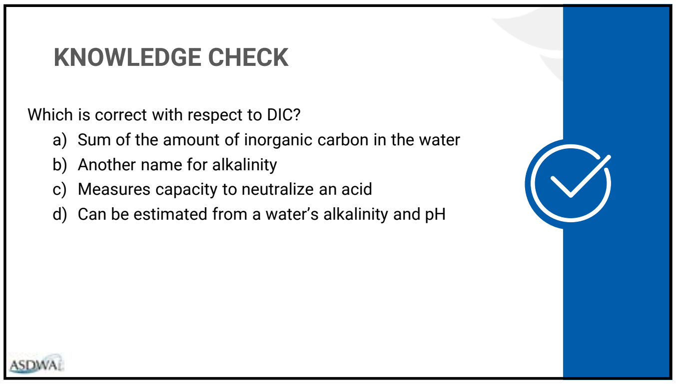

KNOWLEDGE CHECK

Which is correct with respect to DIC?

a) Sum of the amount of inorganic carbon in the water
b) Another name for alkalinity
c) Measures capacity to neutralize an acid
d) Can be estimated from a water's alkalinity and pH

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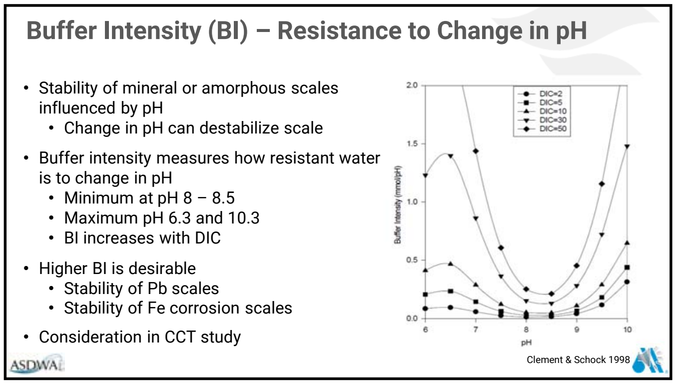

Buffer Intensity (BI) – Resistance to Change in pH

- Stability of mineral or amorphous scales influenced by pH
  - Change in pH can destabilize scale
- Buffer intensity measures how resistant water is to change in pH
  - Minimum at pH 8 – 8.5
  - Maximum pH 6.3 and 10.3
  - BI increases with DIC
- Higher BI is desirable
  - Stability of Pb scales
  - Stability of Fe corrosion scales
- Consideration in CCT study

Clement & Schock 1998

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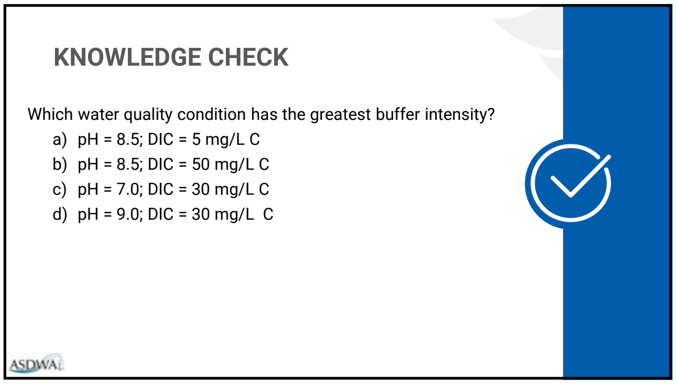

KNOWLEDGE CHECK

Which water quality condition has the greatest buffer intensity?

a) pH = 8.5; DIC = 5 mg/L C
b) pH = 8.5; DIC = 50 mg/L C
c) pH = 7.0; DIC = 30 mg/L C
d) pH = 9.0; DIC = 30 mg/L C

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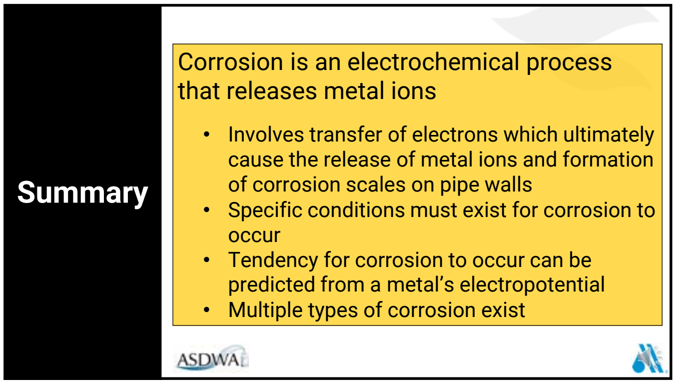

Summary

Corrosion is an electrochemical process that releases metal ions

- Involves transfer of electrons which ultimately cause the release of metal ions and formation of corrosion scales on pipe walls
- Specific conditions must exist for corrosion to occur
- Tendency for corrosion to occur can be predicted from a metal's electropotential
- Multiple types of corrosion exist

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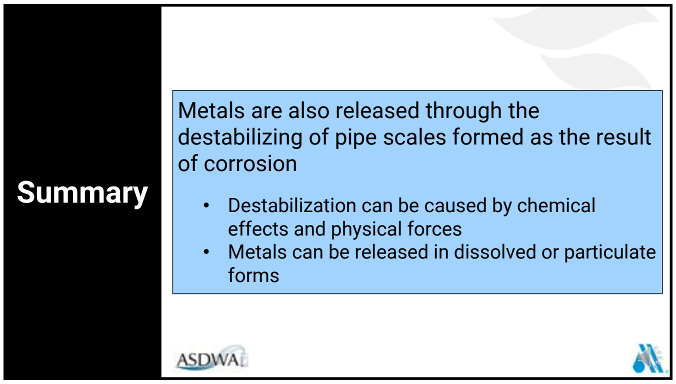

Summary

Metals are also released through the destabilizing of pipe scales formed as the result of corrosion

- Destabilization can be caused by chemical effects and physical forces
- Metals can be released in dissolved or particulate forms

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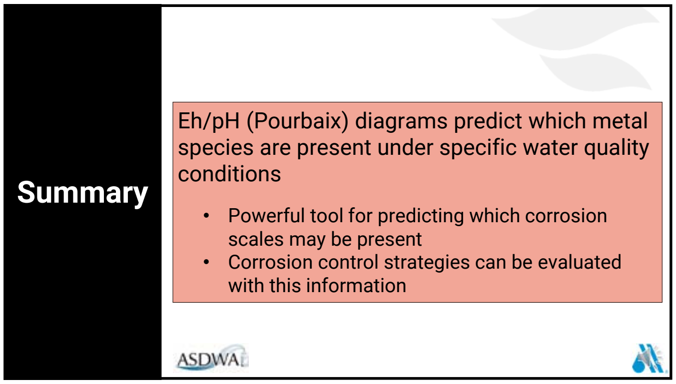
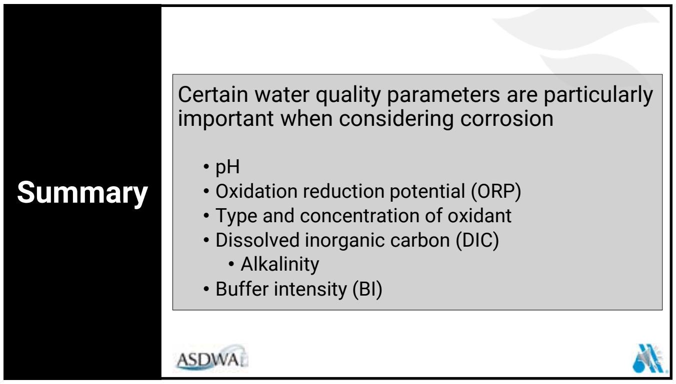


Summary

Eh/pH (Pourbaix) diagrams predict which metal species are present under specific water quality conditions

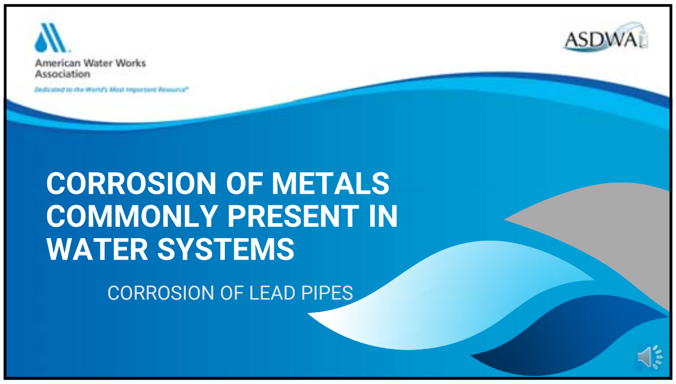
- Powerful tool for predicting which corrosion scales may be present
- Corrosion control strategies can be evaluated with this information



Summary

Certain water quality parameters are particularly important when considering corrosion

- pH
- Oxidation reduction potential (ORP)
- Type and concentration of oxidant
- Dissolved inorganic carbon (DIC)
  - Alkalinity
- Buffer intensity (BI)

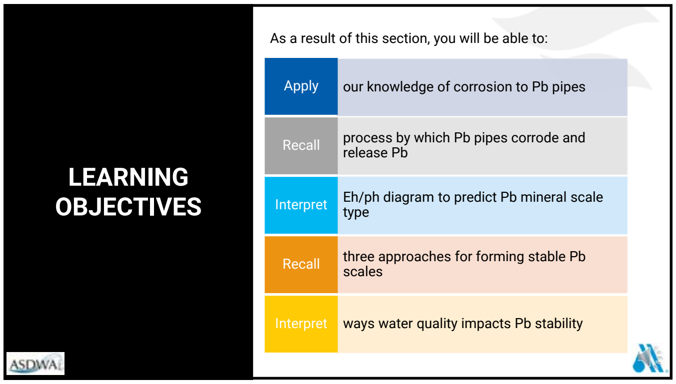


American Water Works Association

Dedicated to the World's Most Important Resource

CORROSION OF METALS COMMONLY PRESENT IN WATER SYSTEMS

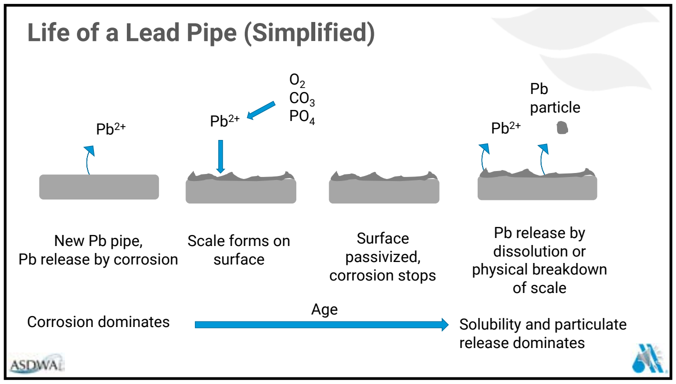
CORROSION OF LEAD PIPES



LEARNING OBJECTIVES

As a result of this section, you will be able to:

Apply	our knowledge of corrosion to Pb pipes
Recall	process by which Pb pipes corrode and release Pb
Interpret	Eh/ph diagram to predict Pb mineral scale type
Recall	three approaches for forming stable Pb scales
Interpret	ways water quality impacts Pb stability



Life of a Lead Pipe (Simplified)

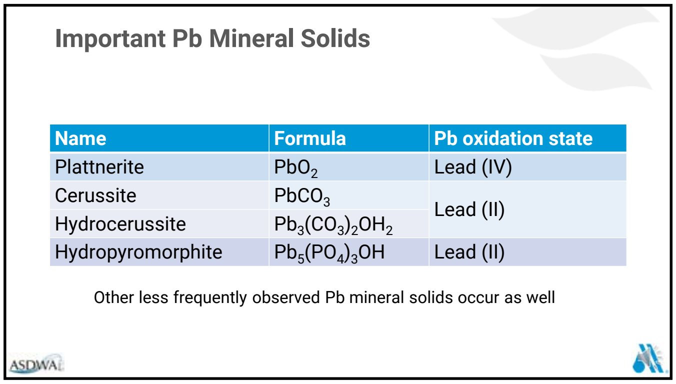
New Pb pipe, Pb release by corrosion

Scale forms on surface

Surface passivized, corrosion stops

Pb release by dissolution or physical breakdown of scale

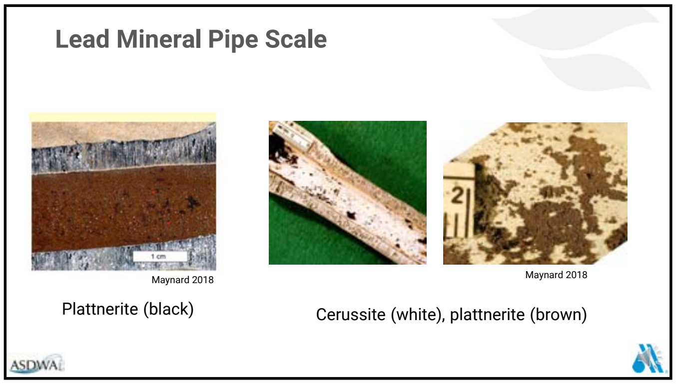
Corrosion dominates → Age → Solubility and particulate release dominates



Important Pb Mineral Solids

Name	Formula	Pb oxidation state
Plattnerite	PbO_2	Lead (IV)
Cerussite	$PbCO_3$	Lead (II)
Hydrocerussite	$Pb_3(CO_3)_2OH_2$	
Hydropyromorphite	$Pb_5(PO_4)_3OH$	Lead (II)

Other less frequently observed Pb mineral solids occur as well



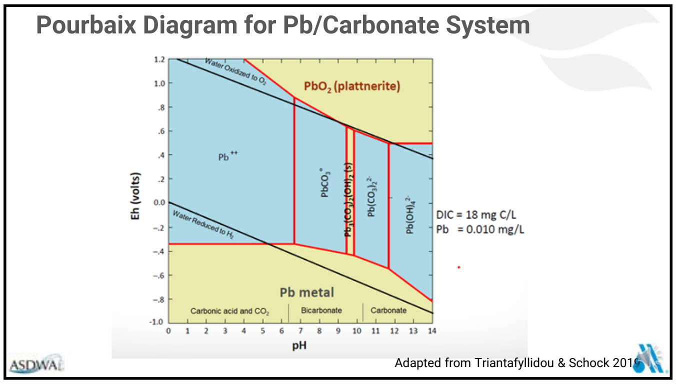
Lead Mineral Pipe Scale

Maynard 2018

Plattnerite (black)

Maynard 2018

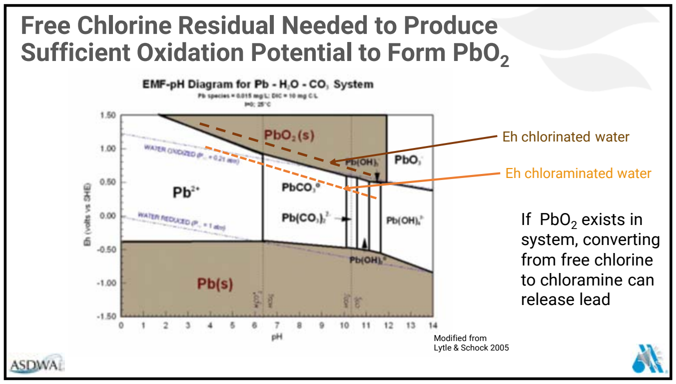
Cerussite (white), plattnerite (brown)



Pourbaix Diagram for Pb/Carbonate System

DIC = 18 mg C/L
Pb = 0.010 mg/L

Adapted from Triantafyllidou & Schock 2016



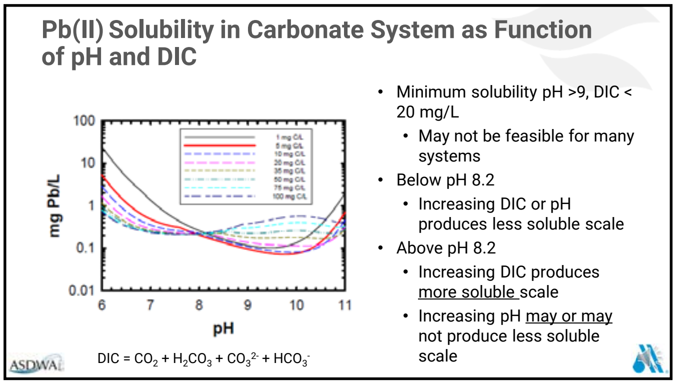
Free Chlorine Residual Needed to Produce Sufficient Oxidation Potential to Form PbO_2

