TREATMENT PROCESSES FOR CORROSIVE WATER

2018 Central West Texas Regional School

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Enprotec / Hibbs & Todd, Inc. (eHT)

Outline

- History of Corrosion Control
- Lead and Copper Background
- Past Corrosion Control Review (Pre-Flint)
- Current Corrosion Control Review (Post-Flint)
- Current Corrosion Control Analyses
- Treatment Options for Corrosion Control
- Summary

History of Corrosion Control

History of Corrosion Control

- Most all forms of corrosion are chemical reactions (erosion is the exception) that require three things:

  - A carrier such as Water that allows the movement of positively charged ions (from Anode+ to Cathode-)
  - A condition (water metal contact) that allows metals to disassociate (ionize) and allows electrons to flow
  - An imbalance that favors the transport of metals or ions to achieve a chemical balance in a water solution.

History of Corrosion Control

- Corrosion Control is employed in water treatment to protect pipeline materials, appurtenances and fittings from leaching problematic (iron) and/or dangerous inorganic chemicals (lead and copper).

- Two types of treatment are generally used:
  - Chemical Adjustment in Water Treatment
  - Post-treatment via Sequestering

- Protection Measures in water system include the use of sacrificial metals and electronic cathodic protection.

History of Corrosion Control

Factors Affecting Corrosion Control

Typical Water Quality Parameters	
pH[1]	Orthophosphate[2]
Alkalinity	Silica[3]
Calcium	Temperature[1]
Conductivity	Hardness

[1] Measured on-site.

[2] Applies when a phosphate-containing inhibitor is used.

[3] Applies when a silicate-containing inhibitor is used.

History of Corrosion Control

Water Hardness

- Hardness in Water causes scaling, causes fibers in clothes to become brittle and increases the amount of soap that must be used for washing
- Hardness in water is caused by the water's Calcium and Magnesium Content
- Water is considered hard when it has a hardness concentration of > 100 mg/L expressed as calcium carbonate equivalent
- Water that hardness < 100 mg/L expressed as CaCO3 is considered soft
- Hardness can either be removed by water treatment or sequestered using phosphates

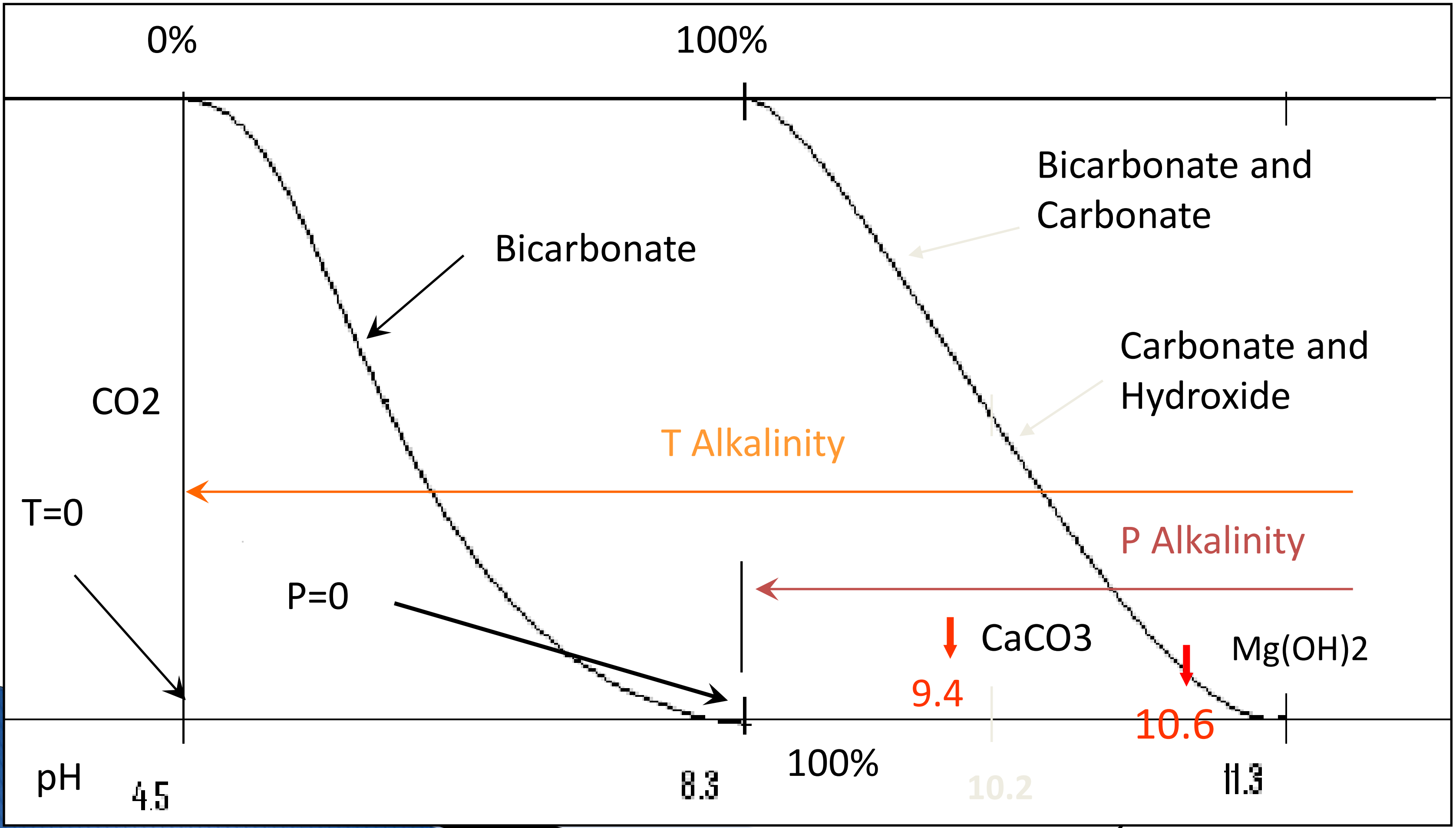
History of Corrosion Control

Water Alkalinity

- The capacity of water to neutralize acids.
- The measure of how much acid must be added to a liquid to lower the pH to 4.5
- It is caused by the water’s content of carbonate, bicarbonate, hydroxide, and occasionally borate, silicate, and phosphate.
- In natural waters, Alkalinity = Bicarbonate Hardness = Total Carbonate Hardness

