ISCO Re-Engineered

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Lets Set the Stage


In-Situ
Beatty

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esident's Hall Foyer

New Technology
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- Chemical oxidation is a long-standing treatment technology with a proven track record
  - first aid
  - water treatment
- Fenton's reactions and ozone were early pioneers for oxidant remediation, with permanganate and persulfate following suit
- ISCO for contaminant remediation has a checkered past, and no one ISCO approach has gained a preferred status

What's the Problem?

- I believe a big obstacle is expectations!
  - ISCO is marketed as a quick remedy – and it can be

> In Situ Chemical Oxidation (ISCO) with sodium permanganate and potassium permanganate is a safe, cost-effective and rapid remediation technology for the treatment of VOCs (e.g. PCE, TCE, DCE VC etc.) in groundwater, soils and sediments.

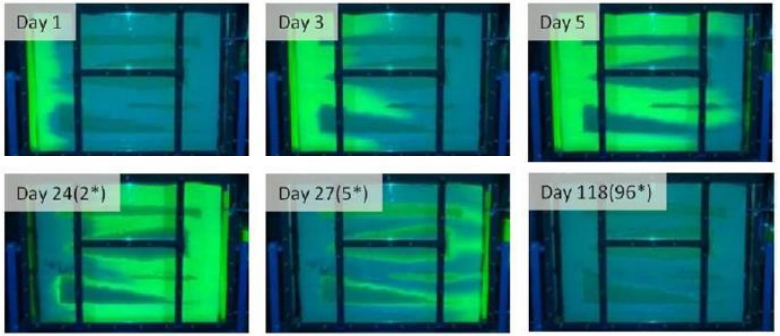
  - Practitioners believe that they can predict ISCO volume needs
    - if you know your contaminant mass
    - if you know your flow characteristics (ROI)
    - if you can get good contact
  - In practice, application is more art than science

Re-Engineered In What Way?

- Realign how we think of ISCO
  - preferred use of the remedial technology
  - short-term vs. long-term expectations
- Reconsider data/monitoring needs
  - decrease reliance on NOD/SOD/TOD testing and contaminant mass calculations
  - increase focus on performance monitoring using key parameters like oxidation potential
  - use caution in over-interpreting color in wells
- Methods of application

Rebound

- A typical response to ISCO at sites which include low K materials, concentrated source areas, and DNAPL
  - we are all aware of the excellent literature and research related to matrix diffusion
  - add complexity of spills maturity
  - and consider site heterogeneity
  - don't necessarily expect that a quick application of ISCO will reverse decades of penetration



* Courtesy of Dr. Tom Sales

Krembs et al.

- 62% of sites had rebound
- Of those, half the wells within the treatment zone exhibited rebound