Eh chlorinated water

Eh chloraminated water

If PbO_2 exists in system, converting from free chlorine to chloramine can release lead

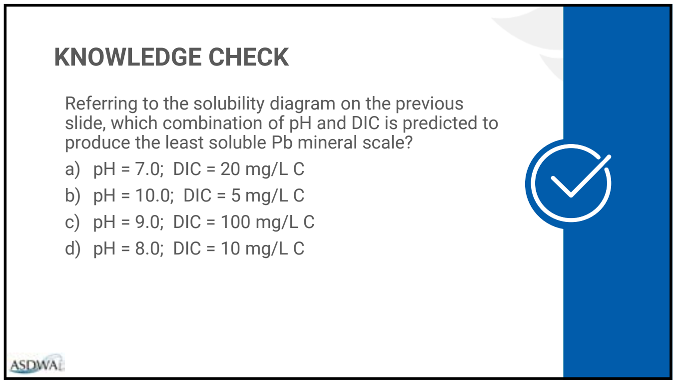
Modified from
Lytle & Schock 2005



Pb(II) Solubility in Carbonate System as Function of pH and DIC

DIC = $CO_2 + H_2CO_3 + CO_3^{2-} + HCO_3^-$

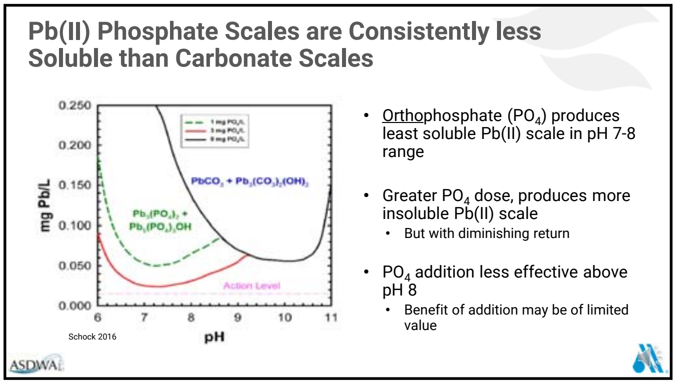
- Minimum solubility pH >9, DIC < 20 mg/L
  - May not be feasible for many systems
- Below pH 8.2
  - Increasing DIC or pH produces less soluble scale
- Above pH 8.2
  - Increasing DIC produces more soluble scale
  - Increasing pH may or may not produce less soluble scale



KNOWLEDGE CHECK

Referring to the solubility diagram on the previous slide, which combination of pH and DIC is predicted to produce the least soluble Pb mineral scale?

a) pH = 7.0; DIC = 20 mg/L C
b) pH = 10.0; DIC = 5 mg/L C
c) pH = 9.0; DIC = 100 mg/L C
d) pH = 8.0; DIC = 10 mg/L C



Pb(II) Phosphate Scales are Consistently less Soluble than Carbonate Scales

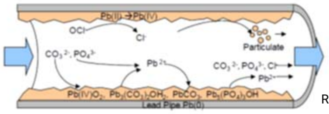
Schock 2016

- Orthophosphate (PO_4) produces least soluble Pb(II) scale in pH 7-8 range
- Greater PO_4 dose, produces more insoluble Pb(II) scale
  - But with diminishing return
- PO_4 addition less effective above pH 8
  - Benefit of addition may be of limited value

Managing Water Quality to Promote Stable Pb Scale Formation

Approach	How	Consideration
Form lead(IV) oxide	High ORP by maintaining elevated Cl_2 residual (1.5-2 mg/L residual)	Difficult to maintain sufficient residual – particularly in premise plumbing DBP formation
Form lead(II) carbonate(s)	Adjust pH and/or DIC (alkalinity) (maintain pH +/- 0.25)	Sensitive to changes in pH and alkalinity May conflict with other compliance requirements
Form lead(II) phosphate(s)	Add **ortho**phosphate (1 – 4 mg/L as PO_4)	Additional chemical Additional nutrient load to WWTP Additional biological activity in distribution system May promote movement of particulate lead

Reality is Far more Complex than Simple Solubility Models

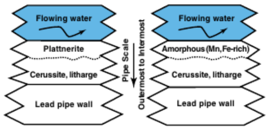


Ref Xie 2010

- Pipe is chemical reactor – not at equilibrium
- Physical integrity of scale is important but not predicted by modeling
- Observed scales are frequently amorphous or with multiple mineral phase
- Deposits from other materials present
- Biological activity and biofilms influence surface characteristics

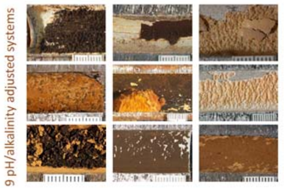
More Realistic Look at Pb Pipe Scale and Deposits

Multiple layers present



Schock et.al. 2014

Non-lead deposits present



Schock 2018

- These factors tend to produce less resilient scale – more particulate Pb
- Cannot be modeled - requires sampling and testing

Impact of Water Quality Parameters on Pb Corrosion and Release

Parameter	Impact
Chloride	Corrosion rates increase with greater chloride levels Sensitive to raw water contamination by road salt
Sulfate	May increase or decrease corrosion rates Ratio with chloride (CSMR) important when galvanic corrosion is present
Natural organic matter (NOM)	Interferes with orthophosphate corrosion inhibitor Produces more porous corrosion scales
Ammonia	Forms combined chlorine in free chlorine systems reducing ORP of water Promotes greater biological activity (nitrification)
Iron	Particulate iron can sorb Pb, which is mobilized with iron particle
Aluminum	Interferes with orthophosphate corrosion inhibitor Aluminum deposition weakens Pb scales/deposits
Assimilable organic carbon	Higher levels encourage bioactivity and biofilms – weakens scale/deposit
Temperature	Increase rate of corrosion

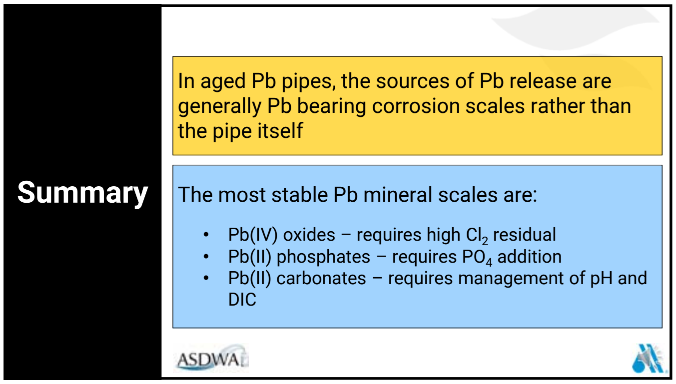
Mn Plays a Large Role in Pb Corrosion and Release

Observation	Impact
Promotes formation amorphous lead scale	Weakens scale increasing risk of lead release
Interferes with formation of lead phosphate scales	Reduces effectiveness of orthophosphate as lead corrosion inhibitor
Acts as lead scavenger	Vector for movement of particulate lead
Mn(IV) acts as electron acceptor during lead oxidation	Release soluble lead
Mn(II) catalyzes Pb(II) oxidation to Pb(IV) in presence of Cl_2	Possible benefit(!) of Mn by promoting formation of PbO_2
Use of polyphosphate to sequester Mn	Causes destabilization of lead scales and lead release

KNOWLEDGE CHECK

Name three ways to promote stable Pb mineral scale formation

a) Control pH and DIC to produce Pb(II) carbonate
b) Maintain high ORP to form Pb(IV) oxides
c) Add orthophosphate as a corrosion inhibitor
d) Add polyphosphate as a corrosion inhibitor

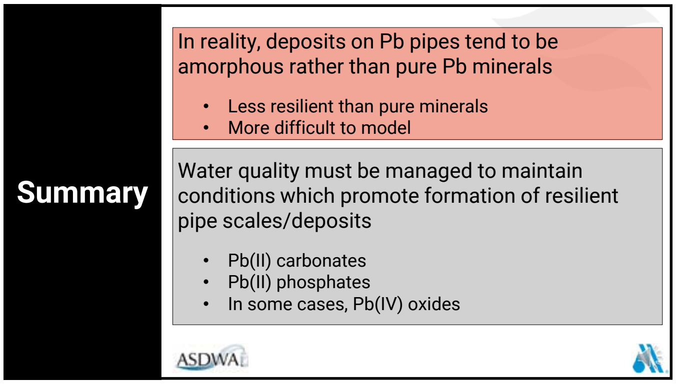


Summary

In aged Pb pipes, the sources of Pb release are generally Pb bearing corrosion scales rather than the pipe itself

The most stable Pb mineral scales are:

- Pb(IV) oxides – requires high Cl_2 residual
- Pb(II) phosphates – requires PO_4 addition
- Pb(II) carbonates – requires management of pH and DIC



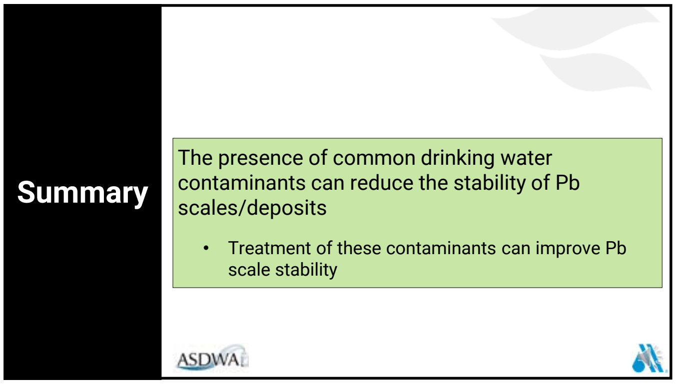
Summary

In reality, deposits on Pb pipes tend to be amorphous rather than pure Pb minerals

- Less resilient than pure minerals
- More difficult to model

Water quality must be managed to maintain conditions which promote formation of resilient pipe scales/deposits

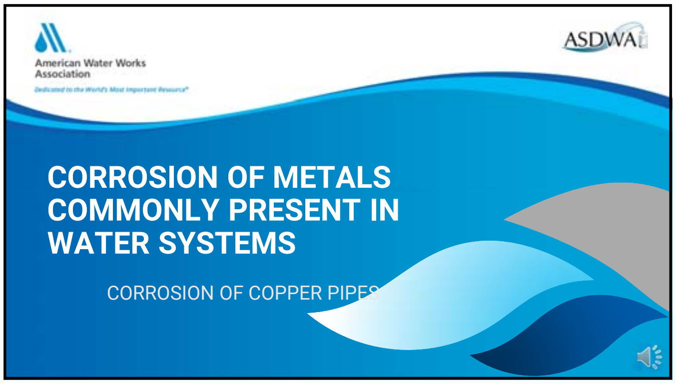
- Pb(II) carbonates
- Pb(II) phosphates
- In some cases, Pb(IV) oxides



Summary

The presence of common drinking water contaminants can reduce the stability of Pb scales/deposits

- Treatment of these contaminants can improve Pb scale stability



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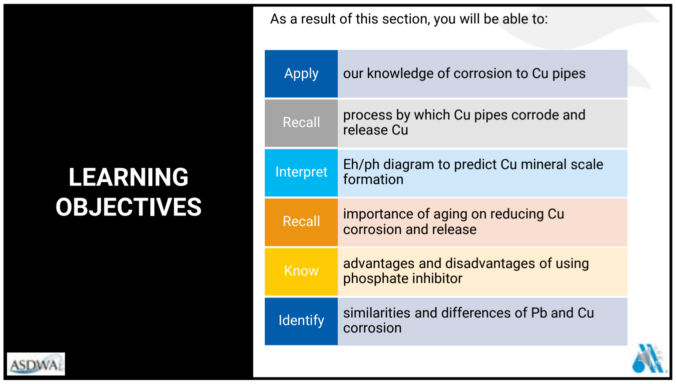
CORROSION OF METALS COMMONLY PRESENT IN WATER SYSTEMS

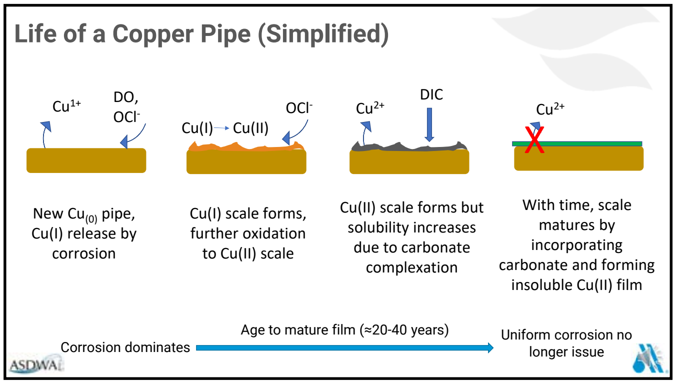
CORROSION OF COPPER PIPES



LEARNING OBJECTIVES

As a result of this section, you will be able to:

Apply	our knowledge of corrosion to Cu pipes
Recall	process by which Cu pipes corrode and release Cu
Interpret	Eh/ph diagram to predict Cu mineral scale formation
Recall	importance of aging on reducing Cu corrosion and release
Know	advantages and disadvantages of using phosphate inhibitor
Identify	similarities and differences of Pb and Cu corrosion



Life of a Copper Pipe (Simplified)

New $Cu_{(0)}$ pipe, Cu(I) release by corrosion

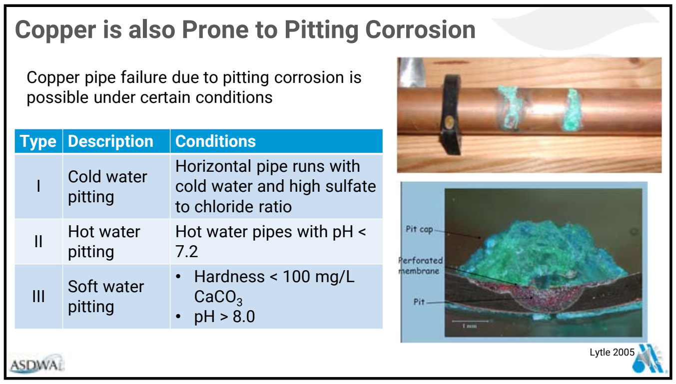
Cu(I) scale forms, further oxidation to Cu(II) scale

Cu(II) scale forms but solubility increases due to carbonate complexation

With time, scale matures by incorporating carbonate and forming insoluble Cu(II) film

Age to mature film (≈20-40 years)

Corrosion dominates → Uniform corrosion no longer issue



Copper is also Prone to Pitting Corrosion

Copper pipe failure due to pitting corrosion is possible under certain conditions

Type	Description	Conditions
I	Cold water pitting	Horizontal pipe runs with cold water and high sulfate to chloride ratio
II	Hot water pitting	Hot water pipes with pH < 7.2
III	Soft water pitting	• Hardness < 100 mg/L $CaCO_3$ • pH > 8.0

Lytle 2005

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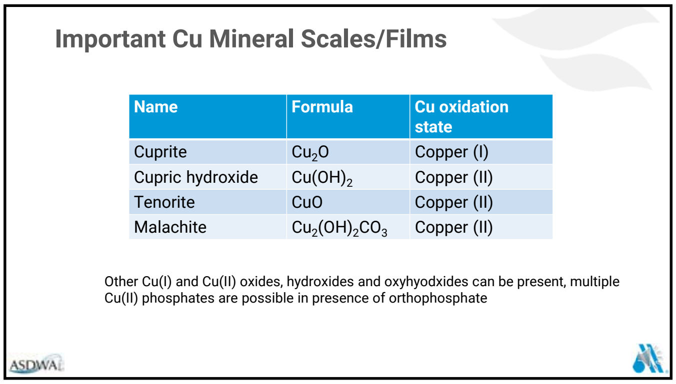

Important Cu Mineral Scales/Films

Name	Formula	Cu oxidation state
Cuprite	Cu_2O	Copper (I)
Cupric hydroxide	$Cu(OH)_2$	Copper (II)
Tenorite	CuO	Copper (II)
Malachite	$Cu_2(OH)_2CO_3$	Copper (II)

