Assessing Secondary Contaminants and Discolored Water in Drinking Water

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Why All the Excitement about Secondary Contaminants?

What They Are:

- Aluminum
- Chloride
- Color
- Copper
- Corrosivity
- Fluoride
- Foaming agents
- Hydrogen sulfide
- Iron
- Manganese
- Odor
- pH
- Silver
- Sulfate
- Total Dissolved Solids
- Zinc

Why All the Excitement about Secondary Contaminants? 2

Common Questions:

- The Secondary Constituent Levels (SCLs) aren’t health-based, right?
- What’s wrong with drinking water that is over the SCLs?
- Does TCEQ enforce the SCLs?

Why All the Excitement about Secondary Contaminants? 3

- TCEQ is obligated by law to monitor the SCLs.
- The federal rules have this to say about secondaries (40 CFR § 143.1):

  "…The regulations in this subpart control contaminants in drinking water that primarily affect the aesthetic qualities relating to the public acceptance of drinking water…"

- The public generally doesn't trust or accept water in which they can taste, smell, or see secondary contaminants.

Why All the Excitement about Secondary Contaminants? 4

- Trends over the last 10 years
  - Significant increase in issuances of violations
  - Increasing legislative interest in response to constituent complaints

What Can Be Done about Secondary Contaminants?

- Let’s focus on the most common* secondary contaminant issues:

  1. Total Dissolved Solids (TDS) > 1,000 mg/L (Saltiness)

  2. Color – usually from iron and/or manganese

*Common to public water systems in Texas

Part 1: Total Dissolved Solids

- How do concentrations > 1,000 mg/L occur?
  - Groundwater
    - Aquifer chemistry
    - Depth
    - Saltwater intrusion
  - Surface water
    - Characteristics of formations where runoff occurs
    - Evaporation
    - Human activities
- Treatment of high TDS water increasing

How is TDS treated?

- Reverse Osmosis (RO)
  - Dissolved salt particles are so small that these are the only membranes that can exclude them.
- Downsides to RO
  - Disposal of a concentrated waste stream
  - Cost

https://www.membracon.co.uk/wp-content/uploads/2023/04/Reverse-Osmosis-Membrane.jpeg

Part 2:
Color from Iron and Manganese

Iron Chemistry

Iron:

- Elemental Symbol: Fe (Latin: ferrum)
- Atomic Mass: 55.845
- Most Common Oxidation States (Valences) in Drinking Water: +2 and +3
- Most common element on earth by mass

Manganese Chemistry

Manganese:

- Elemental Symbol: Mn
- Atomic Mass: 54.938
- Most Common Oxidation States (Valences) in Drinking Water: +2, +3 and +4
- Not found as a free element in nature but in minerals in combination with iron

Oxidation Reactions

$$Fe^{+0} \xrightarrow[\text{Oxidation}]{} Fe^{+2} + 2e^{-}$$

$$Fe^{+2} \xrightarrow[\text{Oxidation}]{} Fe^{+3} + 1e^{-}$$

$$Mn^{+0} \xrightarrow[\text{Oxidation}]{} Mn^{+2} + 2e^{-}$$

$$Mn^{+2} \xrightarrow[\text{Oxidation}]{} Mn^{+3} + 1e^{-}$$

$$Mn^{+3} \xrightarrow[\text{Oxidation}]{} Mn^{+4} + 1e^{-}$$

Oxidation States

Iron (Fe):

- Fe^{+2} Ferrous (soluble, colorless)
- Fe^{+3} Ferric (insoluble) – ferric oxides (Fe_2O_3)

Manganese (Mn):

- Mn^{+2} Manganous (soluble, colorless)
- Mn^{+3} Manganic (insoluble)
- Mn^{+4} (insoluble) – manganese dioxide (MnO_2)

What's So Tricky about Fe and Mn?

