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RemOx[®] SR ISCO Reagent

Liberation Prolongee de Permanganate: barrieres reactives pour un assainissement ecologique et durable

Sustained release permanganate: reactive barriers for Green and sustainable remediation

Lorenzo Sacchetti
EMEA Technical Manager



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What?

- RemOx[®] SR
 - Stable slow release solid permanganate (PCE, TCE, DCE, VC, phenols, PAHs, hydrocarbons, ...)
 - Isolates reactants from instant dissolution in groundwater
 - Nontoxic and biodegradable
 - Facilitates slow sustained release of reactant(s) over long periods of time (e.g., years)

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What?

- 1.35" or 2.5" diameter
- 1' to 3' long



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Why?

Our customers were asking for a low cost, low footprint and easy to use ISCO system and the more we discussed the ideas with our customers the more interest we found.

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Why?

Create an ISCO process that is:

- Simpler to apply
- Offers sustained release
- Lowers total cost to completion
- Provides flexible design
- Allows stepped implementation
- Is safer to use

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Why?

The process began with the idea and research on the RemOx[®] *in situ* wells:

Development of a patentable, cost-effective, low footprint, *in situ* delivery system for long term application of permanganate in both saturated and unsaturated zones.

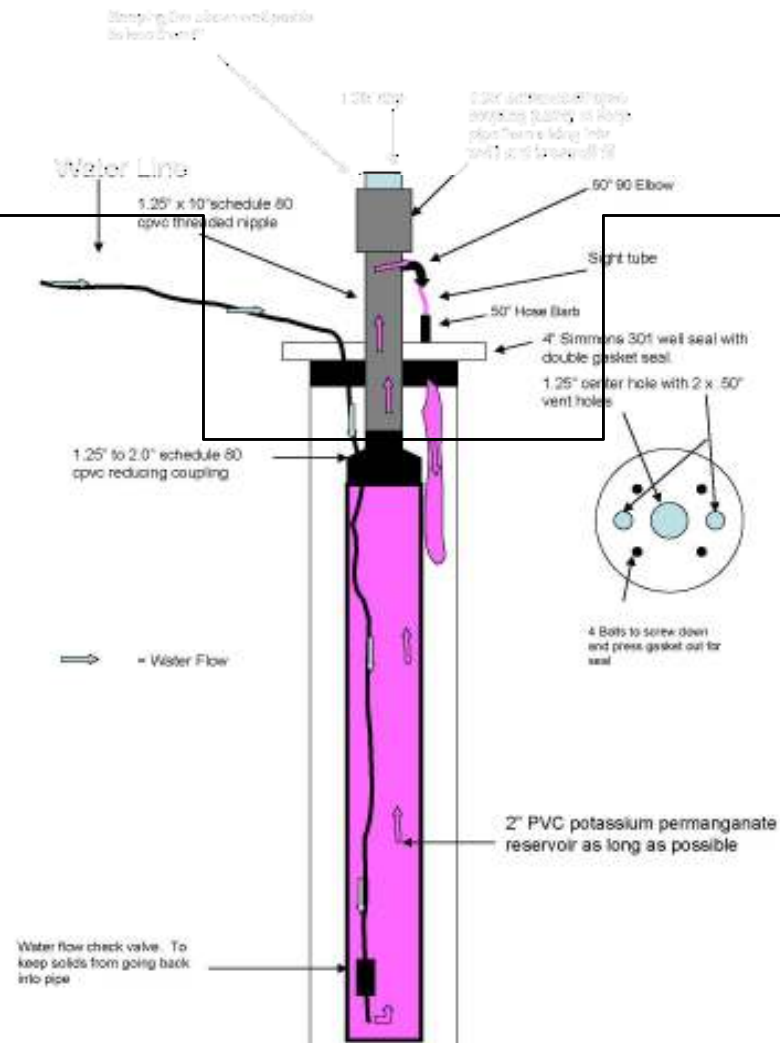
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Why?

Surface



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When?

This product is commercially available

- There are five projects currently under way in the United States
- There are five projects that will be started in the next two months in the United States
- There are four projects that will be started in Europe and South America in the next two months.
- **THIS IS NEW. WE ARE LEARNING!**

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When?

1. At the start of the project as the primary treatment option
2. In combination with other treatment options
 - ISCO and BIO applied at the same field injection
3. As a polishing component to an ISCO project
 - Permanganate, Modified Fenton or activated persulphate to treat residual contamination absorbed to the soil

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Where?

This product is being used as:

- An alternative to a ZVI wall
- A polishing step at a traditional ISCO site
- A way to treat a very tight soils with ISCO
- A way to apply ISCO in a stepped cost approach by property owners (Government)
- A long term slow release “cartridge” in a low flow remotely operated injection system

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RemOx[®] SR

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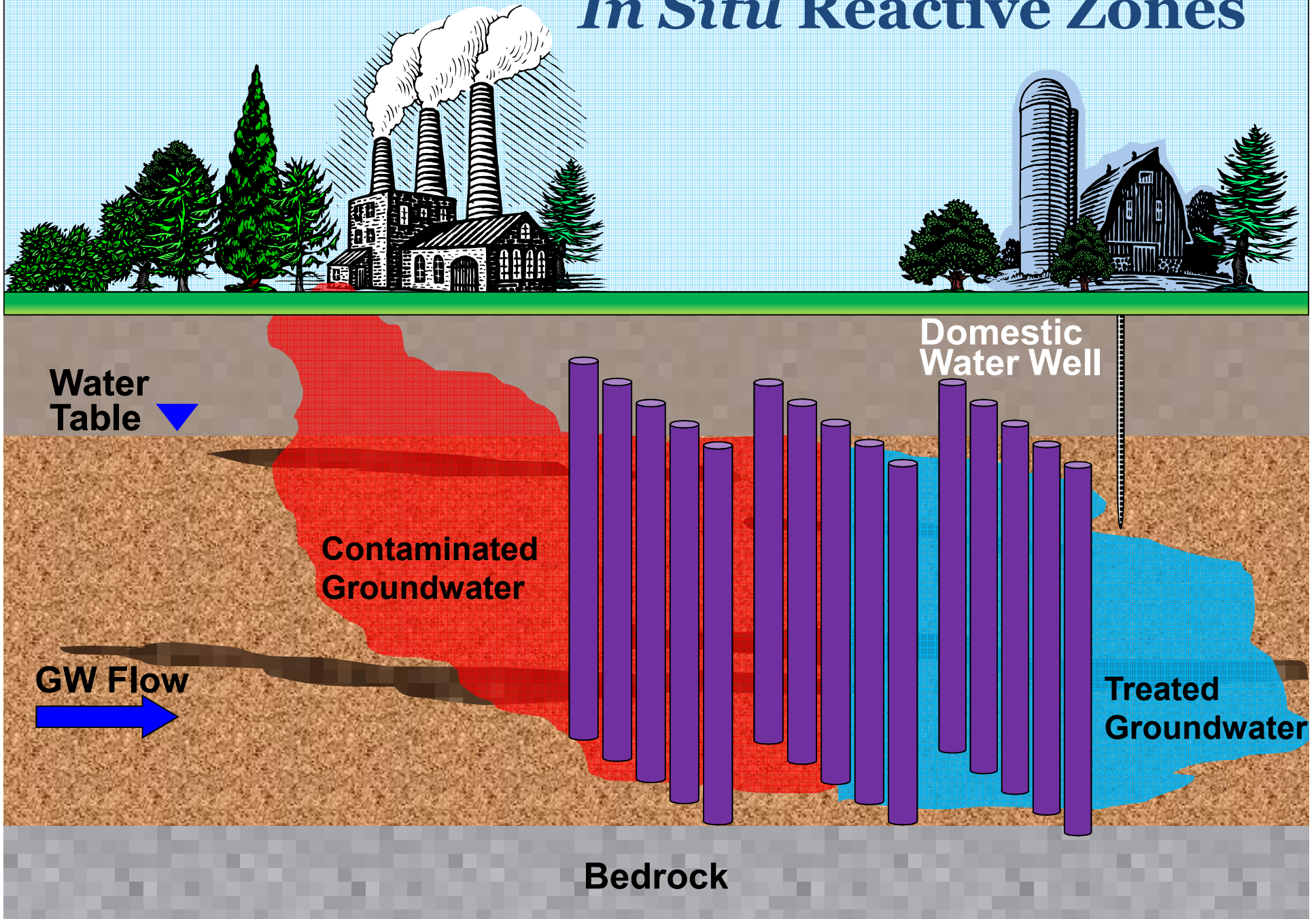


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The Challenge

- All remedial technologies have an environmental impact...
 - Electricity/fossil fuel to power equipment
 - Aboveground treatment of extracted fluids
 - Landfill disposal
 - Health and Safety of injecting liquid oxidants
- Reactive materials have been used successfully to remove contaminants in soil and groundwater
 - Once emplaced, do not require continued supply of electrical/fossil fuel energies
 - Serve as long-term, low-cost passive treatment for destruction/transformation of toxic contaminants