Other Cu(I) and Cu(II) oxides, hydroxides and oxyhyodxides can be present, multiple Cu(II) phosphates are possible in presence of orthophosphate

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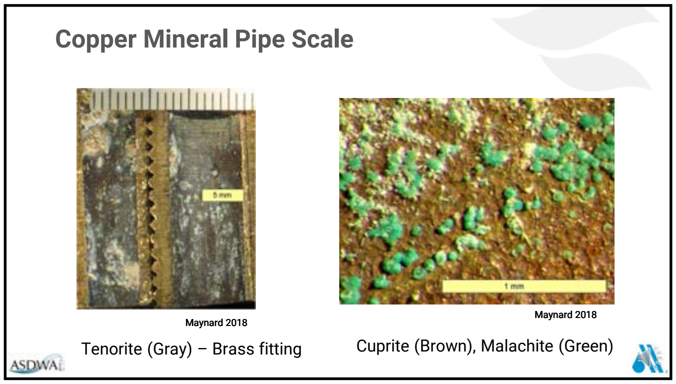

Copper Mineral Pipe Scale

Maynard 2018

Tenorite (Gray) – Brass fitting

Maynard 2018

Cuprite (Brown), Malachite (Green)

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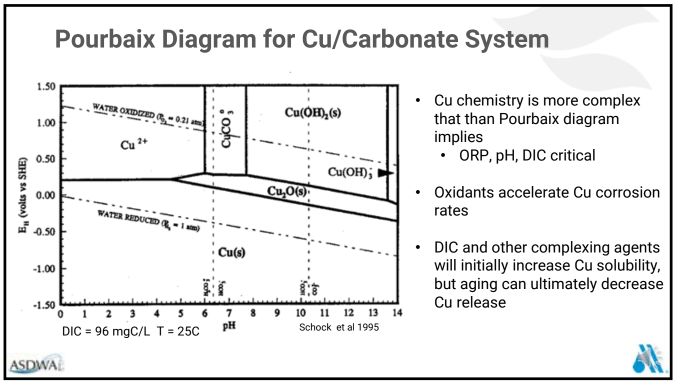

Pourbaix Diagram for Cu/Carbonate System

DIC = 96 mgC/L T = 25C

Schock et al 1995

- Cu chemistry is more complex that than Pourbaix diagram implies
  - ORP, pH, DIC critical
- Oxidants accelerate Cu corrosion rates
- DIC and other complexing agents will initially increase Cu solubility, but aging can ultimately decrease Cu release

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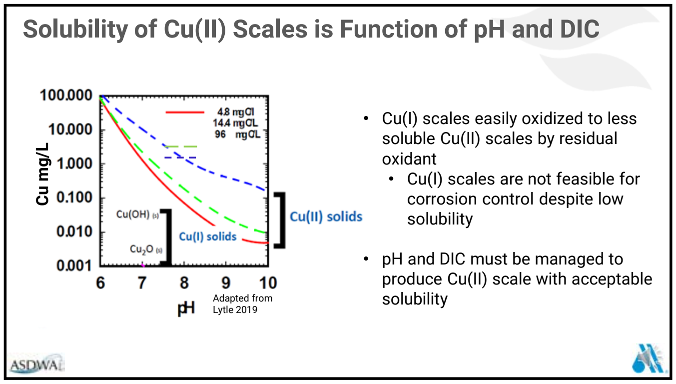

Solubility of Cu(II) Scales is Function of pH and DIC

Adapted from Lytle 2019

- Cu(I) scales easily oxidized to less soluble Cu(II) scales by residual oxidant
  - Cu(I) scales are not feasible for corrosion control despite low solubility
- pH and DIC must be managed to produce Cu(II) scale with acceptable solubility

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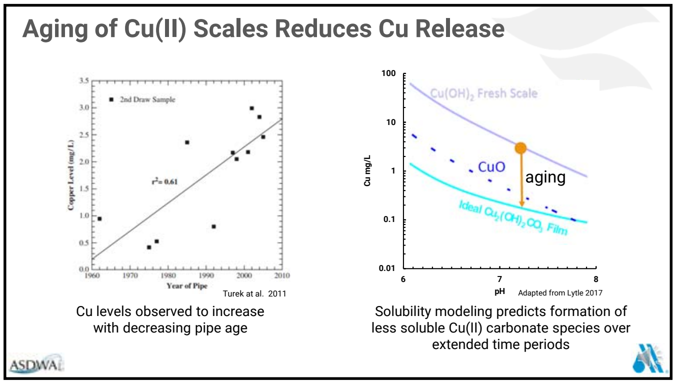

Aging of Cu(II) Scales Reduces Cu Release

Turek at al. 2011

Cu levels observed to increase with decreasing pipe age

Adapted from Lytle 2017

Solubility modeling predicts formation of less soluble Cu(II) carbonate species over extended time periods

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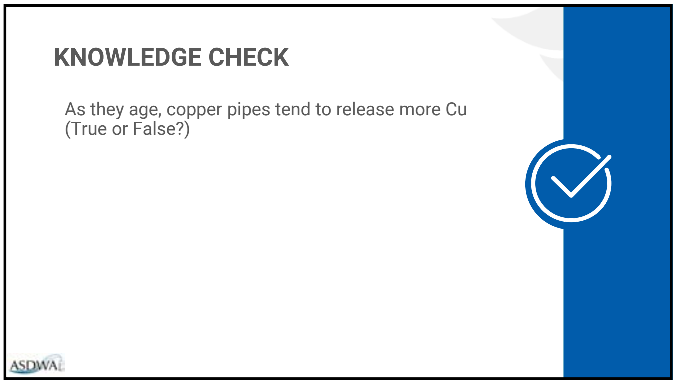
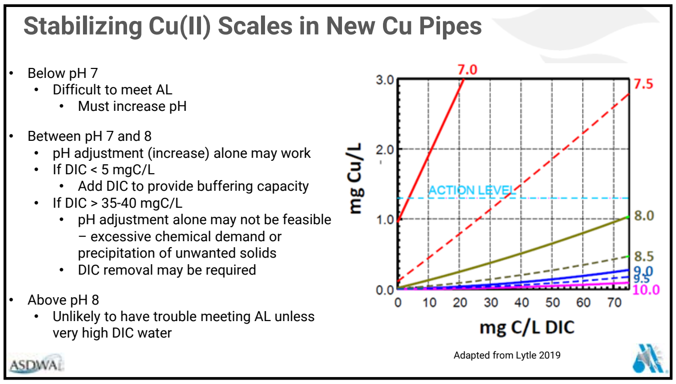


KNOWLEDGE CHECK

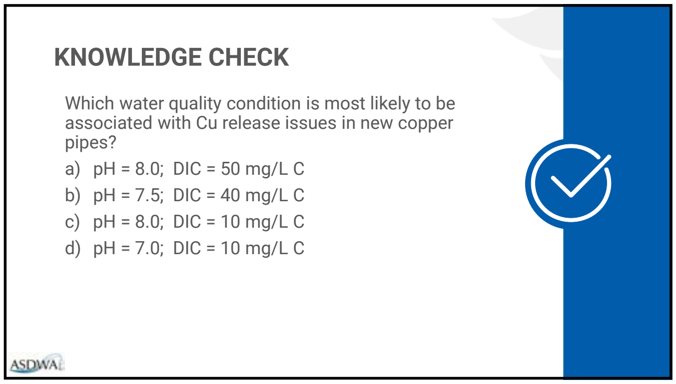
As they age, copper pipes tend to release more Cu (True or False?)



Stabilizing Cu(II) Scales in New Cu Pipes

- Below pH 7
  - Difficult to meet AL
    - Must increase pH
- Between pH 7 and 8
  - pH adjustment (increase) alone may work
  - If DIC < 5 mgC/L
    - Add DIC to provide buffering capacity
  - If DIC > 35-40 mgC/L
    - pH adjustment alone may not be feasible – excessive chemical demand or precipitation of unwanted solids
    - DIC removal may be required
- Above pH 8
  - Unlikely to have trouble meeting AL unless very high DIC water

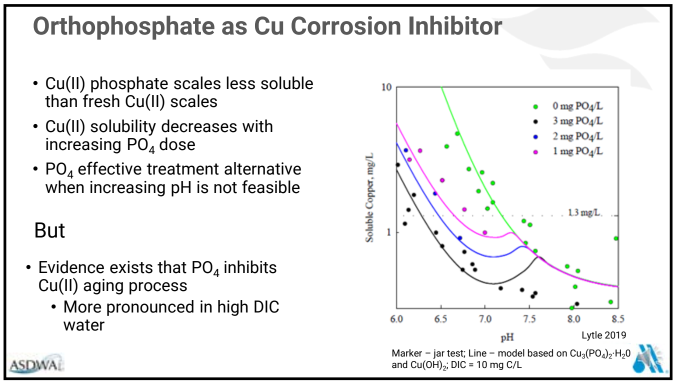
Adapted from Lytle 2019



KNOWLEDGE CHECK

Which water quality condition is most likely to be associated with Cu release issues in new copper pipes?

a) pH = 8.0; DIC = 50 mg/L C
b) pH = 7.5; DIC = 40 mg/L C
c) pH = 8.0; DIC = 10 mg/L C
d) pH = 7.0; DIC = 10 mg/L C



Orthophosphate as Cu Corrosion Inhibitor

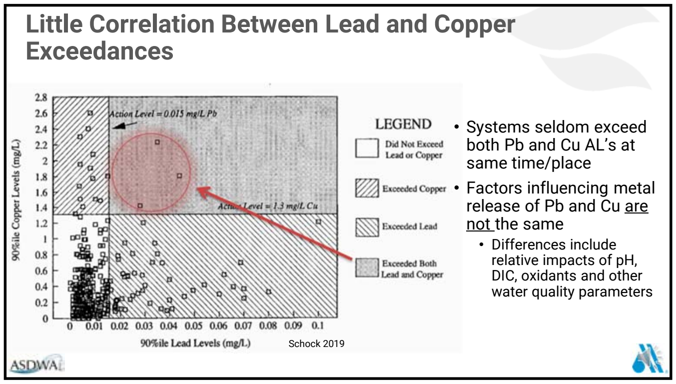
- Cu(II) phosphate scales less soluble than fresh Cu(II) scales
- Cu(II) solubility decreases with increasing PO_4 dose
- PO_4 effective treatment alternative when increasing pH is not feasible

But

- Evidence exists that PO_4 inhibits Cu(II) aging process
  - More pronounced in high DIC water

Lytle 2019

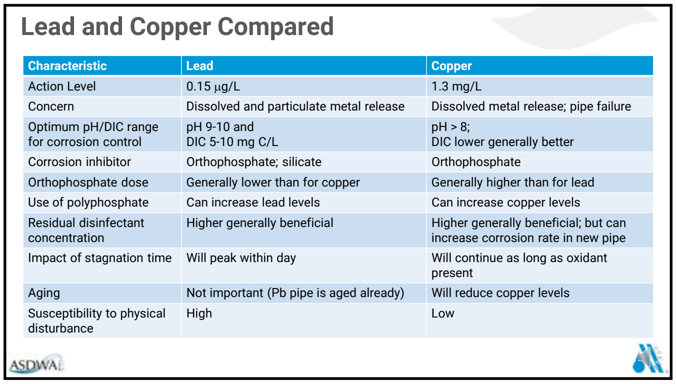
Marker – jar test; Line – model based on $Cu_3(PO_4)_2{\cdot}H_20$ and $Cu(OH)_2$; DIC = 10 mg C/L



Little Correlation Between Lead and Copper Exceedances

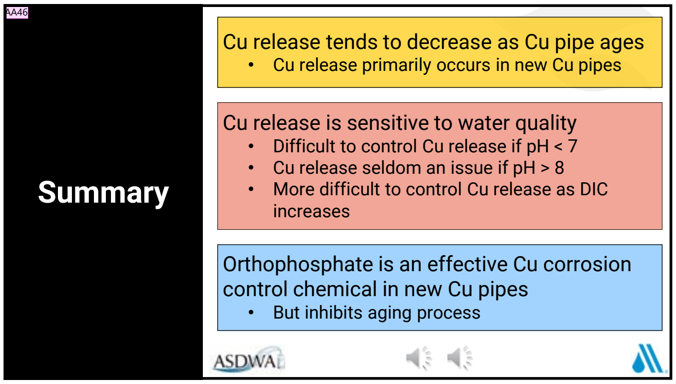
Schock 2019

- Systems seldom exceed both Pb and Cu AL's at same time/place
- Factors influencing metal release of Pb and Cu are not the same
  - Differences include relative impacts of pH, DIC, oxidants and other water quality parameters



Lead and Copper Compared

Characteristic	Lead	Copper
Action Level	0.15 µg/L	1.3 mg/L
Concern	Dissolved and particulate metal release	Dissolved metal release; pipe failure
Optimum pH/DIC range for corrosion control	pH 9-10 and DIC 5-10 mg C/L	pH > 8; DIC lower generally better
Corrosion inhibitor	Orthophosphate; silicate	Orthophosphate
Orthophosphate dose	Generally lower than for copper	Generally higher than for lead
Use of polyphosphate	Can increase lead levels	Can increase copper levels
Residual disinfectant concentration	Higher generally beneficial	Higher generally beneficial; but can increase corrosion rate in new pipe
Impact of stagnation time	Will peak within day	Will continue as long as oxidant present
Aging	Not important (Pb pipe is aged already)	Will reduce copper levels
Susceptibility to physical disturbance	High	Low



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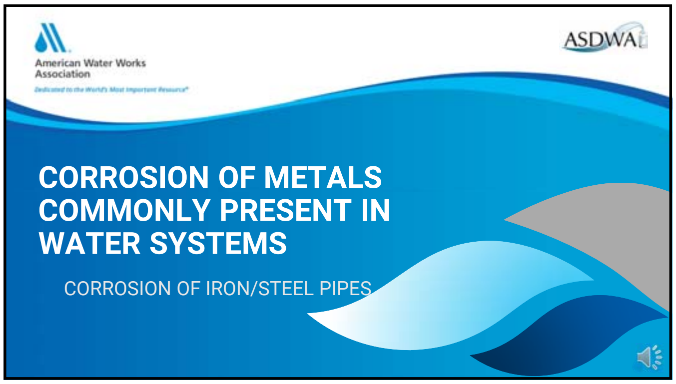
Summary

Cu release tends to decrease as Cu pipe ages
- Cu release primarily occurs in new Cu pipes

Cu release is sensitive to water quality
- Difficult to control Cu release if pH < 7
- Cu release seldom an issue if pH > 8
- More difficult to control Cu release as DIC increases

Orthophosphate is an effective Cu corrosion control chemical in new Cu pipes
- But inhibits aging process



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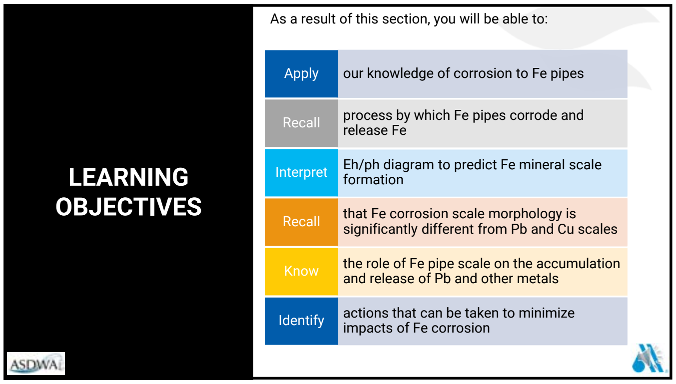
CORROSION OF METALS COMMONLY PRESENT IN WATER SYSTEMS

