ARCADIS Design & Consultancy for natural and built assets

PRECIPITATING SUCCESS; A SOLUTION TO HEAVY METALS IN GROUNDWATER

April 12, 2018

Agenda

- Conceptual Site Model (CSM) of subject site
- Overview of *in situ* chemically induced sulfide precipitation
- Overview of implementation and design rationale
- Review of performance

Site Layout

OU1 Ponds

OU2 Groundwater (GW)

Historical Operations

Current Operations

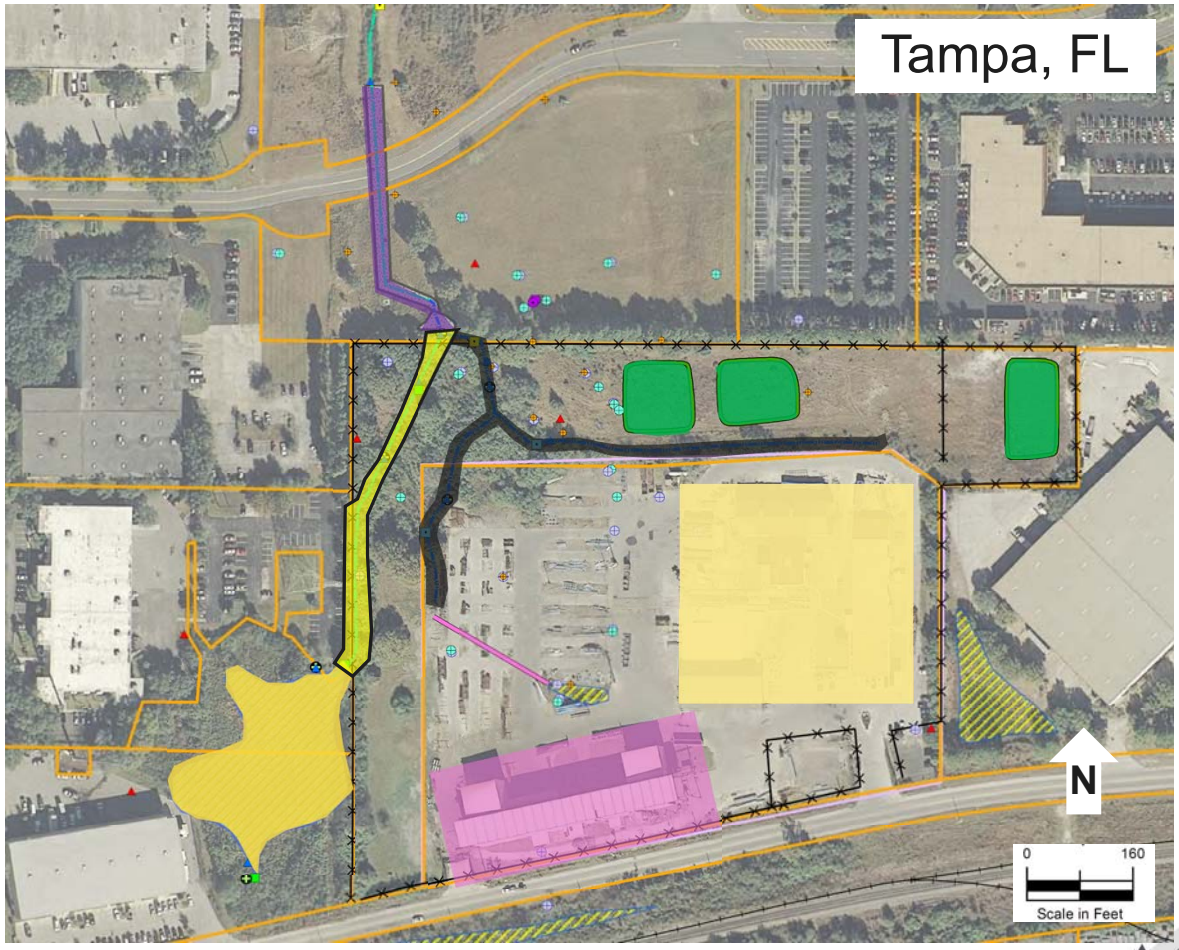
OU3 Surface Water (SW)

North Wetland

Unnamed Creek

Drainage Swale

Surface Water Conveyance

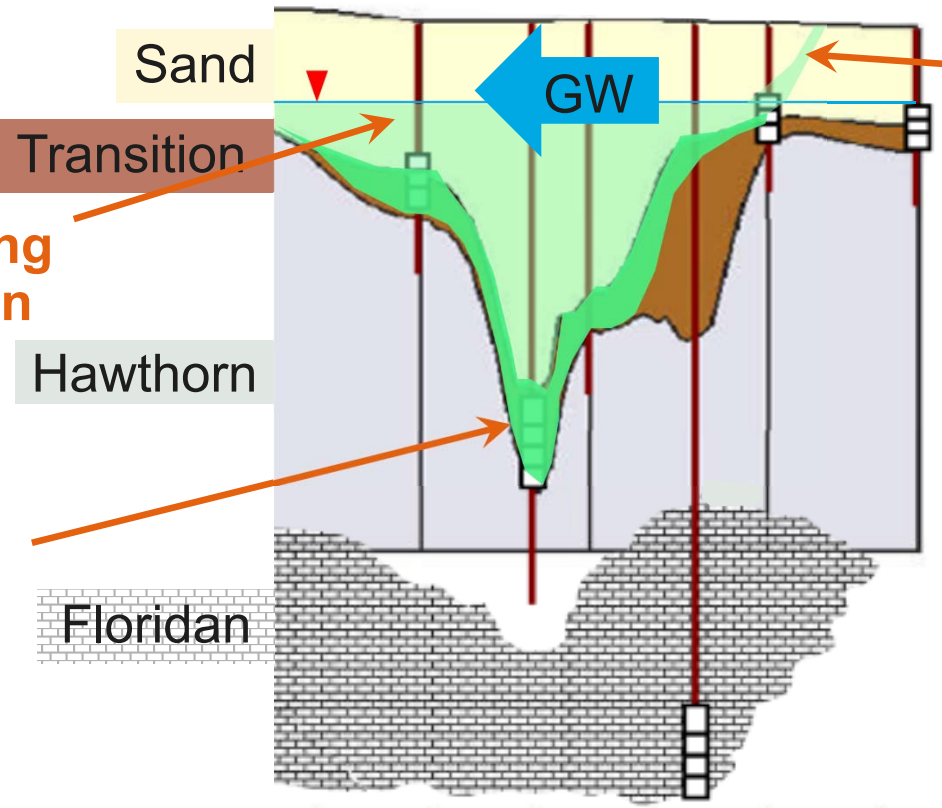


Conceptual Site Model: Tampa, FL

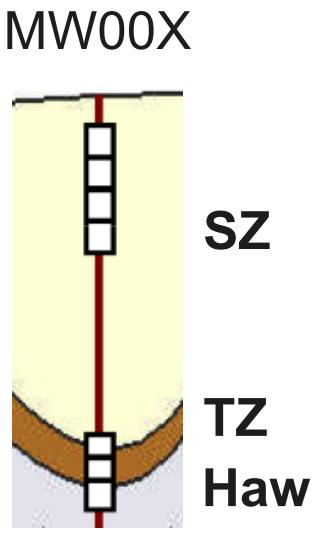
Acidic, high concentration metals release (surface and subsurface)

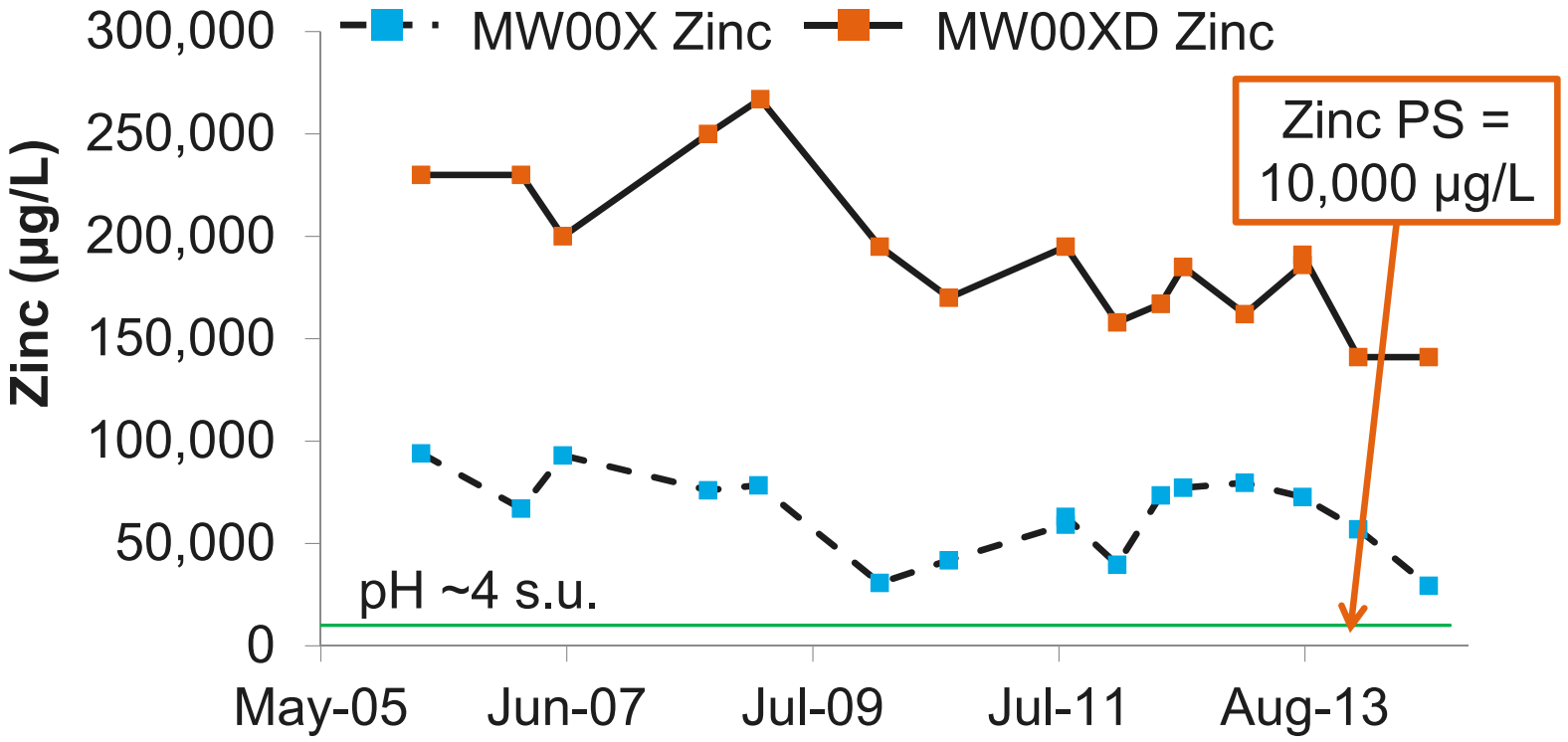
Sand Zone (SZ) impacts less significant; attenuating via dilution/advection

Acidic, high metals concentration groundwater (GW) settling in Transition Zone (TZ)



Conceptual Site Model: Tampa, FL (example)