In Situ Reactive Zones



CRT Technology Development – Sustained-Release Permanganate



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- Promising lab and pilot-scale field studies investigating slow- release permanganate for barrier applications (e.g., Comfort et al. 2011; Dugan et al., 2011; Kang et al. 2004; Lee and Schwartz, 2007; Ross et al. 2005)
- 2003 Specialty Earth Sciences developed methods of encapsulation for sustained-release of reactants
 - *US Patent No. 7,431,849 B1 “Encapsulated Reactant and Process” (2008)*
 - *US Patent App. 12/169,434 “Encapsulated Reactant and Process” (2008)*
 - *US Patent App. 12/269,520 “A Process for Making Environmental Reactants” (2009)*
- Carus holds exclusive licensing rights for manufacturing, sales, and distribution



Technology Development – Sustained-Release Permanganate

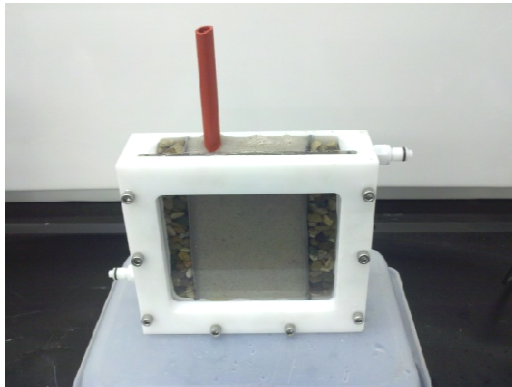
- RemOx[®] SR (Sustained-Release) is a potassium permanganate (KMnO_4)-based product dispersed in a solid paraffin wax matrix (60% to >80% KMnO_4)
- Potential for other reactants to be used (e.g., other oxidants, activators, catalysts, oxygen-release compounds, heavy metal immobilization amendments)

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Experimental Approach



- Column and tank experiments to evaluate permanganate release and treatment performance under dynamic flow conditions

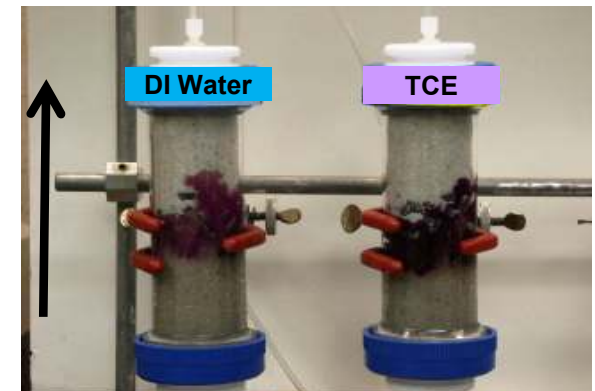
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Experimental Approach - 1-D Column Studies

- Sand Columns (30 cm x 4.8 cm)
 - 20/30 mesh silica sand
 - 35 g SRP 60% mass loading (21 g KMnO_4)
 - DI water or dissolved TCE
 - Influent ~ 0.7 mg/L
 - Flow rates (0.2 or 0.7 mL/min)
- KMnO_4 dissolves and diffuses from wax matrix to react and degrade TCE



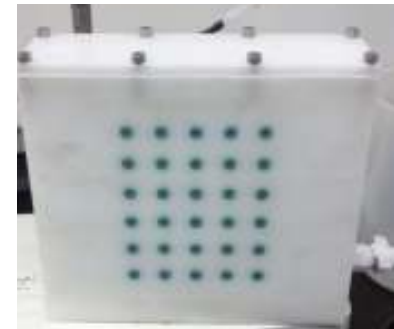
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Experimental Approach: 2-D Tank Studies

- LxWxD = 14x14x2.5 cm
- 20/30 silica sand with one mini-candle (80% KMnO_4)
- Influent = DI water
 - 0.55-0.60 mL/min
- Discrete sampling from rear ports (6)
 - Spatial component of MnO_4^- distribution
- Composite sampling from effluent
 - Temporal component of MnO_4^- distribution

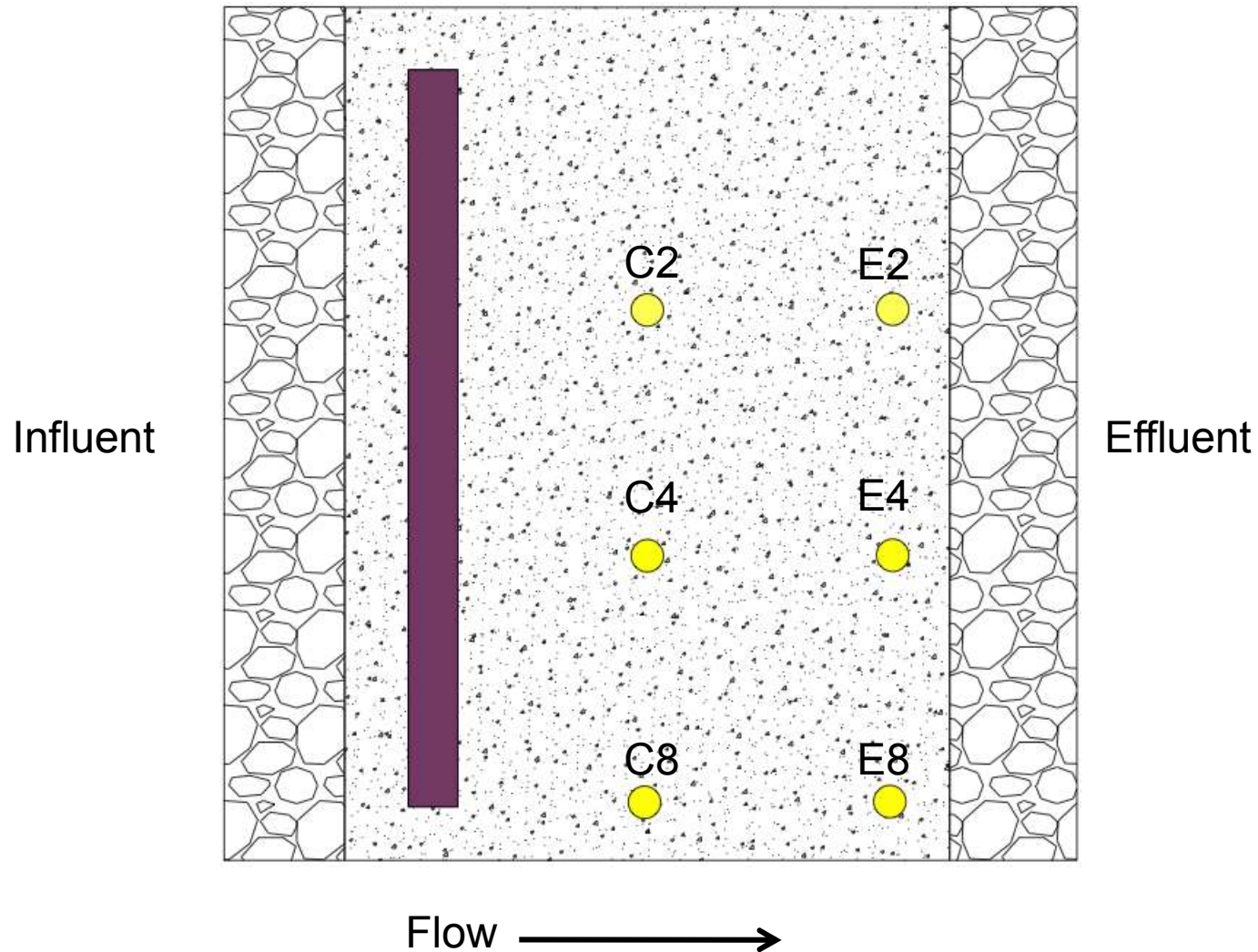


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Experimental Approach: 2-D Tank Studies