History of Corrosion Control

Relationships among pH, Alkalinity and Indicators



History of Corrosion Control

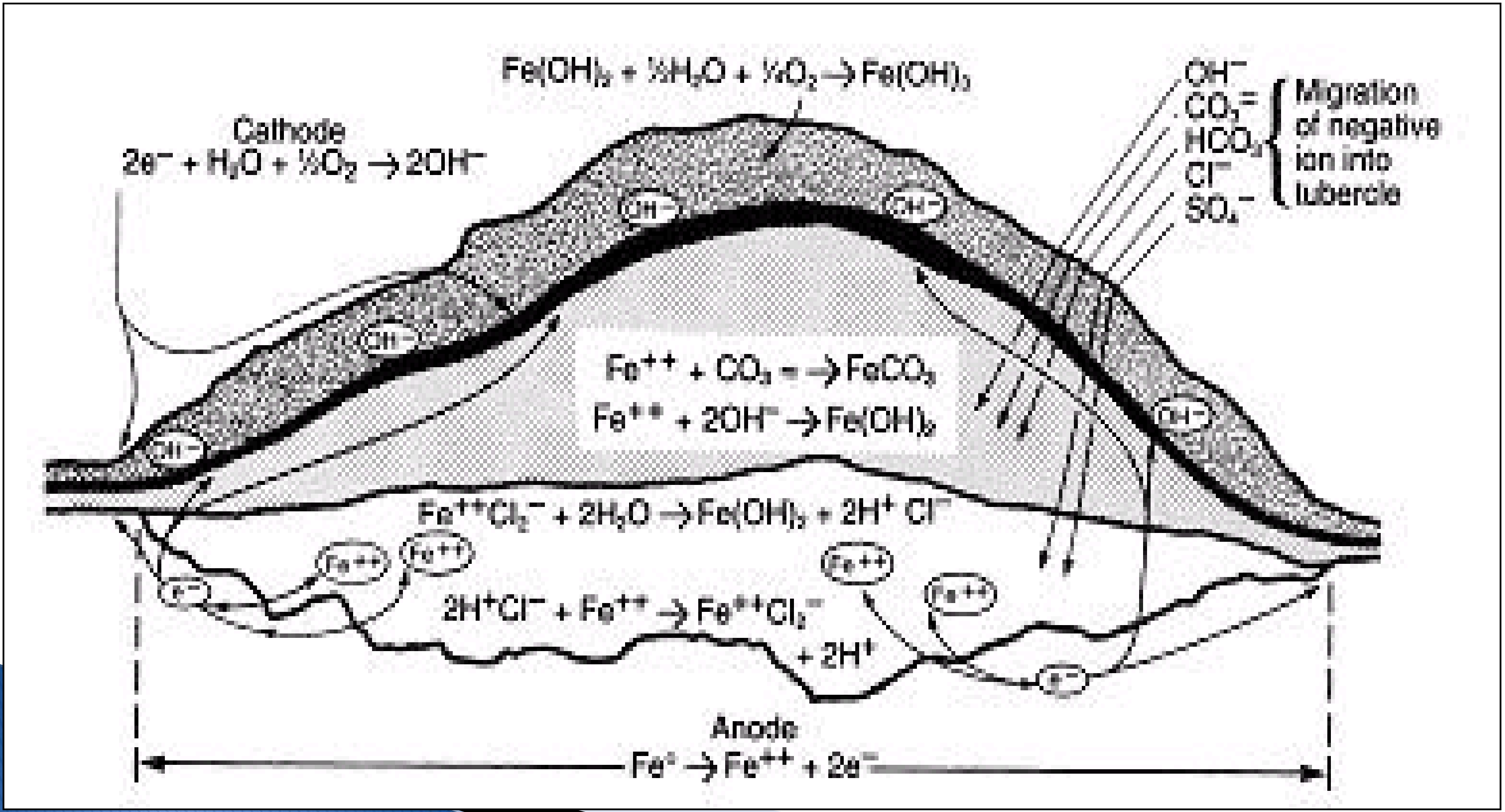
Types of Alkalinity that can be Present at pH Values

- Below 4.5 only CO_2 present, no Alkalinity
- Between 4.5 to 8.3 only Bicarbonate present
- Between 8.3 to 10.2 Bicarbonate & Carbonate.
- Between 10.2 to 11.3 Carbonate & Hydroxide

- At 9.4 Calcium Carbonate becomes insoluble and precipitates
- At 10.6 Magnesium Hydroxide becomes insoluble and precipitates