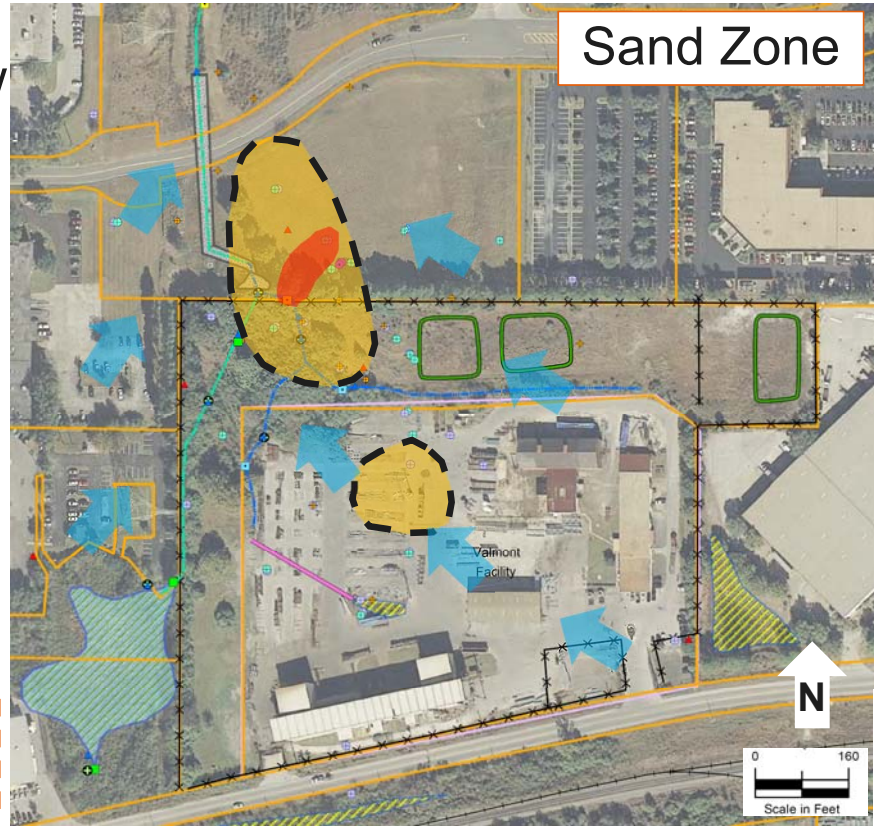
OU2 Groundwater: Nature and Extent

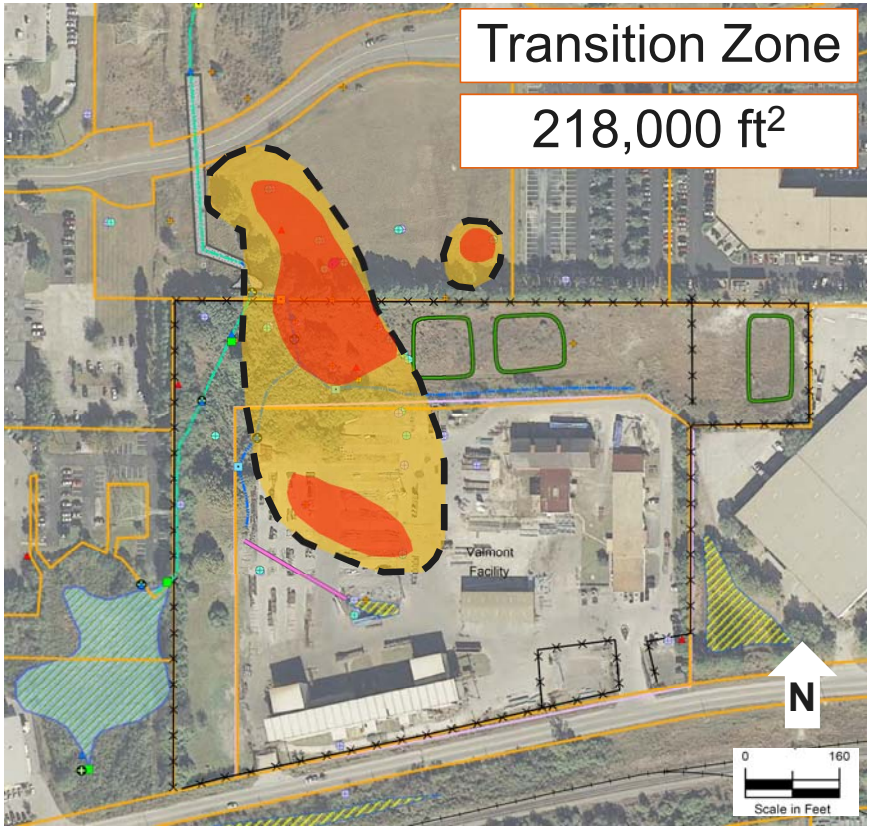
GW Flow Direction

Exceeding PS

Metals listed in the ROD:

As	10 µg/L
Cd	5 µg/L
Cr_{tot}	100 µg/L
Pb	15 µg/L
Ni	100 µg/L
Zn	10,000 µg/L

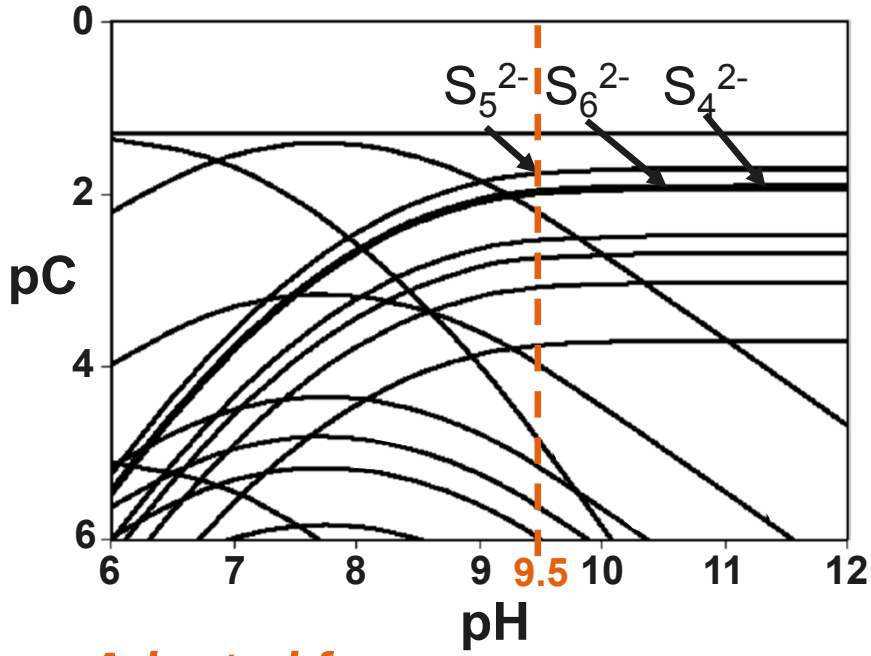




2012, 2015 Analytical Results (**Zinc**)

In Situ Chemically Induced Sulfide Precipitation

- Injection of sulfide into an aquifer to facilitate the formation of comparatively less soluble metal precipitates (versus carbonates and hydroxides).
- Polysulfide is a readily available form of sulfide (S_n^{2-}) (i.e., calcium, potassium, sodium)
- Predicted distribution suggests **n** = 4 to 6 (for pH > 9.5; typical of polysulfide)
- Acidity scavenging and potential formation of hydrogen sulfide (H_2S); Review inert materials (e.g., arsenic, selenium)



Adapted from Kamyshny et al. 2004

In Situ Chemically Induced Sulfide Precipitation

Metal	K_{sp} of MeS	Difference Factor
Cadmium (Cd^{2+})	3.6×10^{-29}	3×10^{8}
Chromium (Cr_{tot})	None	--
Iron (Fe^{2+})	1.1×10^{-19}	5×10^{3}
Copper (Cu^{2+})	8.5×10^{-45}	1×10^{11}
Lead (Pb^{2+})	3.4×10^{-28}	3×10^{8}
Nickel (Ni^{2+})	1.4×10^{-24}	1×10^{7}
Zinc (Zn^{2+})	1.2×10^{-23}	3×10^{8}