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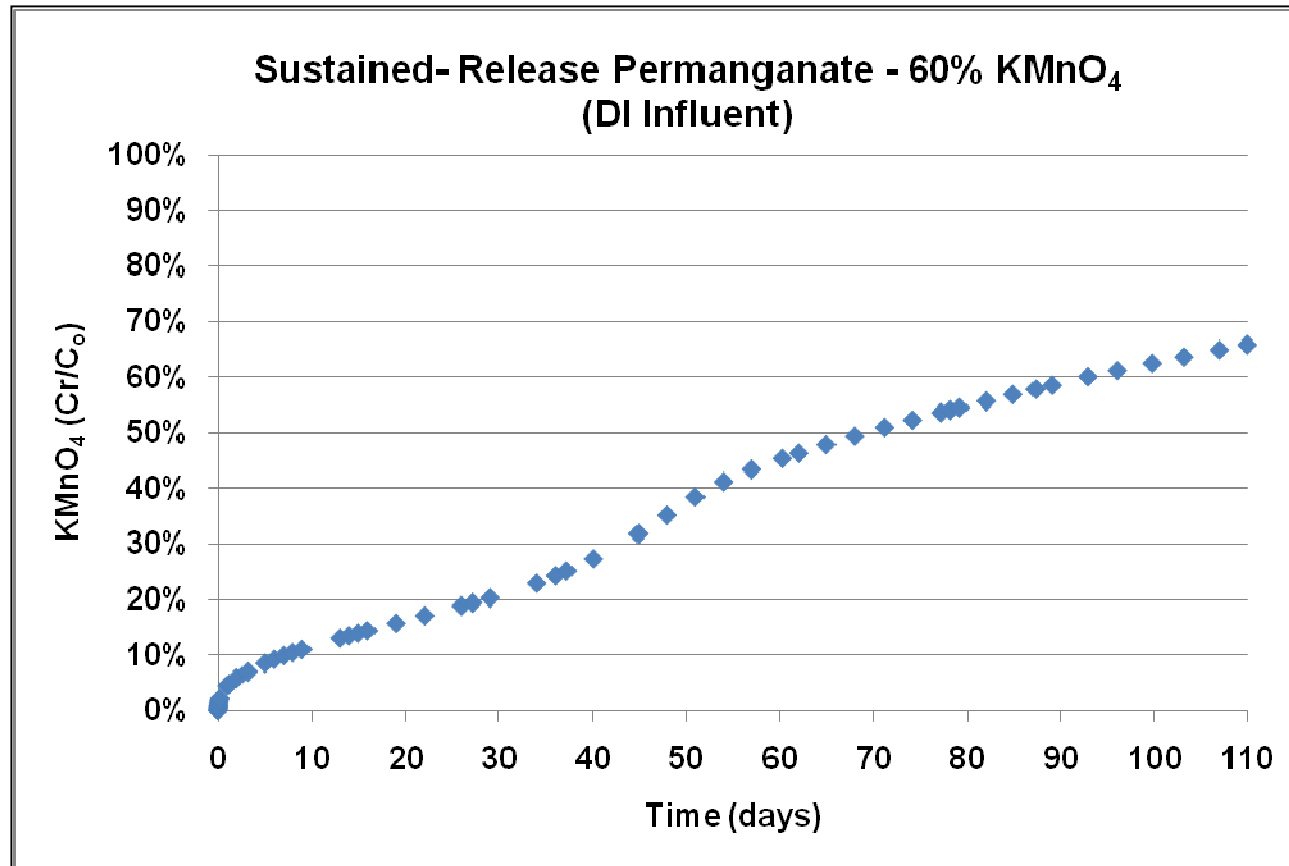
1D Column Results

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Results



During 110 days of operation ~ 70% of the permanganate was released

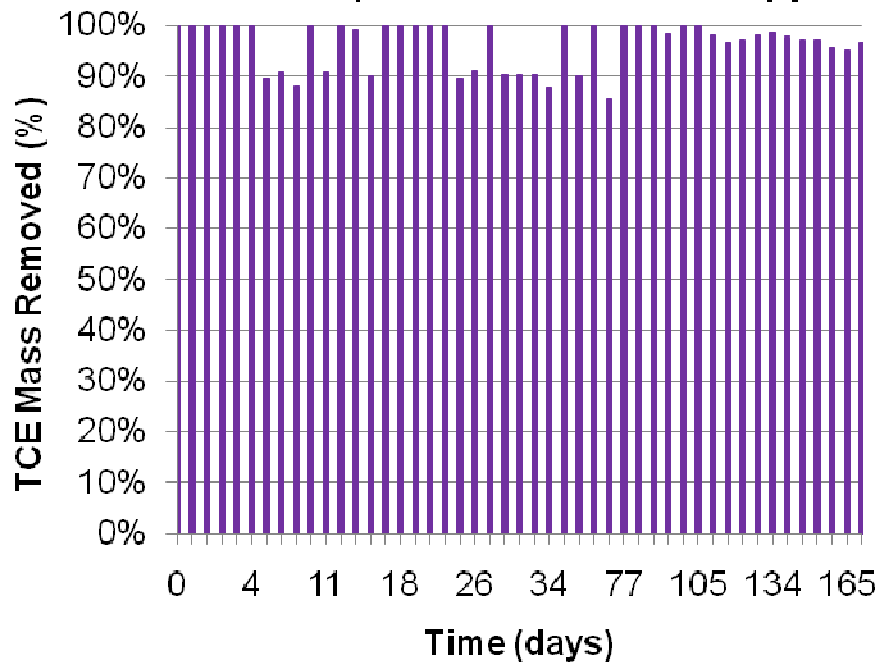
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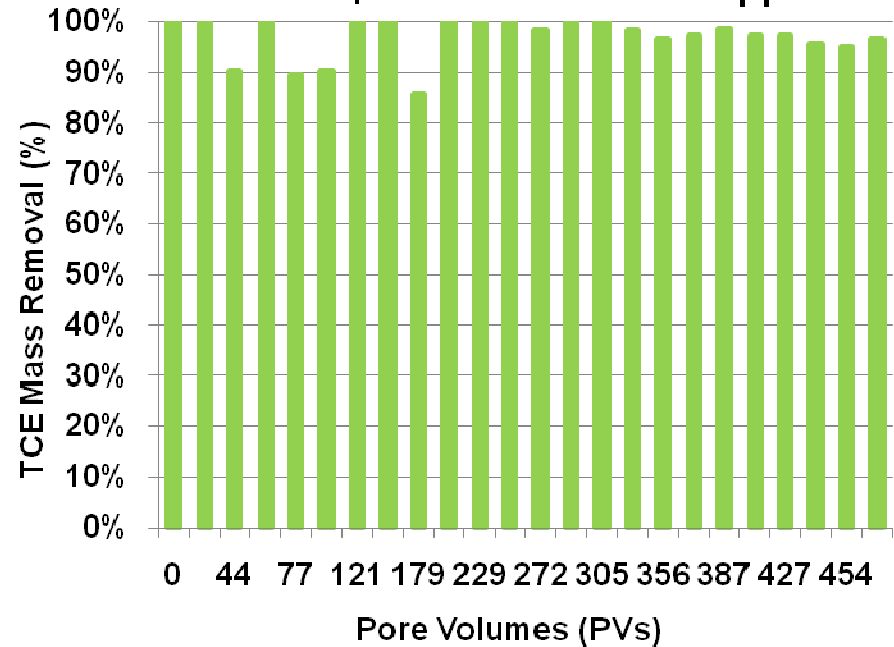
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Results

**Sustained-Release Permanganate
60% KMnO_4 - TCE influent ~ 0.7 ppm**



**Sustained-Release Permanganate
60% KMnO_4 - TCE Influent ~ 0.7 ppm**



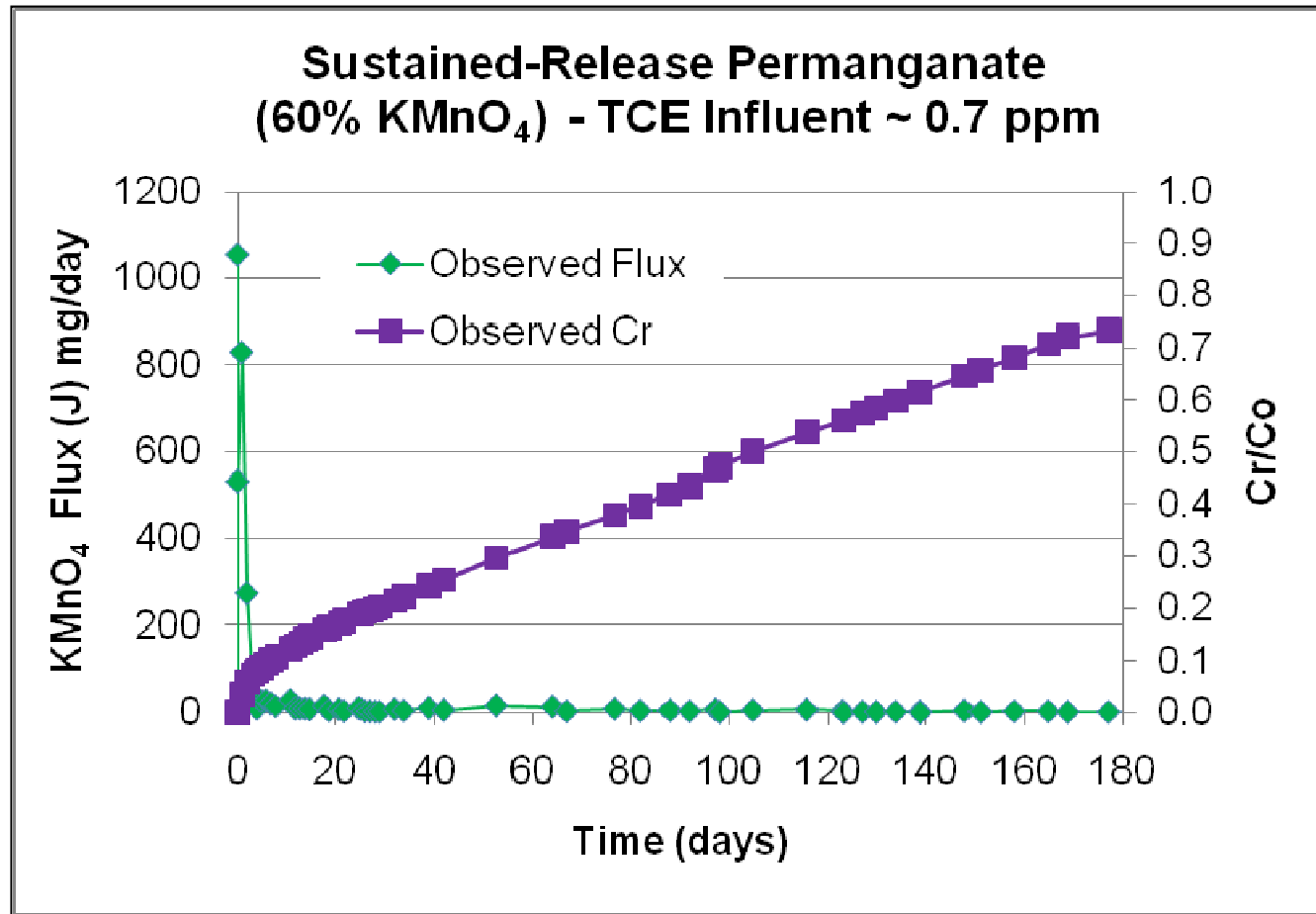
TCE mass removal 86% - 100% over 170 days or > 470 PVs