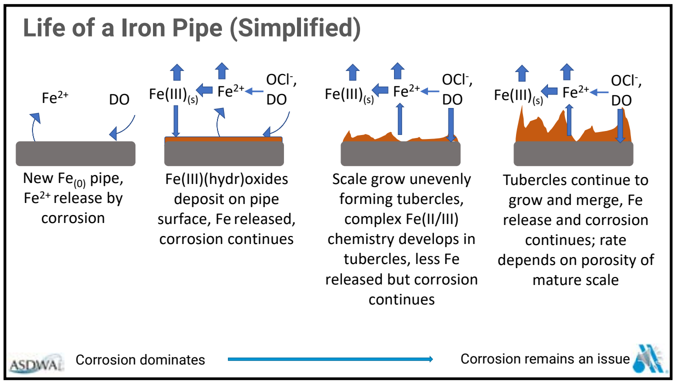
CORROSION OF IRON/STEEL PIPES



LEARNING OBJECTIVES

As a result of this section, you will be able to:

Apply	our knowledge of corrosion to Fe pipes
Recall	process by which Fe pipes corrode and release Fe
Interpret	Eh/ph diagram to predict Fe mineral scale formation
Recall	that Fe corrosion scale morphology is significantly different from Pb and Cu scales
Know	the role of Fe pipe scale on the accumulation and release of Pb and other metals
Identify	actions that can be taken to minimize impacts of Fe corrosion



Life of a Iron Pipe (Simplified)

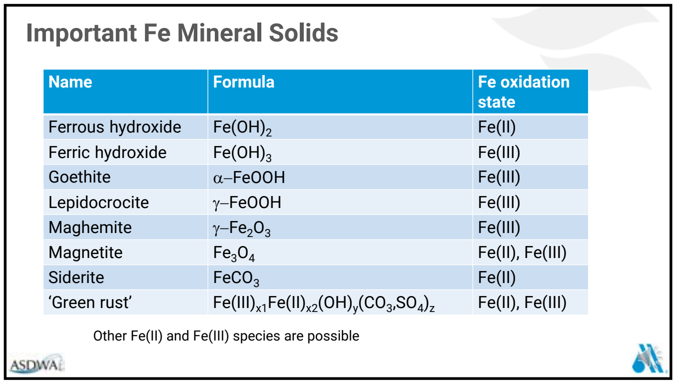
New $Fe_{(0)}$ pipe, Fe^{2+} release by corrosion

Fe(III)(hydr)oxides deposit on pipe surface, Fe released, corrosion continues

Scale grow unevenly forming tubercles, complex Fe(II/III) chemistry develops in tubercles, less Fe released but corrosion continues

Tubercles continue to grow and merge, Fe release and corrosion continues; rate depends on porosity of mature scale

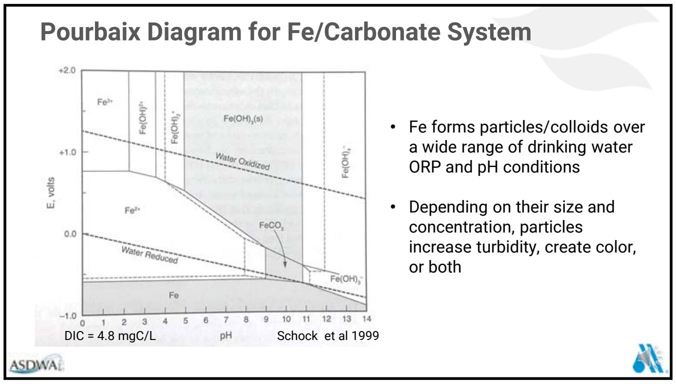
Corrosion dominates → Corrosion remains an issue



Important Fe Mineral Solids

Name	Formula	Fe oxidation state
Ferrous hydroxide	$Fe(OH)_2$	Fe(II)
Ferric hydroxide	$Fe(OH)_3$	Fe(III)
Goethite	α–FeOOH	Fe(III)
Lepidocrocite	γ–FeOOH	Fe(III)
Maghemite	γ–Fe_2O_3	Fe(III)
Magnetite	Fe_3O_4	Fe(II), Fe(III)
Siderite	$FeCO_3$	Fe(II)
'Green rust'	$Fe(III)_{x1}Fe(II)_{x2}(OH)_y(CO_3,SO_4)_z$	Fe(II), Fe(III)

Other Fe(II) and Fe(III) species are possible



Pourbaix Diagram for Fe/Carbonate System

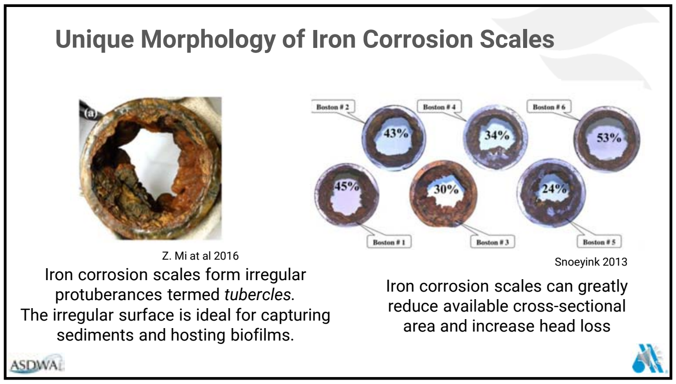
DIC = 4.8 mgC/L

Schock et al 1999

- Fe forms particles/colloids over a wide range of drinking water ORP and pH conditions
- Depending on their size and concentration, particles increase turbidity, create color, or both

Slide 73

AA46 Kris, please combine the two audio files
Andrew Appell, 3/15/2021



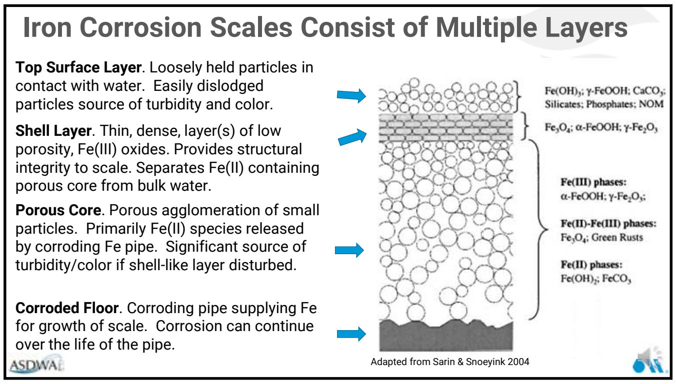
Unique Morphology of Iron Corrosion Scales

Z. Mi at al 2016

Iron corrosion scales form irregular protuberances termed *tubercles.*
The irregular surface is ideal for capturing sediments and hosting biofilms.

Snoeyink 2013

Iron corrosion scales can greatly reduce available cross-sectional area and increase head loss



Iron Corrosion Scales Consist of Multiple Layers

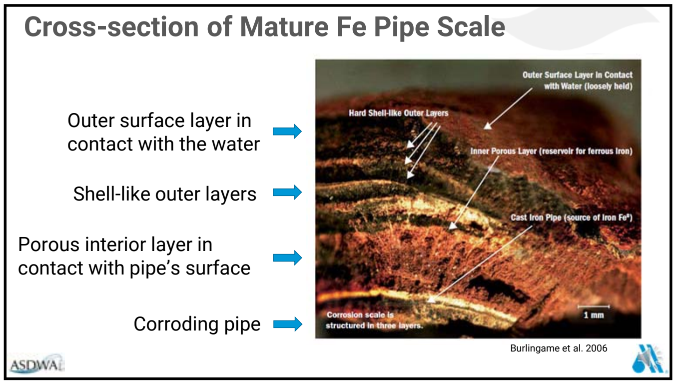
Top Surface Layer. Loosely held particles in contact with water. Easily dislodged particles source of turbidity and color.

Shell Layer. Thin, dense, layer(s) of low porosity, Fe(III) oxides. Provides structural integrity to scale. Separates Fe(II) containing porous core from bulk water.

Porous Core. Porous agglomeration of small particles. Primarily Fe(II) species released by corroding Fe pipe. Significant source of turbidity/color if shell-like layer disturbed.

Corroded Floor. Corroding pipe supplying Fe for growth of scale. Corrosion can continue over the life of the pipe.

Adapted from Sarin & Snoeyink 2004



Cross-section of Mature Fe Pipe Scale

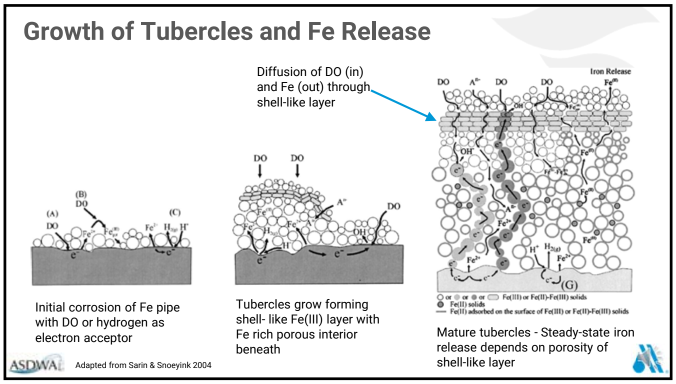
Outer surface layer in contact with the water

Shell-like outer layers

Porous interior layer in contact with pipe's surface

Corroding pipe

Burlingame et al. 2006



Growth of Tubercles and Fe Release

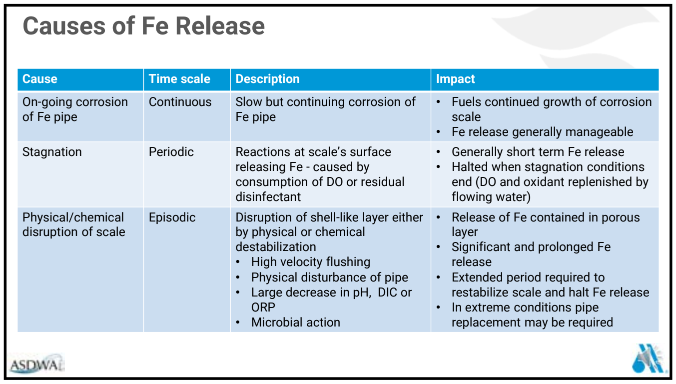
Diffusion of DO (in) and Fe (out) through shell-like layer

Initial corrosion of Fe pipe with DO or hydrogen as electron acceptor

Tubercles grow forming shell- like Fe(III) layer with Fe rich porous interior beneath

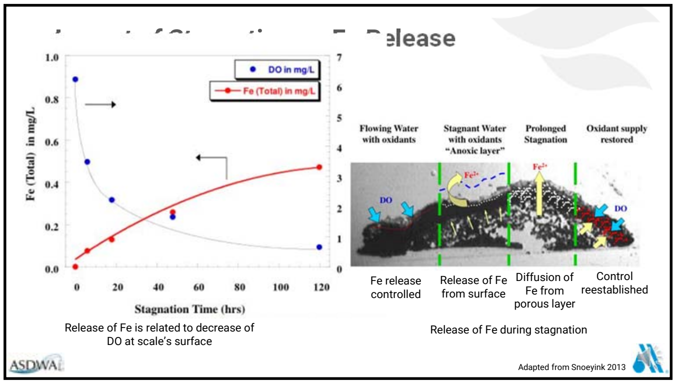
Mature tubercles - Steady-state iron release depends on porosity of shell-like layer

Adapted from Sarin & Snoeyink 2004



Causes of Fe Release

Cause	Time scale	Description	Impact
On-going corrosion of Fe pipe	Continuous	Slow but continuing corrosion of Fe pipe	• Fuels continued growth of corrosion scale • Fe release generally manageable
Stagnation	Periodic	Reactions at scale's surface releasing Fe - caused by consumption of DO or residual disinfectant	• Generally short term Fe release • Halted when stagnation conditions end (DO and oxidant replenished by flowing water)
Physical/chemical disruption of scale	Episodic	Disruption of shell-like layer either by physical or chemical destabilization • High velocity flushing • Physical disturbance of pipe • Large decrease in pH, DIC or ORP • Microbial action	• Release of Fe contained in porous layer • Significant and prolonged Fe release • Extended period required to restabilize scale and halt Fe release • In extreme conditions pipe replacement may be required



elease

Release of Fe is related to decrease of DO at scale's surface

Fe release controlled

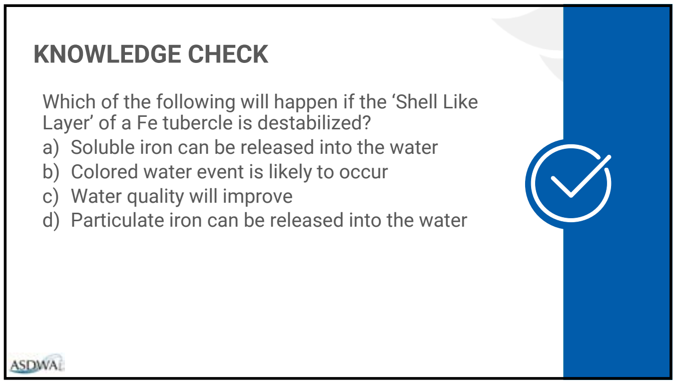
Release of Fe from surface

Diffusion of Fe from porous layer

Control reestablished

Release of Fe during stagnation

Adapted from Snoeyink 2013



KNOWLEDGE CHECK

Which of the following will happen if the ‘Shell Like Layer’ of a Fe tubercle is destabilized?

a) Soluble iron can be released into the water
b) Colored water event is likely to occur
c) Water quality will improve
d) Particulate iron can be released into the water

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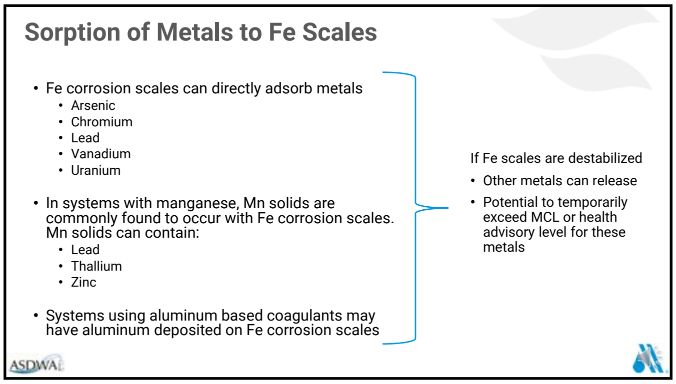

Sorption of Metals to Fe Scales

- Fe corrosion scales can directly adsorb metals
  - Arsenic
  - Chromium
  - Lead
  - Vanadium
  - Uranium
- In systems with manganese, Mn solids are commonly found to occur with Fe corrosion scales. Mn solids can contain:
  - Lead
  - Thallium
  - Zinc
- Systems using aluminum based coagulants may have aluminum deposited on Fe corrosion scales

If Fe scales are destabilized

- Other metals can release
- Potential to temporarily exceed MCL or health advisory level for these metals

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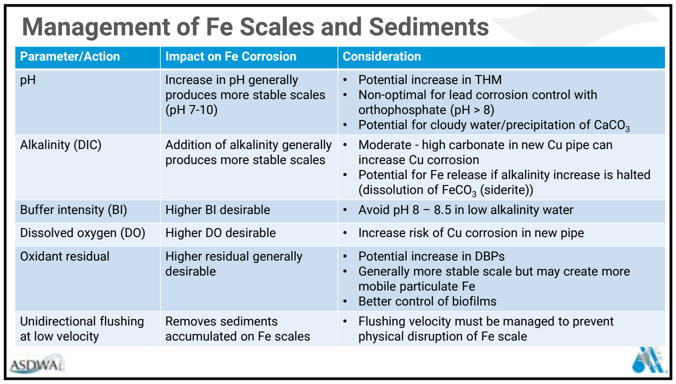

Management of Fe Scales and Sediments

Parameter/Action	Impact on Fe Corrosion	Consideration
pH	Increase in pH generally produces more stable scales (pH 7-10)	• Potential increase in THM • Non-optimal for lead corrosion control with orthophosphate (pH > 8) • Potential for cloudy water/precipitation of $CaCO_3$
Alkalinity (DIC)	Addition of alkalinity generally produces more stable scales	• Moderate - high carbonate in new Cu pipe can increase Cu corrosion • Potential for Fe release if alkalinity increase is halted (dissolution of $FeCO_3$ (siderite))
Buffer intensity (BI)	Higher BI desirable	• Avoid pH 8 – 8.5 in low alkalinity water
Dissolved oxygen (DO)	Higher DO desirable	• Increase risk of Cu corrosion in new pipe
Oxidant residual	Higher residual generally desirable	• Potential increase in DBPs • Generally more stable scale but may create more mobile particulate Fe • Better control of biofilms
Unidirectional flushing at low velocity	Removes sediments accumulated on Fe scales	• Flushing velocity must be managed to prevent physical disruption of Fe scale

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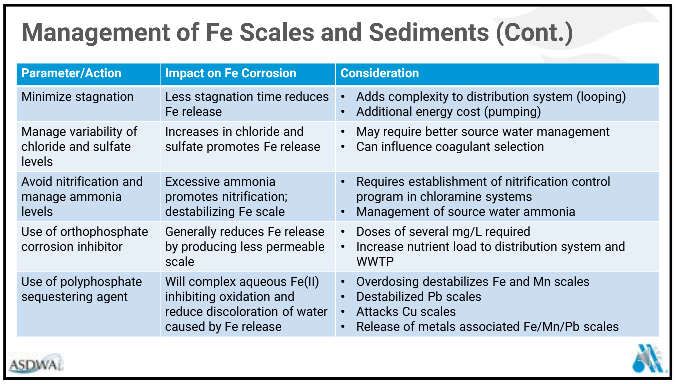

Management of Fe Scales and Sediments (Cont.)