2012 Perspective

Environmental Science & Technology

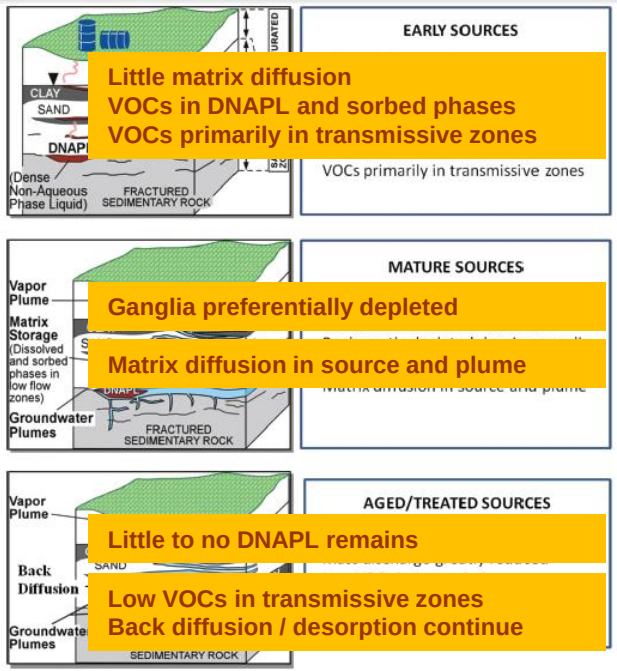
Feature

pubs.acs.org/est

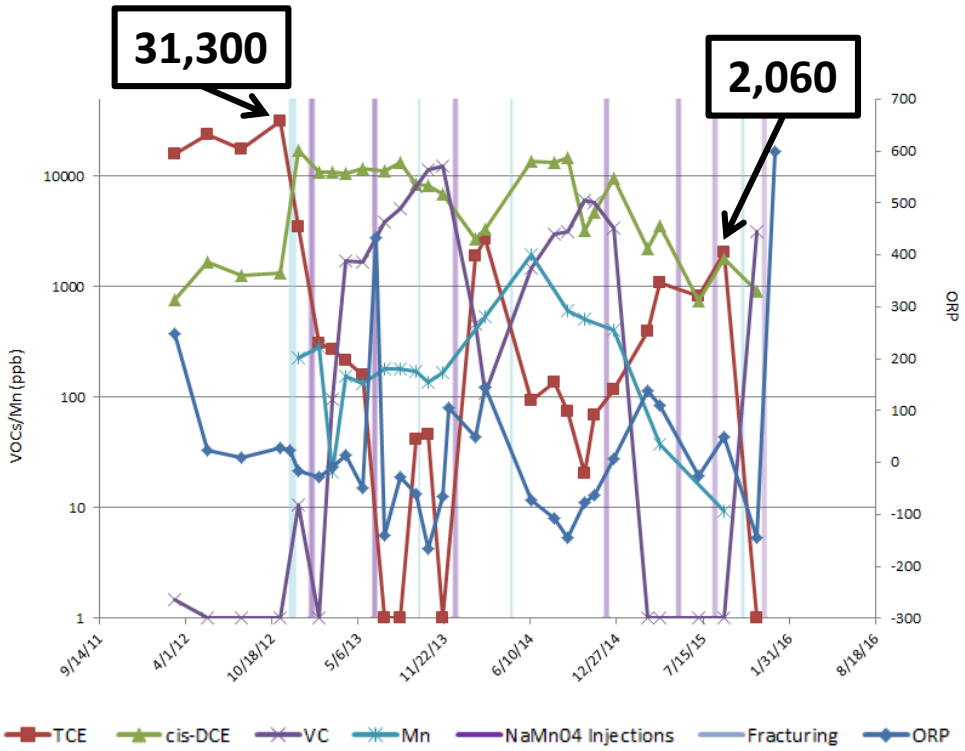
Chlorinated Ethene Source Remediation: Lessons Learned

Hans F. Stroo,[†,*] Andrea Leeson,[‡] Jeffrey A. Marqusee,[‡] Paul C. Johnson,[§] C. Herb Ward,[∥] Michael C. Kavanaugh,[⊥] Tom C. Sale,[#] Charles J. Newell,[▽] Kurt D. Pennell,[○] Carmen A. Lebrón,[◆] and Marvin Unger[†]

- 60-80% reductions for injection-based remedies
- ISCO rapidly destroys chloroethenes, but has important limitations
- ISCO has been a marginally successful source treatment
- Reactants are short-lived
- May disrupt natural attenuation
- Sorbed mass may be released
- One study found average maximum decreases if 55%



Typical Batch Injection



- CVOCs decrease after each batch
- May note Mn, MnO4-, chlorides or purple color inc.
- DO or ORP may bounce around
- Low chemical data density compared to potential geochemical changes

Client/Regulator Perspective

- Is this the right remedy for the site?
- Why does it keep rebounding?
- Are you simply pushing contaminants around?
- How much longer will this take?
- You want how much more money?
- Will we really get to closure?
- Can you guarantee a fixed price?

So, Re-Engineer ISCO

- Limit rebound, and lower the cost of ISCO
- Reduce batch injection labor, which is about 50% of injection cost
- Maybe simply add oxidant until done
  - try considering ISCO as a long-term remedy approach
  - eliminates guess work of oxidant mass needed
  - avoids need to evaluate NOD
  - mechanize injection to reduce consultant costs, put $ to the remedy
- Need to address
  - having enough storage volume
  - security
  - potential health and safety issues

How?