Conner 1990

$$DF = \frac{K_{sp} of\ Me(OH)_x}{K_{sp}\ of\ MeS}$$

DF = Difference Factor

K_{sp} = Solubility product

$Me(OH)_x$ = Metal hydroxide

MeS = Metal sulfide

In Situ Chemically Induced Sulfide Precipitation

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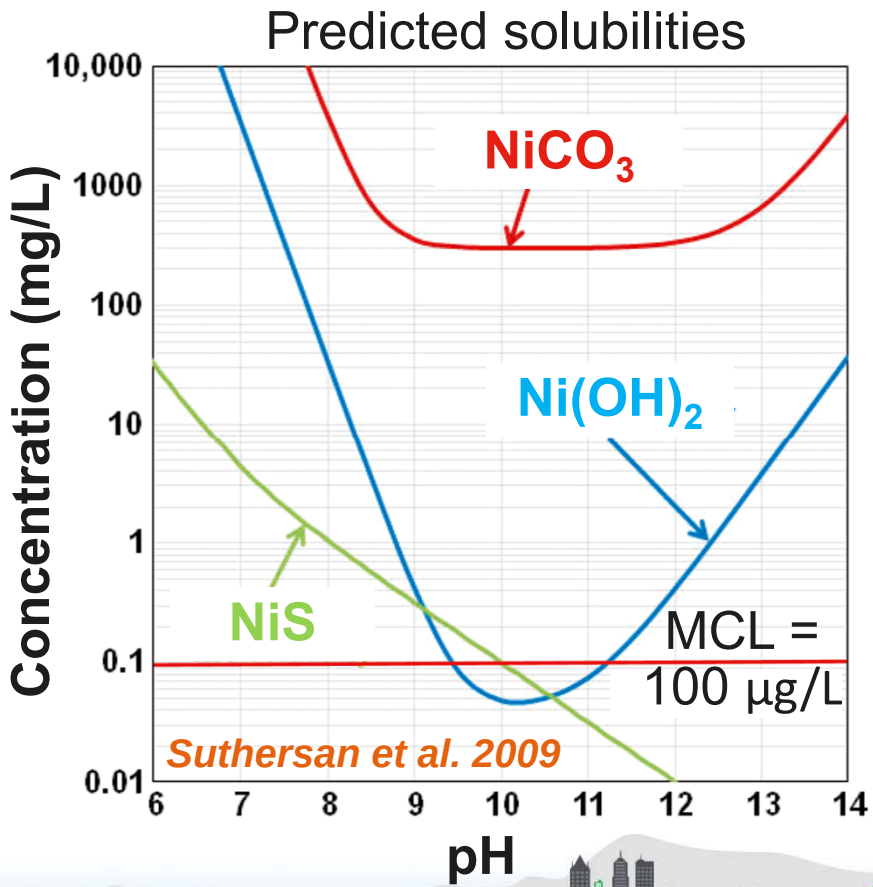
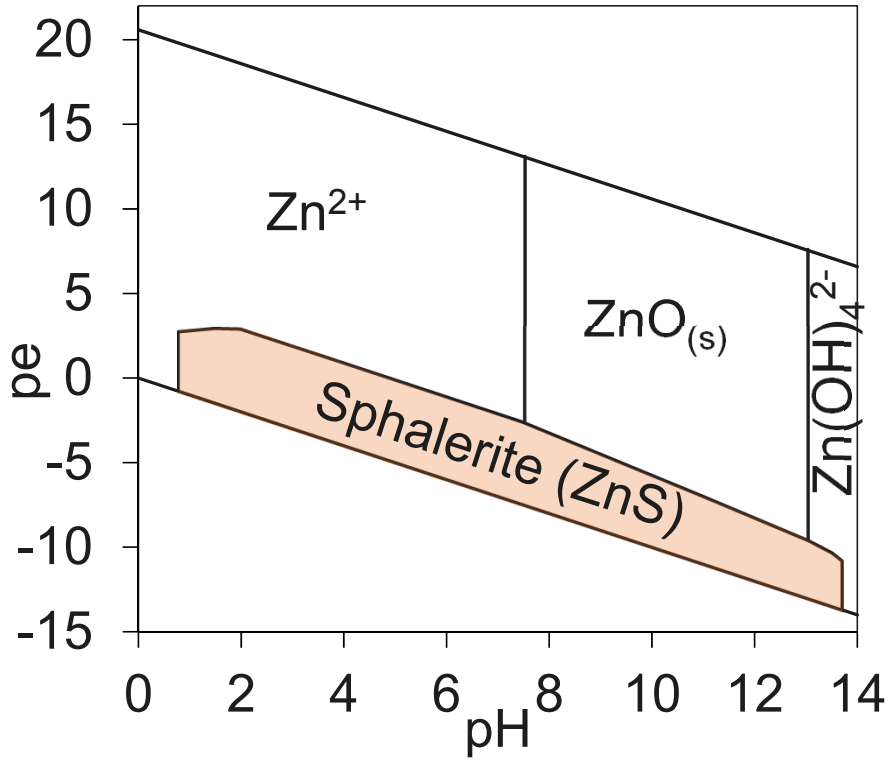
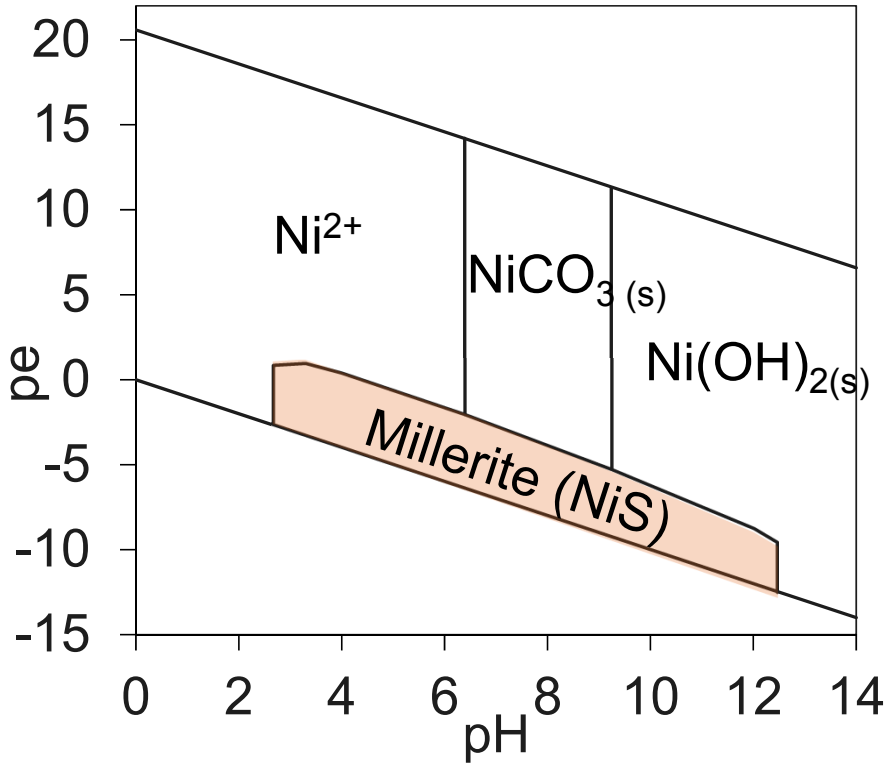


In Situ Chemically Induced Sulfide Precipitation



PHREEQC (wateq database)



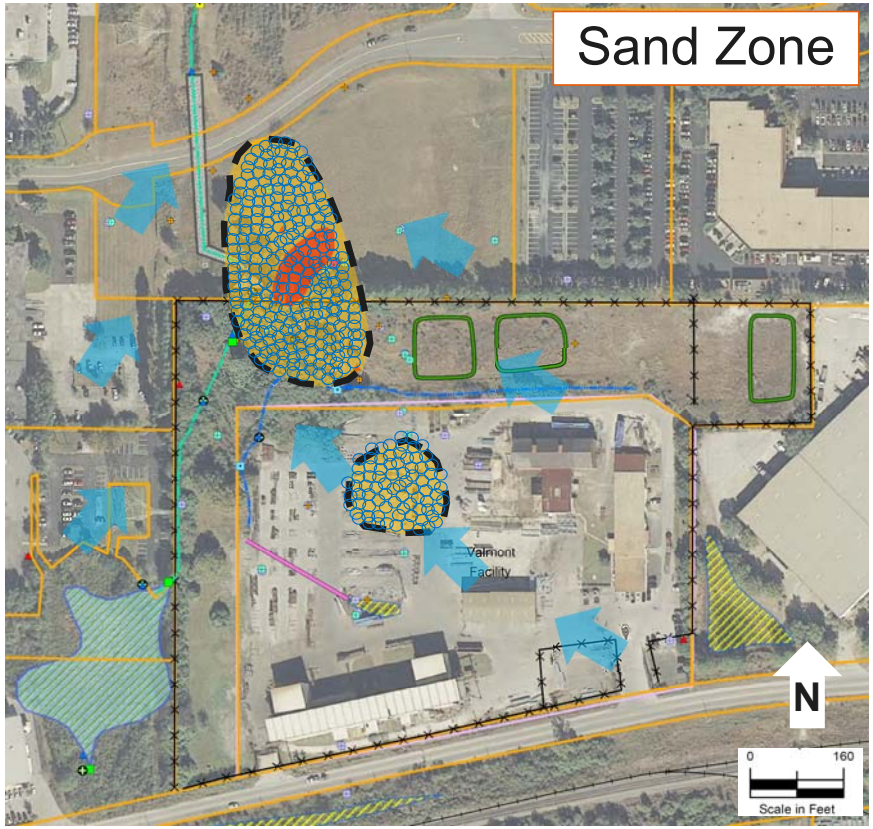
PHREEQC (wateq database)

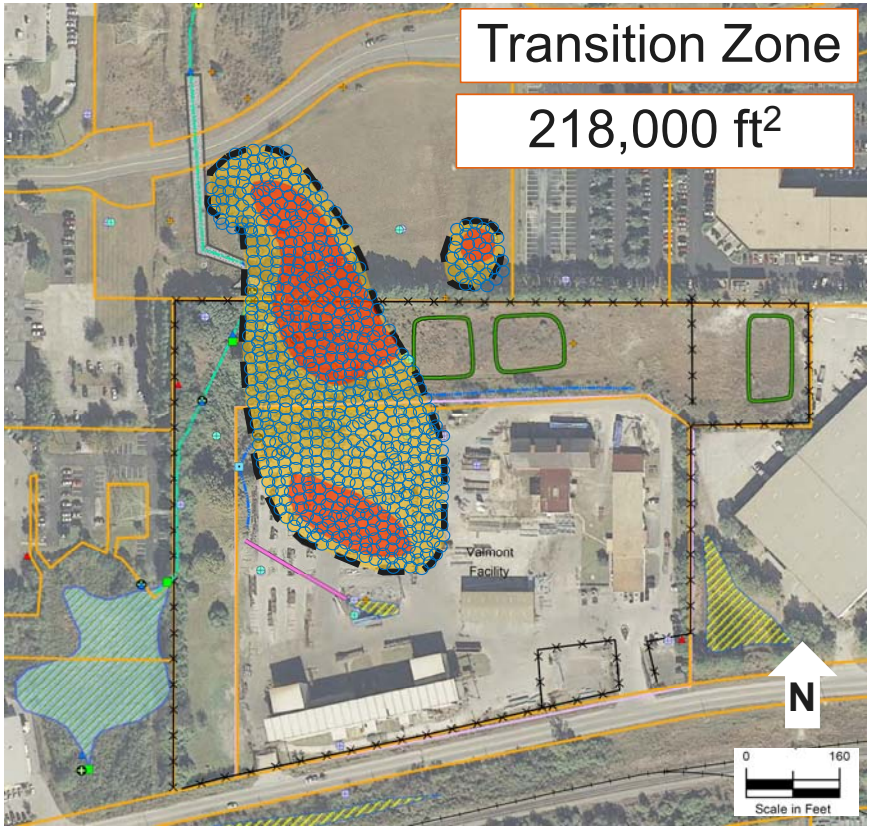
Design Overview

GW Flow Direction

Exceeding PS

10 ft Radius of Influence





2012, 2015 Analytical Results (**Zinc**)

Design Overview (cont.)

Metric	May 2016 to May 2017
Points Completed:	787 points
Na_2S_x Injected (35.5% assay):	69,080 gal
NaOH Injected (50% assay):	5,520 gal
Water Injected:	1,651,340 gal
Total Volume Injected:	1,705,980 gal
Na_2S_x Injection Concentration (as sulfide):	1.93% by wt
NaOH Injection Concentration:	0.24% by wt

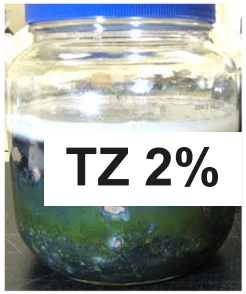
Design Overview (cont.)

20 to 30 simultaneous DPT injection locations through an active facility

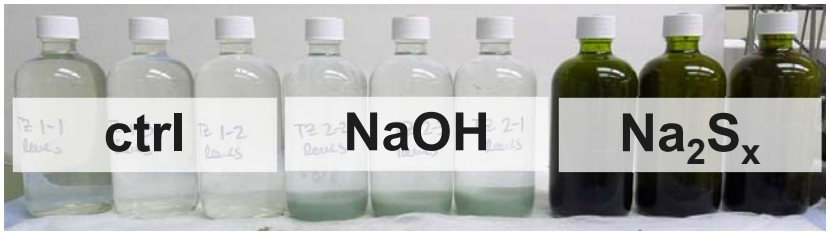
One of two 16-leg injection manifolds

Na_2S_x/NaOH shipments via tanker truck; Bulk onsite storage in secondary containment