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Results

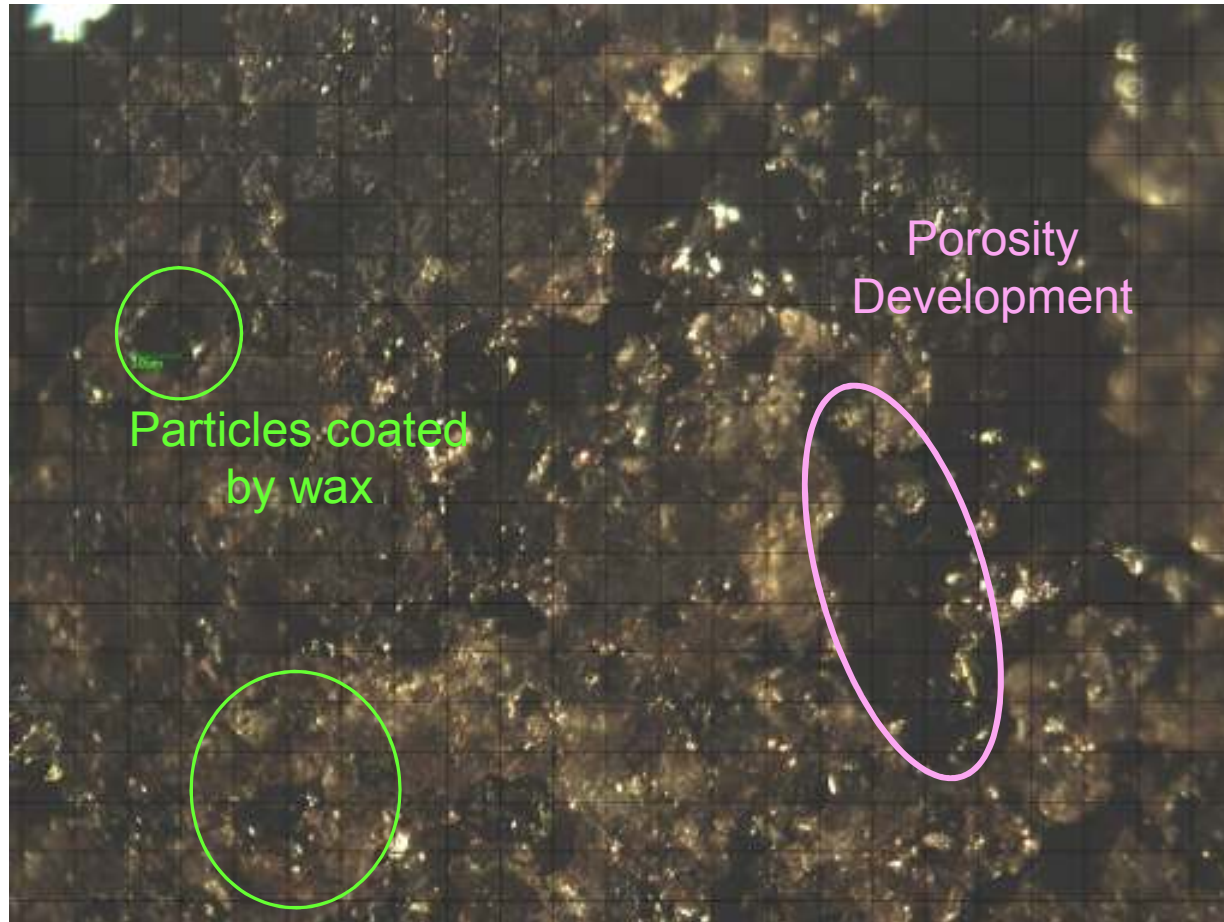


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Results



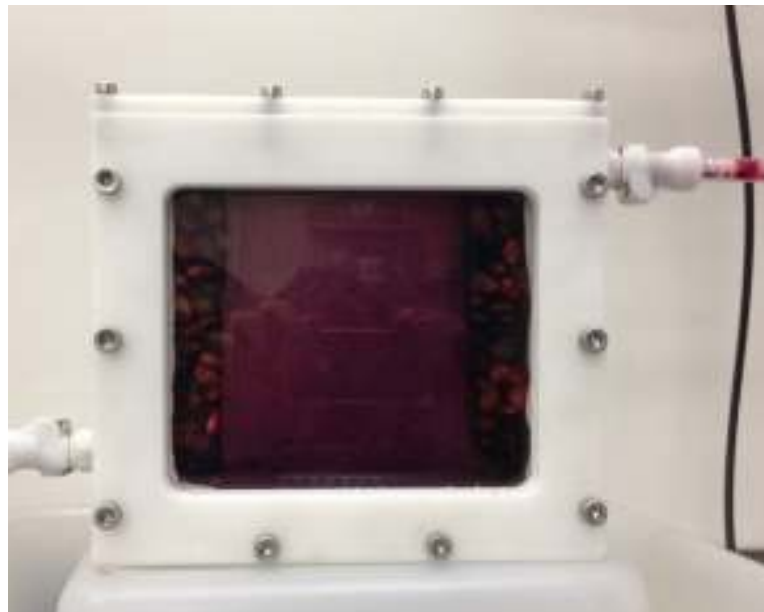
~70% $KMnO_4$ reacted-released over 170 days..increased mass loading to enhance $KMnO_4$ utilization

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Preliminary Results 2D Tanks