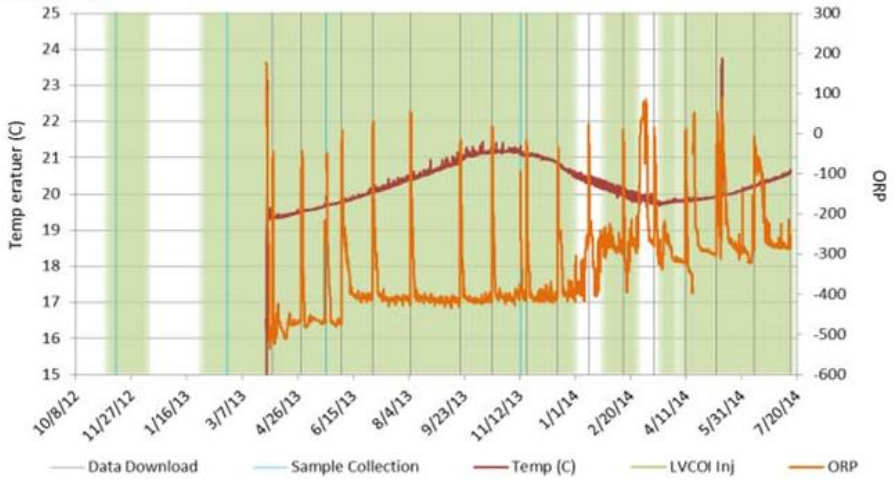
Concern/Issue	Mitigation
Limit Rebound	• Promote and maintain a reactive treatment environment sufficient to degrade contaminants
Reduce Labor/Costs	• Mechanize injections • Use instrumentation for real-time monitoring
Chemical Storage	• Reduce storage requirements by injecting higher concentrations • reduce injection volumes accordingly
Security	• Include shelters appropriate to location
Health and Safety	• Reduced contact, but at higher concentrations

“Reactive Treatment”

- Simple addition of an oxidant may not show benefits because of
  - lack of contact (hydraulics)
  - insufficient volume (scope, cost)
  - insufficient concentration
- There is a threshold point for each site – and I propose that it is based on achieving a suitable oxidation potential.
- Once that threshold is achieved, it needs to be maintained until treatment is accomplished.
- Time needed to maintain that environment is variable, and may be long.

One Option - LVCOI

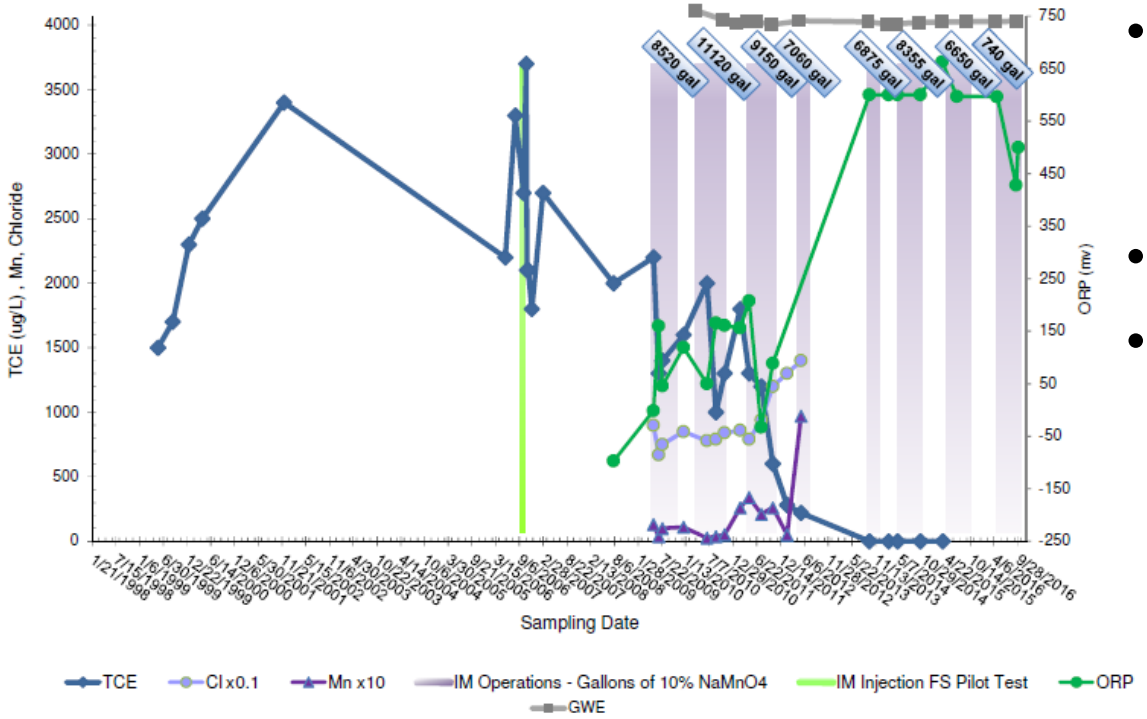
- Considering Low Volume Chemical Oxidant Injection (LVCOI) as a long-term option allows for management of process and costs
- Avoid the cyclic environment associated with batch injections using
  - more frequent applications, or
  - continuous injection
- Avoid concerns of hydraulically pushing contaminants away from the high concentration areas using lower volumes



