



Permanganate Treatment of Oilfield Produced Water

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Produced Water Society Permian Basin

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Midland TX

Presentation Topics

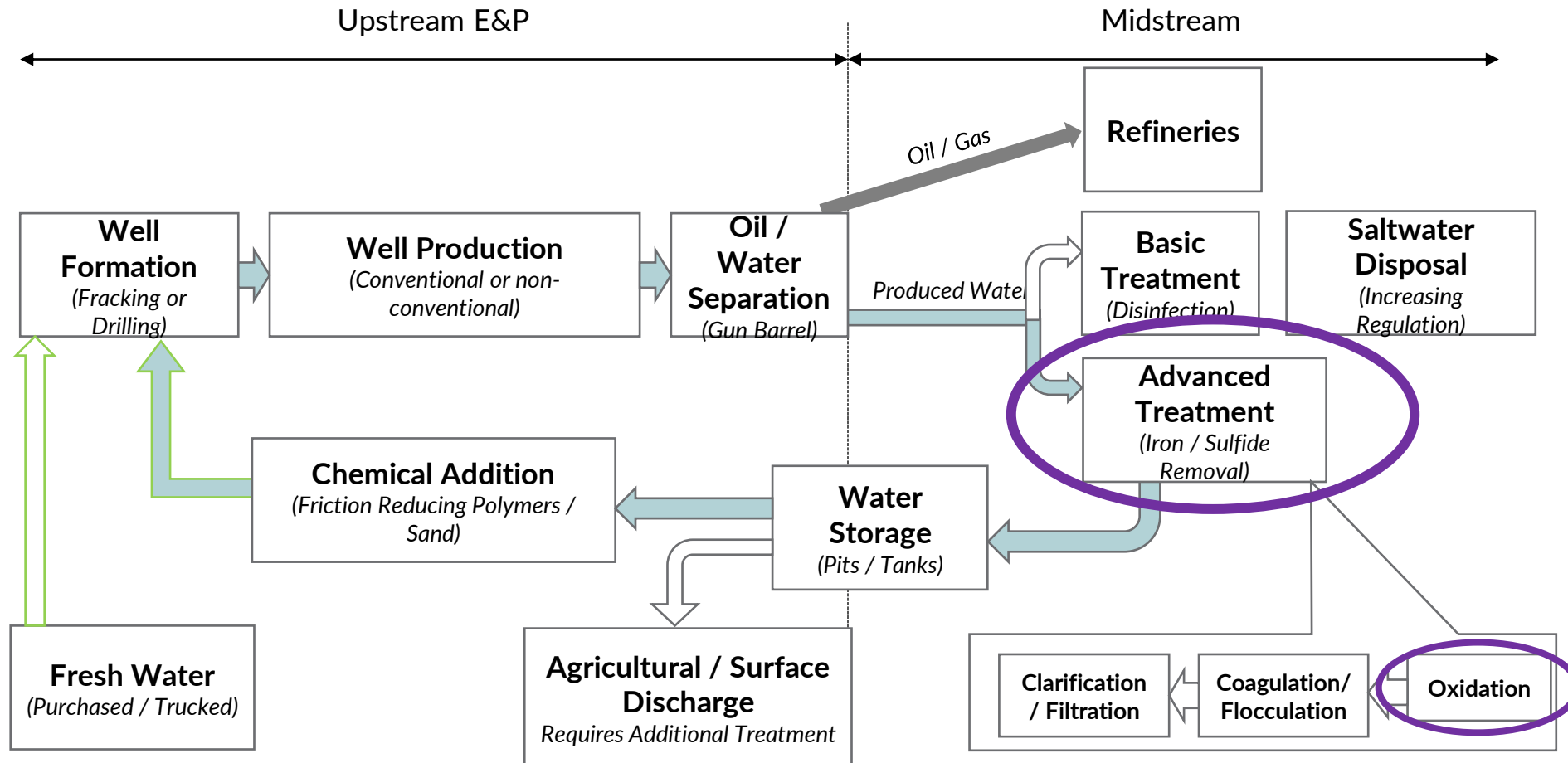
- Oxidation and PW treatment
- Properties and reactions of permanganate
- Common key performance indicators (KPIs)
- PW treatment goals:
 - Iron removal
 - Oxidation-Reduction Potential (ORP)
 - Water Clarification
- Comparison of permanganate and hydrogen peroxide
 - Field and laboratory data from Permian Basin

Key Messages

Permanganate Treatment of Produced Water

- Offers a rapid and effective pre-treatment alternative to oxidation with hydrogen peroxide
- Eliminates the need for addition of inorganic coagulant, allowing a simplified 2-product treatment program
- Reduces required doses of polymer/flocculant chemicals
- Can provided an optimized, cost-effective total treatment strategy

Produced Water Treatment Flowchart



Common Oxidizers



Chemical oxidizers are applied to:

- Oxidize iron and other metals, dissolved sulfides, and H₂S
- Increase oxidation-reduction potential (ORP)
- Assist solids removal and water clarification

Reference:
Produced Water Treatment Fundamentals, Module 2
Lisa Henthorne, President
Produced Water Society