Parameter/Action	Impact on Fe Corrosion	Consideration
Minimize stagnation	Less stagnation time reduces Fe release	• Adds complexity to distribution system (looping) • Additional energy cost (pumping)
Manage variability of chloride and sulfate levels	Increases in chloride and sulfate promotes Fe release	• May require better source water management • Can influence coagulant selection
Avoid nitrification and manage ammonia levels	Excessive ammonia promotes nitrification; destabilizing Fe scale	• Requires establishment of nitrification control program in chloramine systems • Management of source water ammonia
Use of orthophosphate corrosion inhibitor	Generally reduces Fe release by producing less permeable scale	• Doses of several mg/L required • Increase nutrient load to distribution system and WWTP
Use of polyphosphate sequestering agent	Will complex aqueous Fe(II) inhibiting oxidation and reduce discoloration of water caused by Fe release	• Overdosing destabilizes Fe and Mn scales • Destabilized Pb scales • Attacks Cu scales • Release of metals associated Fe/Mn/Pb scales

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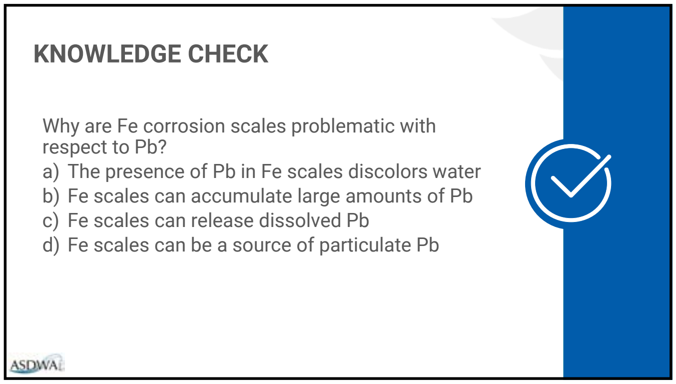

KNOWLEDGE CHECK

Why are Fe corrosion scales problematic with respect to Pb?

a) The presence of Pb in Fe scales discolors water
b) Fe scales can accumulate large amounts of Pb
c) Fe scales can release dissolved Pb
d) Fe scales can be a source of particulate Pb

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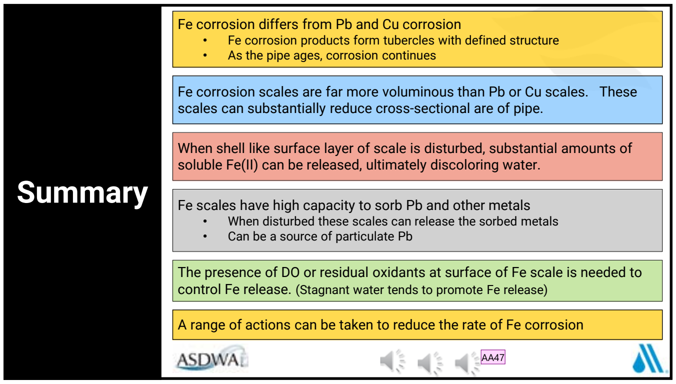

Summary

Fe corrosion differs from Pb and Cu corrosion
- Fe corrosion products form tubercles with defined structure
- As the pipe ages, corrosion continues

Fe corrosion scales are far more voluminous than Pb or Cu scales. These scales can substantially reduce cross-sectional are of pipe.

When shell like surface layer of scale is disturbed, substantial amounts of soluble Fe(II) can be released, ultimately discoloring water.

Fe scales have high capacity to sorb Pb and other metals
- When disturbed these scales can release the sorbed metals
- Can be a source of particulate Pb

The presence of DO or residual oxidants at surface of Fe scale is needed to control Fe release. (Stagnant water tends to promote Fe release)

A range of actions can be taken to reduce the rate of Fe corrosion

AA47

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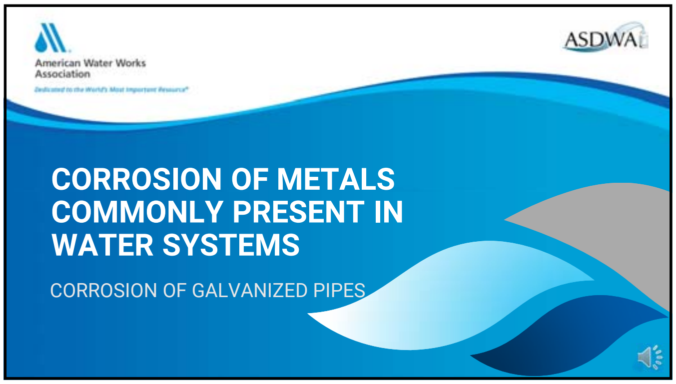
Slide 90

AA47 Kris please combine 3 audio files
Andrew Appell, 3/15/2021



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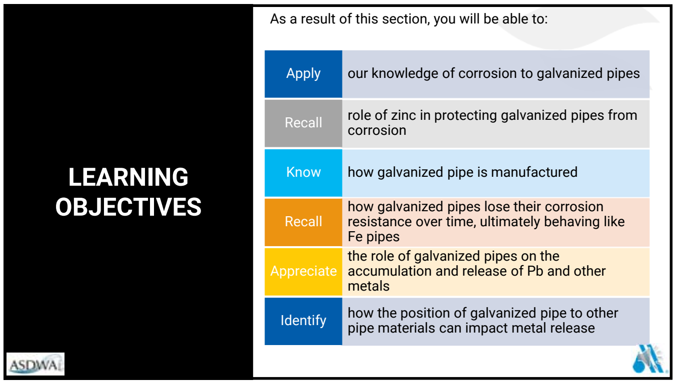
ASDWA

CORROSION OF METALS COMMONLY PRESENT IN WATER SYSTEMS

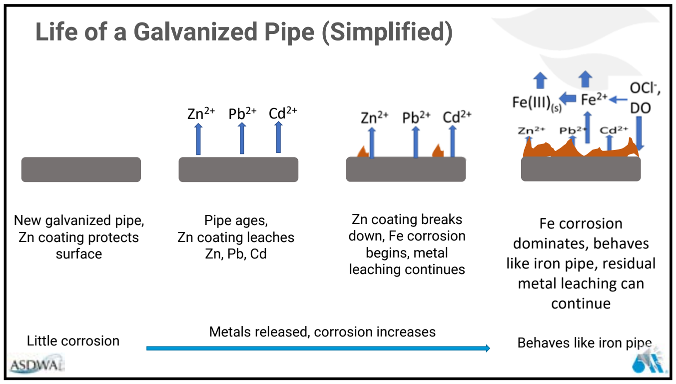
CORROSION OF GALVANIZED PIPES



LEARNING OBJECTIVES

As a result of this section, you will be able to:

Apply	our knowledge of corrosion to galvanized pipes
Recall	role of zinc in protecting galvanized pipes from corrosion
Know	how galvanized pipe is manufactured
Recall	how galvanized pipes lose their corrosion resistance over time, ultimately behaving like Fe pipes
Appreciate	the role of galvanized pipes on the accumulation and release of Pb and other metals
Identify	how the position of galvanized pipe to other pipe materials can impact metal release



Life of a Galvanized Pipe (Simplified)

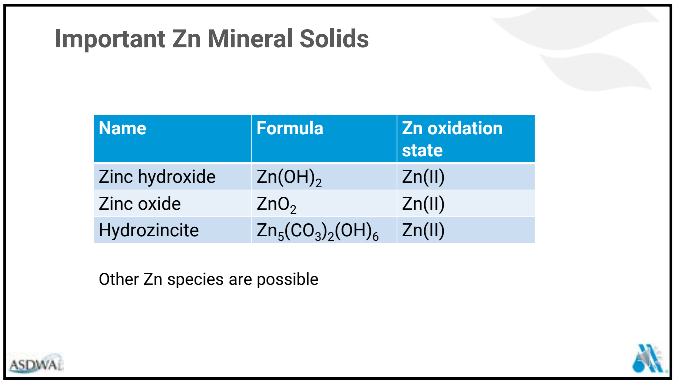
New galvanized pipe, Zn coating protects surface

Pipe ages, Zn coating leaches Zn, Pb, Cd

Zn coating breaks down, Fe corrosion begins, metal leaching continues

Fe corrosion dominates, behaves like iron pipe, residual metal leaching can continue

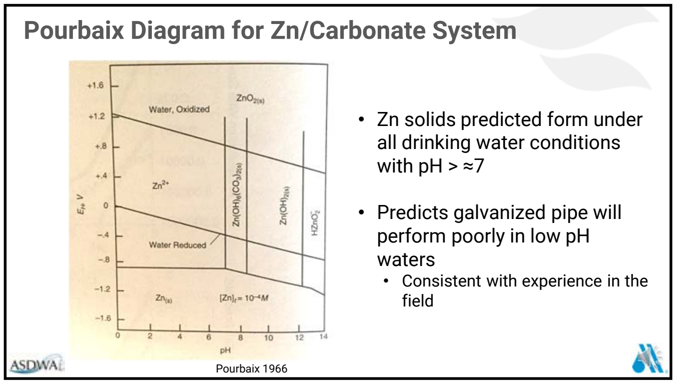
Little corrosion → Metals released, corrosion increases → Behaves like iron pipe



Important Zn Mineral Solids

Name	Formula	Zn oxidation state
Zinc hydroxide	$Zn(OH)_2$	Zn(II)
Zinc oxide	ZnO_2	Zn(II)
Hydrozincite	$Zn_5(CO_3)_2(OH)_6$	Zn(II)

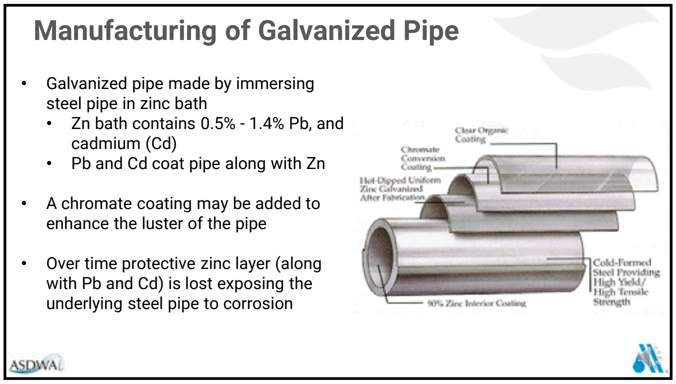
Other Zn species are possible



Pourbaix Diagram for Zn/Carbonate System

Pourbaix 1966

- Zn solids predicted form under all drinking water conditions with pH > ≈7
- Predicts galvanized pipe will perform poorly in low pH waters
  - Consistent with experience in the field



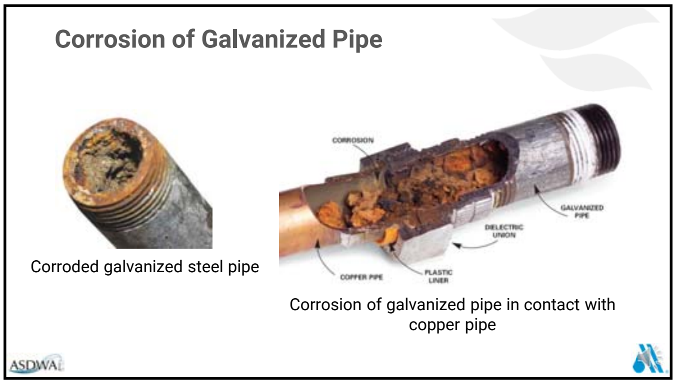
Manufacturing of Galvanized Pipe

- Galvanized pipe made by immersing steel pipe in zinc bath
  - Zn bath contains 0.5% - 1.4% Pb, and cadmium (Cd)
  - Pb and Cd coat pipe along with Zn
- A chromate coating may be added to enhance the luster of the pipe
- Over time protective zinc layer (along with Pb and Cd) is lost exposing the underlying steel pipe to corrosion

Protection of Steel Pipe by Sacrificial Zinc Coating

Material	Anode reaction	Potential (volts)
Magnesium	$Mg_{(s)} \rightarrow Mg^{2+} + 2e^-$	+2.37
Zinc	$Zn_{(s)} \rightarrow Zn^{2+} + 2e^-$	+0.76
Steel, iron	$Fe_{(s)} \rightarrow Fe^{2+} + 2e^-$	+0.44
Cast iron	$Fe_{(s)} \rightarrow Fe^{2+} + 2e^-$	+0.44
Tin	$Sn_{(s)} \rightarrow Sn^{2+} + 2e^-$	+0.14
Lead	$Pb_{(s)} \rightarrow Pb^{2+} + 2e^-$	+0.13
Brass	-	≈ -0.34
Bronze	-	≈ -0.31
Copper	$Cu_{(s)} \rightarrow Cu^{2+} + 2e^-$	-0.35
Gold	$Au_{(s)} \rightarrow Au^{3+} + 3e^-$	-1.5

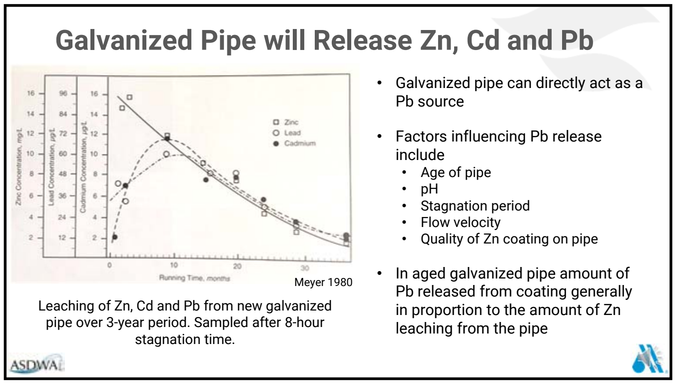
- Zn less noble, corrodes in preference to iron.
  - Zn provides protection for steel pipe
- Exposed Zn surface forms an oxide coating
  - Slows rate of Zn corrosion.
  - Extends time the steel pipe protected.
- Zn coating is lost
  - steel pipe is subject to increasing amount of iron corrosion
  - Pipe typically remains in service after Zn coating no longer provides protection



Corrosion of Galvanized Pipe

Corroded galvanized steel pipe

Corrosion of galvanized pipe in contact with copper pipe

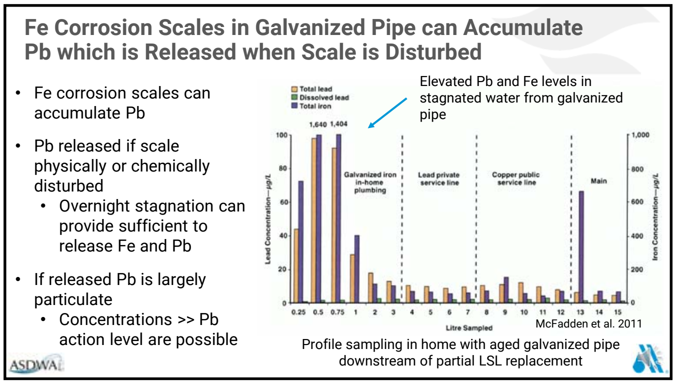


Galvanized Pipe will Release Zn, Cd and Pb

Meyer 1980

Leaching of Zn, Cd and Pb from new galvanized pipe over 3-year period. Sampled after 8-hour stagnation time.