“LVCOI”

- LVCOI is based on the consistent application of oxidant to reach and maintain a reactive degradation environment
  - the amount and frequency of injection is site dependent
  - the amount and frequency can be assessed monitoring the oxidation front
- About 10 years of site experience support this approach
  - dramatic improvements have been observed in some source zones
  - impacts have been documented significant distances from injection locations
  - observed slow but steady improvements in low K materials

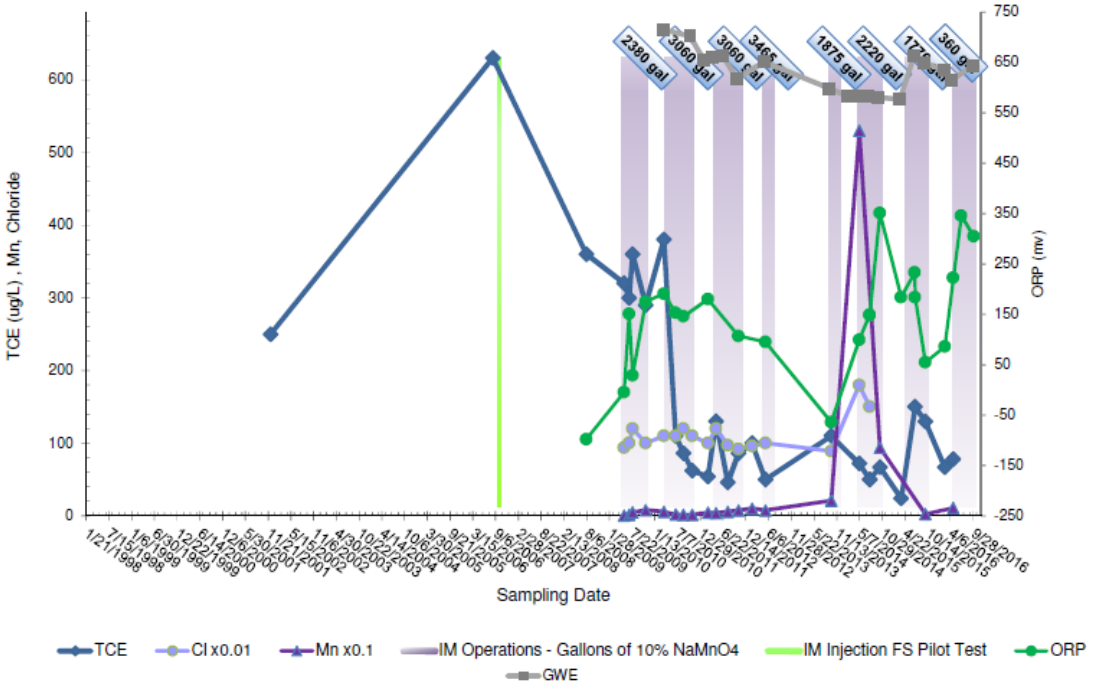
Initiating LVCOI



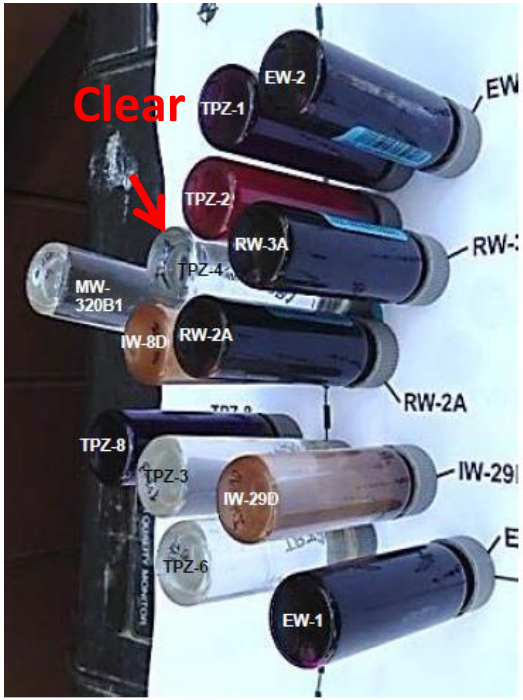