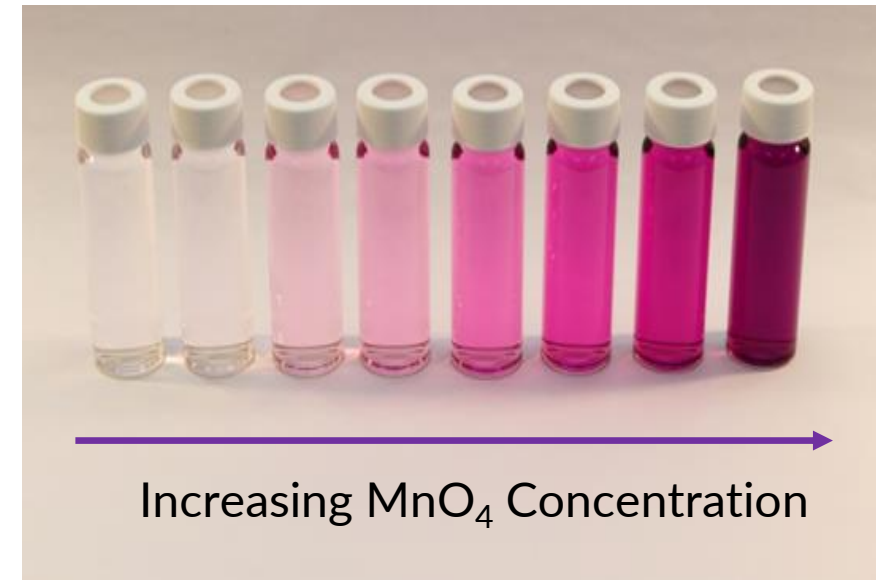
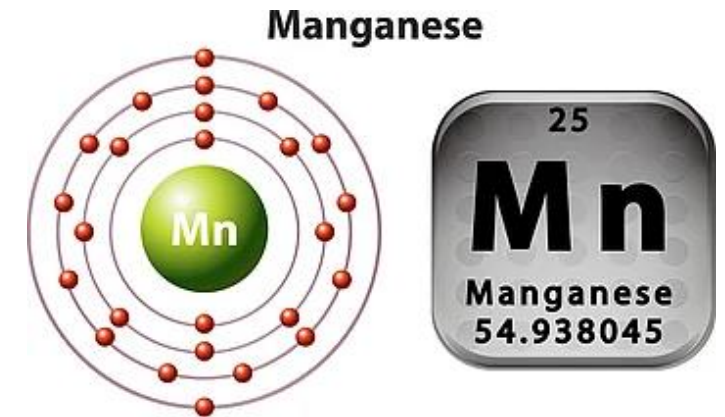
Oxidant: Pros and Cons

Purpose: precipitate metals and H₂S to enable efficient separation in downstream equipment.

Chemical	Pros	Cons
Potassium Permanganate	• Effective oxidant • Available as solid chemical – easier and less costly to transport • Relatively safe to use	• Somewhat more costly to procure than alternatives • Less recognized in the oil and gas industry • If overdosed, a pink color results – can be used as indicator
Chlorine Dioxide	• Strong oxidant • Effective treatment at low doses • Relatively inexpensive to procure • Well understood	• Use of explosive gas in chemical makeup process poses HSE risk • Requires complex onsite generation procedure • Challenging to store
Hydrogen Peroxide	• Strong oxidant • Effective treatment at low doses • Inexpensive • Safe to use compared to other oxidants	• Liquid form makes transportation more expensive option. • May require more storage volume than other oxidants • pH adjustment often required • Will readily consume light oils
Ozone	• Very strong oxidant with OH radical • Alkalinity reduces ozone decomposition • Insitu generation	• Limited residual properties • OH radical non-selective, assimilable organics may increase • May be more expensive than alternatives • Supply chain more limited

Permanganate Products

- Permanganate is a highly oxidized form of manganese
- CAIROX® potassium permanganate:
 - Crystalline solids, 97% or greater assay
- CARUSOL® liquid permanganate:
 - Concentrated liquids, 20% or 40% as pre-dissolved water solutions