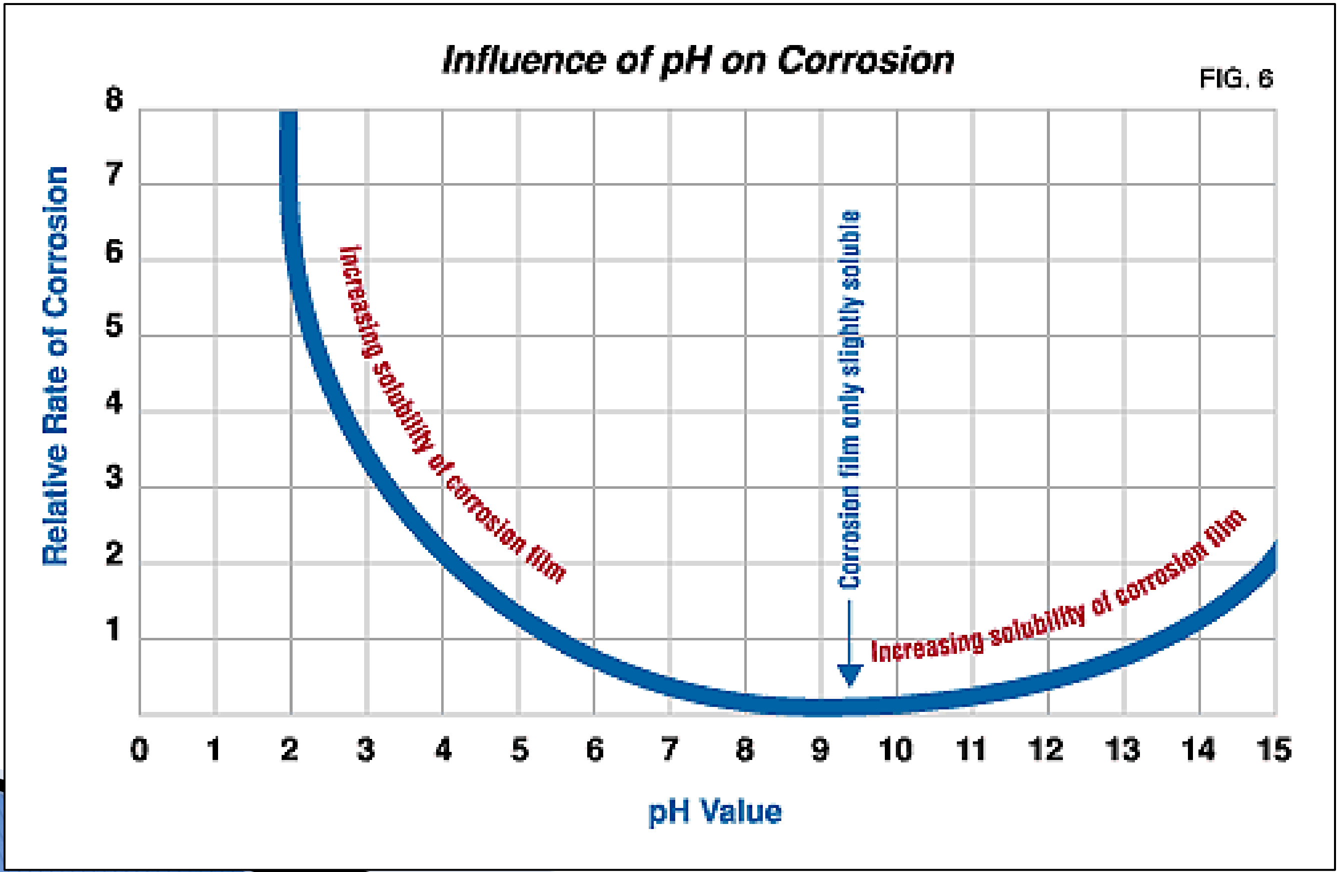
History of Corrosion Control

- Cathodic Action Resulting in Tuberculation in Water Pipelines



History of Corrosion Control

- Effects of pH on the Rate of Corrosion of Iron in Water

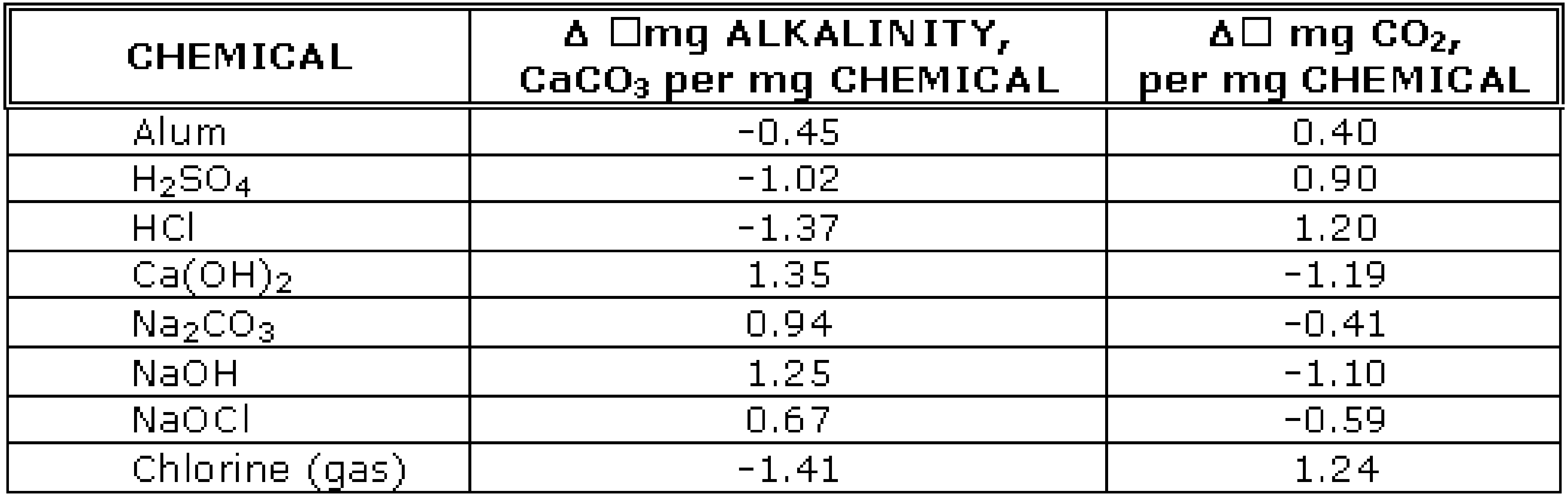


Influence of pH on Corrosion

FIG. 6

History of Corrosion Control

- Effects of Raising or Lowering Alkalinity and CO_2 by Chemical Addition

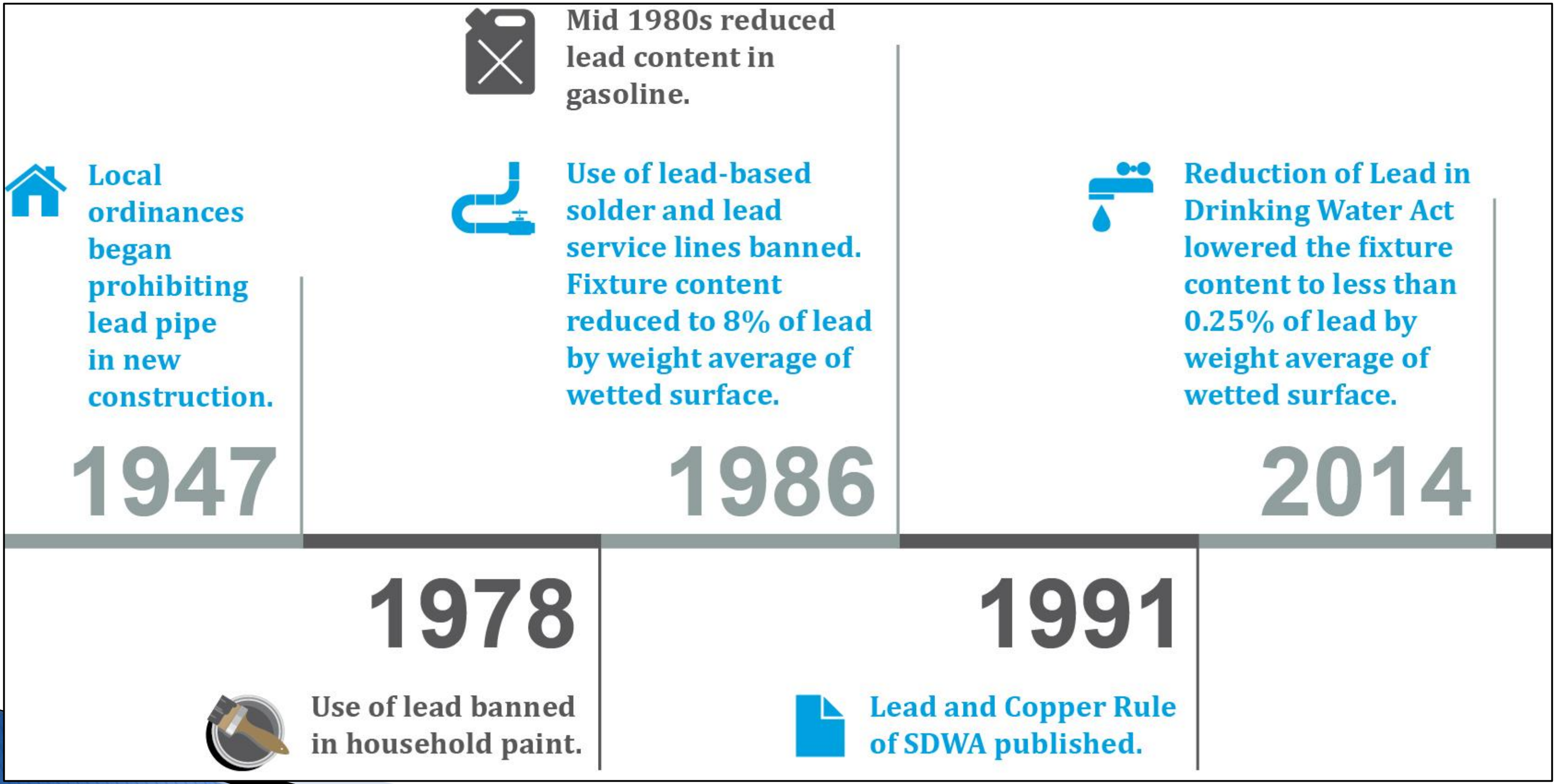


CHEMICAL	Δ □mg ALKALINITY, $CaCO_3$ per mg CHEMICAL	Δ□ mg CO_2, per mg CHEMICAL
Alum	-0.45	0.40
H_2SO_4	-1.02	0.90
HCl	-1.37	1.20
$Ca(OH)_2$	1.35	-1.19
Na_2CO_3	0.94	-0.41
NaOH	1.25	-1.10
NaOCl	0.67	-0.59
Chlorine (gas)	-1.41	1.24

Lead and Copper Background

Lead and Copper Background

History of Lead Regulations



1947

Local ordinances began prohibiting lead pipe in new construction.

1978

Use of lead banned in household paint.

Mid 1980s reduced lead content in gasoline.

1986

Use of lead-based solder and lead service lines banned. Fixture content reduced to 8% of lead by weight average of wetted surface.

1991

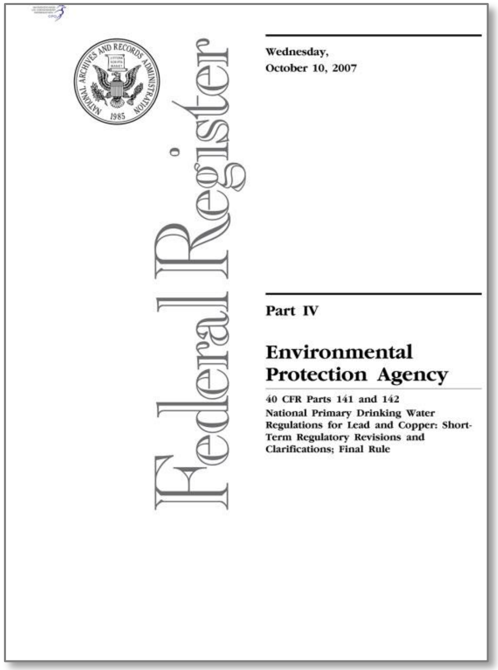
Lead and Copper Rule of SDWA published.

2014

Reduction of Lead in Drinking Water Act lowered the fixture content to less than 0.25% of lead by weight average of wetted surface.