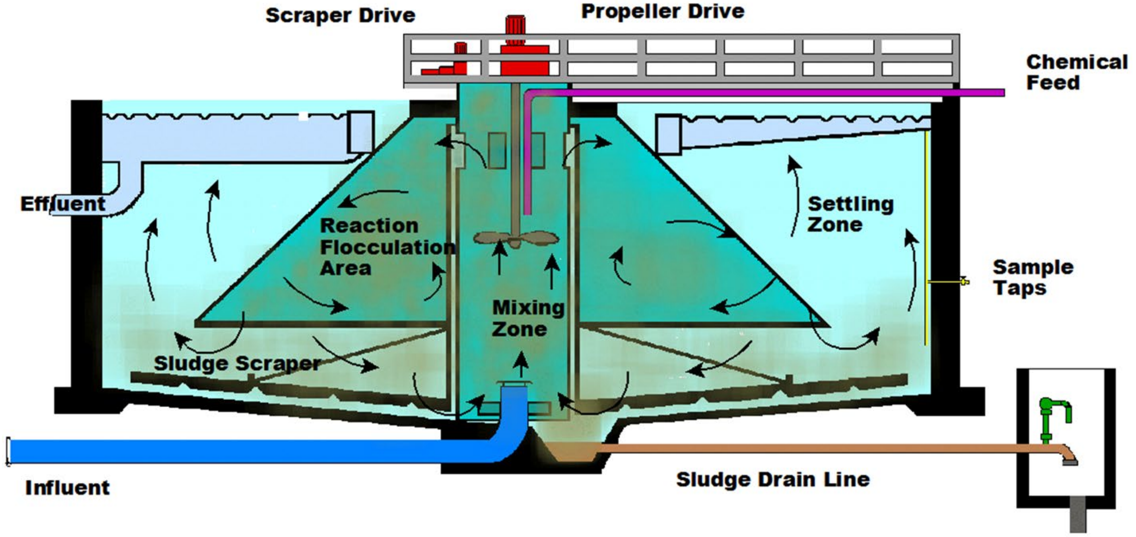
- The insoluble forms of Fe (Fe^{+3}) and Mn (Mn^{+3} and Mn^{+4}) cause color at sufficiently high concentrations
  - Generally, around the SCL concentrations
  - Iron SCL = 0.3 mg/L
  - Mn SCL = 0.05 mg/L
  - However, concentrations lower than the SCL can cause color.

What's So Tricky about Fe and Mn? 2

- It is difficult to maintain Fe and Mn in their soluble (clear) forms.
  - Water systems are required to apply and maintain a disinfectant (oxidant) concentration in plants and through distribution.

Common Fe and Mn Treatment Strategies

- Removal (Gold Standard)
  1. Pretreatment
  2. Coagulation
  3. Flocculation
  4. Sedimentation
  5. Filtration



Removal

- For removal, soluble iron and manganese must be changed to their insoluble forms.

  For example:

  - Soluble (Fe^{2+}) to Insoluble (Fe^{3+})
  - Soluble (Mn^{2+}) to Insoluble (Mn^{4+})

- This may be done using pretreatment (chemical and non-chemical means)

Chemical/Non-Chemical Pretreatment

Chemical Oxidants:

- Chlorine
- Permanganates (Sodium/Potassium)
- Chlorine dioxide
- Ozone

Chemicals for pH Adjustment

- Caustic
- Lime

Non-Chemical:

- Aeration

Chemical Oxidants

Chemical oxidants can be used to either:

- Oxidize soluble iron and manganese to their insoluble forms;
- Recharge/restore adsorption properties of filter media (e.g. $KMnO_4$ for greensand and chlorine for microsand); or
- Both

pH Adjustment

pH adjustment can be used to:

- Improve coagulation
- Optimize oxidation of iron (lower pH) and manganese (higher pH)
- Achieve optimum pH for coagulants and organic polymers
- Achieve optimum pH for hydrogen sulfide removal and oxidation of iron and manganese
- Facilitate softening

Aeration

Aeration can be used to:

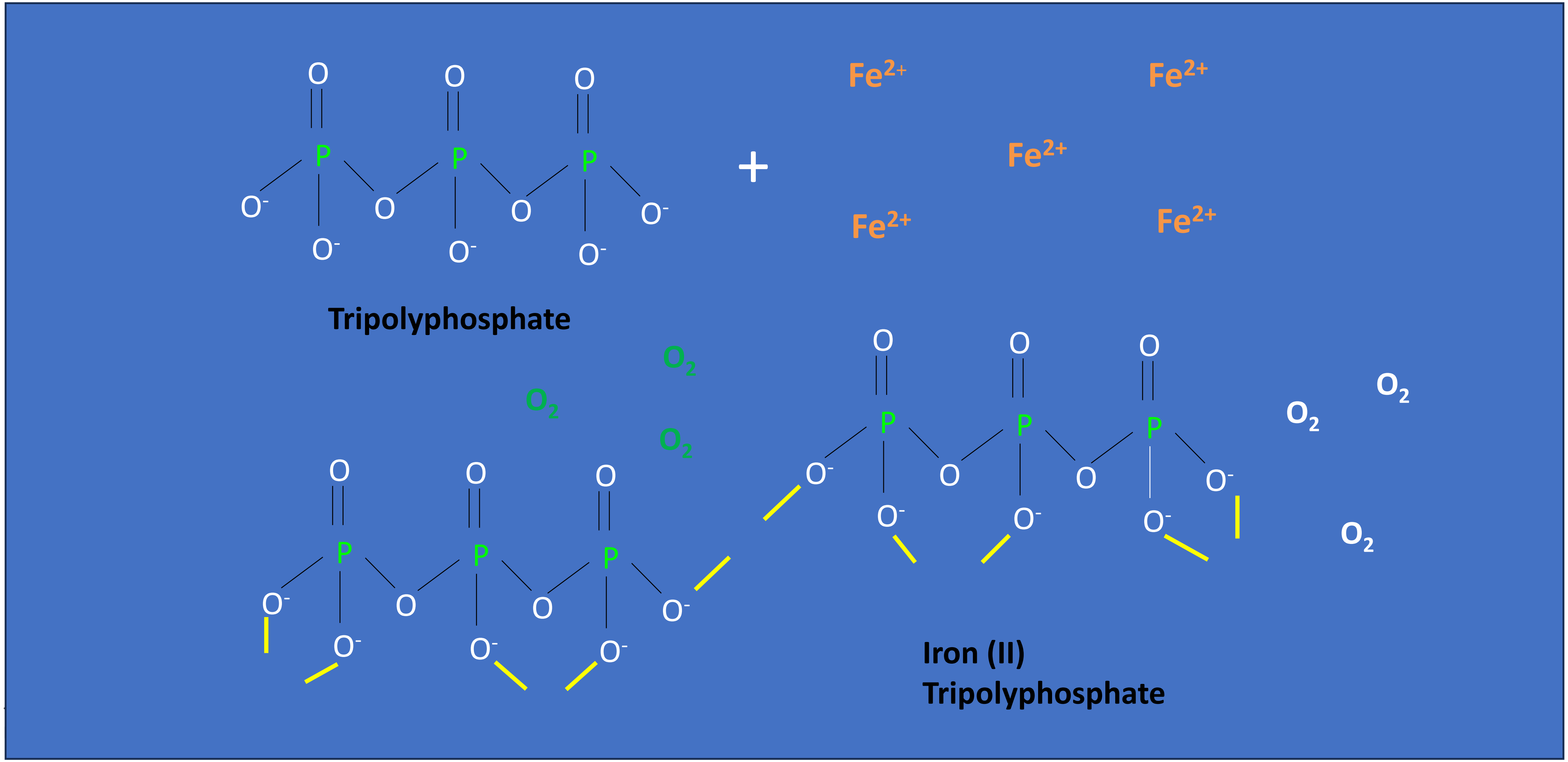
- Oxidize soluble iron (not so practical for oxidizing soluble manganese)
- Help remove demand such as hydrogen sulfide
- Increase pH by removing carbon dioxide

Removal: Bottom Line

- Relatively costly
- Reliable

Common Fe and Mn Treatment Strategies

Sequestration with Polyphosphate



Sequestration: Chemical Effectiveness

Depends on many factors:

- Adequate mixing
  - Need adequate chemical dispersion before adding oxidant
- Location of feeding point
  - Should be as close to the raw source as possibly and always before the chlorine feed
- Temperature
  - Water temperatures above 120ºF can lead to the dissociation of sequestering complexes (e.g. water heaters)