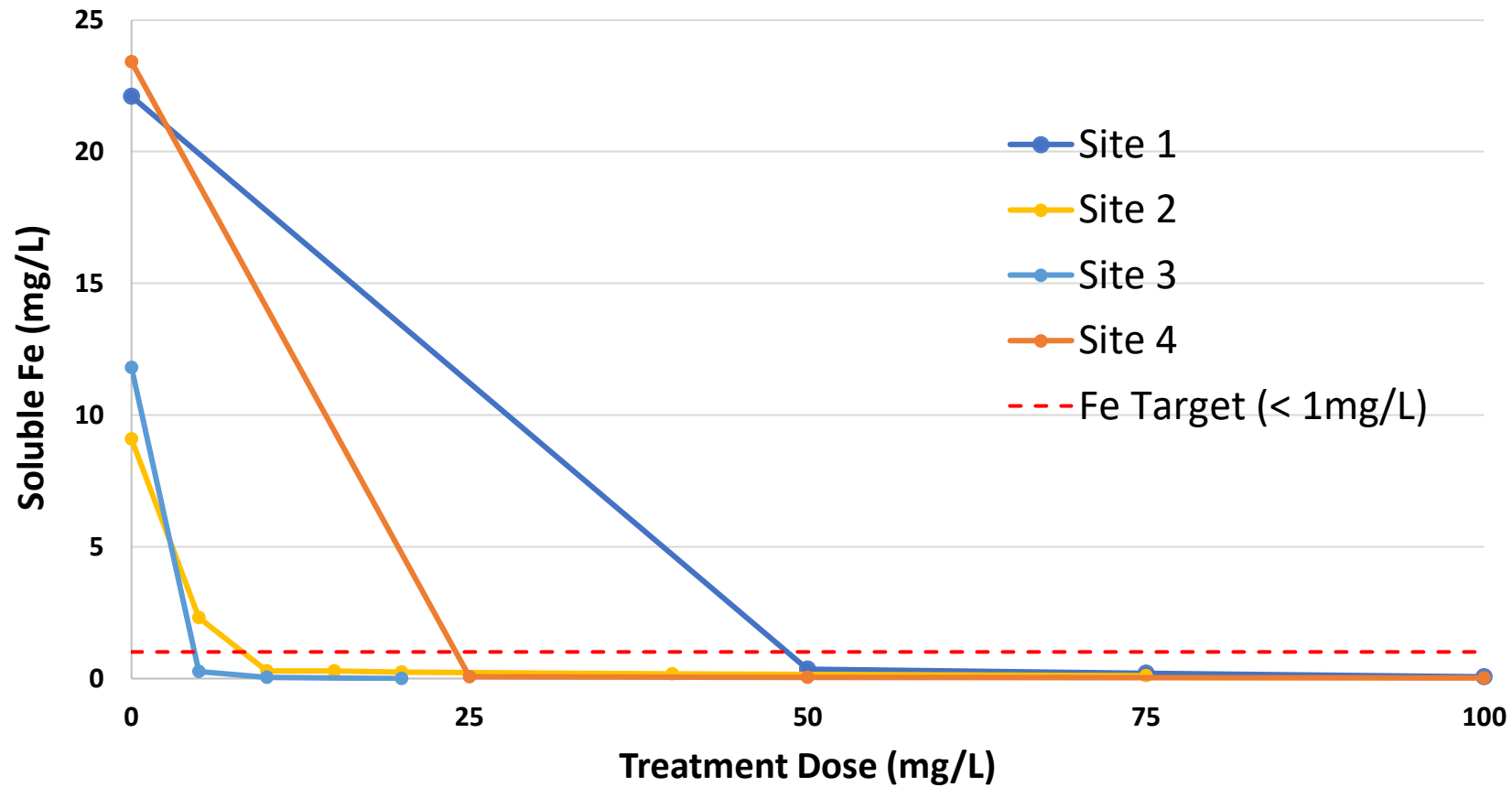
Permanganate Reactivity

Permanganate Reactivity with Selected Inorganic Compounds	
Very Fast (1 second)	Sulfites (IV), Sodium bisulfite
Fast (20 seconds)	Nitrite (III)
	Iron (II) $3 \text{Fe}^{+2} + \text{MnO}_4^- + 7 \text{H}_2\text{O} \longrightarrow 3 \text{Fe}(\text{OH})_3 + \text{MnO}_2 + 5 \text{H}^+$
	Arsenic (III) $3 \text{As}^{+3} + 2 \text{MnO}_4^- + 4 \text{H}_2\text{O} \longrightarrow 3 \text{As}^{+5} + 2 \text{MnO}_2 + 8 \text{OH}^-$
Medium Fast (5 minutes)	Sulfide $3 \text{H}_2\text{S} + 4 \text{MnO}_4^- \longrightarrow 2 \text{SO}_4^{-2} + \text{S} + 3 \text{H}_2\text{O} + 3 \text{MnO} + \text{MnO}_2$
	Manganese (II) $3 \text{Mn}^{+2} + 2 \text{MnO}_4^- + 2 \text{H}_2\text{O} \longrightarrow 5 \text{MnO}_2 + 4 \text{H}^+$

Treatment Goals and KPIs

KPI	Common Limits
Total Iron	< 2 mg/L
Oxidation-Reduction Potential (ORP)	> 300 mV
Turbidity	10 - 100 NTU
Sulfides (including H ₂ S)	0 ppm (for H ₂ S)
pH	6-8
Microbiology	< 100 ng/mL ATP