Lead and Copper Background

- Published in 1991 and required first round of sampling in 1992
- Identified corrosion control as method to reduce the risk of lead and copper leaching into drinking water
- Requires monitoring at high risk sites every 3 years if compliance has been maintained
- Only SDWA rule that is monitored at water consumer's tap



Federal Register

Wednesday,
October 10, 2007

Part IV

Environmental
Protection Agency

40 CFR Parts 141 and 142
National Primary Drinking Water Regulations for Lead and Copper: Short-Term Regulatory Revisions and Clarifications; Final Rule

Lead and Copper Background

- Rarely from source water or distribution mains
- Service lines
  - Lead service lines, on either side of the meter
  - Goosenecks or pigtails
- Customer plumbing
  - Solder
  - Plumbing fixtures

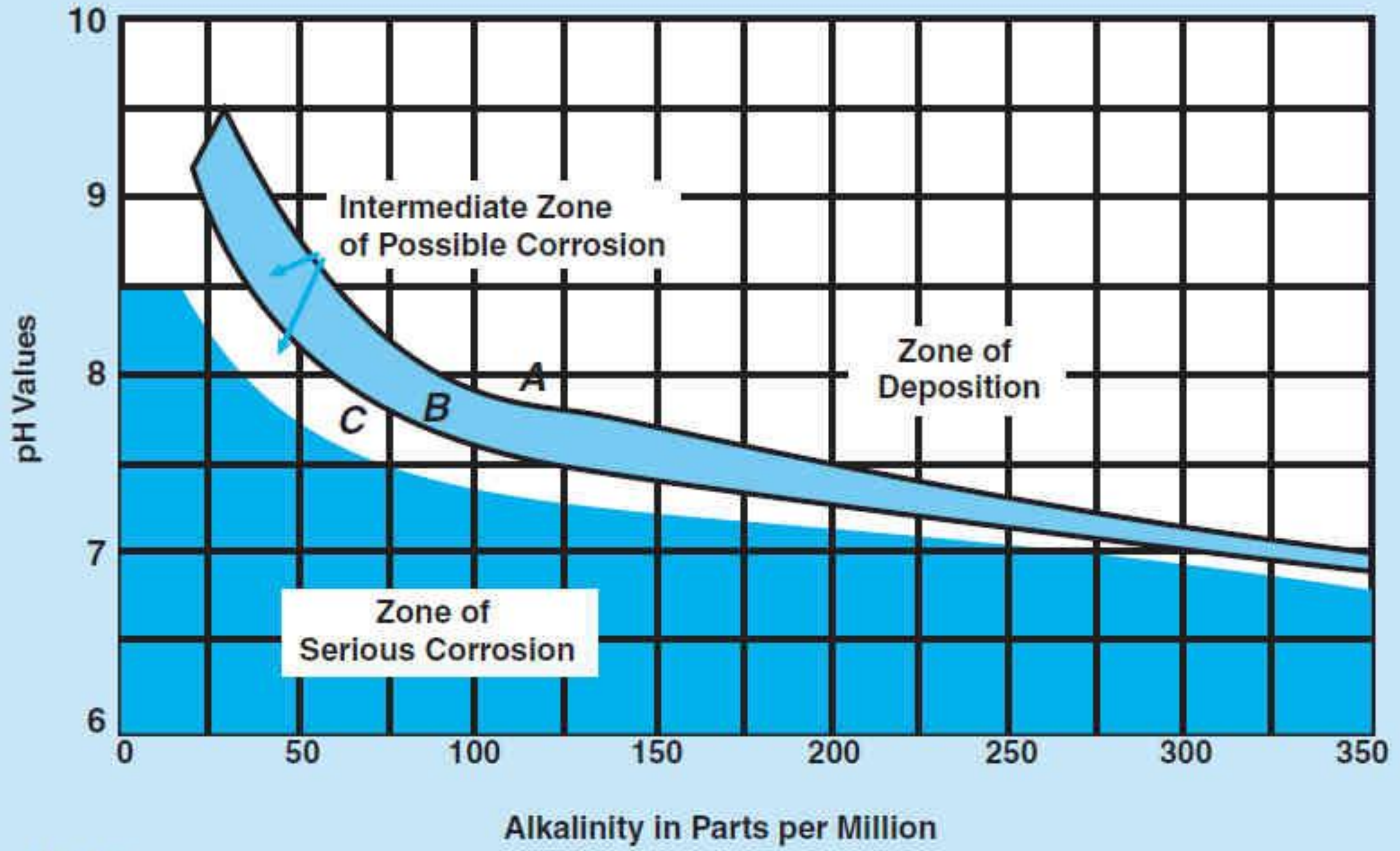
Lead and Copper Background

- Exposure to copper can cause stomach and intestinal distress, liver and kidney damage, and complications of Wilson’s disease.
- EPA set an MCLG of 1.3 mg/L

BB Matt (eee.sxc.hu.com)

Past Corrosion Control Review (Pre-Flint)

Past Corrosion Control Review (Pre-Flint)



Note:
- A = Curve of values necessary to produce a coating of calcium carbonate.
- B = Curve of calcium carbonate equilibrium.
- C = Curve of values necessary to prevent iron stains.

Past Corrosion Control Review (Pre-Flint)

Baylis Curve Example

$$pH = \log \left\{2.2 \times 10^6 \text{ X } \frac{\text{(Alkalinity in mg/L as CaCO3)}}{(CO_2 \text{ in mg/L})}\right\}$$

Measured Alkalinity

60 mg/L as $CaCO_3$

Measured CO_2

= 7.4 mg/L

$pH = \log \{2.2 \times 10^6 \text{ X } 60/7.4\} = 7.25$

Need to increase pH to reduce corrosivity

Past Corrosion Control Review (Pre-Flint)

Use of the Langelier Saturation Index (LSI) for Determining Water Stability

- Every water has a particular pH value where the water will neither deposit scale nor cause corrosion.
- A stable condition is termed saturation.
- Saturation (pHs), varies depending on calcium hardness, alkalinity, TDS, and temperature.
- LSI = pH – pHs

Corrosive < LSI = 0 > Scale Forming

Past Corrosion Control Review (Pre-Flint)

LSI	Description	General Recommendation
- 5	Severe Corrosion	Treatment Recommended
- 4	Severe Corrosion	Treatment Recommended
- 3	Moderate Corrosion	Treatment Recommended
- 2	Moderate Corrosion	Treatment May Be Needed
-1	Mild Corrosion	Treatment May Be Needed
-0.5	Mild Corrosion	Treatment May Be Needed
0	Near Balanced	Probably No Treatment
0.5	Some Faint Coating	Probably No Treatment
1	Mild Scale Coating	Treatment May Be Needed
2	Mild to Moderate Coatings	Treatment May Be Needed
3	Moderate Scale Forming	Treatment Advisable
4	Severe Scale Forming	Treatment Advisable

Past Corrosion Control Review (Pre-Flint)

Water Characteristic	Likely Cause
Red/reddish-brown Water	**Distribution Pipe Corrosion**
Blueish Stains on fixtures	**Copper Line Corrosion**
Black Water	**Sulfide Corrosion of Iron**
Foul Tastes and Odors	**By-Products of Bacteria**
Loss of Pressure	**Tuberculation**
Lack of Hot Water	**Scaling**
Reduced Life of Plumbing	**Pitting from Corrosion**
Tastes Like Garden Hose	**Backflow From Hose**