- Galvanized pipe can directly act as a Pb source
- Factors influencing Pb release include
  - Age of pipe
  - pH
  - Stagnation period
  - Flow velocity
  - Quality of Zn coating on pipe
- In aged galvanized pipe amount of Pb released from coating generally in proportion to the amount of Zn leaching from the pipe



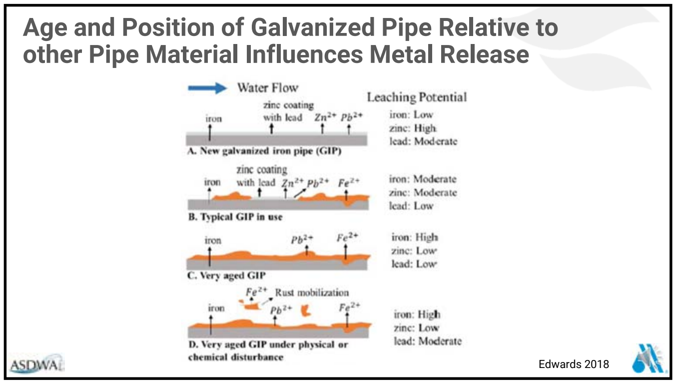
Fe Corrosion Scales in Galvanized Pipe can Accumulate Pb which is Released when Scale is Disturbed

- Fe corrosion scales can accumulate Pb
- Pb released if scale physically or chemically disturbed
  - Overnight stagnation can provide sufficient to release Fe and Pb
- If released Pb is largely particulate
  - Concentrations >> Pb action level are possible

Elevated Pb and Fe levels in stagnated water from galvanized pipe

McFadden et al. 2011

Profile sampling in home with aged galvanized pipe downstream of partial LSL replacement



Age and Position of Galvanized Pipe Relative to other Pipe Material Influences Metal Release

Leaching Potential

A. New galvanized iron pipe (GIP)

iron: Low
zinc: High
lead: Moderate

B. Typical GIP in use

iron: Moderate
zinc: Moderate
lead: Low

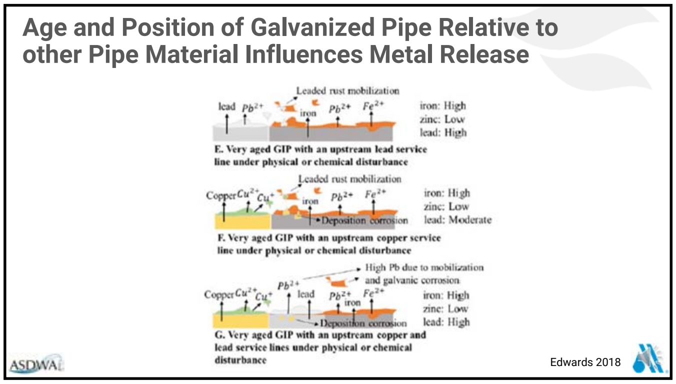
C. Very aged GIP

iron: High
zinc: Low
lead: Low

D. Very aged GIP under physical or chemical disturbance

iron: High
zinc: Low
lead: Moderate

Edwards 2018



Age and Position of Galvanized Pipe Relative to other Pipe Material Influences Metal Release

E. Very aged GIP with an upstream lead service line under physical or chemical disturbance

iron: High
zinc: Low
lead: High

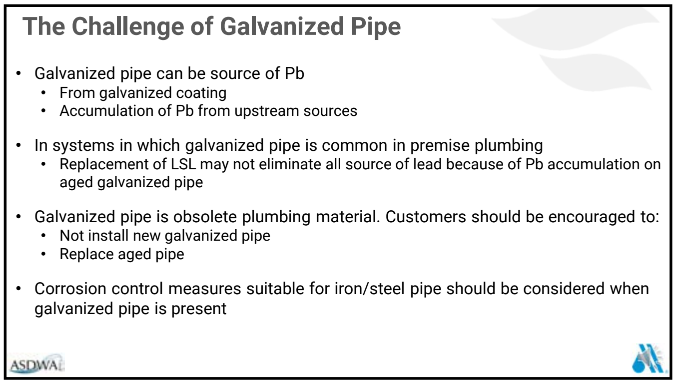
F. Very aged GIP with an upstream copper service line under physical or chemical disturbance

iron: High
zinc: Low
lead: Moderate

G. Very aged GIP with an upstream copper and lead service lines under physical or chemical disturbance

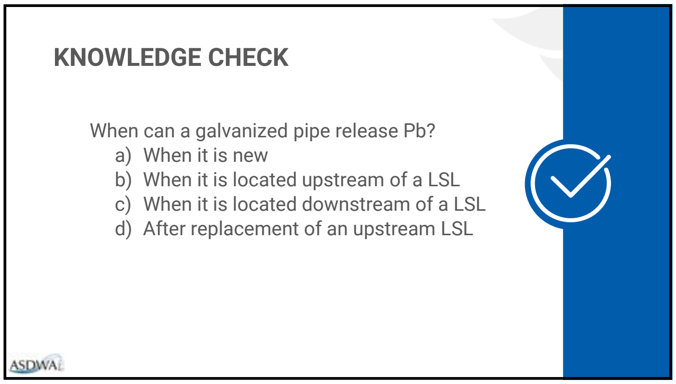
iron: High
zinc: Low
lead: High

Edwards 2018



The Challenge of Galvanized Pipe

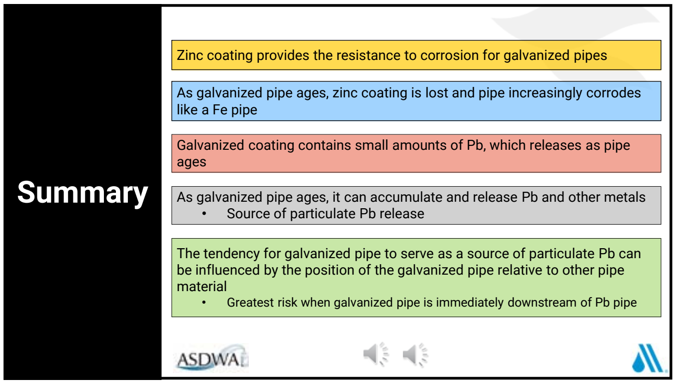
- Galvanized pipe can be source of Pb
  - From galvanized coating
  - Accumulation of Pb from upstream sources
- In systems in which galvanized pipe is common in premise plumbing
  - Replacement of LSL may not eliminate all source of lead because of Pb accumulation on aged galvanized pipe
- Galvanized pipe is obsolete plumbing material. Customers should be encouraged to:
  - Not install new galvanized pipe
  - Replace aged pipe
- Corrosion control measures suitable for iron/steel pipe should be considered when galvanized pipe is present



KNOWLEDGE CHECK

When can a galvanized pipe release Pb?

a) When it is new
b) When it is located upstream of a LSL
c) When it is located downstream of a LSL
d) After replacement of an upstream LSL



Summary

- Zinc coating provides the resistance to corrosion for galvanized pipes
- As galvanized pipe ages, zinc coating is lost and pipe increasingly corrodes like a Fe pipe
- Galvanized coating contains small amounts of Pb, which releases as pipe ages
- As galvanized pipe ages, it can accumulate and release Pb and other metals
  - Source of particulate Pb release
- The tendency for galvanized pipe to serve as a source of particulate Pb can be influenced by the position of the galvanized pipe relative to other pipe material
  - Greatest risk when galvanized pipe is immediately downstream of Pb pipe

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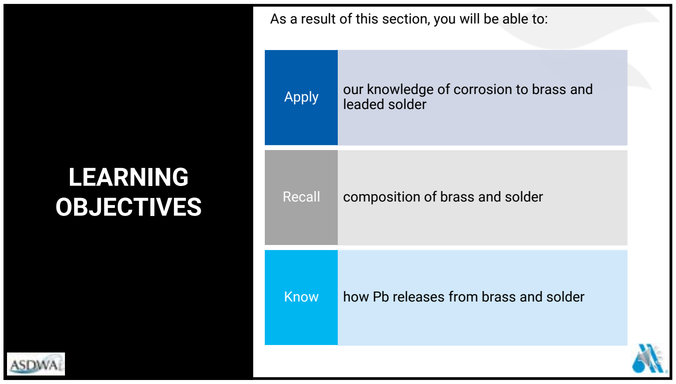
CORROSION OF METALS COMMONLY PRESENT IN WATER SYSTEMS

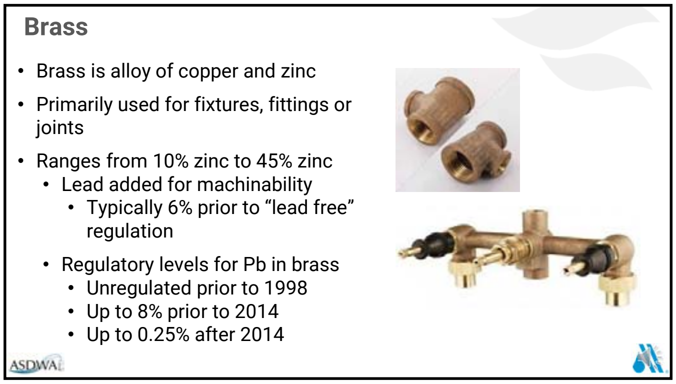
CORROSION OF BRASS AND LEADED SOLDER



LEARNING OBJECTIVES

As a result of this section, you will be able to:

Apply	our knowledge of corrosion to brass and leaded solder
Recall	composition of brass and solder
Know	how Pb releases from brass and solder



Brass

- Brass is alloy of copper and zinc
- Primarily used for fixtures, fittings or joints
- Ranges from 10% zinc to 45% zinc
  - Lead added for machinability
    - Typically 6% prior to "lead free" regulation
  - Regulatory levels for Pb in brass
    - Unregulated prior to 1998
    - Up to 8% prior to 2014
    - Up to 0.25% after 2014

Corrosion Concerns Related to Brass

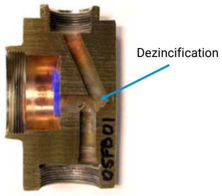
Concern	Description	Comment
Leaching of lead	Lead leaches from brass fixture	• Not concern for brass manufactured after 2014
Galvanic corrosion between brass and Pb pipe or gooseneck	Lead is less noble than brass; will release Pb via galvanic corrosion	• Problem with new connections • Older connections generally are passivized but may become active after physical/chemical disturbance
Dezincification	Selective leaching of Zn from brass	• Forms deposits reducing flow (meringue deposit) • Weakens fitting, prone to leaks/failure • May increase Pb release from leaded brass • More likely at high chloride and pH > ≈ 8.3

Brass Corrosion

Corrosion at Pb/brass joint

Maynard 2018

Dezincified brass faucet housing



Maynard 2018

Leaded and Lead Free Solder

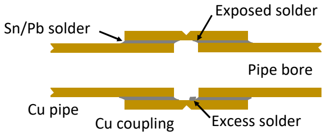
- <u>Leaded</u> plumbing solder mixture of Pb and Sn
  - Typically 40:60 to 50:50 ratio Pb to Sn
  - Low melting point (≈ 360°F)
  - Pb improved strength of joint
  - Standard practice for Cu/Cu or Cu/brass sweated joints prior to ban in 1986
- Lead free solder required post 1986
  - Pb free defined as < 0.2% Pb
  - Mixture of Sn with Cu, Sb, and/or Ag
    - Melting point typically > 440 °F

Sweated Cu/Cu and Cu/Brass Joints

- Procedure for sweating joint
  - Clean Cu surface
  - Add flux to dissolve oxide layer
  - Heat > 450°F
  - Melt solder, capillary action draws solder into joint
  - Wipe flux from joint
- Many factors influence quality of joint and the total surface area of solder in contact with water
  - Cleaning
  - Flux
  - Actual temperature reached during procedure
  - Excess solder

Corrosion of Sweated Sn/Pb Solder Joint

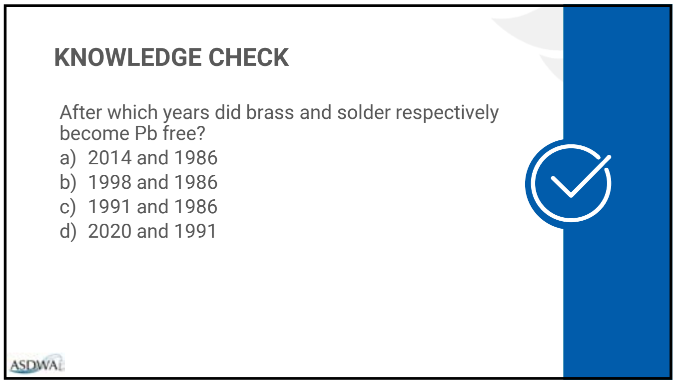
Cross section of sweated Cu/Cu joint



Characteristics
- Small area of solder exposed to water
- Large electrochemical driving force
  - Sn/Pb anode; Cu cathode
- Area of anode small compared to cathode
- Exposed excess solder in poorly sweated joints

Corrosion of Sweated Sn/Pb Solder Joint

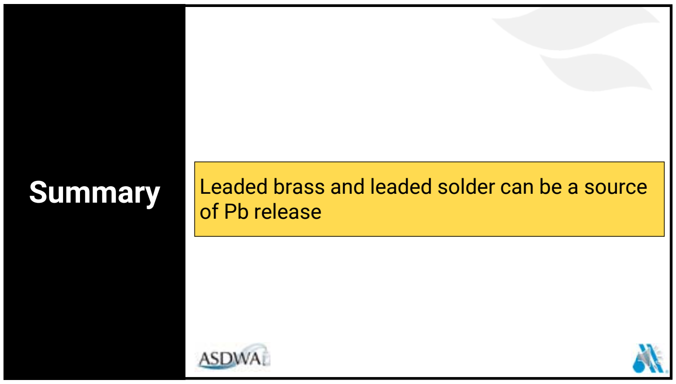
- Galvanic corrosion is primary mechanism for Pb release
  - Pb release by dissolution of corrosion products is not as important
- Pb release decreases with time as passivation reduces galvanic current
- Galvanic corrosion rate sensitive to increase in
  - Chloride/Sulfate Mass Ratio (CSMR)
  - Nitrate
  - Phosphate
- Given their age (prior to 1986), undisturbed leaded solder joints generally are passivized and not a major source of Pb release



KNOWLEDGE CHECK

After which years did brass and solder respectively become Pb free?