Design Rationale: Treatability Testing



SZ and TZ 2-L jars dosed with 2% wt Na_2S_x

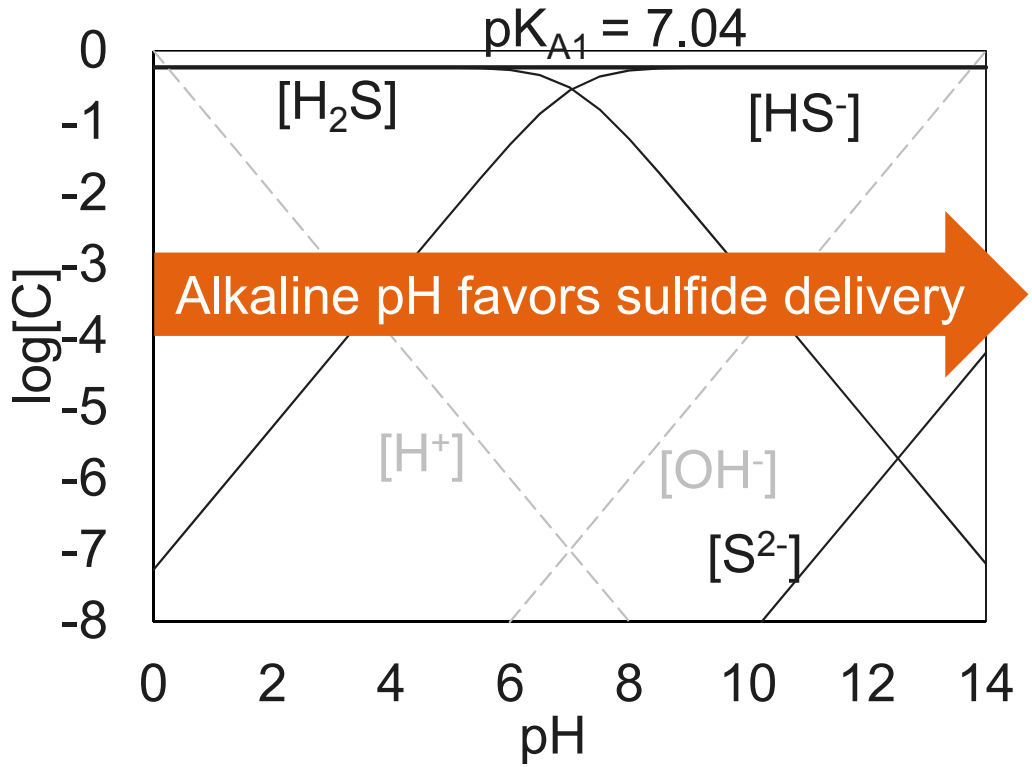


SZ and TZ jars with 0.25% wt NaOH and 2% wt Na_2S_x

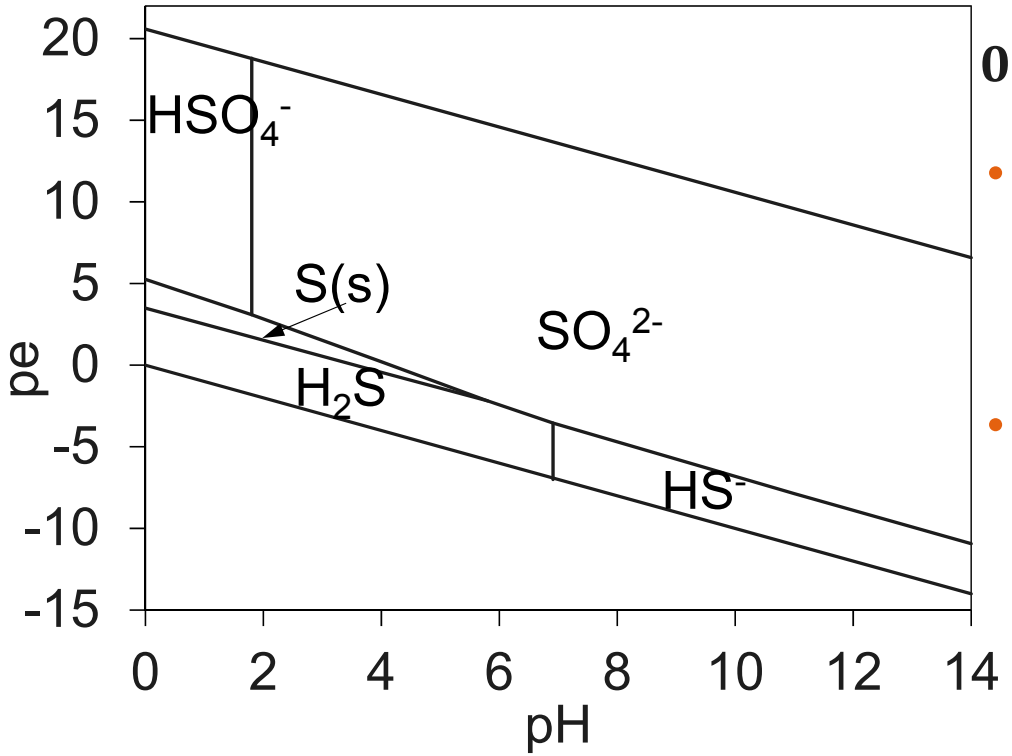
- ✓ Confirmed efficacy for metals removal
- ? Highlight challenges associated with Ni removal
- ✓ Confirmed importance of co-precipitation for Ni removal
- ✓ Confirmed 2% by weight Na_2S_x and 0.25 NaOH combined dose

Design Rationale: Polysulfide Management

- Sulfide can scavenge acidity; forms hydrogen sulfide (H_2S) (flammable, asphyxiant, toxic)
- Solubility of H_2S in water ~ 4 to 5 grams per liter (g/L)
- Injection concentration: ~20 g/L as sulfide; H_2S represents potential inefficient reactive sulfide delivery
- NaOH can be a sacrificial acidity scavenger; optimize polysulfide distribution



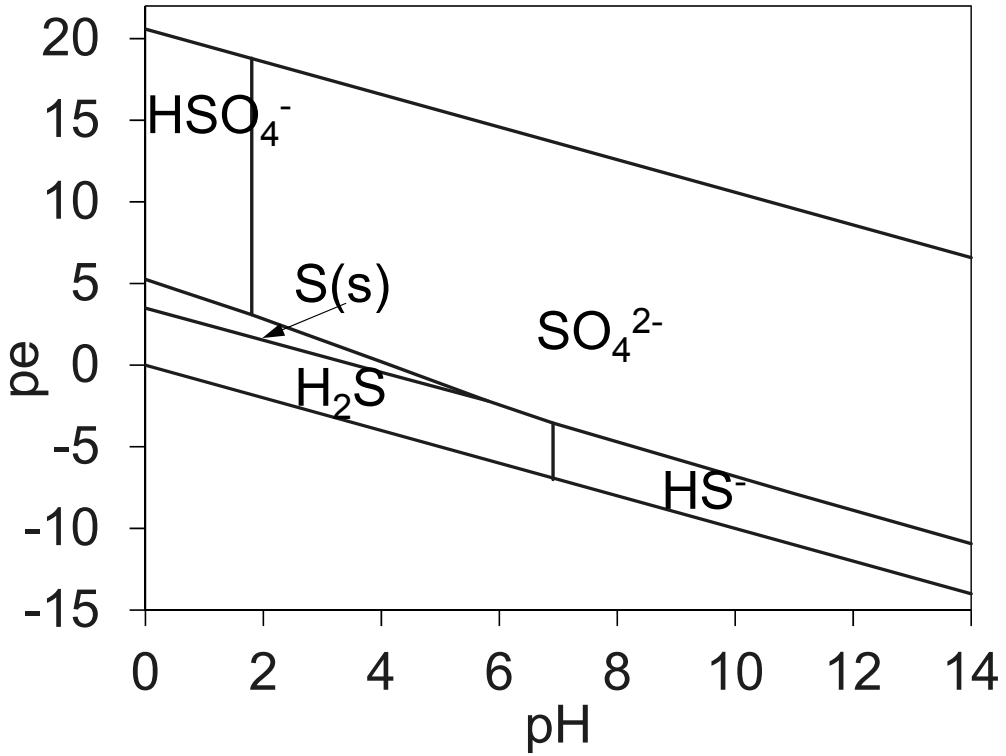
Design Rationale: Reagent Mixing



$$0.5O_2 + Na_2S_5 + 2H^+ \rightarrow 2Na^+ + H_2O + 5S_{(s)}$$

- 2,400 gallons of 2% by wt as sulfide per point results in ~1 kg $S_{(S)}$ lost/generated per point with batch/in-line mixing.
- Batch mixing and in-line dilution will result in formation of elemental sulfur ($S_{(s)}$) precipitate

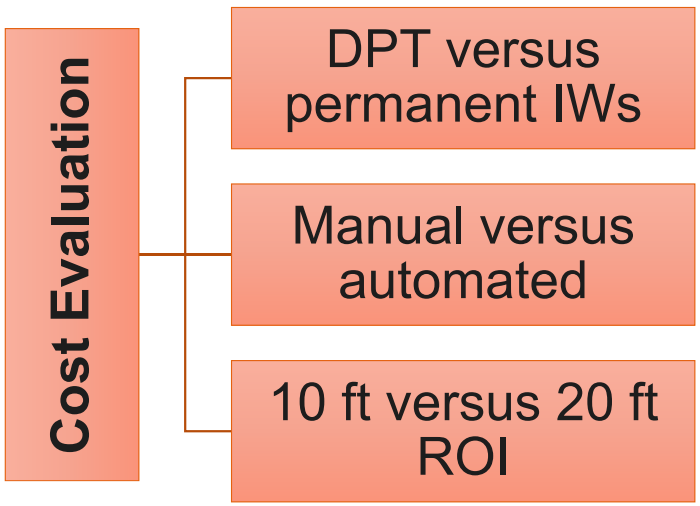
Design Rationale: Reagent Mixing (cont.)

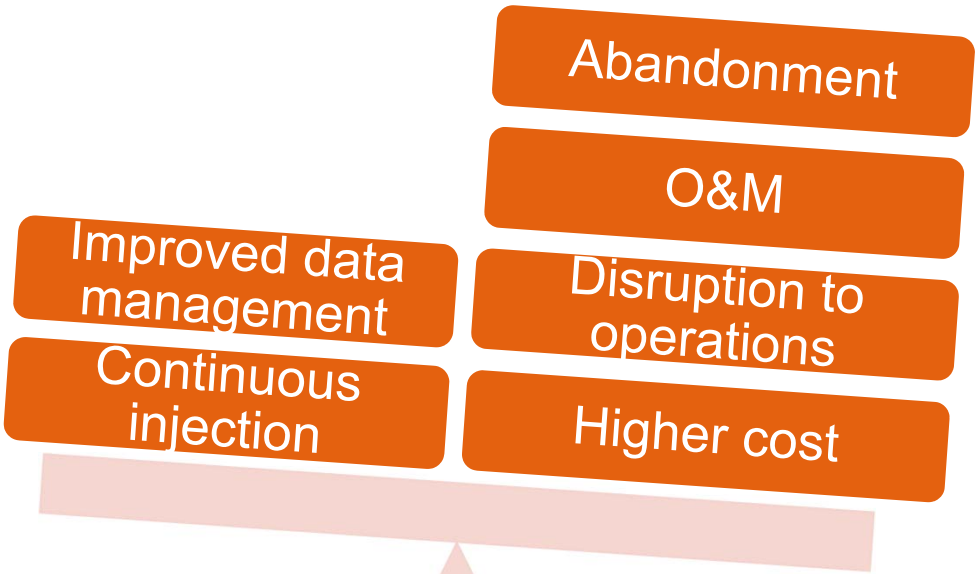


Full-strength pulsed dosing of polysulfide and alkaline water optimizes sulfide distribution and conveyance.