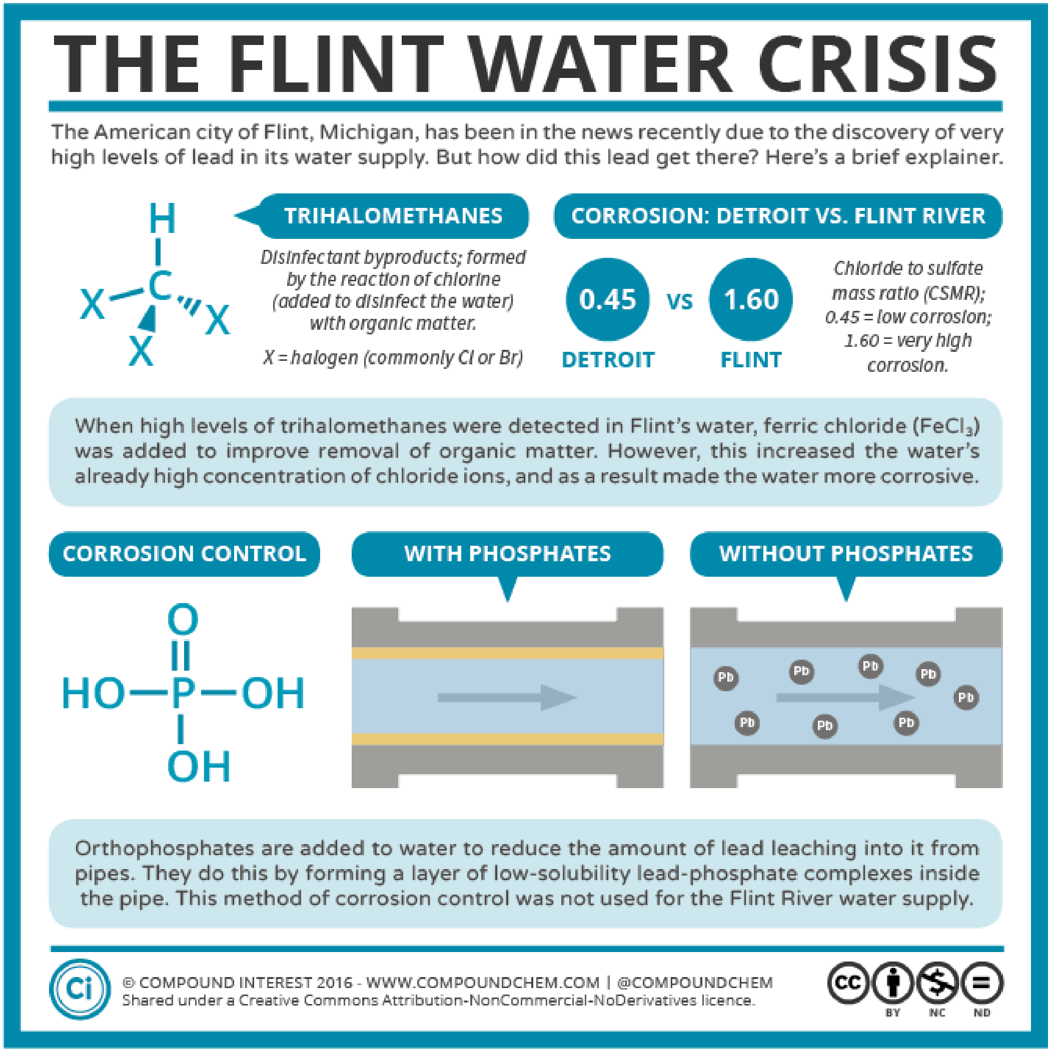
Past Corrosion Control Review (Pre-Flint)

Development and Review of Corrosion Control Study with TCEQ

- WQPs Reviewed
  - Calcium, Alkalinity, Conductivity, TDS, pH, Temperature
- Historical analyses completed
  - LSI
  - Aggressiveness
- Most common treatment method was pH adjustment via sodium hydroxide (caustic) addition

Current Corrosion Control Review
(Post-Flint)

Current Corrosion Control Review (Post-Flint)



THE FLINT WATER CRISIS

The American city of Flint, Michigan, has been in the news recently due to the discovery of very high levels of lead in its water supply. But how did this lead get there? Here's a brief explainer.

TRIHALOMETHANES

Disinfectant byproducts; formed by the reaction of chlorine (added to disinfect the water) with organic matter.

X = halogen (commonly Cl or Br)

CORROSION: DETROIT VS. FLINT RIVER

0.45 vs **1.60**

DETROIT **FLINT**

Chloride to sulfate mass ratio (CSMR); 0.45 = low corrosion; 1.60 = very high corrosion.

When high levels of trihalomethanes were detected in Flint's water, ferric chloride ($FeCl_3$) was added to improve removal of organic matter. However, this increased the water's already high concentration of chloride ions, and as a result made the water more corrosive.

CORROSION CONTROL

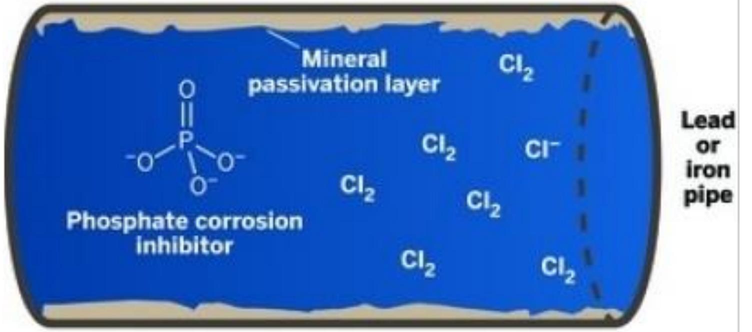
WITH PHOSPHATES

WITHOUT PHOSPHATES

Orthophosphates are added to water to reduce the amount of lead leaching into it from pipes. They do this by forming a layer of low-solubility lead-phosphate complexes inside the pipe. This method of corrosion control was not used for the Flint River water supply.

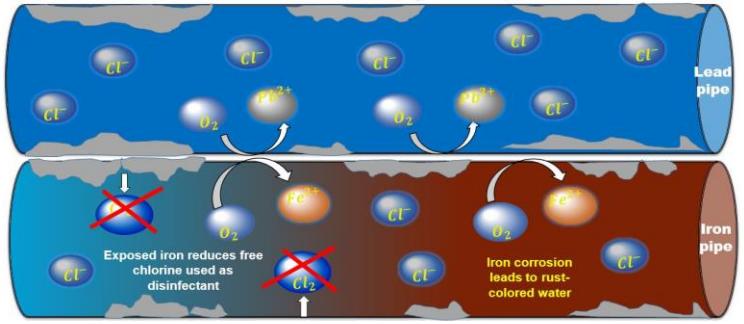
Before: Treated Detroit water

Phosphate corrosion inhibitor helps maintain a mineral passivation layer on the inside of Flint's pipes, protecting them from corrosion. With little corrosion, chlorine disinfectant levels remain stable.



After: Treated Flint River Water

Lack of corrosion inhibitor, high chloride levels, and other factors cause the passivation layer to dissolve and fall off, leading to increased corrosion in pipes. As pipes corrode, chlorine disinfection breaks down. Oxides such as dissolved O_2 corrode pipes and leach soluble metal.



Current Corrosion Control Review (Post-Flint)

- Texas Legislature Response to Flint:
  - “We will not let Flint happen in Texas…period.”

Current Corrosion Control Review (Post-Flint)

- **How did it happen here?**

  - Source water quality changes not accounted for
  - Equipment calibration not current (pH meters)
  - Focusing only on finished turbidity
  - Focusing only on DBP levels
  - Not maintaining a stable monochloramine
  - Letting nitrification get out of control in distribution

Current Corrosion Control Review (Post-Flint)

- **What do we do about it?**
  - If you already have lead and copper spikes, or the potential for it due to corrosive water…
    - You must develop an Optimal Corrosion Control Treatment (OCCT) approach
    - Site-specific – What works for your neighbor may not work for you…

Current Corrosion Control Review (Post-Flint)

- **Optimal corrosion control treatment (OCCT)**
  - Chemical treatment designed to reduce the corrosivity of water
    - Raising pH to make water less acidic
    - Adding buffering to make water more stable
    - Adding corrosion inhibitors to create a barrier to inhibit metals release
  - OCCT required for large systems
  - Required for small/medium systems only if the action level is exceeded
    - Recommended if finished water quality is corrosive or almost corrosive

Current Corrosion Control Analyses

Current Corrosion Control Analyses

Use of the Langelier Saturation Index (LSI) for Determining Water Stability

- Every water has a particular pH value where the water will neither deposit scale nor cause corrosion.
- A stable condition is termed saturation.
- Saturation (pHs), varies depending on calcium hardness, alkalinity, TDS, and temperature.
- LSI = pH – pHs
  - Corrosive = LSI <= 0
  - Slightly Scale Forming >= 0.25
  - Moderately Scale Forming >= 0.5

Current Corrosion Control Analyses

LSI	Description	General Recommendation
- 5	Severe Corrosion	Treatment Recommended
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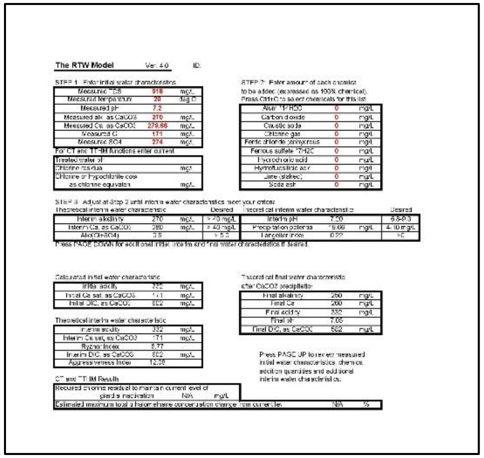
Current Corrosion Control Analyses