- Initial pilot test data resulted in less than optimal results
- Change in consultants
- LVCOI implemented during 2009
  - remote site
  - long-term outlook
  - source area application
  - delayed ORP response

Reviewing LVCOI Data

- Common data trends illustrate an initial decline, then plateau in concentration
- ORP has a higher plateau, then some rise
- Many wells have an ORP plateau at about 150-200 mV
- Mn data is inconsistent from site-to-site, likely related to metals Eh-pH mineralization



Impact of Low K

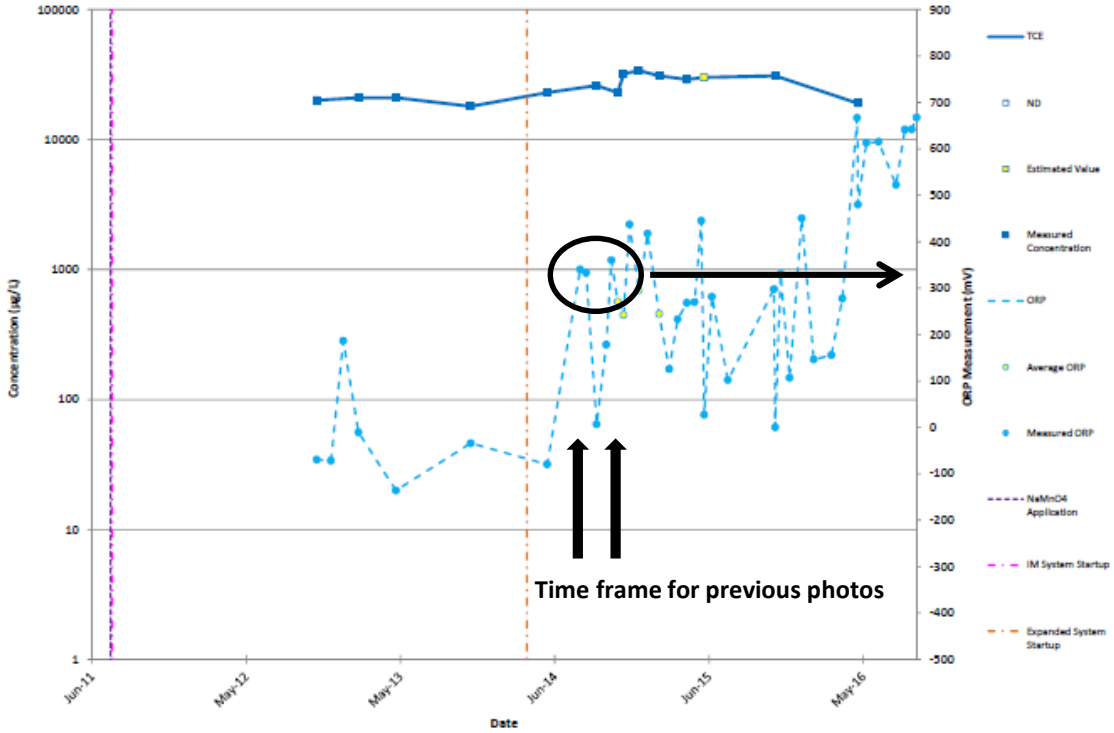


Upper Shallow Zone – 8/14/2014
(4.5 months post-startup)