Design Rationale: Temporary DPT Points

Benefits and Weakness of Automated System with permanent injections wells (IWs)



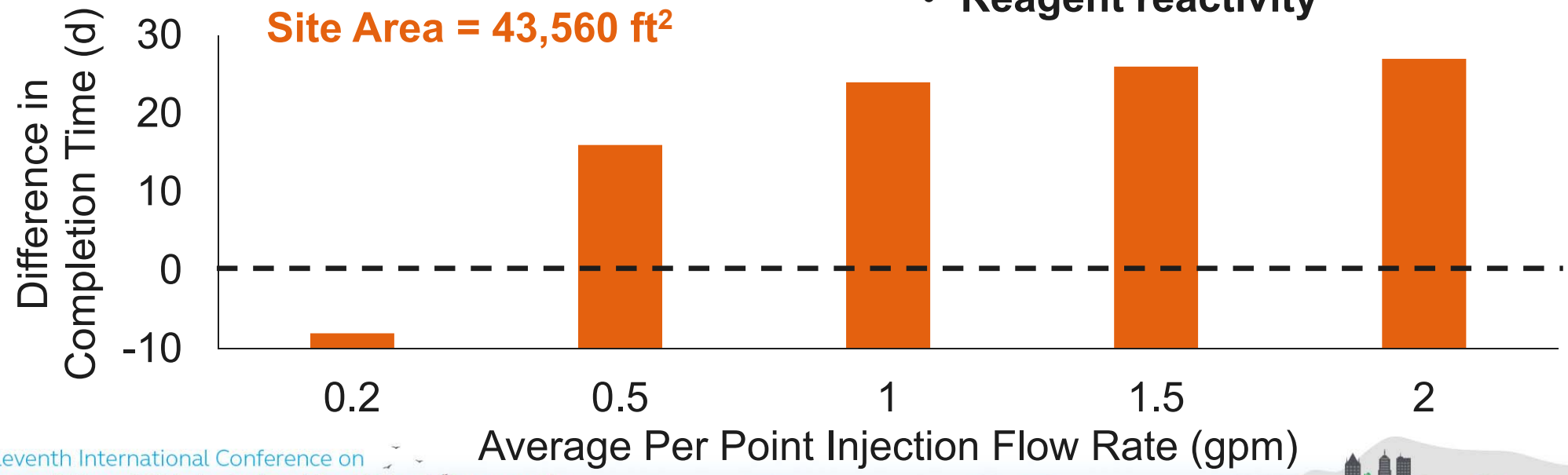


Design Rationale: 10 ft ROI versus 20 ft ROI

Low injection flow rates support greater injection point density (cost and distribution).

Efficacy of reagent distribution influences ROI selection

- **Injection hydraulics AND**
- **Reagent reactivity**



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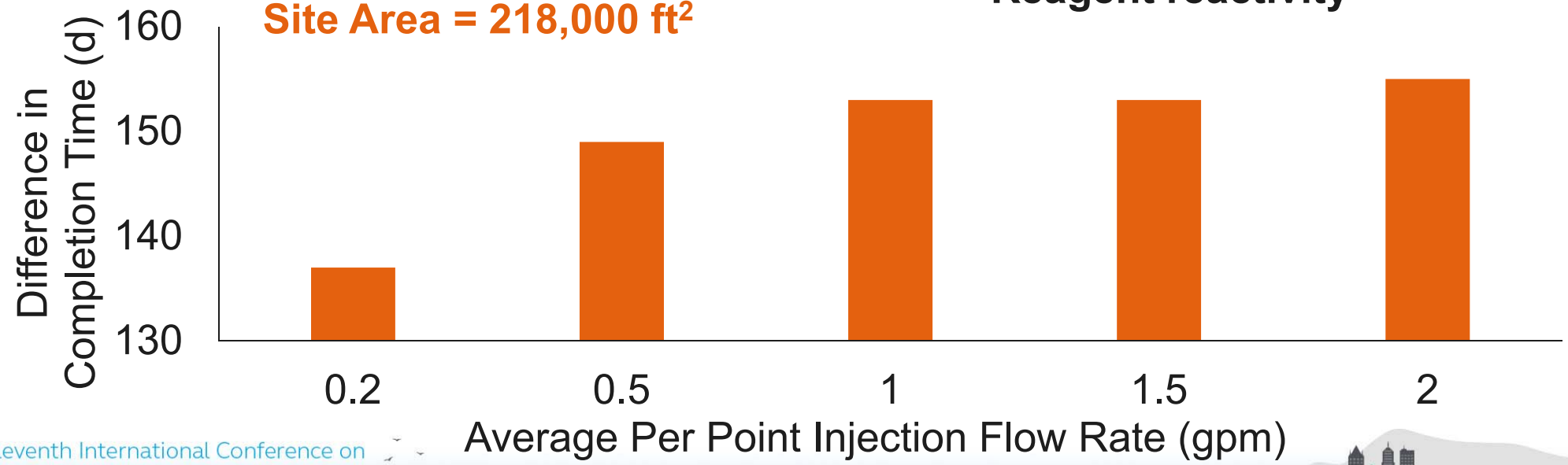
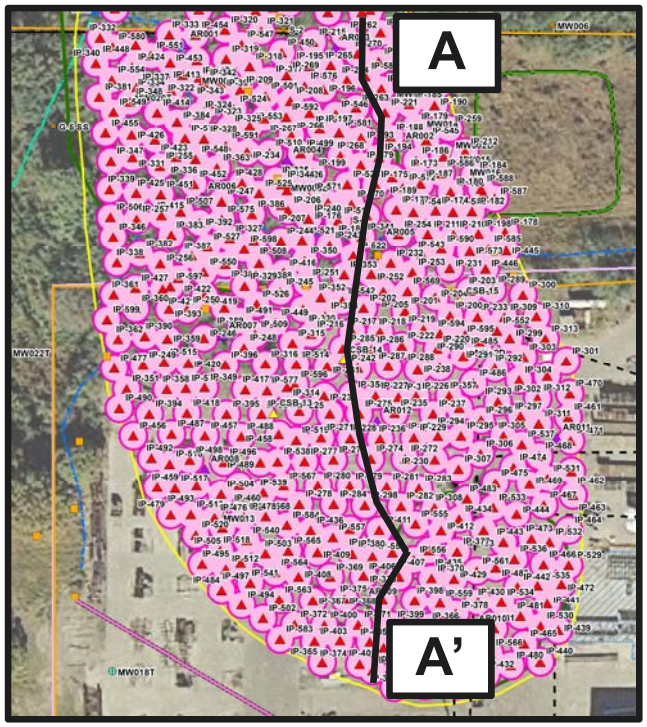
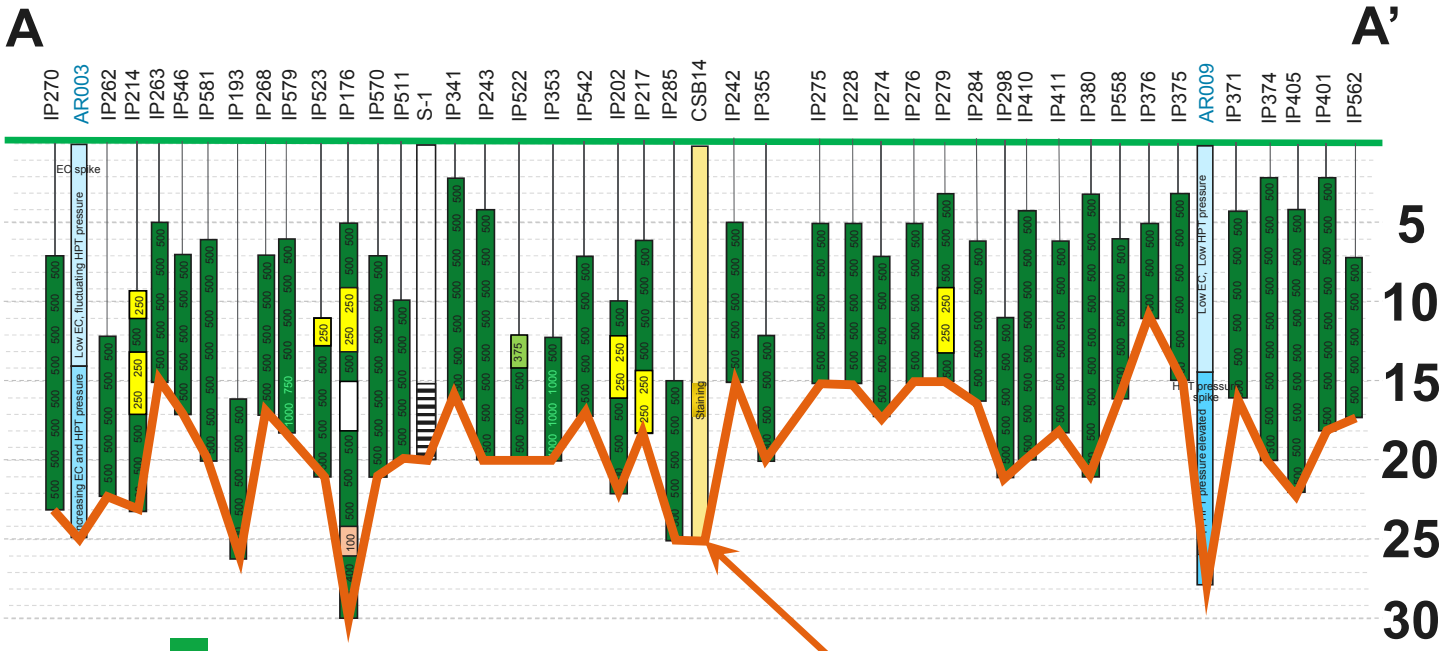
Site Area = 218,000 ft²



Performance: Reagent Distribution





Full Targeted Volume

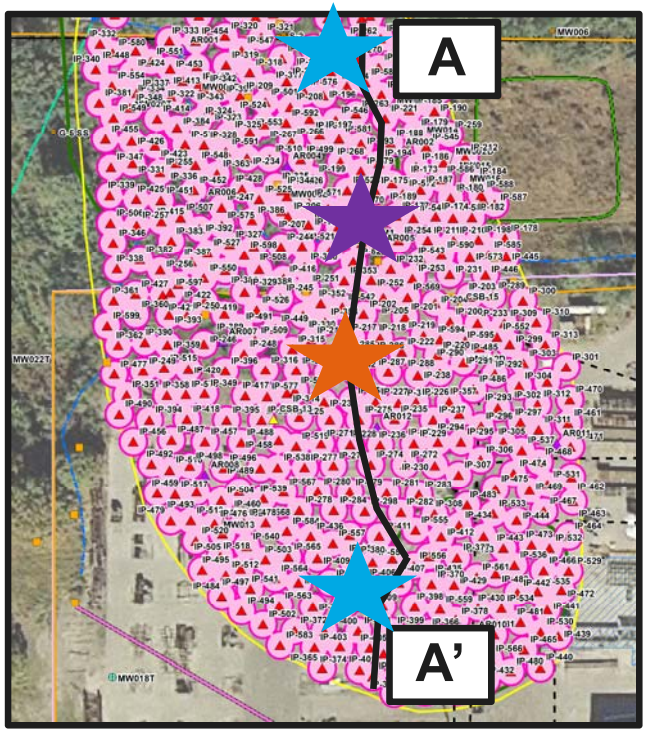
Target volume:

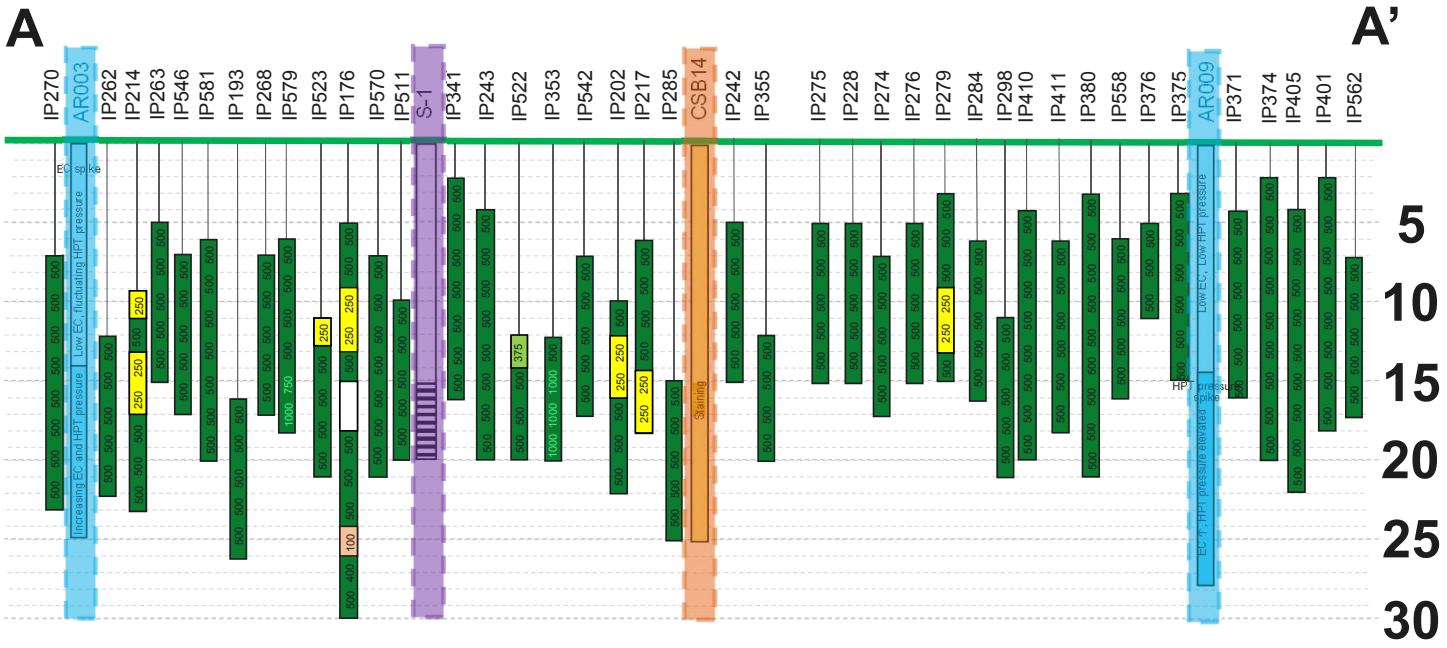
~470 gal/ 2 ft interval

Poor Volume Injected

Anticipated undulating Hawthorne surface

Performance: Reagent Distribution

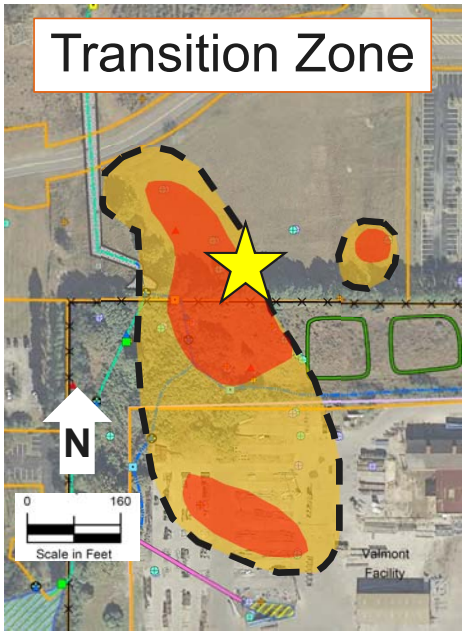




Dose response confirmed through multiple lines of evidence:

★ Hydraulic Profiling Tool ★ Monitoring Well ★ Confirmatory Soil Borings

Performance: Analytical Data (MW-A)