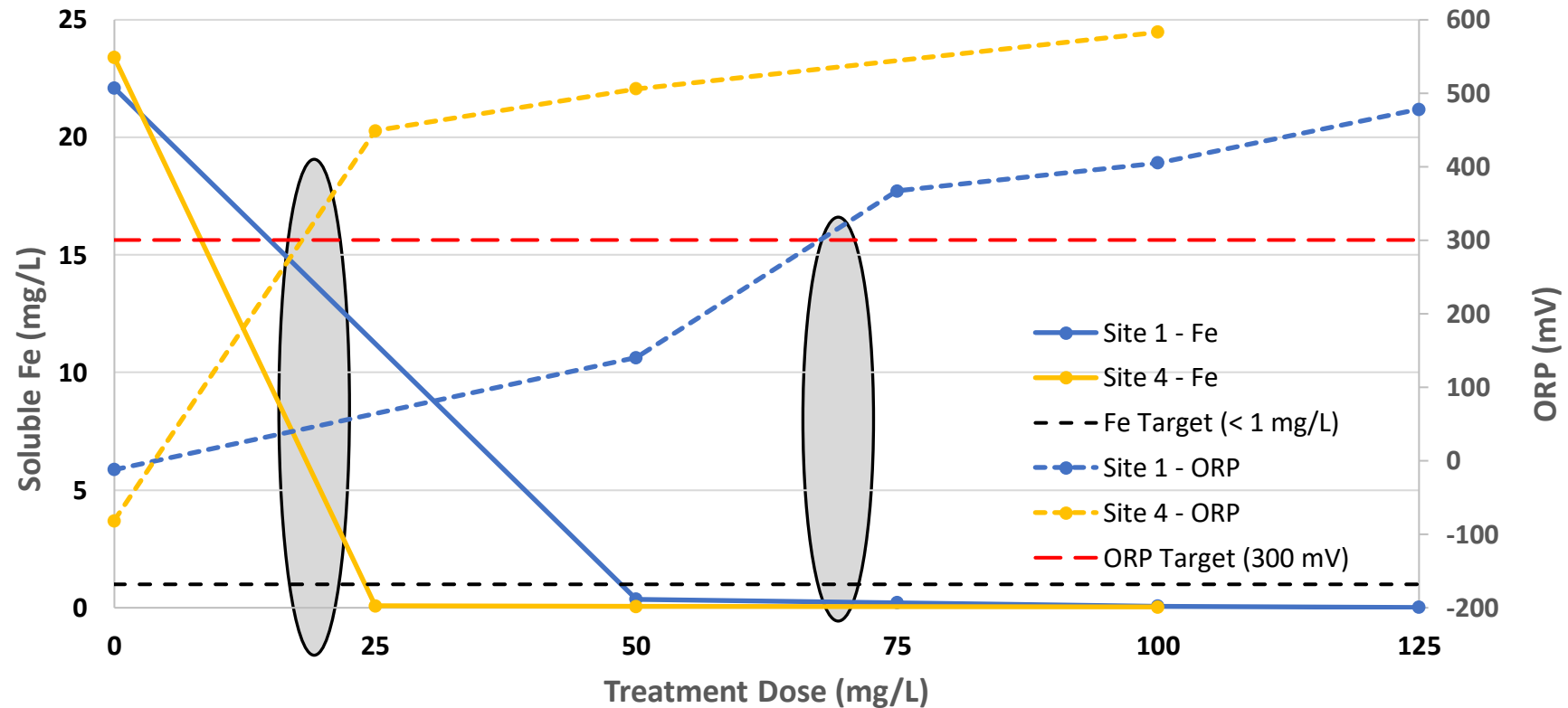
Iron Oxidation



- Rapid oxidation of soluble iron (Fe^{+2}) to insoluble iron (Fe^{+3})