Upper Shallow Zone – 11/11/2014
(7.5 months post-startup)

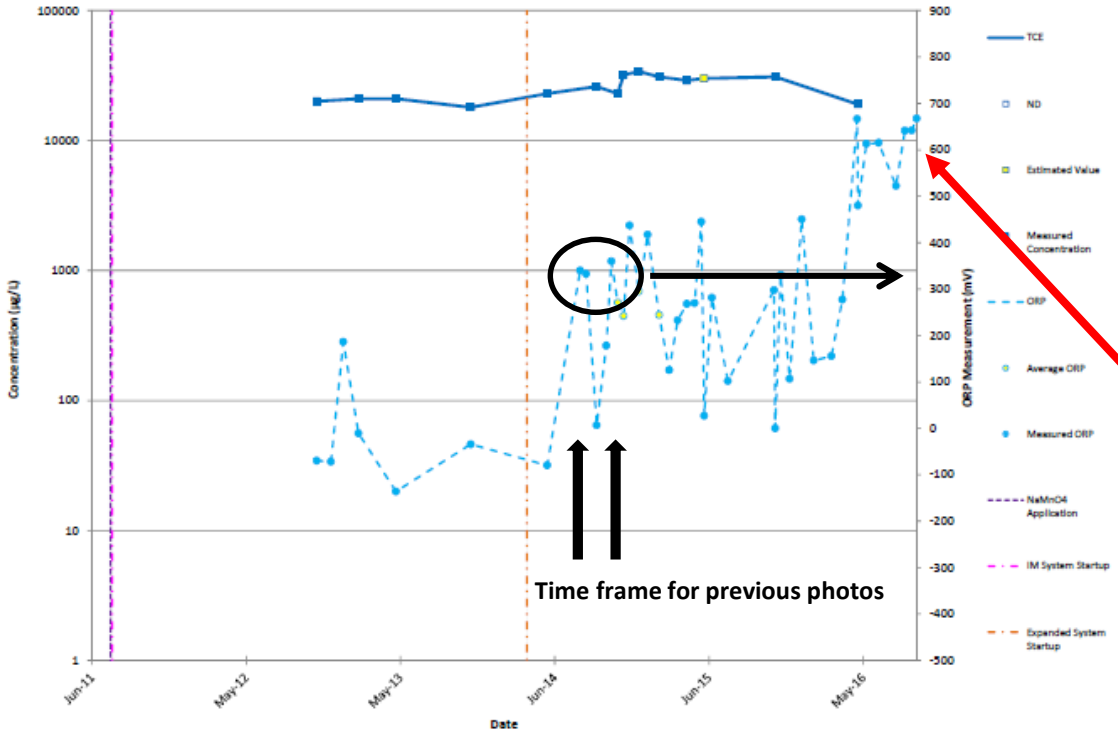
Upper Shallow Zone – 11/25/2014
(8 months post-startup)

Impact of Low K



- Less common – data trends don't illustrate an initial decline then plateau in concentration
- ORP has a higher plateau, then some rise
- ORP plateaus at about 350 mV for approximately 2 years, but wells remained clear
- Note no decrease in TCE