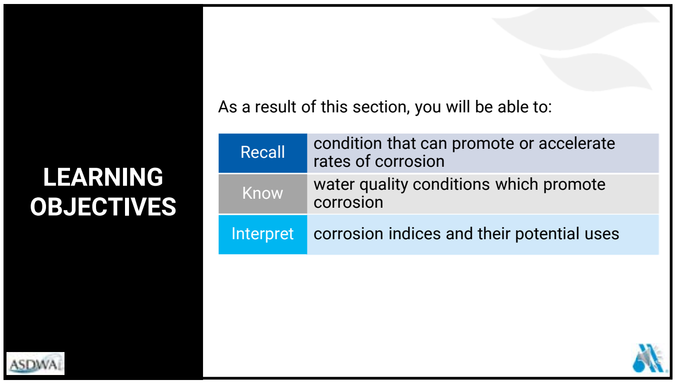
a) 2014 and 1986
b) 1998 and 1986
c) 1991 and 1986
d) 2020 and 1991



Summary

Leaded brass and leaded solder can be a source of Pb release

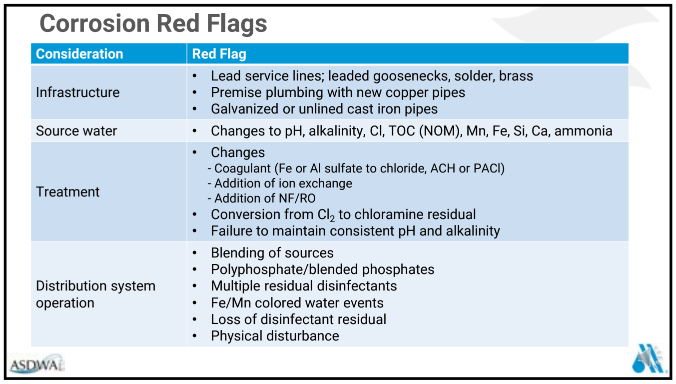
PREDICTING THE RISK FOR CORROSION AND METAL RELEASE



LEARNING OBJECTIVES

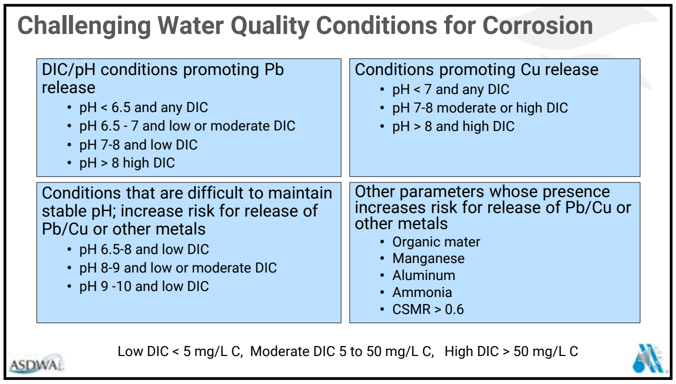
As a result of this section, you will be able to:

Recall	condition that can promote or accelerate rates of corrosion
Know	water quality conditions which promote corrosion
Interpret	corrosion indices and their potential uses



Corrosion Red Flags

Consideration	Red Flag
Infrastructure	• Lead service lines; leaded goosenecks, solder, brass • Premise plumbing with new copper pipes • Galvanized or unlined cast iron pipes
Source water	• Changes to pH, alkalinity, Cl, TOC (NOM), Mn, Fe, Si, Ca, ammonia
Treatment	• Changes - Coagulant (Fe or Al sulfate to chloride, ACH or PACl) - Addition of ion exchange - Addition of NF/RO • Conversion from Cl_2 to chloramine residual • Failure to maintain consistent pH and alkalinity
Distribution system operation	• Blending of sources • Polyphosphate/blended phosphates • Multiple residual disinfectants • Fe/Mn colored water events • Loss of disinfectant residual • Physical disturbance



Challenging Water Quality Conditions for Corrosion

DIC/pH conditions promoting Pb release
- pH < 6.5 and any DIC
- pH 6.5 - 7 and low or moderate DIC
- pH 7-8 and low DIC
- pH > 8 high DIC

Conditions promoting Cu release
- pH < 7 and any DIC
- pH 7-8 moderate or high DIC
- pH > 8 and high DIC

Conditions that are difficult to maintain stable pH; increase risk for release of Pb/Cu or other metals
- pH 6.5-8 and low DIC
- pH 8-9 and low or moderate DIC
- pH 9 -10 and low DIC

Other parameters whose presence increases risk for release of Pb/Cu or other metals
- Organic mater
- Manganese
- Aluminum
- Ammonia
- CSMR > 0.6

Low DIC < 5 mg/L C, Moderate DIC 5 to 50 mg/L C, High DIC > 50 mg/L C

Variable Water Quality is Undesirable

- Rapid changes in water quality destabilize scales and deposits
- Parameters impacting metal release
  - pH
  - DIC
  - ORP
  - Residual disinfectant
  - Chloride
  - Hardness
  - TDS

- Large day-to-day variations in treated water quality produces less stable scales.
- Long term changes to treated water quality should be implemented slowly and include a program of additional sampling and flushing.

Corrosion Indices Involving Calcium Carbonate Stability

Index	Equation	Indicator		Useful for
Langelier Saturation Index	LSI = pH_{actual}-pH_{sat}	LSI>0 LSI<0	Supersaturated, tends to precipitate $CaCO_3$ Undersaturated, tends to dissolve $CaCO_3$	Estimate condition relative to $CaCO_3$ saturation
Stiff and Davis Stability index	S&DSI = pH_{actual}-pH_{sat}	S&DSI >0 S&DSI <0	Supersaturated, tends to precipitate $CaCO_3$ Undersaturated, tends to dissolve $CaCO_3$	Estimate condition relative to $CaCO_3$ saturation for waters > 10,000 mg/L TDS
Ryznar Stability Index	RSI = 2pH_{sat}-pH_{actual}	RSI>6 RSI<6	Undersaturated, tends to dissolve $CaCO_3$ Supersaturated, tends to precipitate $CaCO_3$	Estimate condition relative to $CaCO_3$ saturation
Puckorius Scaling Index	PSI = 2pH_{sat}-pH_{eq}	PSI>6 PSI<6	Undersaturated, tends to dissolve $CaCO_3$ Supersaturated, tends to precipitate $CaCO_3$	Estimate condition relative to $CaCO_3$ saturation

Corrosion Indices Involving Calcium Carbonate Stability (cont.)

Index	Equation	Indicator		Useful for
Calcium Carbonate Precipitation Potential	CCPP = Caactual-Casat	CCPP>0 0 to -5 -5 to -10 < -10	$CaCO_3$ scaling will occur Passive Moderate Aggressive	Estimate quantity of $CaCO_3$ precipitated or dissolved
McCauley's Driving Force Index	DFI = (Ca^{2+} x CO_3^-)/ (K_{sp} x 10^{10})	DFI>1 RSI<1	Undersaturated, tends to dissolve $CaCO_3$ Supersaturated, tends to precipitate $CaCO_3$	Estimate condition relative to $CaCO_3$ saturation

These indices do not predict the corrosivity towards metals (Pb, Cu, Fe or brass)

Corrosion Indices Involving Iron, Steel or AC Pipe

Index	Equation	Indicator		Useful for
Larson Index	LI=([Cl^-]+2[SO_4^{2-}])/ [HCO_3^-]	LI>0.5 LI<0.5	Corrosion possible Corrosion unlikely	Corrosion of iron and steel
Larson Scold Index	LS=[Cl^-+SO_4^{2-}]/ Alkalinity	LS<0.8 0.8<LS<1.2 LS>1.2	Chloride & sulfate will not interfere with natural film formation Chloride & sulfate may interfere with natural film formation Tendency toward higher localized corrosion	Aggressiveness to mild steel
Aggressive Index	AI=pH+ log(AH) A=Alkalinity H= Ca hardness	AI<10 10<AI<12 AI>12	Highly Aggressive Moderately Aggressive Non-aggressive	Aggressiveness to AC or concrete lined pipes

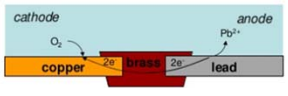
These corrosion indices may be useful in predicting aggressiveness of water to ferrous or concrete lined pipes

KNOWLEDGE CHECK

Which indices involving calcium carbonate stability best predicts a water's corrosivity?

a) LSI
b) CCPP
c) RSI
d) None

Chloride to Sulfate Mass Ratio and Galvanic Corrosion

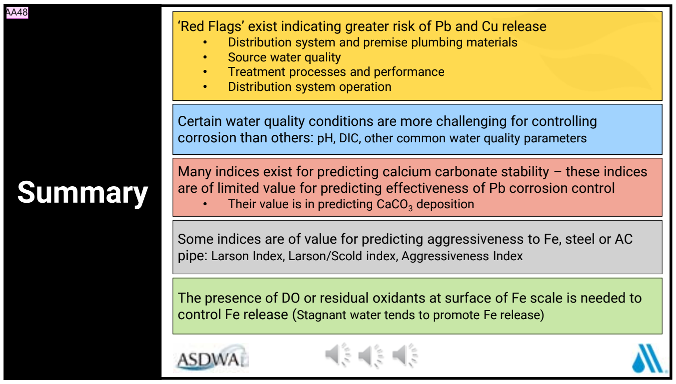


DeSantis 2009

- When possibility of galvanic corrosion is present, ratio of chloride to sulfate (CSMR) is important

$$CSMR = \frac{Chloride\ (\frac{mg}{L})}{Sulfate\ (\frac{mg}{L})}$$

- It has been observed that CSMR above threshold of 0.6 may accelerate galvanic corrosion
- Avoid CSMR > 0.6
  - Particularly in water with alkalinity < 50 mg/L $CaCO_3$



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Summary

'Red Flags' exist indicating greater risk of Pb and Cu release
- Distribution system and premise plumbing materials
- Source water quality
- Treatment processes and performance
- Distribution system operation

Certain water quality conditions are more challenging for controlling corrosion than others: pH, DIC, other common water quality parameters

Many indices exist for predicting calcium carbonate stability – these indices are of limited value for predicting effectiveness of Pb corrosion control
- Their value is in predicting $CaCO_3$ deposition

Some indices are of value for predicting aggressiveness to Fe, steel or AC pipe: Larson Index, Larson/Scold index, Aggressiveness Index

The presence of DO or residual oxidants at surface of Fe scale is needed to control Fe release (Stagnant water tends to promote Fe release)

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CORROSION CONTROL THEORY AND TREATMENT OPTIONS

CORROSION CONTROL TREATMENT METHODS

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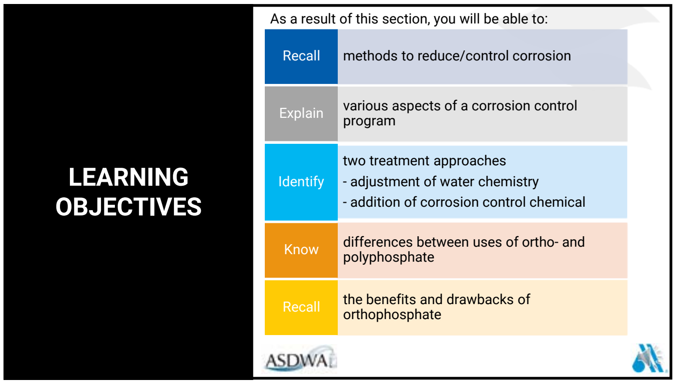

LEARNING OBJECTIVES

As a result of this section, you will be able to:

Recall	methods to reduce/control corrosion
Explain	various aspects of a corrosion control program
Identify	two treatment approaches - adjustment of water chemistry - addition of corrosion control chemical
Know	differences between uses of ortho- and polyphosphate
Recall	the benefits and drawbacks of orthophosphate

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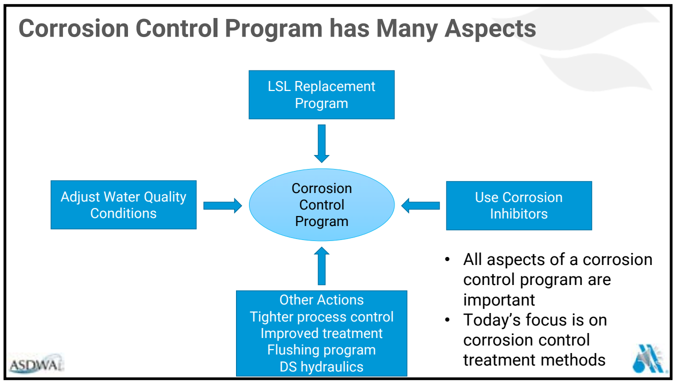

Corrosion Control Program has Many Aspects

- All aspects of a corrosion control program are important
- Today's focus is on corrosion control treatment methods

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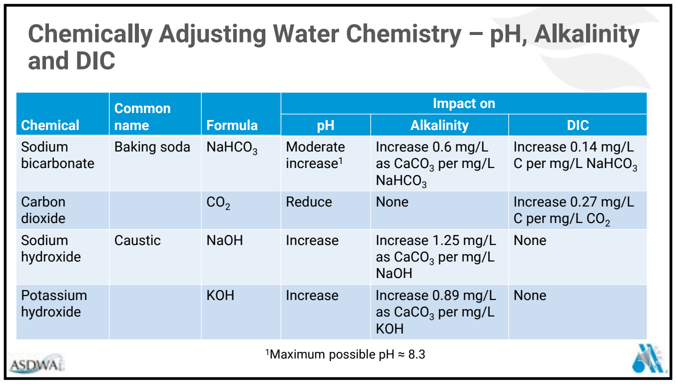

Chemically Adjusting Water Chemistry – pH, Alkalinity and DIC

Chemical	Common name	Formula	Impact on		
			pH	Alkalinity	DIC
Sodium bicarbonate	Baking soda	$NaHCO_3$	Moderate increase[1]	Increase 0.6 mg/L as $CaCO_3$ per mg/L $NaHCO_3$	Increase 0.14 mg/L C per mg/L $NaHCO_3$
Carbon dioxide		CO_2	Reduce	None	Increase 0.27 mg/L C per mg/L CO_2
Sodium hydroxide	Caustic	NaOH	Increase	Increase 1.25 mg/L as $CaCO_3$ per mg/L NaOH	None
Potassium hydroxide		KOH	Increase	Increase 0.89 mg/L as $CaCO_3$ per mg/L KOH	None

[1] Maximum possible pH ≈ 8.3

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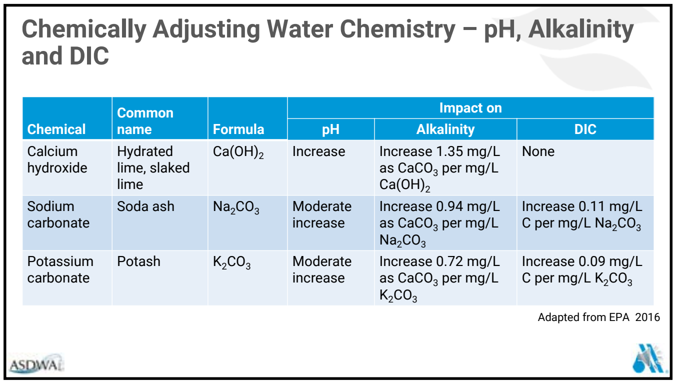

Chemically Adjusting Water Chemistry – pH, Alkalinity and DIC

Chemical	Common name	Formula	Impact on		
			pH	Alkalinity	DIC
Calcium hydroxide	Hydrated lime, slaked lime	$Ca(OH)_2$	Increase	Increase 1.35 mg/L as $CaCO_3$ per mg/L $Ca(OH)_2$	None
Sodium carbonate	Soda ash	Na_2CO_3	Moderate increase	Increase 0.94 mg/L as $CaCO_3$ per mg/L Na_2CO_3	Increase 0.11 mg/L C per mg/L Na_2CO_3
Potassium carbonate	Potash	K_2CO_3	Moderate increase	Increase 0.72 mg/L as $CaCO_3$ per mg/L K_2CO_3	Increase 0.09 mg/L C per mg/L K_2CO_3

Adapted from EPA 2016

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Adjusting Water Chemistry with Aeration

- Aeration can be used to strip excess CO_2 from raw water raw water. Under certain conditions this can:
  - Increase pH
  - Remove DIC
  - Not change alkalinity
- Suitable for water with
  - Low pH (< ≈7.2)
    and
  - Elevated DIC (> ≈15 mg/L C)
    and
  - CO_2 > ≈ 4 mg/L

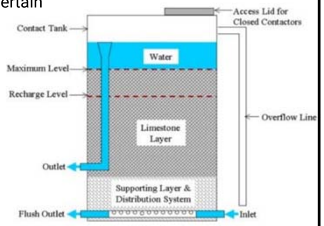
Ideal conditions for Cu corrosion

- Other potential benefits
  - Fe and H_2S removal
- Not suitable for anoxic raw water
  - Aeration increases DO and consequently corrosivity of water

Cascade aeration

Adjusting Water Chemistry with Limestone Contactors

- Limestone contactors can be used to equilibrate raw water with calcium carbonate. Under certain conditions this can:
  - Increase pH
  - Increase DIC
  - Increase alkalinity
- Suitable for water with
  - Low pH (< ≈7.2)
    and
  - Moderate alkalinity (< ≈100 mg/L $CaCO_3$)
    and
  - Ca < ≈ 60 mg/L
- Applicability limited to small systems
  - Maximum hydraulic loading rate ≈ 1 GPM/Ft^2



Jalil 2003

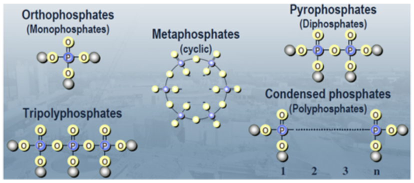
Limestone contactor

KNOWLEDGE CHECK

It is possible to simultaneously increase pH and reduce alkalinity using common water treatment chemicals (True/False)

Phosphate Chemistry – Orthophosphate vs. Polyphosphate

- Orthophosphate
  - Phosphorus atom surrounded by four oxygens
  - Basic building block for phosphate chemistry
- Polyphosphates link orthophosphates together by sharing an oxygen atom. Polyphosphates can form
  - Linear structures
  - Cyclic structures



Britton et al. 2008

Orthophosphate and Polyphosphate Compared

- Orthophosphate
  - Corrosion control chemical
  - Forms anion with -1 or -2 charge at drinking water pHs
  - Reacts with metals to form stable mineral precipitates
    - Fe, Pb, Cu, Ca, Mg and others
- Polyphosphates
  - Is a sequestrant
    - Masks color caused by Fe, Mn; ties up Ca
  - Chelates ions to form complexes of variable stability
    - Fe, Pb, Cu, Ca, Mg, Mn, NOM and others
  - Can increase levels of dissolved, colloidal and particulate Pb in systems where Pb is present

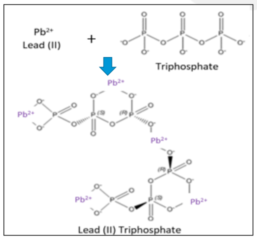
Blended phosphates are a combination of ortho- and polyphosphates.
- Composition of blends is considered proprietary by suppliers
- Often exact formulation is unknown to the user.