Sequestration: Chemical Effectiveness 2

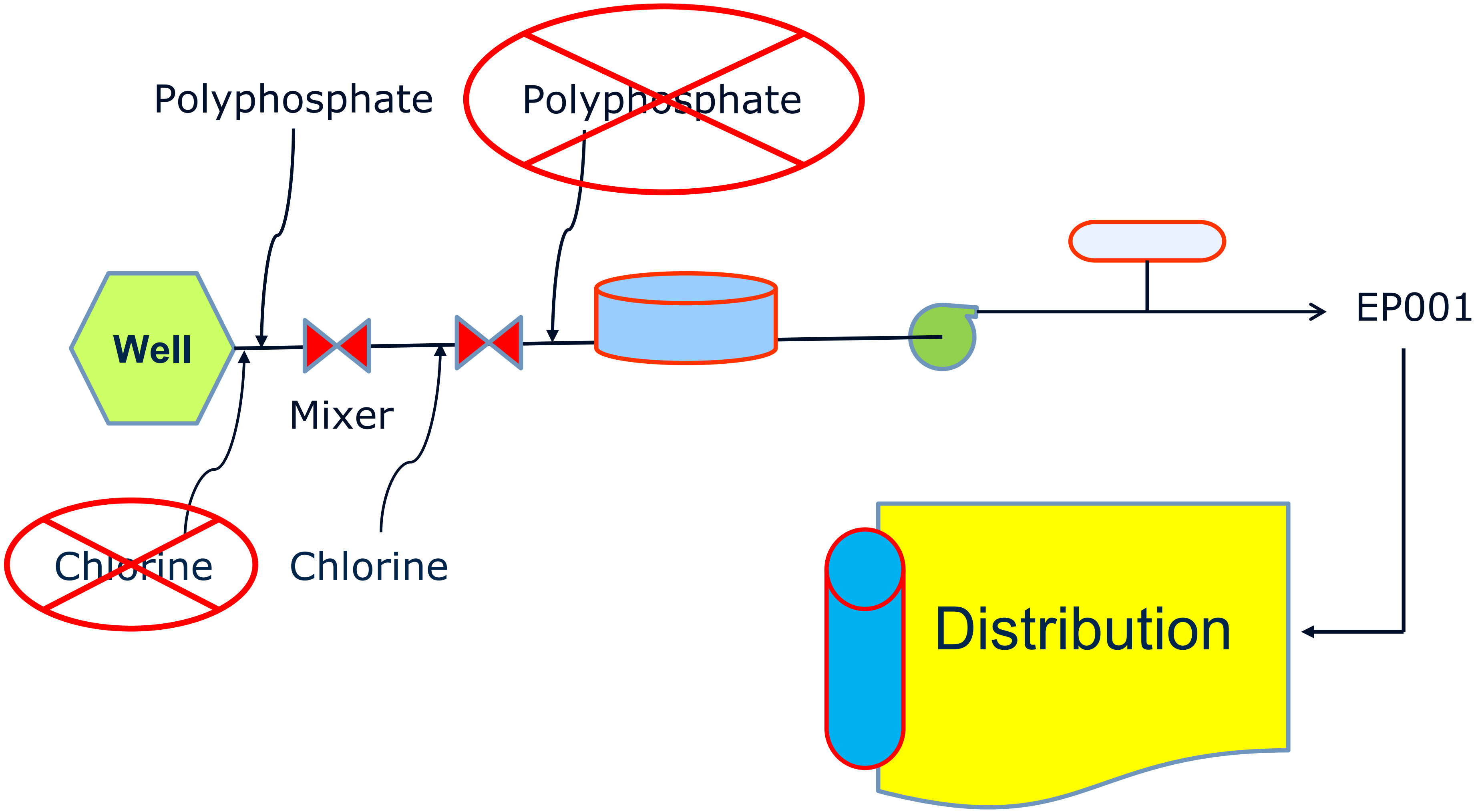
- pH
  - Each sequestering agent has an optimum pH range and it's highly recommended to follow it.

- Water age
  - Sequestering agents are usually reliable for approximately 3 to 5 days depending on temperature.

Sequestration: Chemical Effectiveness 3

- Hardness (Calcium Ca^{2+} and Magnesium Mg^{2+})
  - Moderate to high water hardness significantly limits the effectiveness of polyphosphates.
- Dosage control (normally 1-3 ppm) unless high hardness
- Concentration of iron and manganese (when combined concentrations are above 1 ppm, sequestering not usually effective).

Where to Feed Sequestering Agent?



Sequestration: Bottom Line

- Many complicating factors
- No guarantee of success
- It's popular because it's cheaper than removal
  - WHEN IT WORKS

- Removal is more reliable (Gold Standard)

Fe and Mn: Other Important Topics (But We Don't Have Time to Cover)

- Assessing treatment effectiveness
  - Special sampling techniques required to determine what fractions are soluble and insoluble.
  - Critical sampling points

- Troubleshooting

Questions?

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Join us at the Public Drinking Water (PDW) Conference on in August 2025!

- Email me to suggest potential topics.