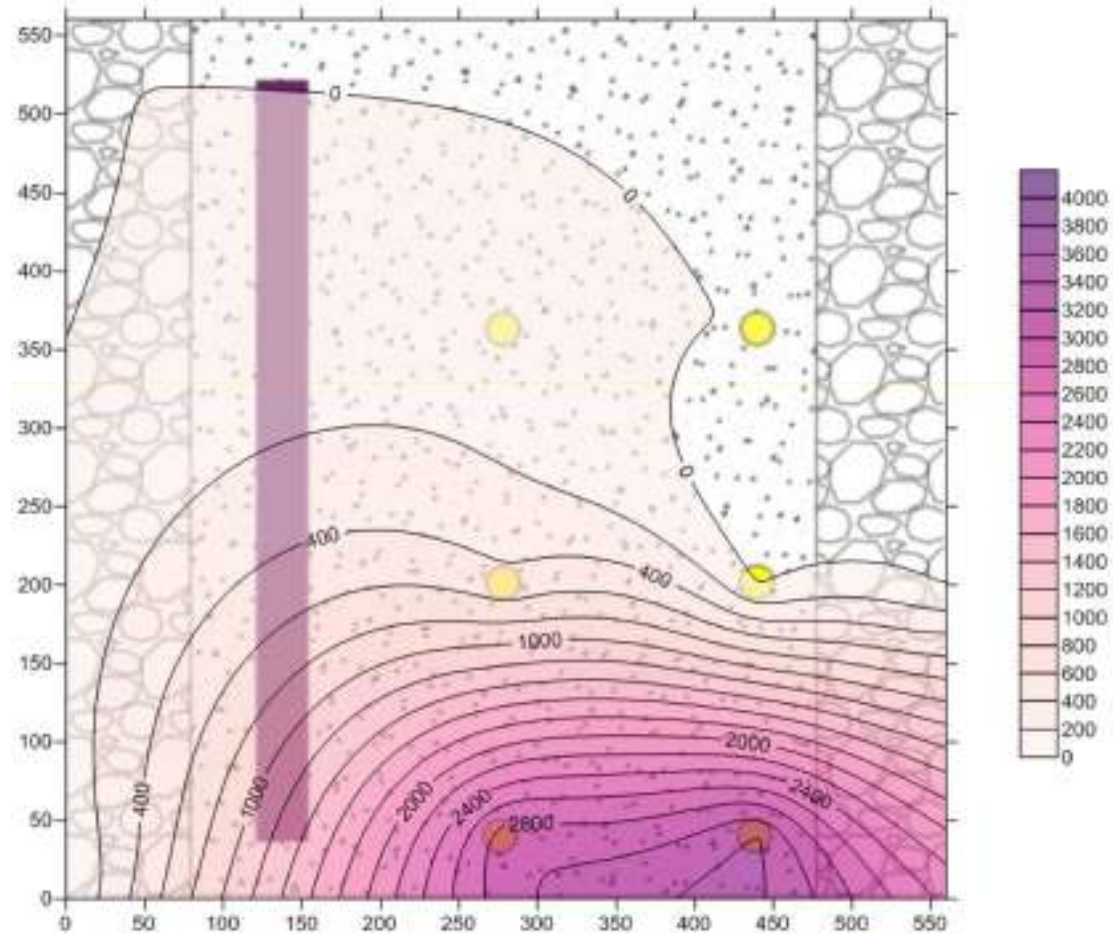


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MnO_4^- distribution (t=2 hours)

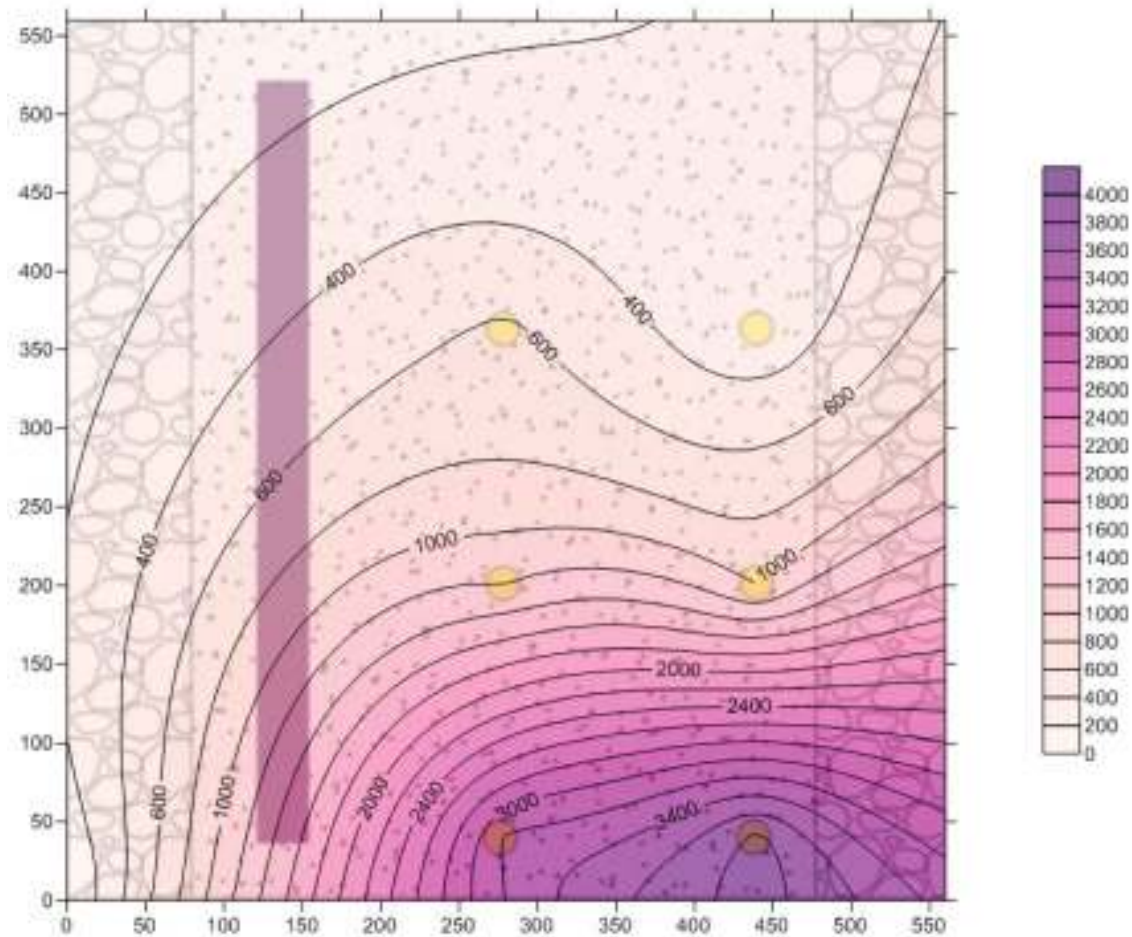


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MnO_4^- distribution (t=8 hours)

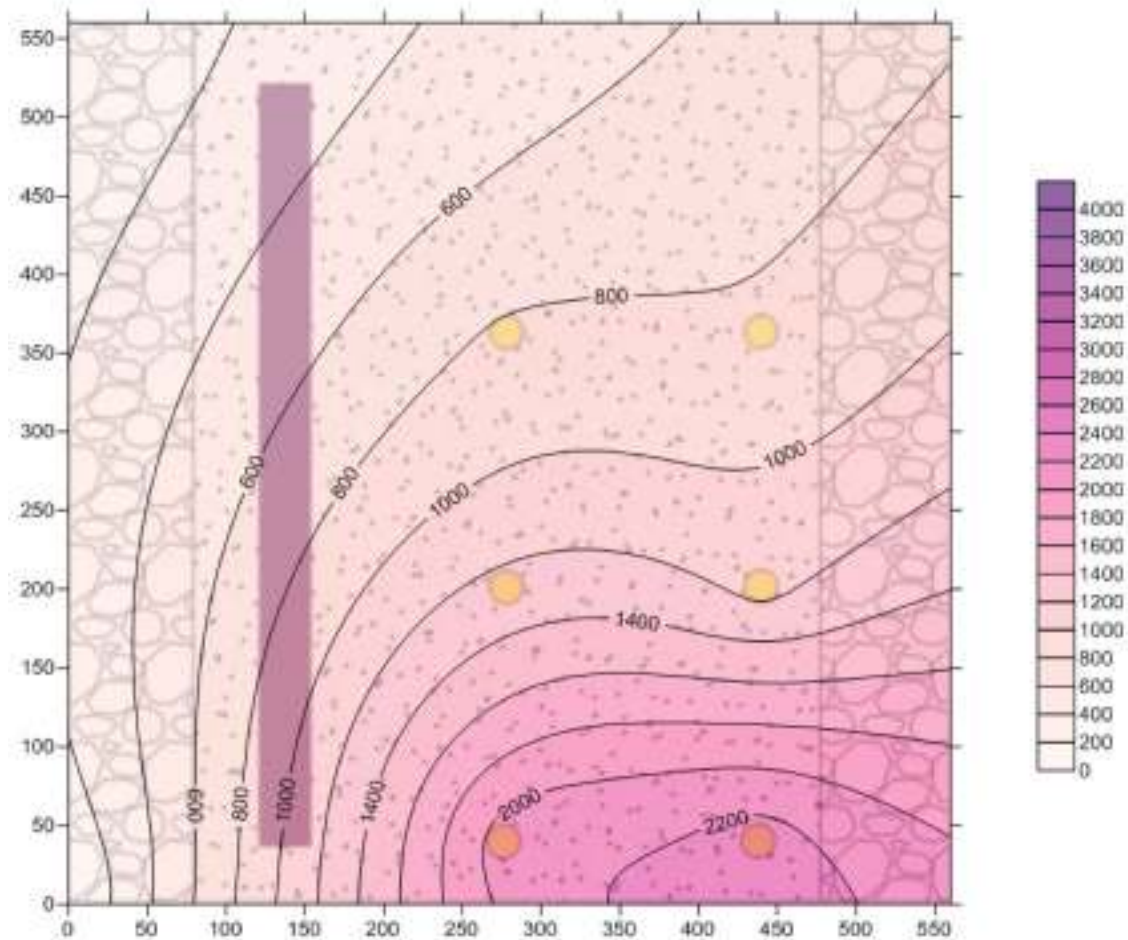


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MnO_4^- Distribution (t=26 hours)