- Two Primary Approaches for Analyses:

- RTW Model (AKA TetraTech Calculator)
    - Rapid analysis of LSI and CCPP based on water quality data
    - Allows for chemical feed adjustment to quickly gauge changes to LSI and CCPP

- EPA OCCT Guidance Manual Evaluation
    - Longer analysis, but also includes corrosion inhibitor options not included in the RTW model



The RTW Model Ver. 4.0 ID:

STEP 1: Enter initial water characteristics

Measured TDS	916	mg/L
Measured temperature	20	deg C
Measured pH	7.2	
Measured alk. as CaCO3	270	mg/L
Measured Ca. as CaCO3	279.86	mg/L
Measured Cl	171	mg/L
Measured SO4	274	mg/L

For CT and TTHM functions enter current:

Treated water pH	
Chlorine residual	mg/L
Chlorine or hypochlorite dose as chlorine equivalent	mg/L

STEP 2: Enter amount of each chemical to be added (expressed as 100% chemical). Press Ctrl+C to select chemicals for this list

Alum (14 H2O)	0	mg/L
Carbon dioxide	0	mg/L
Caustic soda	0	mg/L
Chlorine gas	0	mg/L
Ferric chloride (anhydrous)	0	mg/L
Ferrous sulfate (7H2O)	0	mg/L
Hydrochloric acid	0	mg/L
Hydrofluosilicic acid	0	mg/L
Lime (slaked)	0	mg/L
Soda ash	0	mg/L

STEP 3: Adjust at Step 2 until interim water characteristics meet your criteria

Theoretical interim water characteristic			Desired	Theoretical interim water characteristic			Desired
Interim alkalinity	270	mg/L	> 40 mg/L	Interim pH	7.20		6.8-9.3
Interim Ca, as CaCO3	280	mg/L	> 40 mg/L	Precipitation potential	19.66	mg/L	4-10 mg/L
Alk/(Cl+SO4)	3.5		> 5.0	Langelier index	0.22		>0

Press PAGE DOWN for additional initial, interim and final water characteristics if desired.

Calculated initial water characteristic

Initial acidity	332	mg/L
Initial Ca sat, as CaCO3	171	mg/L
Initial DIC, as CaCO3	602	mg/L

Theoretical final water characteristic after CaCO3 precipitation

Final alkalinity	260	mg/L
Final Ca	260	mg/L
Final acidity	332	mg/L
Final pH	7.05	
Final DIC, as CaCO3	582	mg/L

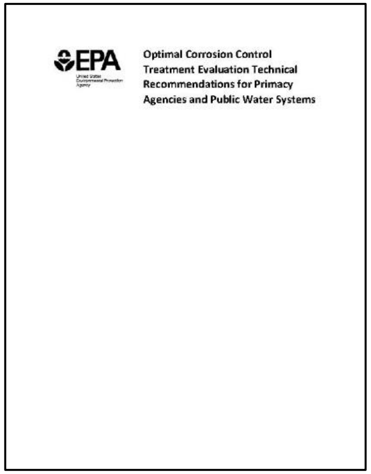
Theoretical interim water characteristic

Interim acidity	332	mg/L
Interim Ca sat, as CaCO3	171	mg/L
Ryznar index	6.77	
Interim DIC, as CaCO3	602	mg/L
Aggressiveness index	12.38	

Press PAGE UP to review measured initial water characteristics, chemical addition quantities and additional interim water characteristics.

CT and TTHM Results

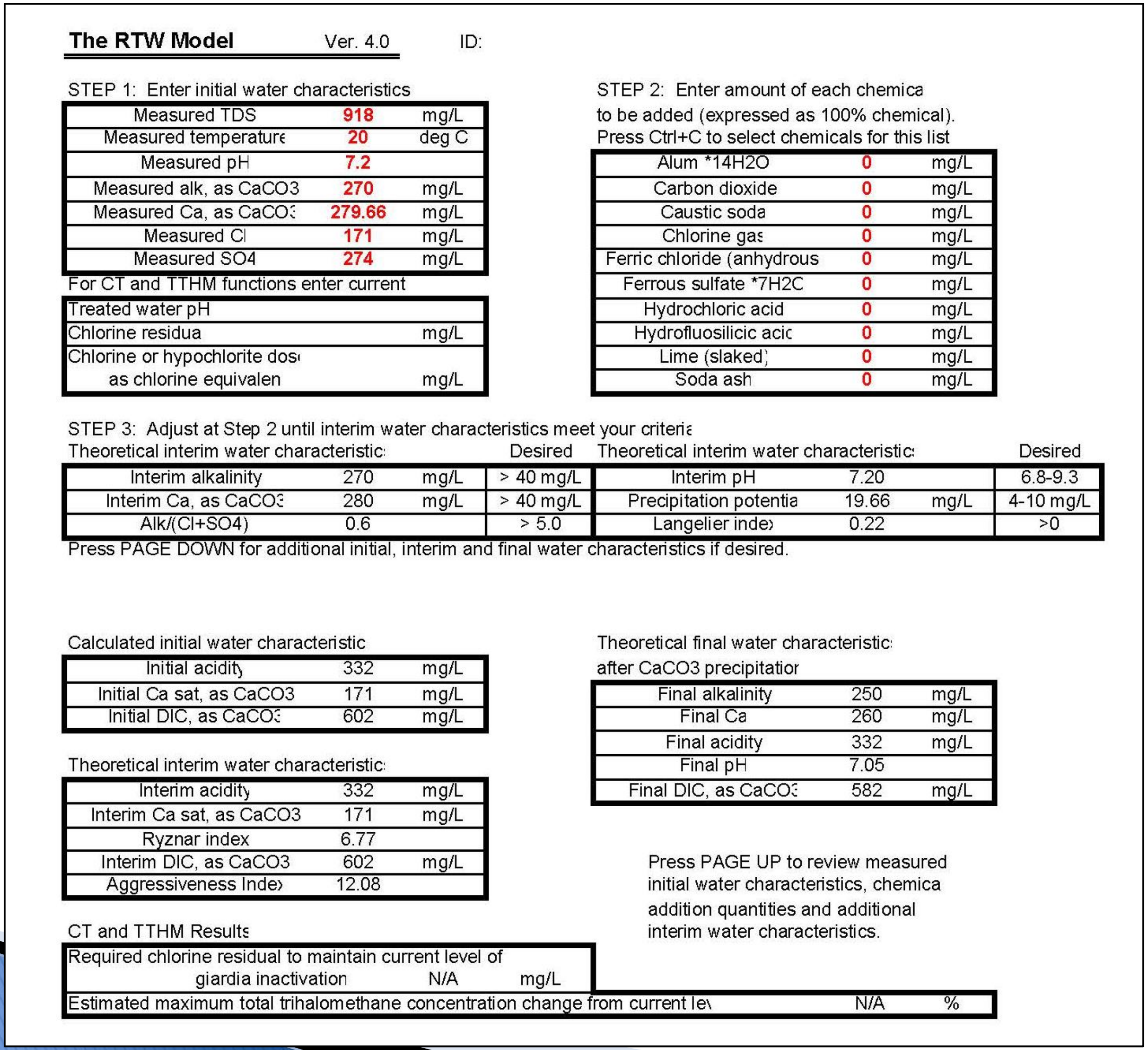
Required chlorine residual to maintain current level of giardia inactivation	N/A	mg/L
Estimated maximum total trihalomethane concentration change from current level	N/A	%



EPA
United States Environmental Protection Agency

Optimal Corrosion Control
Treatment Evaluation Technical
Recommendations for Primacy
Agencies and Public Water Systems

Current Corrosion Control Analyses



The RTW Model Ver. 4.0 ID:

STEP 1: Enter initial water characteristics

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Measured SO4	274	mg/L

For CT and TTHM functions enter current

Treated water pH	
Chlorine residua	mg/L
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STEP 2: Enter amount of each chemica
to be added (expressed as 100% chemical).
Press Ctrl+C to select chemicals for this list