When blended phosphates are used
- Pb scales tend to be more amorphous and less mineral compared to orthophosphate alone.
- Amorphous scales are more vulnerable to disturbance than mineral scales.

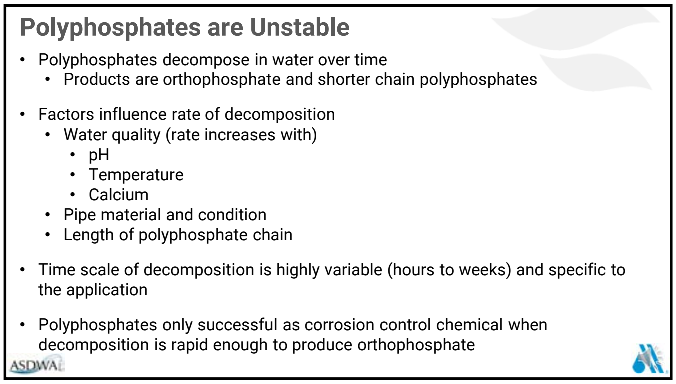
An Example - Reactions Between Pb(II) and Ortho- or Polyphosphate are Very Different

$$5Pb^{2+} + 3PO_4^{3-} + H_2O$$
$$\downarrow$$
$$Pb_5(PO_4)_3OH_{(s)}\downarrow + H^+$$
$$\text{Log } K_{sp} = -62.83$$

Pb(II) and orthophosphate form the mineral hydropyromorphite

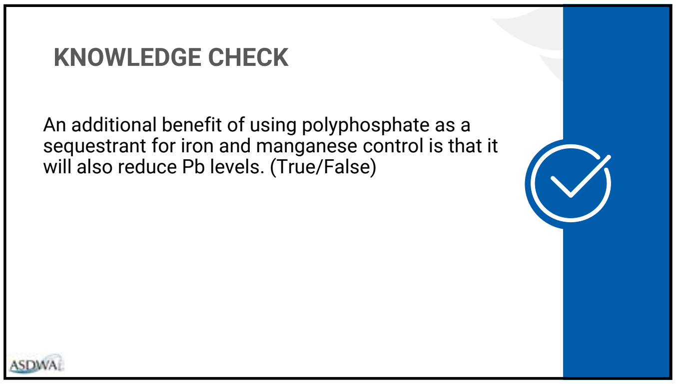


Pb(II) and triphosphate form the chemical complex lead (II) triphosphate



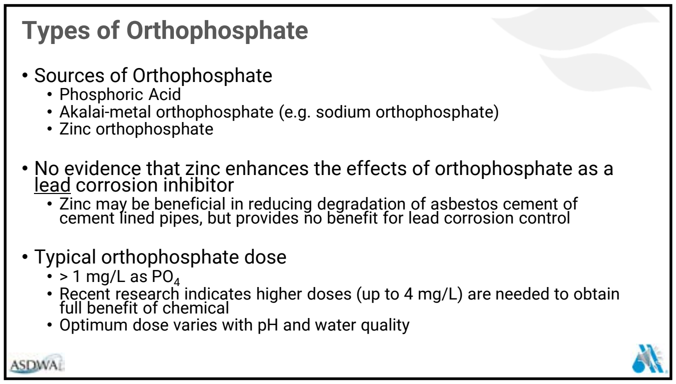
Polyphosphates are Unstable

- Polyphosphates decompose in water over time
  - Products are orthophosphate and shorter chain polyphosphates
- Factors influence rate of decomposition
  - Water quality (rate increases with)
    - pH
    - Temperature
    - Calcium
  - Pipe material and condition
  - Length of polyphosphate chain
- Time scale of decomposition is highly variable (hours to weeks) and specific to the application
- Polyphosphates only successful as corrosion control chemical when decomposition is rapid enough to produce orthophosphate



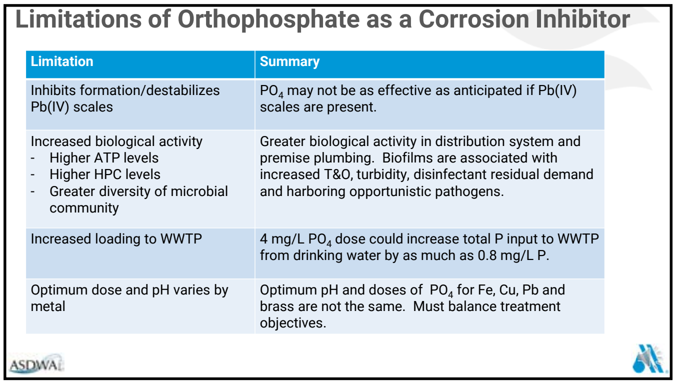
KNOWLEDGE CHECK

An additional benefit of using polyphosphate as a sequestrant for iron and manganese control is that it will also reduce Pb levels. (True/False)



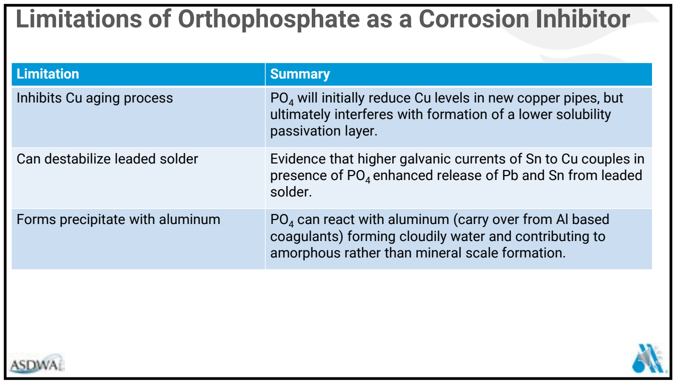
Types of Orthophosphate

- Sources of Orthophosphate
  - Phosphoric Acid
  - Akalai-metal orthophosphate (e.g. sodium orthophosphate)
  - Zinc orthophosphate
- No evidence that zinc enhances the effects of orthophosphate as a lead corrosion inhibitor
  - Zinc may be beneficial in reducing degradation of asbestos cement of cement lined pipes, but provides no benefit for lead corrosion control
- Typical orthophosphate dose
  - > 1 mg/L as PO_4
  - Recent research indicates higher doses (up to 4 mg/L) are needed to obtain full benefit of chemical
  - Optimum dose varies with pH and water quality



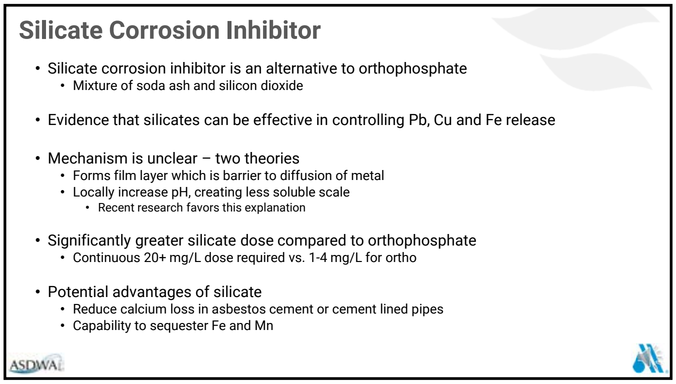
Limitations of Orthophosphate as a Corrosion Inhibitor

Limitation	Summary
Inhibits formation/destabilizes Pb(IV) scales	PO_4 may not be as effective as anticipated if Pb(IV) scales are present.
Increased biological activity - Higher ATP levels - Higher HPC levels - Greater diversity of microbial community	Greater biological activity in distribution system and premise plumbing. Biofilms are associated with increased T&O, turbidity, disinfectant residual demand and harboring opportunistic pathogens.
Increased loading to WWTP	4 mg/L PO_4 dose could increase total P input to WWTP from drinking water by as much as 0.8 mg/L P.
Optimum dose and pH varies by metal	Optimum pH and doses of PO_4 for Fe, Cu, Pb and brass are not the same. Must balance treatment objectives.



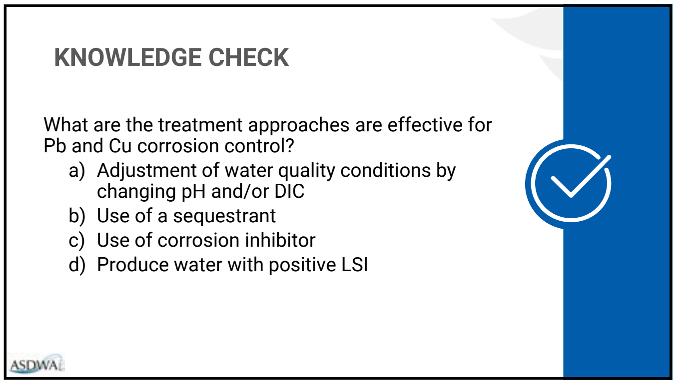
Limitations of Orthophosphate as a Corrosion Inhibitor

Limitation	Summary
Inhibits Cu aging process	PO_4 will initially reduce Cu levels in new copper pipes, but ultimately interferes with formation of a lower solubility passivation layer.
Can destabilize leaded solder	Evidence that higher galvanic currents of Sn to Cu couples in presence of PO_4 enhanced release of Pb and Sn from leaded solder.
Forms precipitate with aluminum	PO_4 can react with aluminum (carry over from Al based coagulants) forming cloudily water and contributing to amorphous rather than mineral scale formation.



Silicate Corrosion Inhibitor

- Silicate corrosion inhibitor is an alternative to orthophosphate
  - Mixture of soda ash and silicon dioxide
- Evidence that silicates can be effective in controlling Pb, Cu and Fe release
- Mechanism is unclear – two theories
  - Forms film layer which is barrier to diffusion of metal
  - Locally increase pH, creating less soluble scale
    - Recent research favors this explanation
- Significantly greater silicate dose compared to orthophosphate
  - Continuous 20+ mg/L dose required vs. 1-4 mg/L for ortho
- Potential advantages of silicate
  - Reduce calcium loss in asbestos cement or cement lined pipes
  - Capability to sequester Fe and Mn



KNOWLEDGE CHECK

What are the treatment approaches are effective for Pb and Cu corrosion control?

a) Adjustment of water quality conditions by changing pH and/or DIC
b) Use of a sequestrant
c) Use of corrosion inhibitor
d) Produce water with positive LSI

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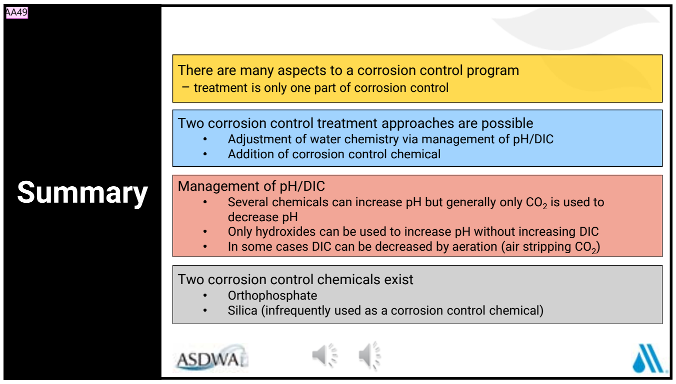

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Summary

There are many aspects to a corrosion control program
– treatment is only one part of corrosion control

Two corrosion control treatment approaches are possible
- Adjustment of water chemistry via management of pH/DIC
- Addition of corrosion control chemical

Management of pH/DIC
- Several chemicals can increase pH but generally only CO_2 is used to decrease pH
- Only hydroxides can be used to increase pH without increasing DIC
- In some cases DIC can be decreased by aeration (air stripping CO_2)

Two corrosion control chemicals exist
- Orthophosphate
- Silica (infrequently used as a corrosion control chemical)

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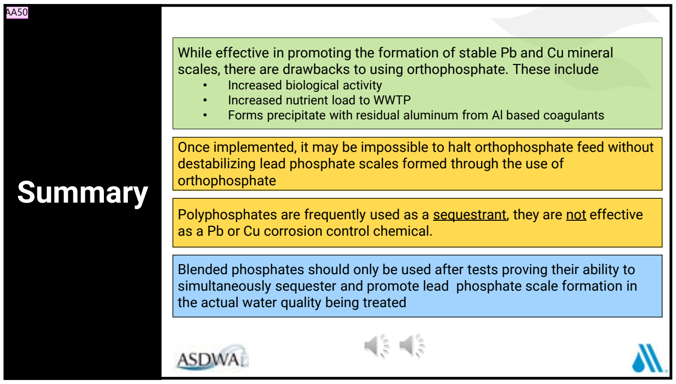

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Summary

While effective in promoting the formation of stable Pb and Cu mineral scales, there are drawbacks to using orthophosphate. These include
- Increased biological activity
- Increased nutrient load to WWTP
- Forms precipitate with residual aluminum from Al based coagulants

Once implemented, it may be impossible to halt orthophosphate feed without destabilizing lead phosphate scales formed through the use of orthophosphate

Polyphosphates are frequently used as a sequestrant, they are not effective as a Pb or Cu corrosion control chemical.

Blended phosphates should only be used after tests proving their ability to simultaneously sequester and promote lead phosphate scale formation in the actual water quality being treated

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CONCLUSIONS

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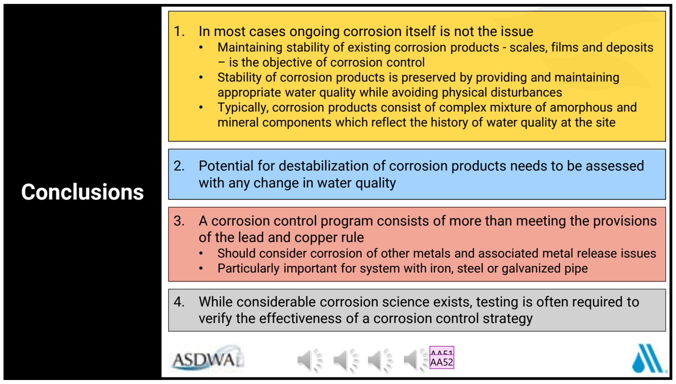

Conclusions

1. In most cases ongoing corrosion itself is not the issue
   - Maintaining stability of existing corrosion products - scales, films and deposits – is the objective of corrosion control
   - Stability of corrosion products is preserved by providing and maintaining appropriate water quality while avoiding physical disturbances
   - Typically, corrosion products consist of complex mixture of amorphous and mineral components which reflect the history of water quality at the site
2. Potential for destabilization of corrosion products needs to be assessed with any change in water quality
3. A corrosion control program consists of more than meeting the provisions of the lead and copper rule
   - Should consider corrosion of other metals and associated metal release issues
   - Particularly important for system with iron, steel or galvanized pipe
4. While considerable corrosion science exists, testing is often required to verify the effectiveness of a corrosion control strategy

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