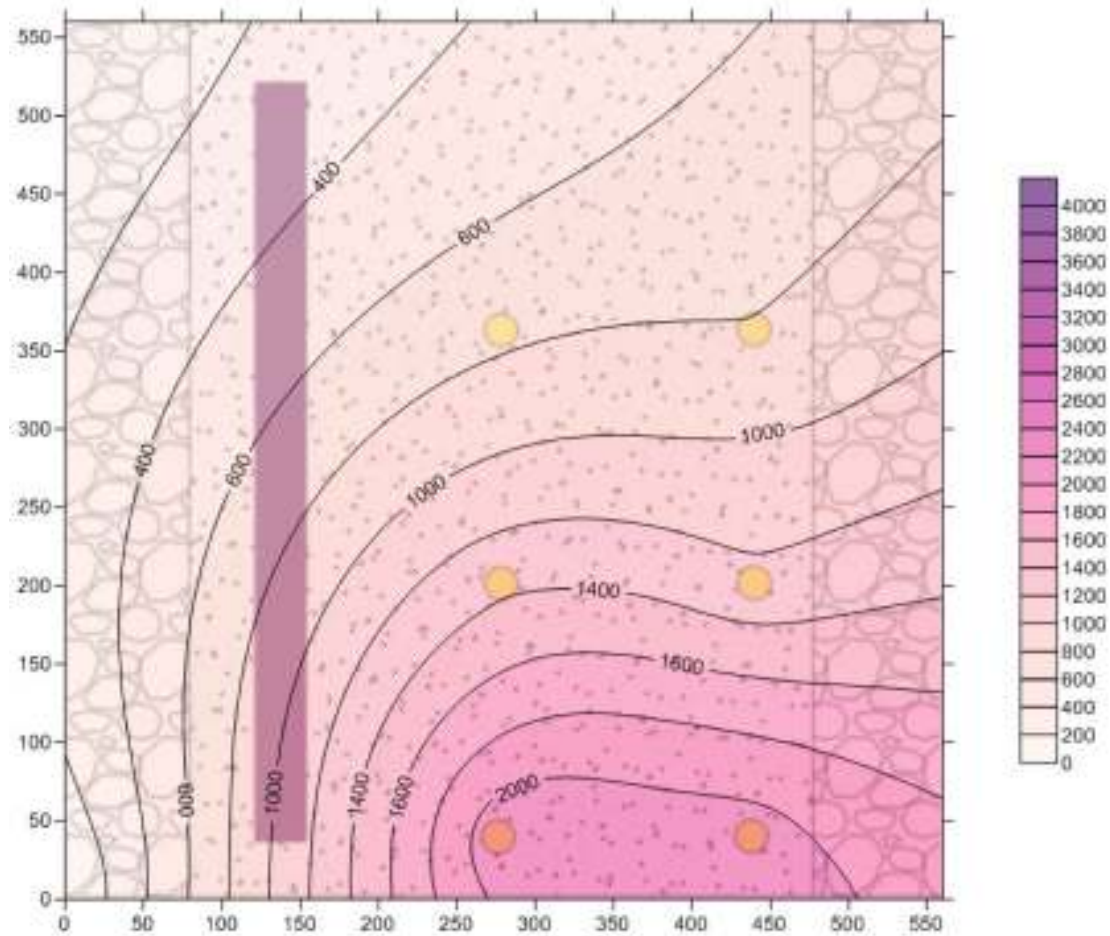


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MnO_4^- Distribution (t=32 hours)

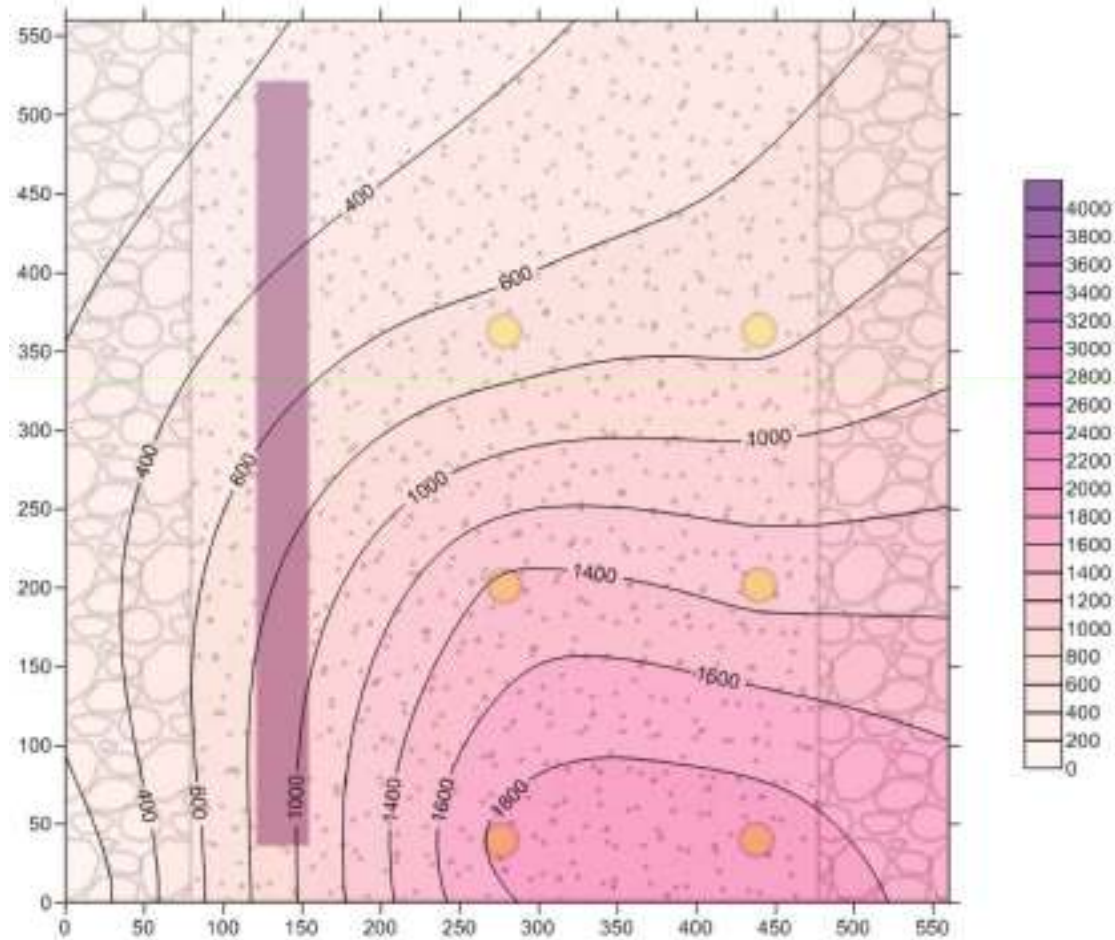


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MnO_4^- Distribution (t=50 hours)

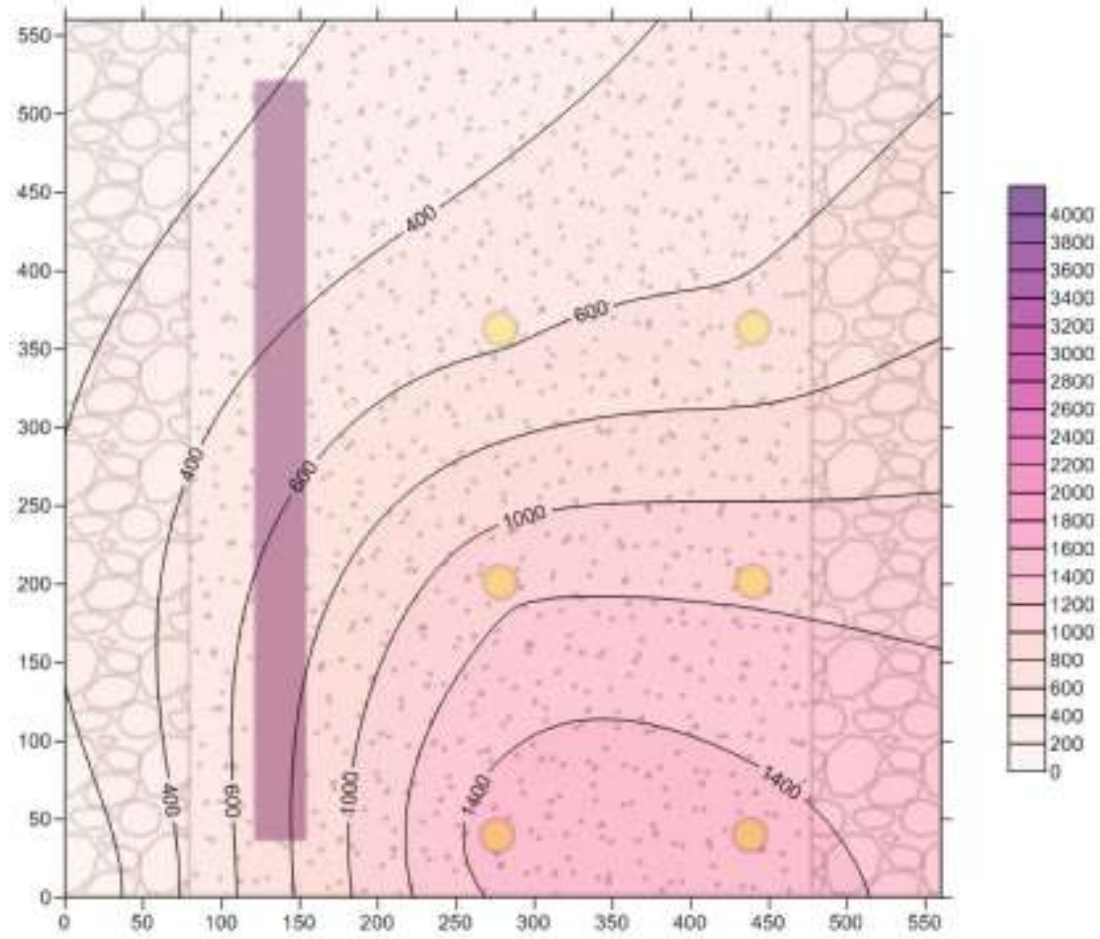


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MnO_4^- Distribution (t=74 hours)