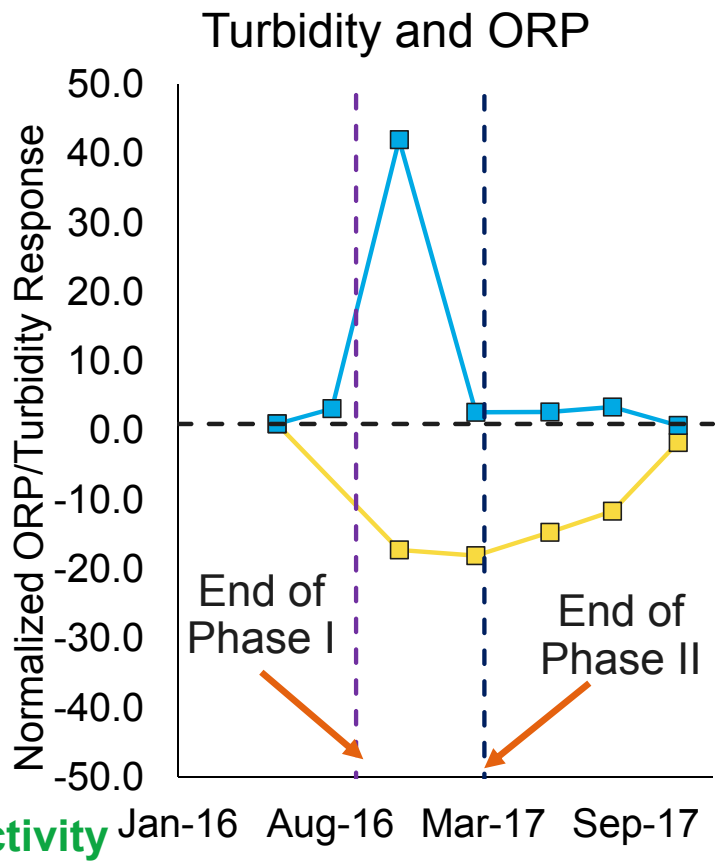


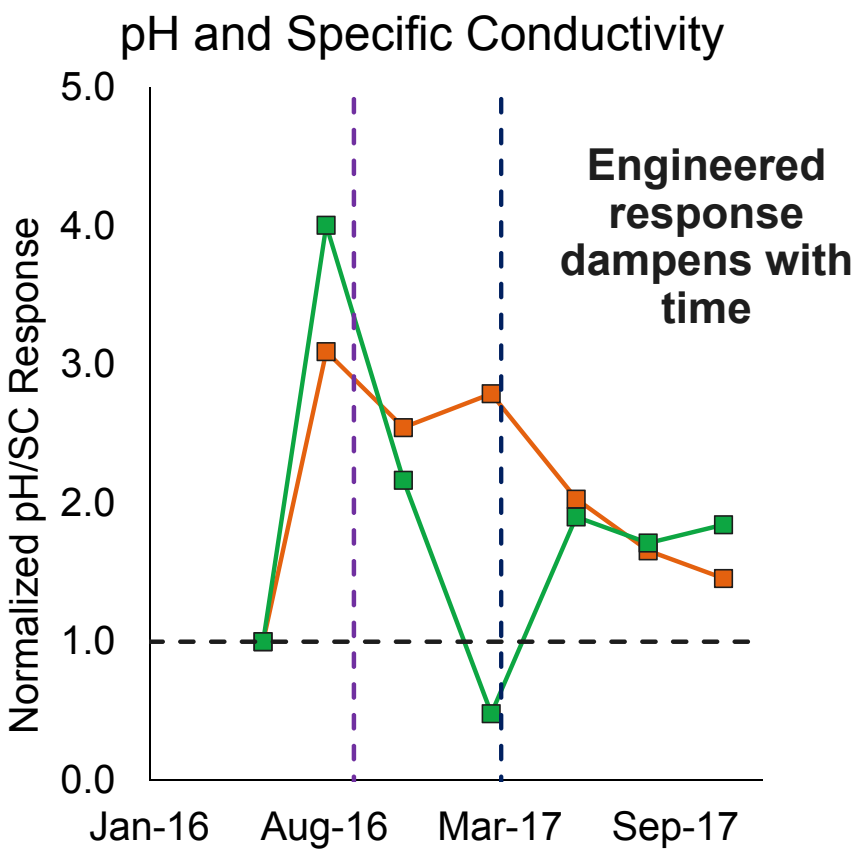
Turbidity

ORP

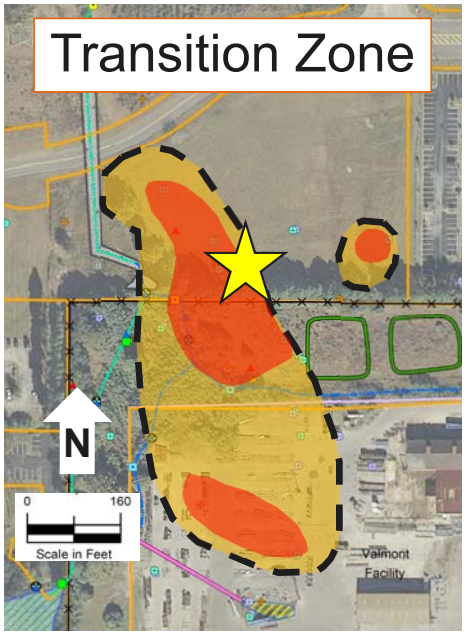
pH

Specific Conductivity

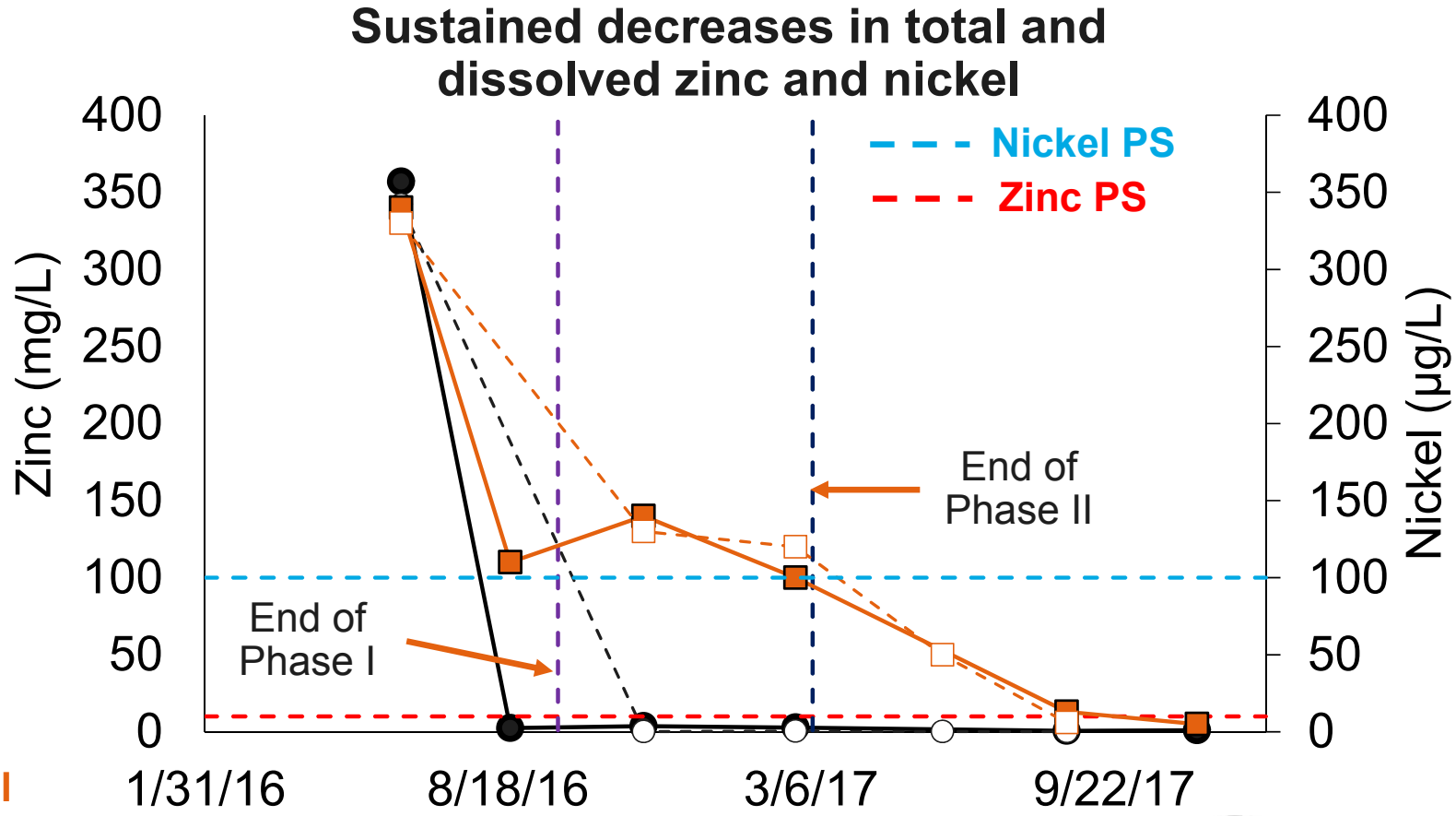




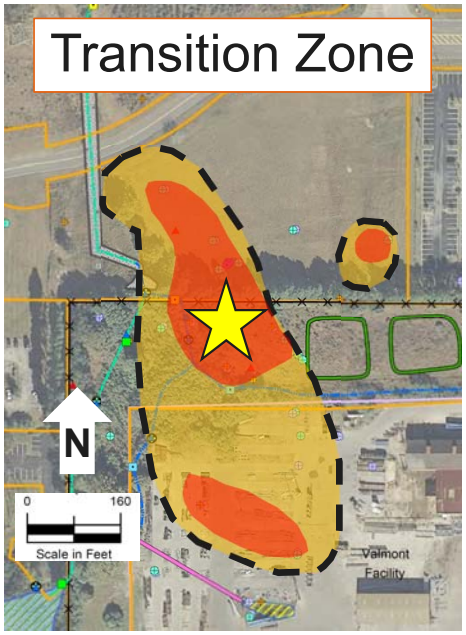
Performance: Analytical Data (MW-A)



Total Zn
Dissolved Zn
Total Nickel
Dissolved Nickel



Performance: Analytical Data (MW-B)

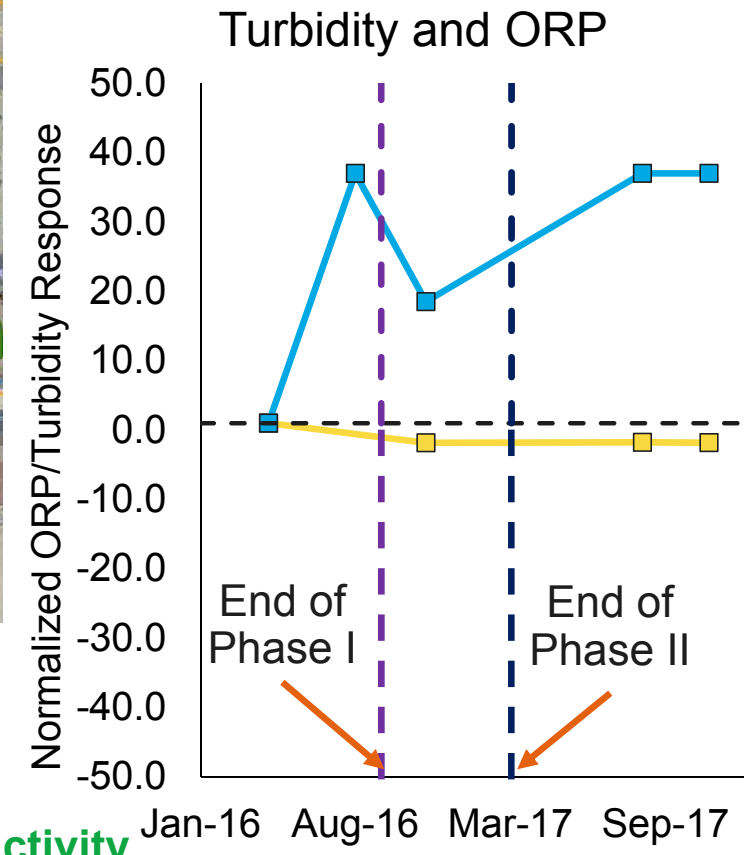


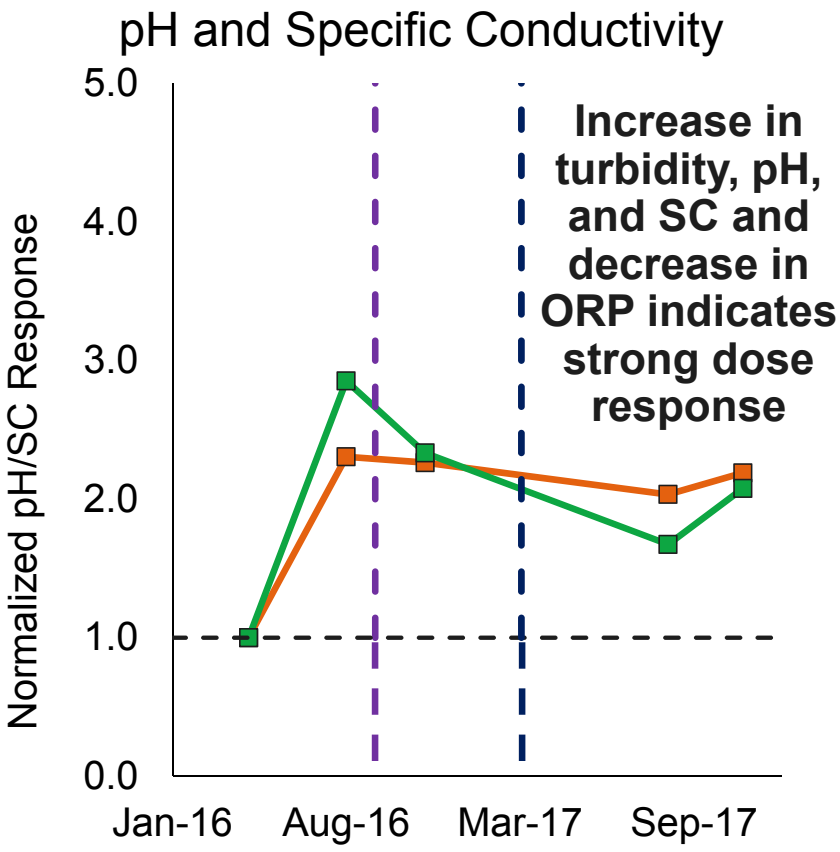
Turbidity

ORP

pH

Specific Conductivity



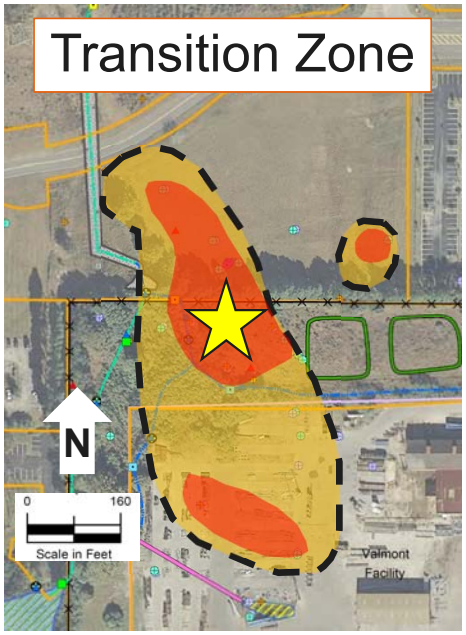


Influence at MW-B

“Rotten egg odor,” black streaking, strong field parameter response

Fluidized; poor recovery; field parameters = solution field parameters

Performance: Analytical Data (MW-B)



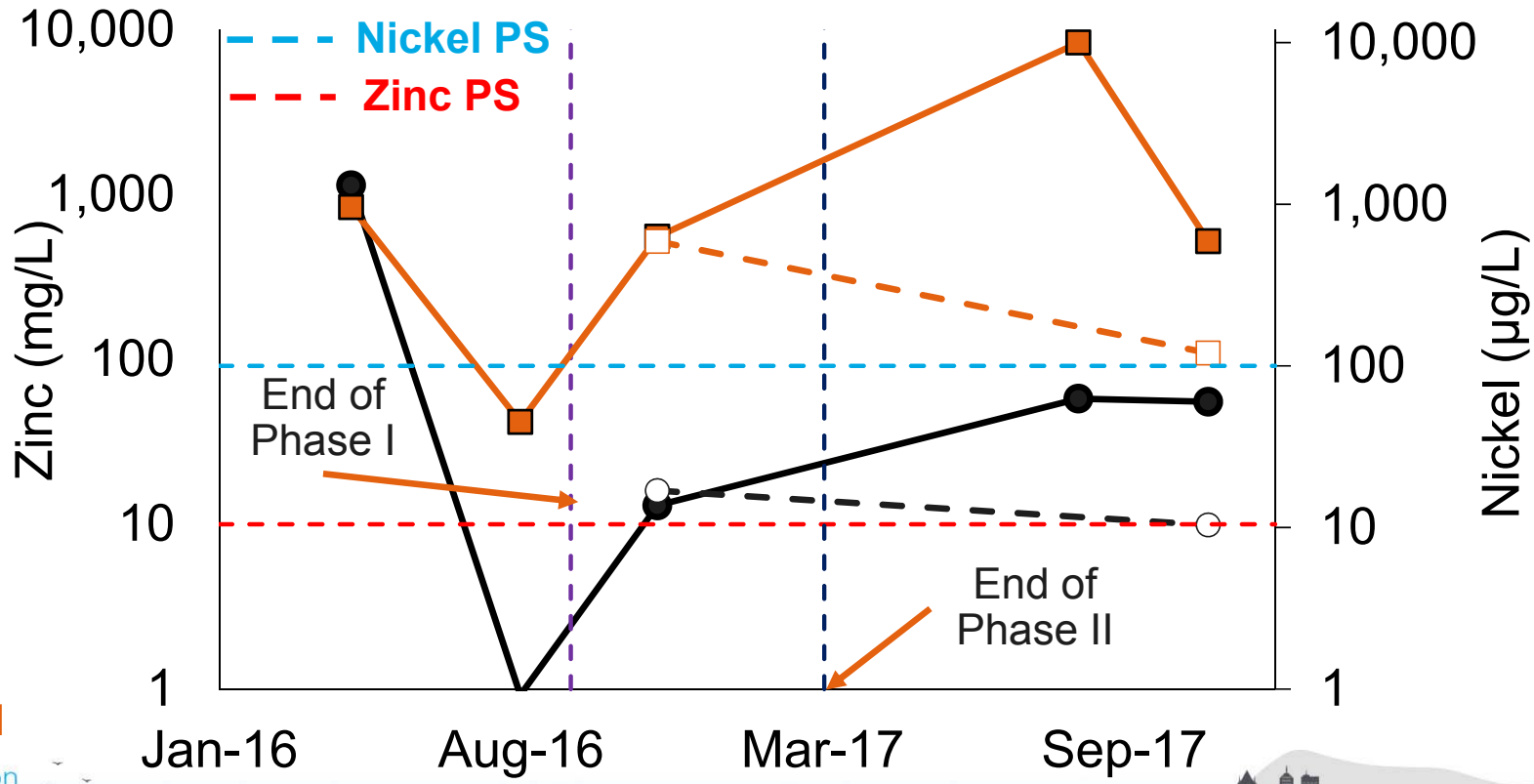
Total Zn

Dissolved Zn

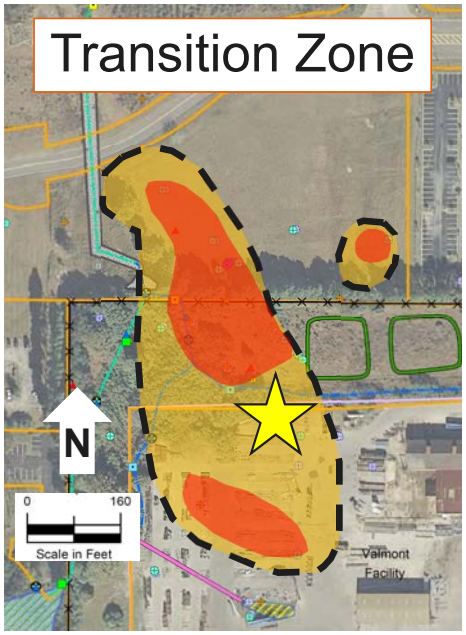
Total Nickel

Dissolved Nickel

Elevated total dissolved solids requires filtration to understand dissolved metals