Alum *14H2O	0	mg/L
Carbon dioxide	0	mg/L
Caustic soda	0	mg/L
Chlorine gas	0	mg/L
Ferric chloride (anhydrous	0	mg/L
Ferrous sulfate *7H2	0	mg/L
Hydrochloric acid	0	mg/L
Hydrofluosilicic aci	0	mg/L
Lime (slaked	0	mg/L
Soda ash	0	mg/L

STEP 3: Adjust at Step 2 until interim water characteristics meet your criteri

Theoretical interim water characteristic			Desired
Interim alkalinity	270	mg/L	> 40 mg/L
Interim Ca, as CaCO	280	mg/L	> 40 mg/L
Alk/(Cl+SO4)	0.6		> 5.0

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Theoretical final water characteristic
after CaCO3 precipitatior

Final alkalinity	250	mg/L
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Final DIC, as CaCO	582	mg/L

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CT and TTHM Results

Required chlorine residual to maintain current level of giardia inactivation	N/A	mg/L
Estimated maximum total trihalomethane concentration change from current le	N/A	%

Current Corrosion Control Analyses

Exhibit E.1: Identification of Potential Corrosion Control Treatment Options

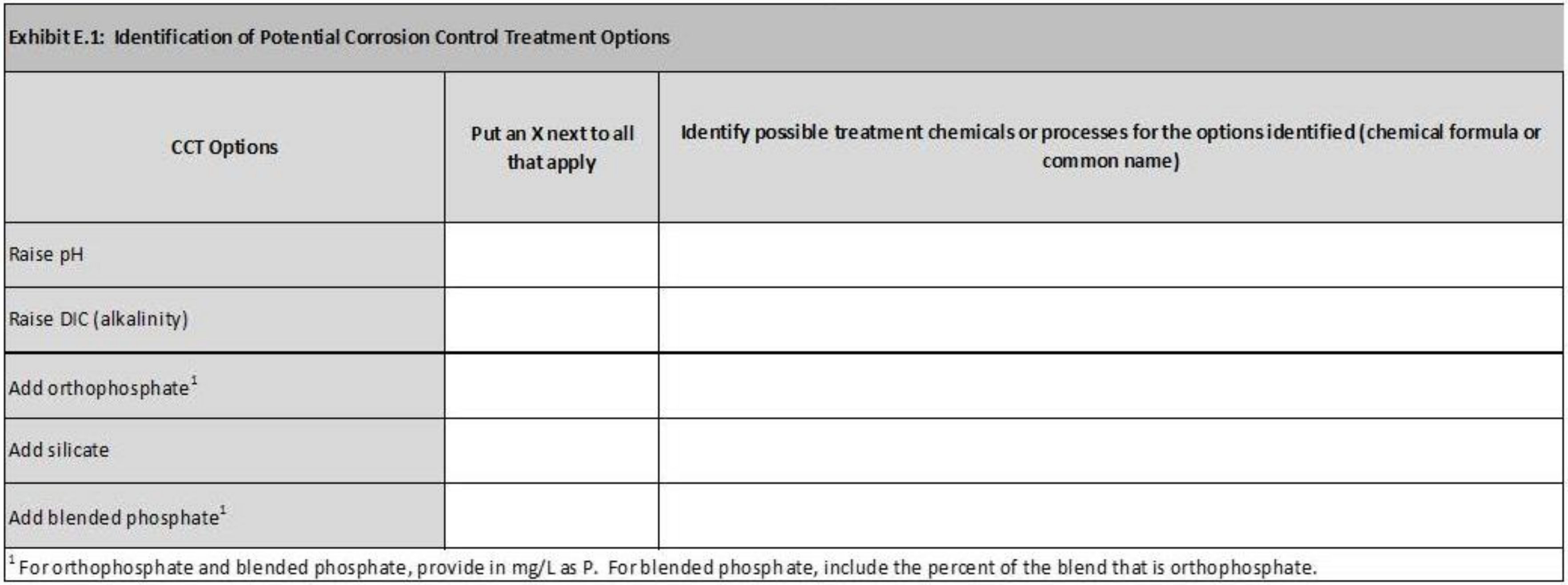


Exhibit E.1: Identification of Potential Corrosion Control Treatment Options		
CCT Options	Put an X next to all that apply	Identify possible treatment chemicals or processes for the options identified (chemical formula or common name)
Raise pH		
Raise DIC (alkalinity)		
Add orthophosphate[1]		
Add silicate		
Add blended phosphate[1]		

[1] For orthophosphate and blended phosphate, provide in mg/L as P. For blended phosphate, include the percent of the blend that is orthophosphate.

Current Corrosion Control Analyses

Additional Corrosion Potential Parameters – Modifed Larson's Ratio (LRM)

- Focused on the potential for iron corrosion based on the ratio of chloride, sulfate and sodium to alkalinity
- LRM = $((Cl^- + SO_4^{2-} + Na^+)^{1/2} / Alk) \times (T/25) \times (HRT)$
    - Corrosive = LRM > 0.5
    - Moderately Scale Forming < 0.5

Current Corrosion Control Analyses

Additional Corrosion Potential Parameters – Ryznar Stability Index (RSI)

- Focused on the relationship of forming and maintaining a stable calcium carbonate scale film with the given water quality
- $RSI = 2(pH_S) - pH$
  - Corrosive = RSI > 8
  - Neutral = RSI = 6-7
  - Moderately Scale Forming = RSI < 6

Current Corrosion Control Analyses

Additional Corrosion Potential Parameters – Aggressiveness Index (AI)

- Originally intended to determine the minimum water quality needed to prevent degradation of AC pipe
- $AI = pH + \log(AH) = pH + \log A + \log H$
  - Corrosive = $AI < 10$
  - Neutral = AI = 10-12
  - Non-Corrosive = $AI > 12$

Current Corrosion Control Analyses

Current TCEQ Focus:

- LSI
  - Starting point:
    - LSI of 0.25-0.50 at Point of Entry
- CCPP
  - Starting point:
    - CCPP of 4-10 mg/L at Point of Entry

Current Corrosion Control Analyses

Why do we say “starting point”?

- Example of Water Quality #1
  - TDS = 500 mg/L
  - Temp. = 20 C
  - pH = 7
  - Alkalinity = 50 mg/L
  - Calcium = 100 mg/L
  - Chloride = 150 mg/L
  - Sulfate = 150 mg/L

- Calculated LSI = -1.11
- Calculated CCPP = -17.05 mg/L
- Considered “corrosive” likely to leach lead and copper where available

Current Corrosion Control Analyses

Why do we say “starting point”?

- Modification of Water Quality #1
  - Raise pH to 8 via caustic addition (dose of approx. 30 mg/L)
  - Calculated LSI = -0.09
  - Calculated CCPP = -0.7 mg/L
  - Considered “slightly corrosive”, still may leach lead and copper where available
- Further Modification of Water Quality #1
  - Raise pH to 8.5 via caustic addition (dose of approx. 36 mg/L)
  - Calculated LSI = 0.47
  - Calculated CCPP = 2.82 mg/L
  - While considered “not corrosive”, the low CCPP value means that a calcium carbonate passivation layer may not extend to the furthest reaches of your distribution system

Current Corrosion Control Analyses

So we just need to stay above 8.5 pH, right?