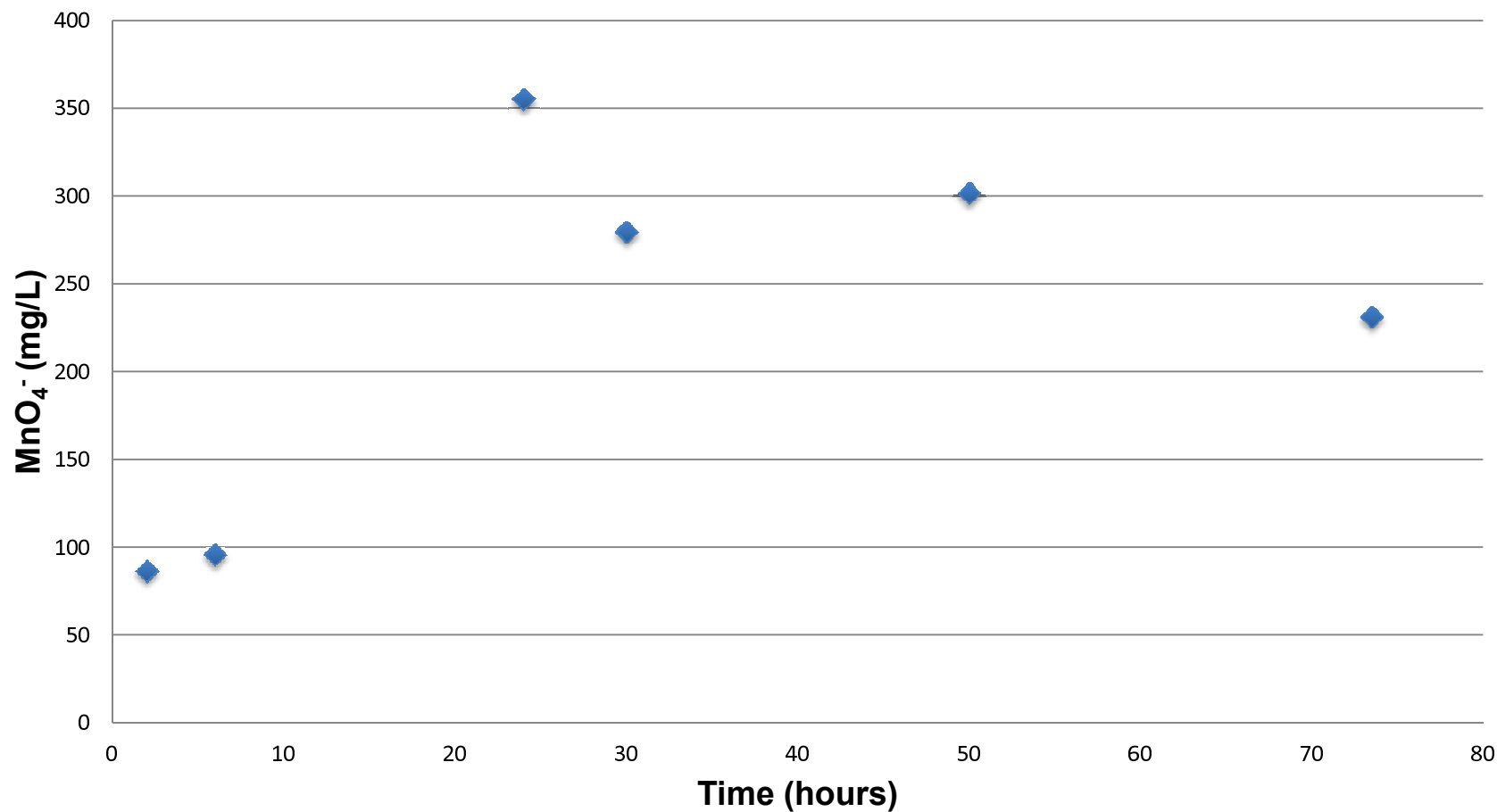


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MnO_4^- Concentration Effluent



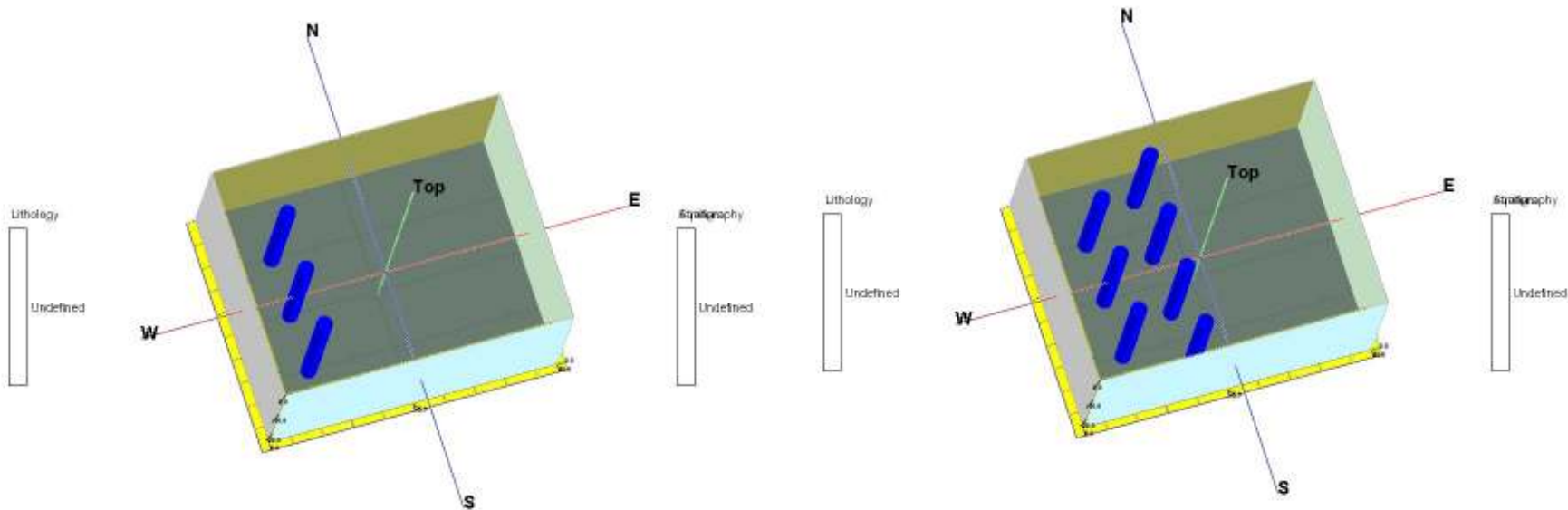
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Next Steps: 3-D Tanks/Design Tool

- 3-D Tanks to evaluate effect of ROI, PNOD, heterogeneities, GW velocity on candle performance
- Develop design tool (Collaboration with Clarkson)



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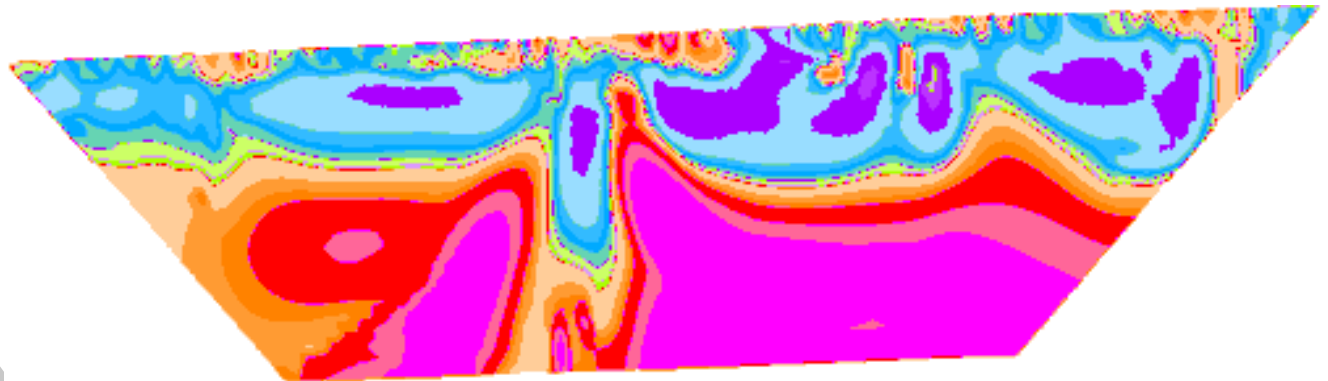