Impact of Low K



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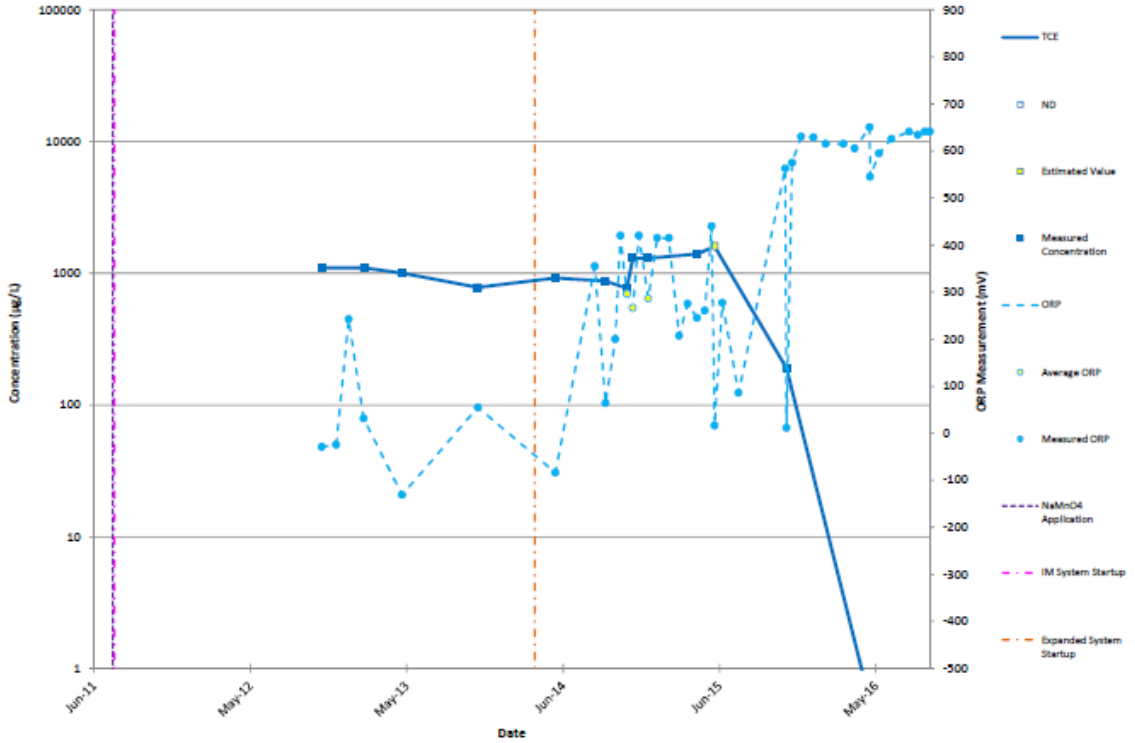
Paired Deeper Well