- Not exactly.
  - Finished water pH above 8.5 is a challenging area to operate in
  - Scale formation is highest at the plant, and can cause scaling issues with tanks, pumps, piping and instrumentation at the plant
  - Monochloramine formation begins to transition to dichloramine and trichloramine formation, which can result in loss of total chlorine residual in distribution and accelerated nitrification
  - Increases in nitrification in distribution will use up alkalinity, which will result in a drop in pH as total chlorine breaks down
    - In other words, increasing pH above 8.5 can actually result in a **reduction** of pH in distribution!
  - If treatment at the plant is not enough, post-treatment in distribution may be necessary

Treatment Options for Corrosion Control

Treatment Options for Corrosion Control

- Treatment Options
  - Treatment Goals
    - Raise pH
      - Biggest impact to LSI
    - Increase Alkalinity
      - Biggest impact to CCPP
    - Increase Calcium
      - Biggest impact to CCPP

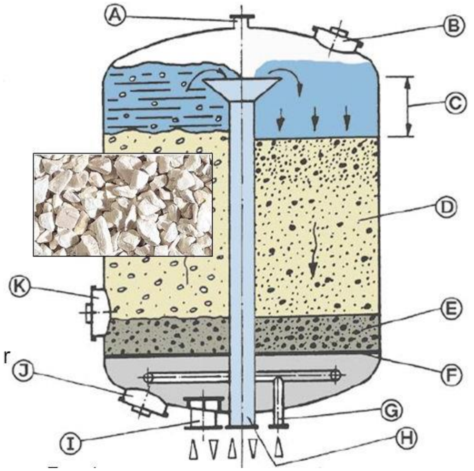
Treatment Options for Corrosion Control

- Most Common Treatment Options

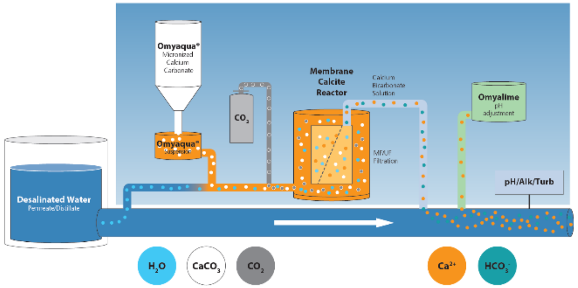
Chemical	Use	Composition	Alkalinity Change per mg/L of Chemical
Caustic Soda (NaOH)	Raise pH	• 93% purity • Storage at less than 50% strength to prevent freezing	1.55 mg/L CaCO3
Lime (Ca[OH]2)	Raise pH	• 95-98% purity • Dry storage with slurry feed	1.21 mg/L CaCO3
Sodium Bicarbonate (NaHCO3)	Little increase in pH	• 98% purity • Dry storage with solution feed	0.60 mg/L CaCO3
Soda Ash (Na2CO3)	Moderate increase in pH	• 95% purity • Dry storage with solution feed	0.90 mg/L CaCO3

Treatment Options for Corrosion Control

- New Treatment Options on the Horizon?
  - Calcite Contactors
    - Flow through calcite packed bed contactors (or inject calcite solution) to dissolve additional calcium and alkalinity back into the finished water

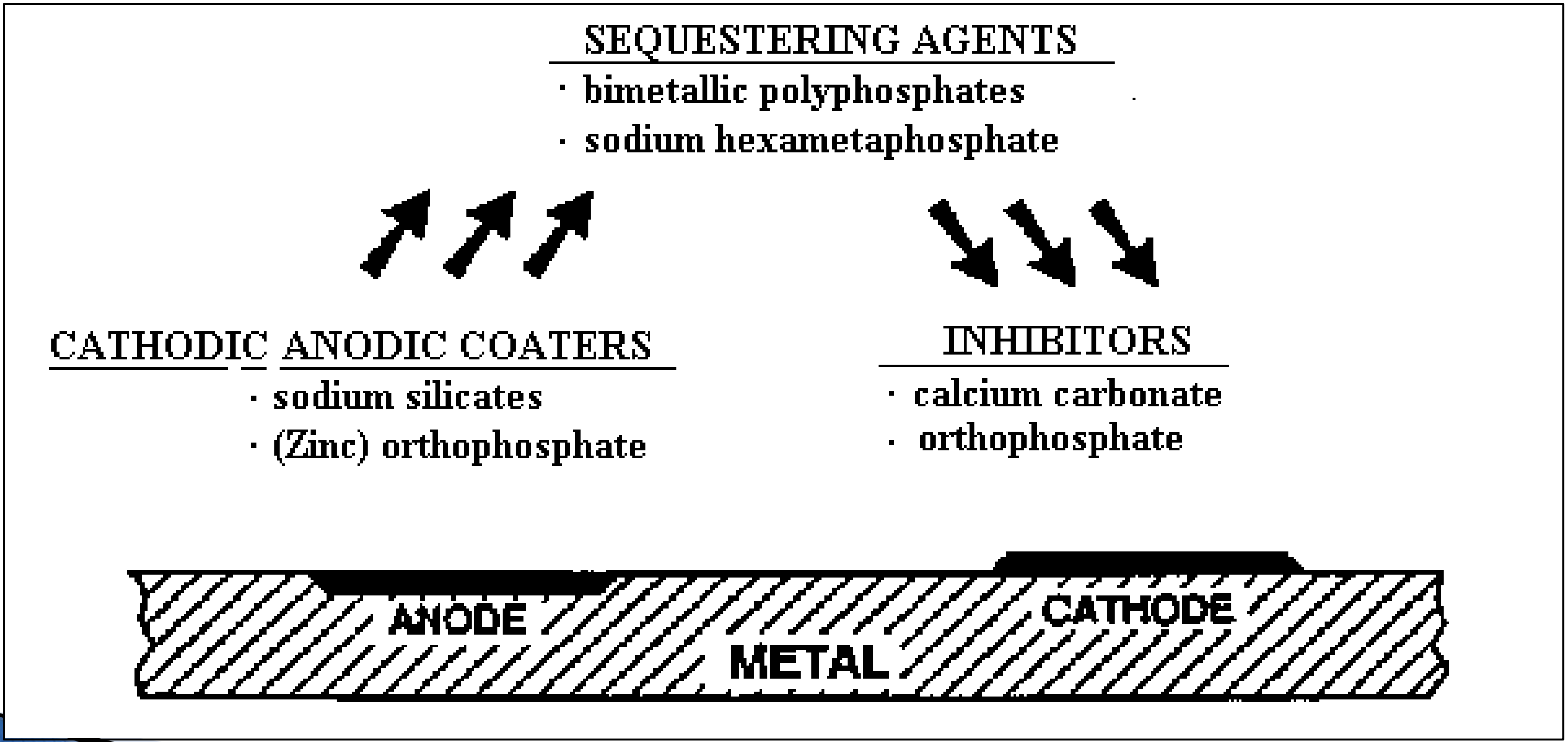


  - Micronized Calcium Carbonate
    - Feed of powdered lime or calcite to target the necessary calcium, alkalinity and pH levels needed (more appropriate for systems greater than 1 MGD at this time however)



Treatment Options for Corrosion Control

- Sequestering Action of Poly and Ortho Phosphates



SEQUESTERING AGENTS
- bimetallic polyphosphates
- sodium hexametaphosphate

CATHODIC ANODIC COATERS
- sodium silicates
- (Zinc) orthophosphate

INHIBITORS
- calcium carbonate
- orthophosphate

Treatment Options for Corrosion Control

- Post-Treatment - Use of Orthophosphates for Sequestering
  - Orthophosphate is used to sequester iron ions at pipe surfaces
  - The Sequestering forms a protective coating that prevents further iron migration
  - Ortho/Poly Blends provide both sequestering of soluble iron and iron movement from pipelines under corrosive conditions

Treatment Options for Corrosion Control

- Treat, Post-Treat, or Do Both?

	Treatment Only	Post-Treatment Only	Do Both?
Advantages	One point of control	Lower capital cost	"Belt and suspenders" approach
	May address corrosion issue without post-treatment	Possibly lower O&M cost	Can balance costs
Disadvantages	Limited impact on WQ at water age > 3-5 days	Need to re-dose after 3-5 days water age	Multiple points of possible failure
	Higher capital cost	Increase in phosphate load to WWTP	More strain on wholesale customers
	Possibly higher O&M cost	Overdosing is just as problematic as underdosing	Overdosing is just as problematic as underdosing
	May not completely address corrosion issue alone	More strain on wholesale customers	Increase in phosphate load to WWTP

Summary

Summary

- We are in a new era following Flint…
- Every major treatment change will now require an evaluation of impacts on corrosion potential
- Source water quality changes (especially seasonal changes) mean re-checking your corrosion control approach
- What works for you may not work for your neighbor, and vice versa!
- Make sure you have used all the tools in your treatment toolbox before taking steps to implement post-treatment (one point of control)
- Some water sources may require treatment and post-treatment – wholesale customers should consider treatment and post-treatment options as well
- Last but not least – coordinate with TCEQ on what you want to do, how you want to do it, and when you want to do it!