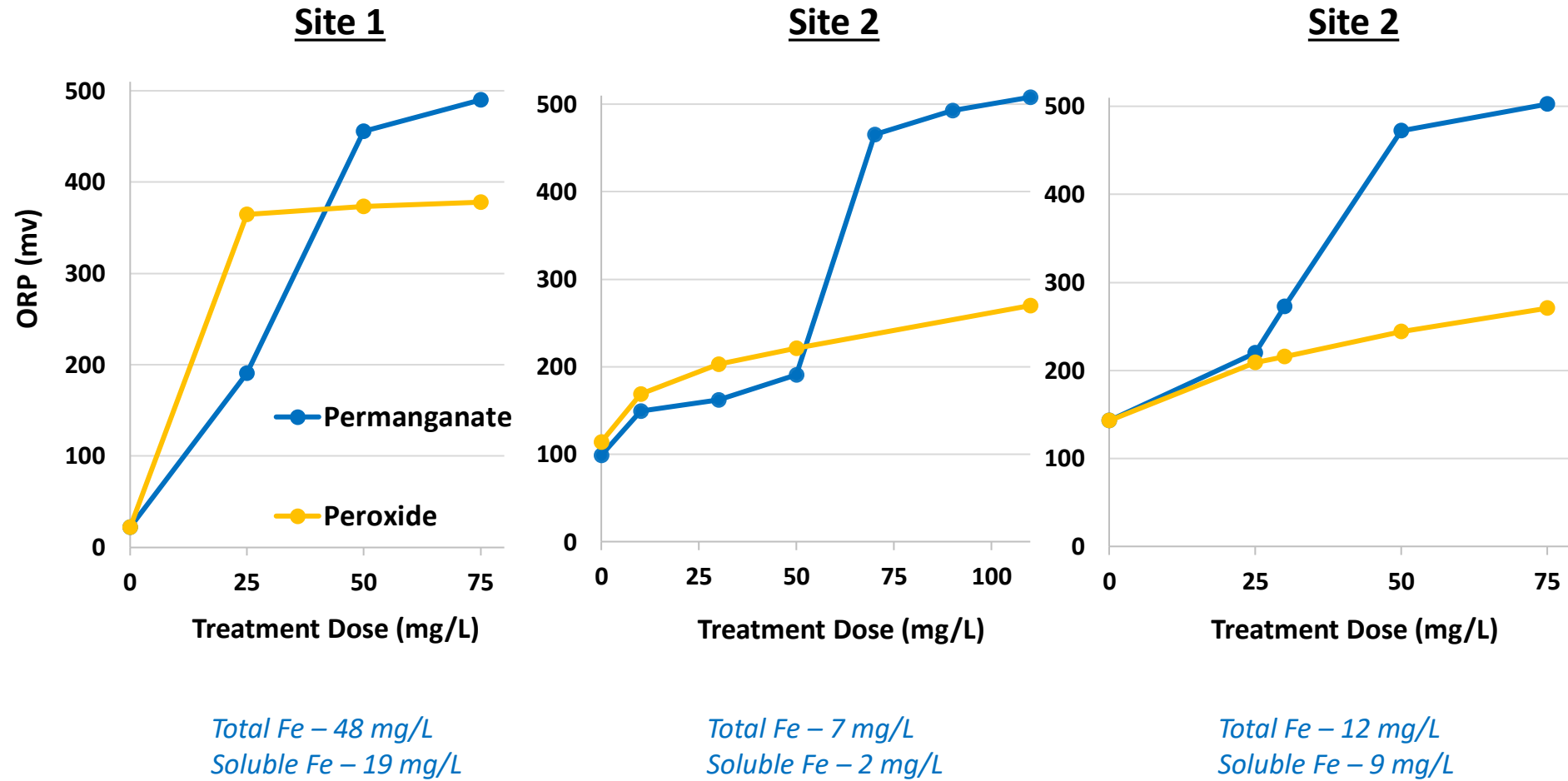
ORP v. Iron Removal

Site 1 and 4 – ORP v. Soluble Iron



- Rapid increase in ORP as soluble iron is oxidized and precipitated

ORP - MnO_4^- v. H_2O_2

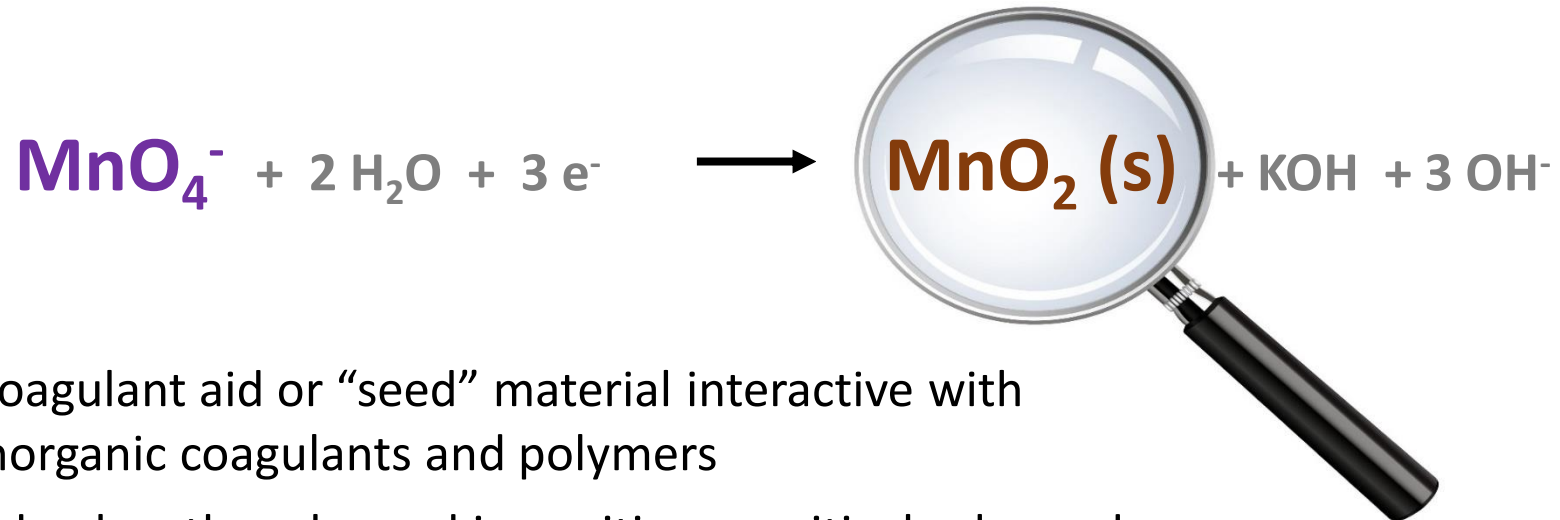


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Permanganate Reaction Product - MnO₂

Look closely at the manganese dioxide (MnO₂) precipitate that forms when permanganate reacts. It has some great benefits...



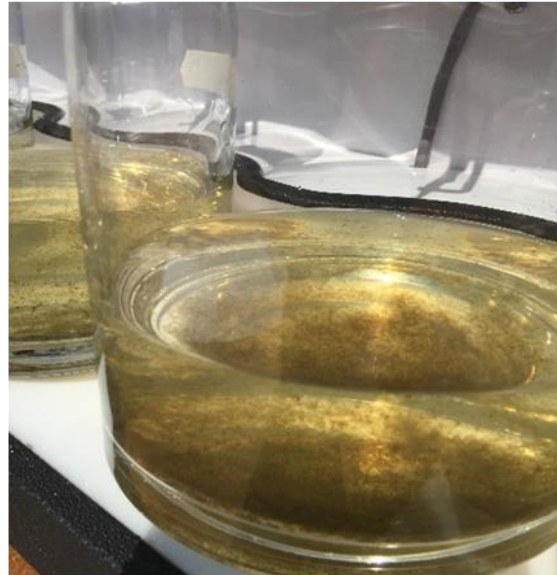
- Coagulant aid or “seed” material interactive with inorganic coagulants and polymers
- Adsorbs other charged impurities - positively charged ions, and some organics
- Provides an active surface for the oxidation of sulfides by dissolved oxygen