Performance: Analytical Data (MW-C)

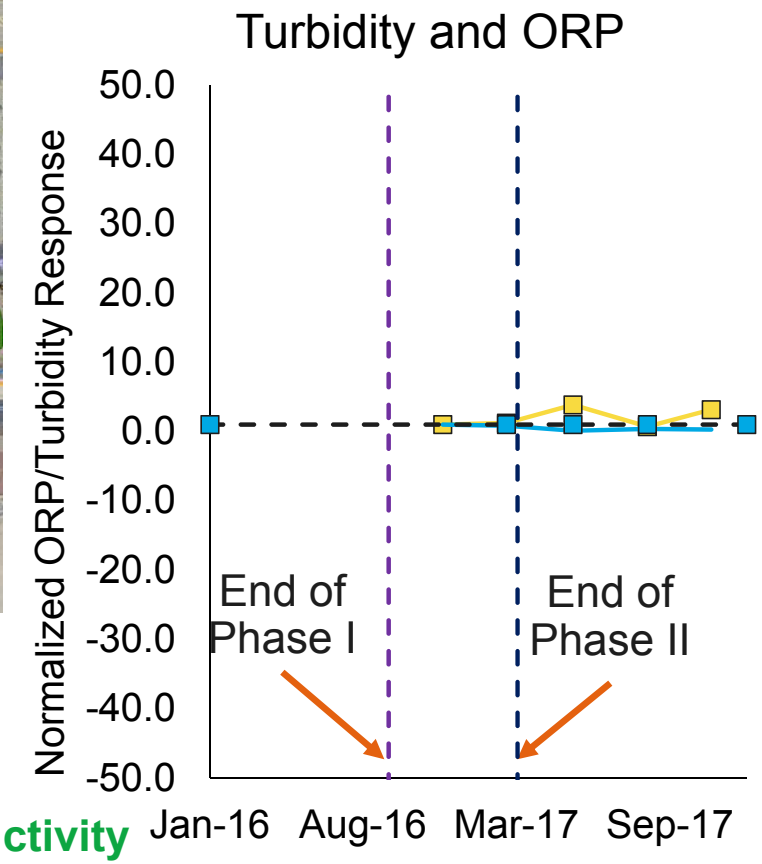


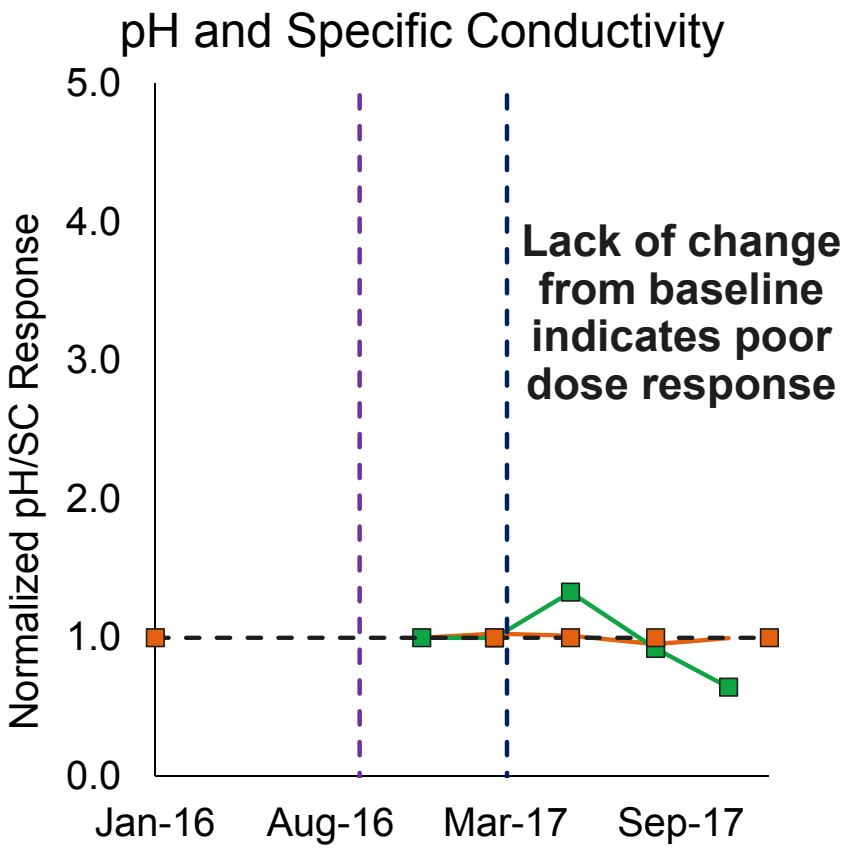
Turbidity

ORP

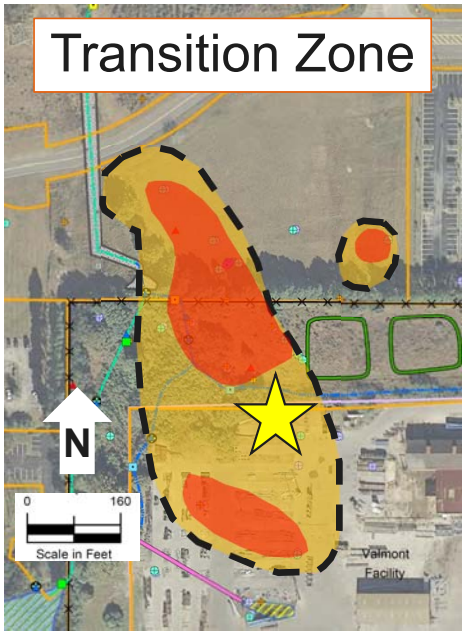
pH

Specific Conductivity



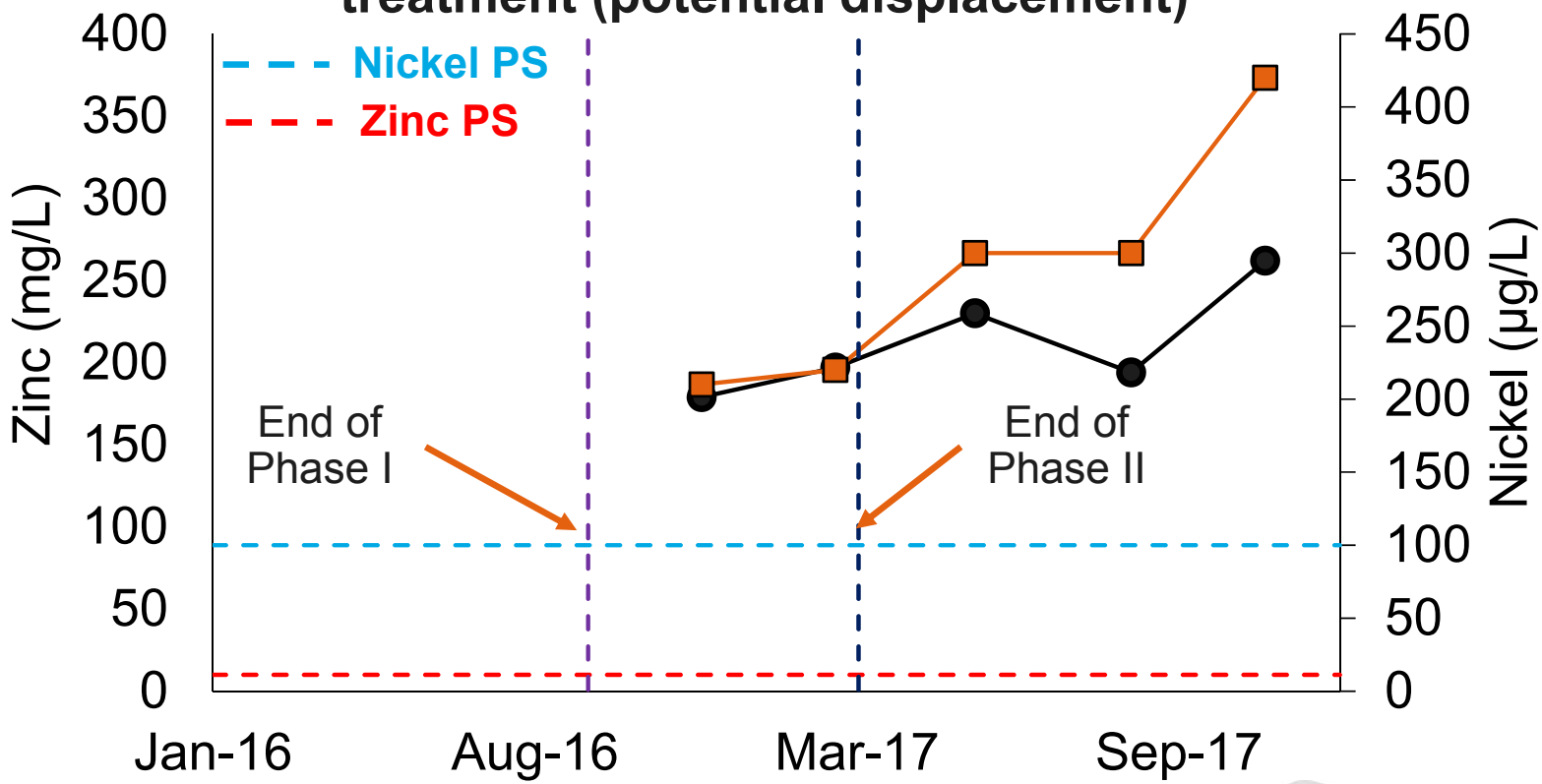


Performance: Analytical Data (MW-C)



Total Zn
Dissolved Zn
Total Nickel
Dissolved Nickel

Poor dose response results in lack of treatment (potential displacement)



Summary

- Approximately 1.7 million gallons of a ~2% by weight Na_2S_x and 0.25% by weight NaOH solution was injected to address acidic groundwater with heavy metal impacts.
- Polysulfide can be used as a form of reactive sulfide and can be engineered to improve both *in situ* distribution and *ex situ* conveyance.
- Temporary injection points can provide an increased certainty of distribution and implementation flexibility to adapt to changing injection hydraulics.
- *In situ* chemically induced sulfide precipitation is an effective strategy for immobilizing heavy metals and its effectiveness is based on achieving sufficient distribution of a highly reactive reagent.

Your Presenter(s)

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