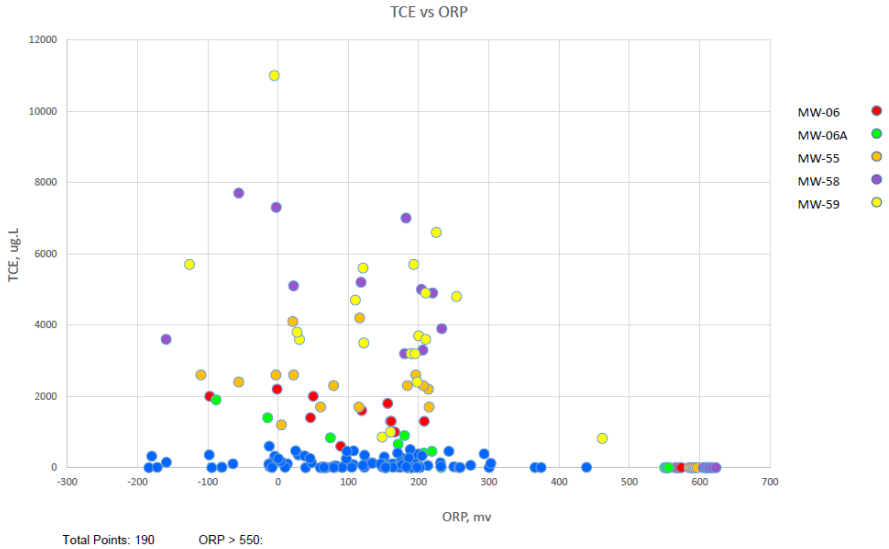


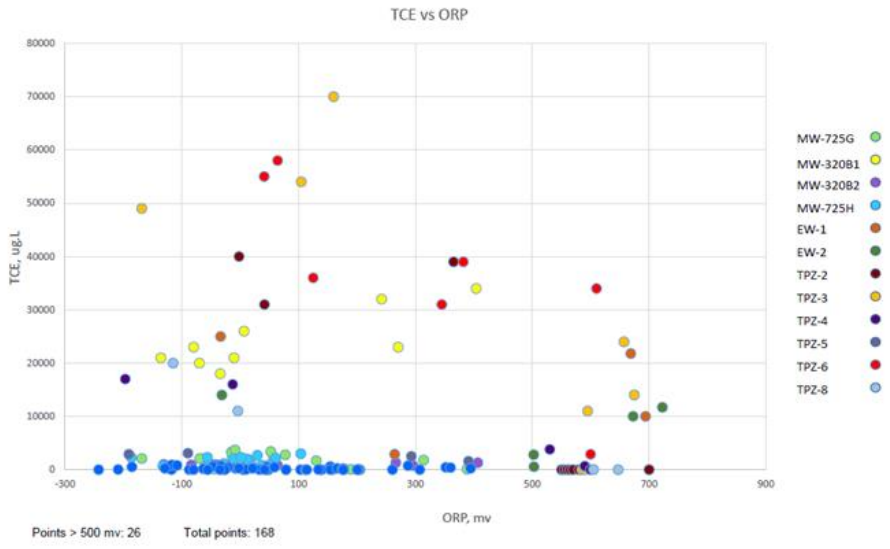
- Although the deeper well responded sooner than its shallow partner, the same trends formed
- At this location, ORP had to increase to about 600 mV to achieve meaningful TCE degradation

LVCOI vs Batch Injection

- The long-term chemical trends collected from high- and low-K sites demonstrate the necessity of achieving and holding an elevated ORP for considerable periods of time
- Batch injections won't maintain reactive oxidation conditions at sites that have separate phase or appreciable mass sorbed into low K materials due to
  - consumption of the oxidant
  - hydraulic migration
  - insufficient chemical gradient to reach sorbed contaminants

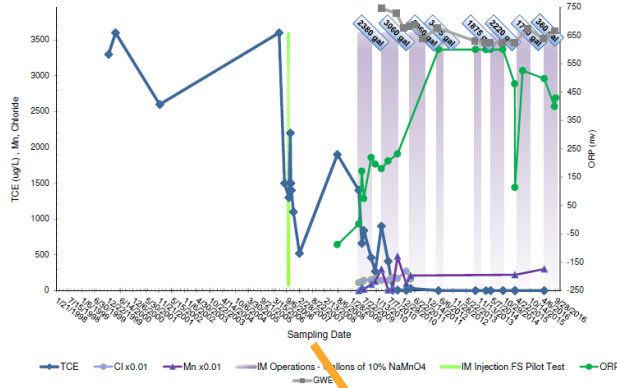
How Much ORP is Needed?

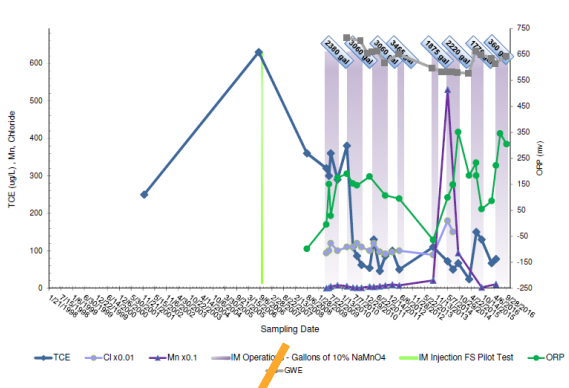


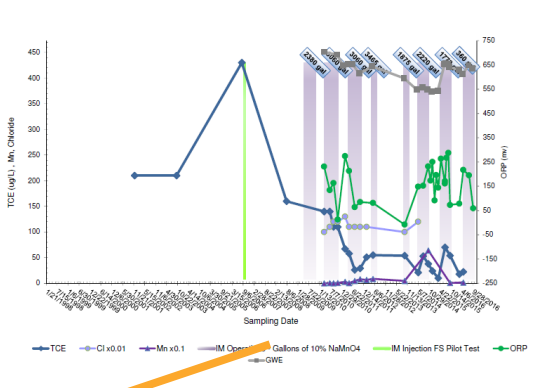


- Data to date does not definitively answer this question , but suggest elevated ORPs of 250-600 are required

Not a Typical ROI







LVCOI Benefits

- Long-term approach has cash flow benefits
- LVCOI reduces consultant field time
- Allows for data trends to develop, improving interpretation of remedy success
- Improved remedy success for low-K materials

ISCO Re-Engineered – Questions?

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Evolution of Application