Manganese Dioxide - Clarification Aid



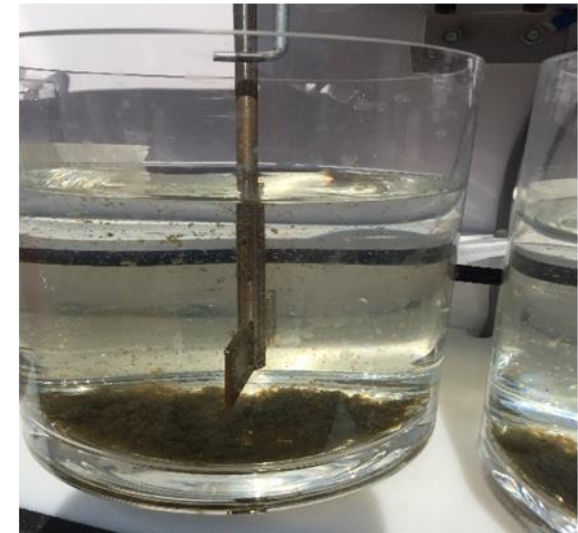
Produced Water Raw

PW + 25 ppm CAIROX®
Potassium Permanganate



Floc formation with MnO_2

PW + 25 ppm CAIROX®
+ Anionic Emulsion Polymer



No additional coagulant required

Manganese Oxide – Clarification Aid



Flowback Water + 80 ppm
CAIROX® Potassium Permanganate

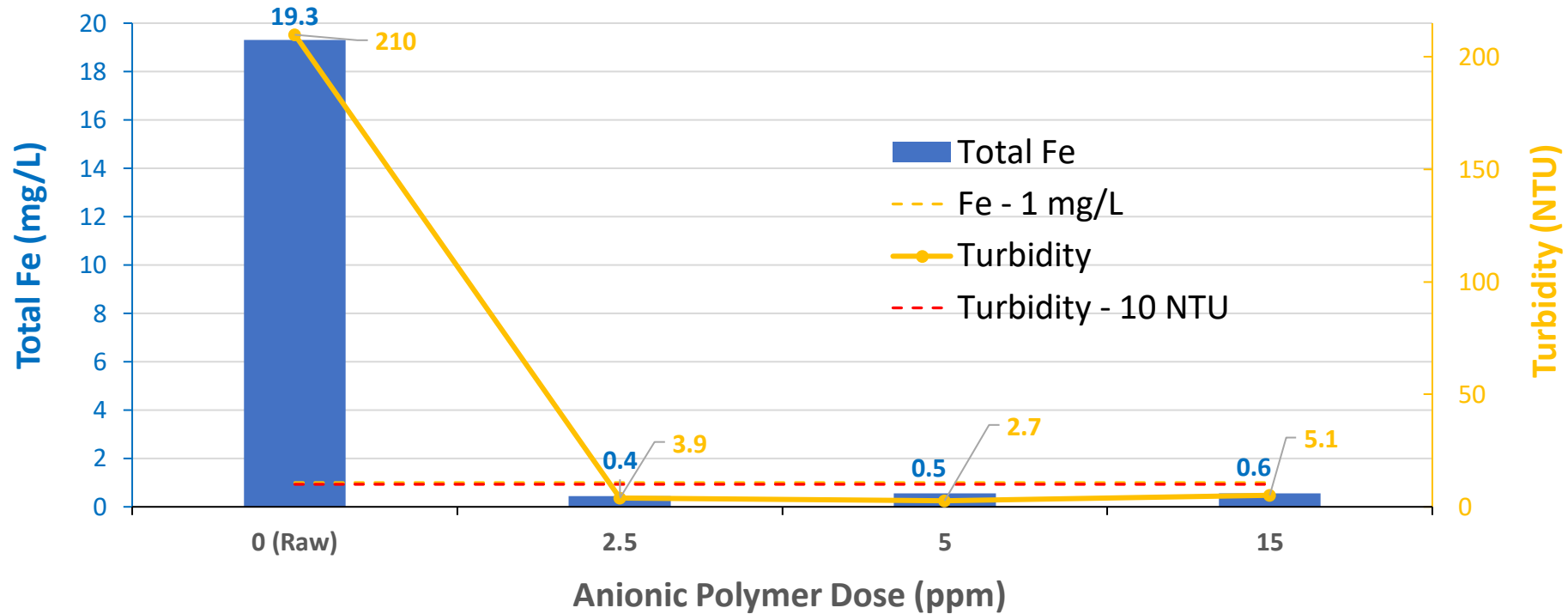
Flowback Water + 80 ppm CAIROX® +
Anionic Emulsion Polymer



No additional coagulant required

Coagulation of Solids with MnO₂

Site 4 – Total Iron and Turbidity Removal

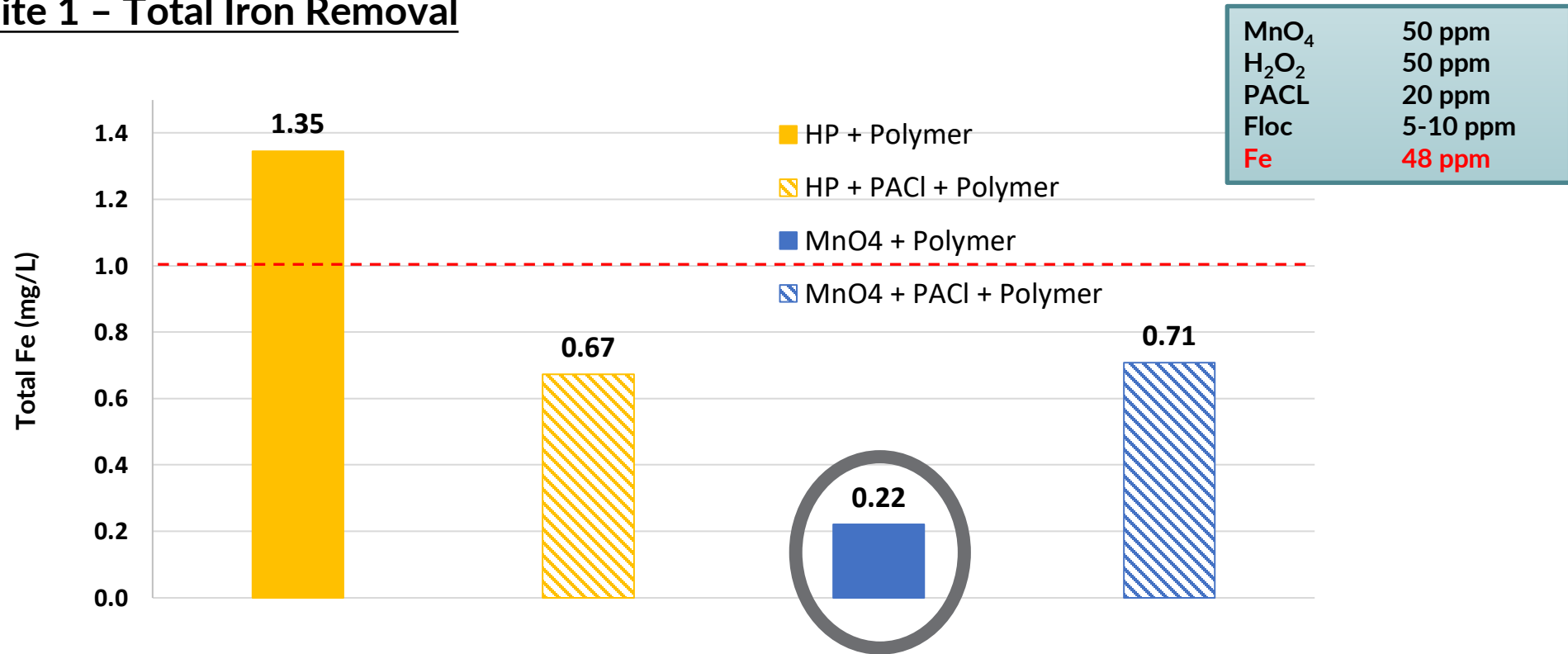


Target KPIs achieved with:

- Low MnO₄ dose (10 ppm), no coagulant, 2-product program, 8x lower polymer dose (v. peroxide)

Total Iron Removal – MnO_4 v. H_2O_2

Site 1 – Total Iron Removal

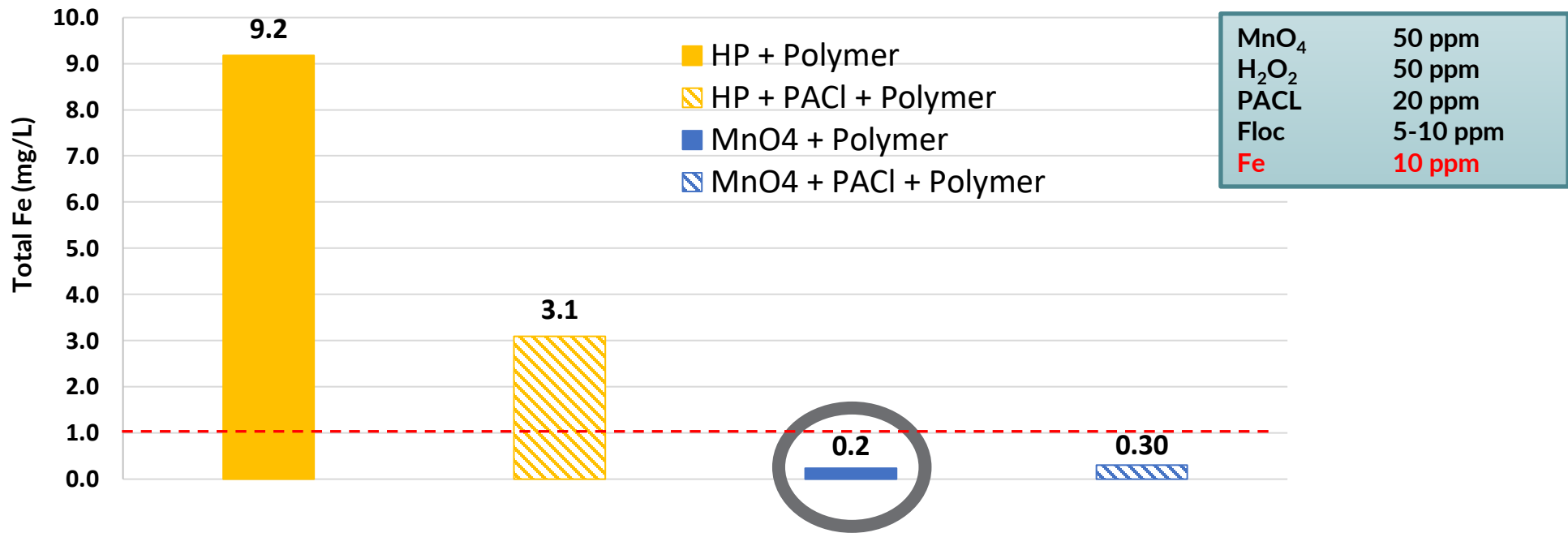


Permanganate achieved target iron levels (< 1 mg/L) with:

- 2-product program
- No inorganic coagulant
- 2x lower polymer dose

Total Iron Removal – MnO_4 v. H_2O_2

Site 2 – Total Iron Removal

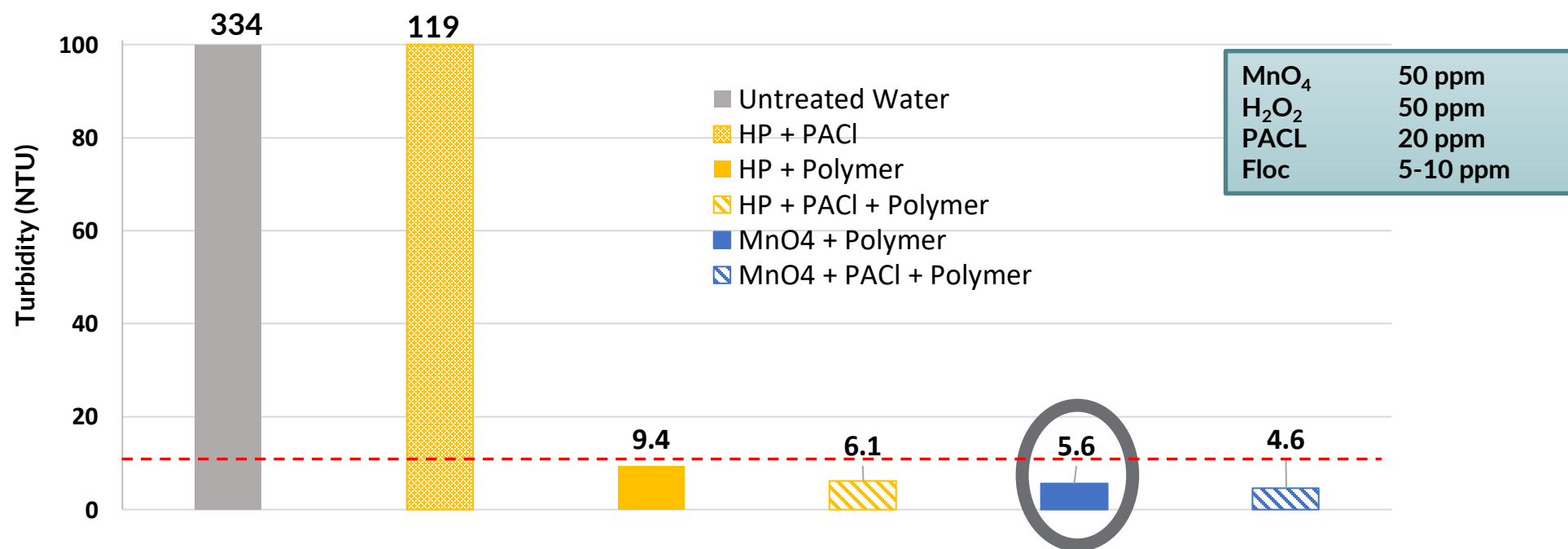


Permanganate achieved target iron levels (< 1 mg/L) with:

- 2-product program No inorganic coagulant 2x lower polymer dose

Clarification – MnO_4 v. H_2O_2

Site 1 – Clarification/Turbidity

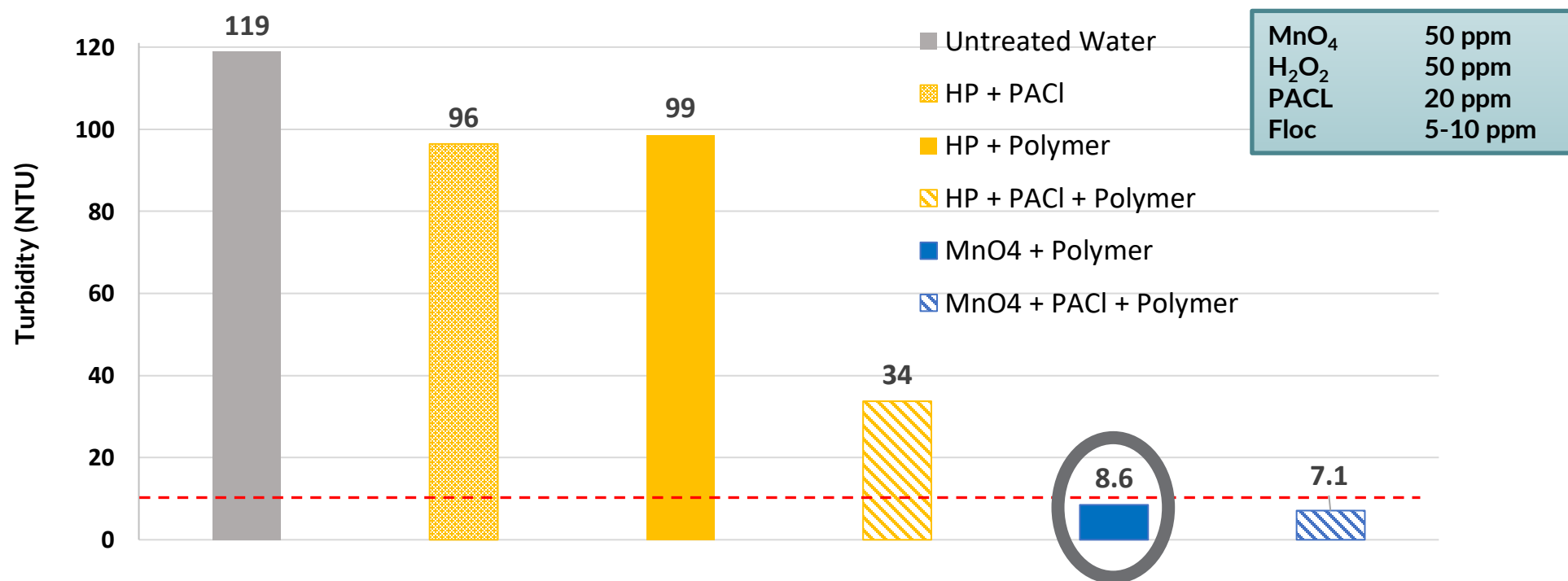


Permanganate achieved target turbidity (< 10 NTU) with:

- 2-product program No inorganic coagulant 2x lower polymer dose

Clarification – MnO_4 v. H_2O_2

Site 2 – Clarification/Turbidity



Permanganate achieved target turbidity (< 10 NTU) with:

- 2-product program
- No inorganic coagulant
- 2x lower polymer dose

Summary

Permanganate Treatment of Produced Water:

- Offers a rapid and effective pre-treatment alternative to oxidation with hydrogen peroxide
- Provides an excellent in-situ coagulation aid for solids removal and clarification
- Eliminates the need for addition of inorganic coagulant - simplified 2-product treatment program
- Reduces required doses of polymer/flocculant chemicals
- May provide more consistent treatment efficiency and performance for variable incoming water composition

Contact Us



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