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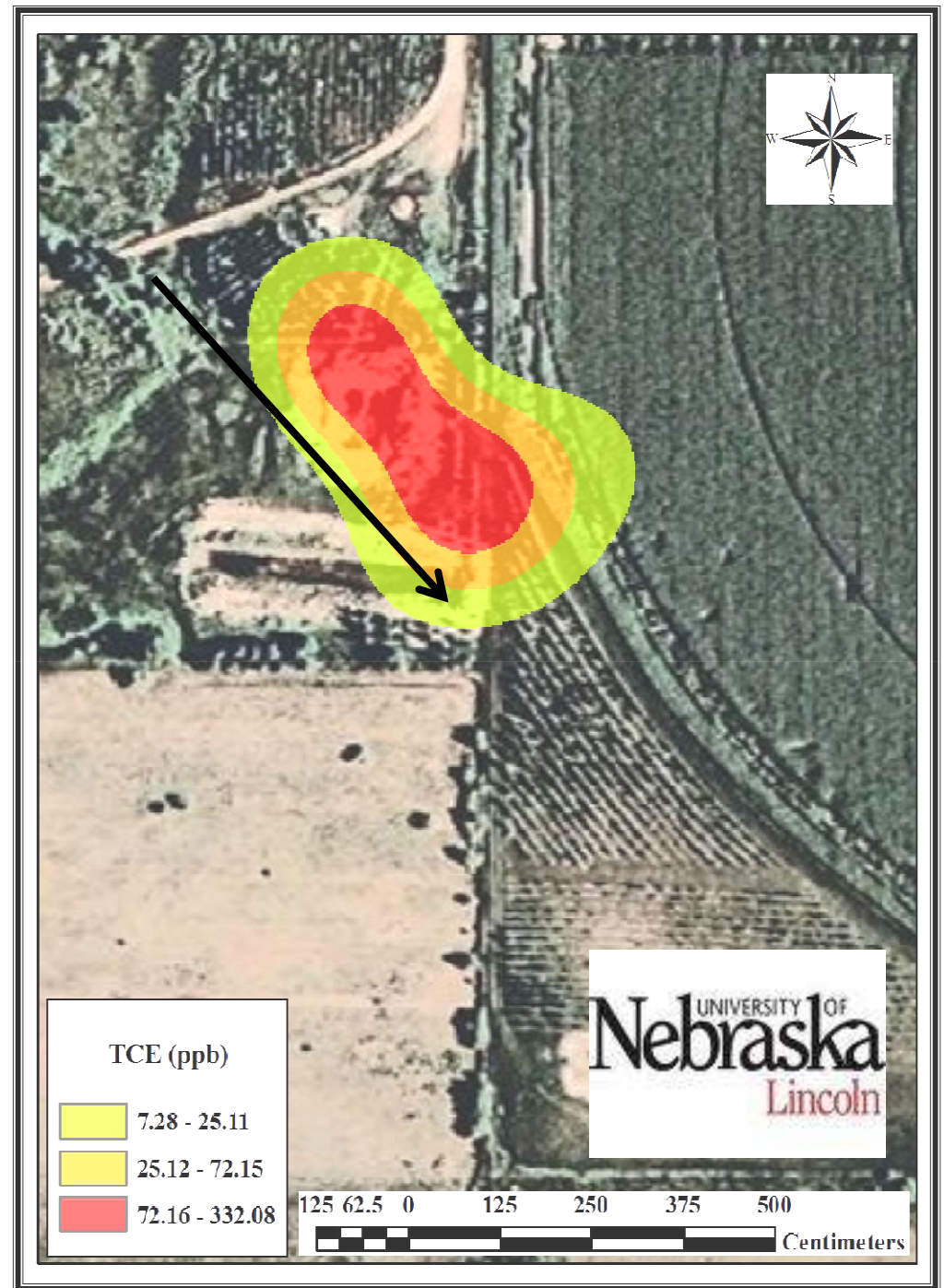
RemOx[®] SR Early Field Applications

Cozad Former Solid Waste Disposal Site

University of Nebraska
Dr. Steve Comfort



- Facility closed after TCE contamination found in underlying aquifer
- Majority of TCE in a low permeable silty-clay unit near surface of water table
- TCE (100-600 ppb)
- Darcy velocity = 0.045 in/day
- UNL with NDEQ wanted to implement low-cost passive system for TCE treatment in low permeability unit





**3-in
well
candles**

In situ
candle
holder &
insertion
tool to
emplace
SRPCs in
3-inch
wells



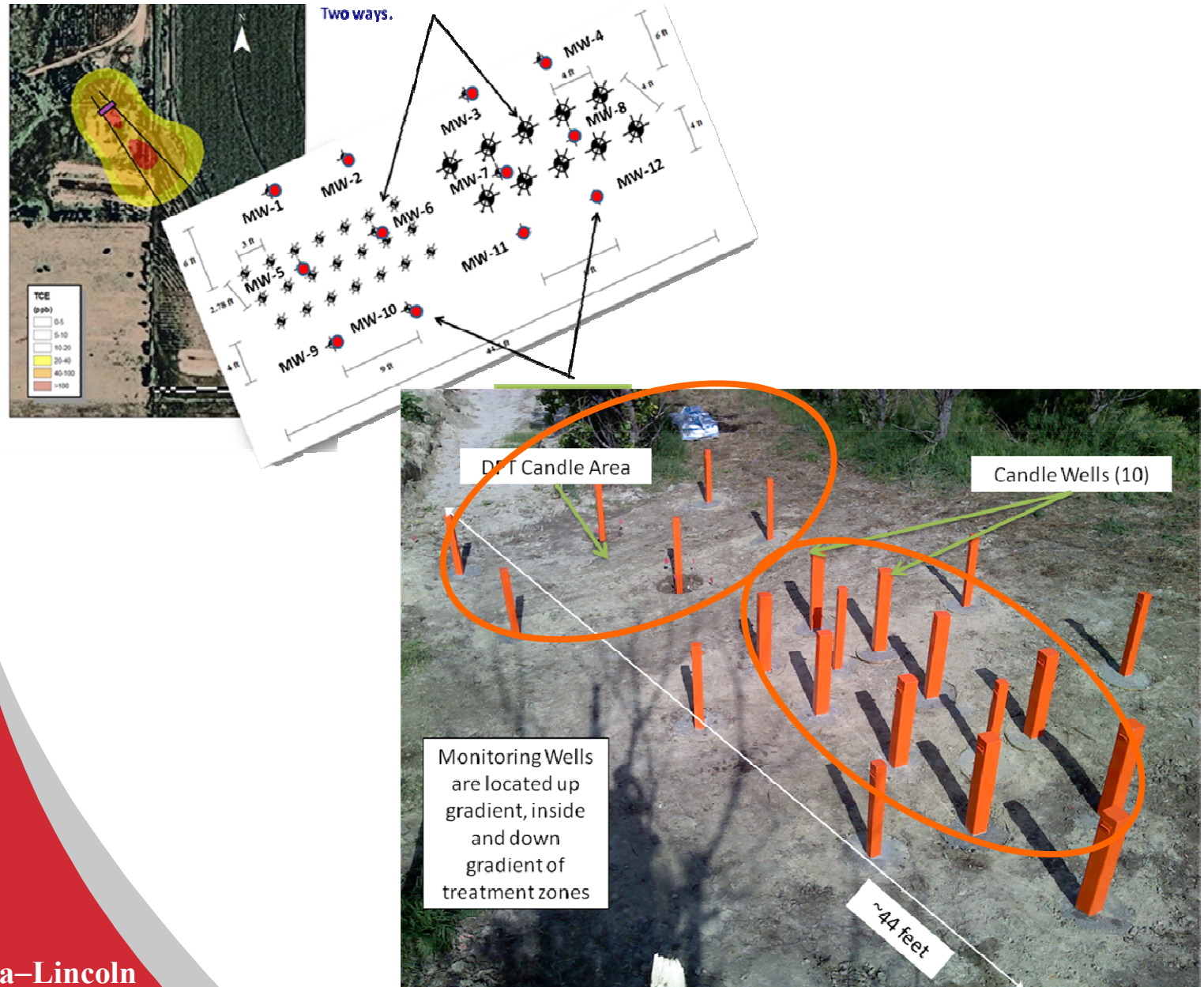
**2-in
DPT candles**

SRPC Reactive Barrier Installation

- 50 three inch injection well SRPCs
- 105 two inch DPT SRPCs

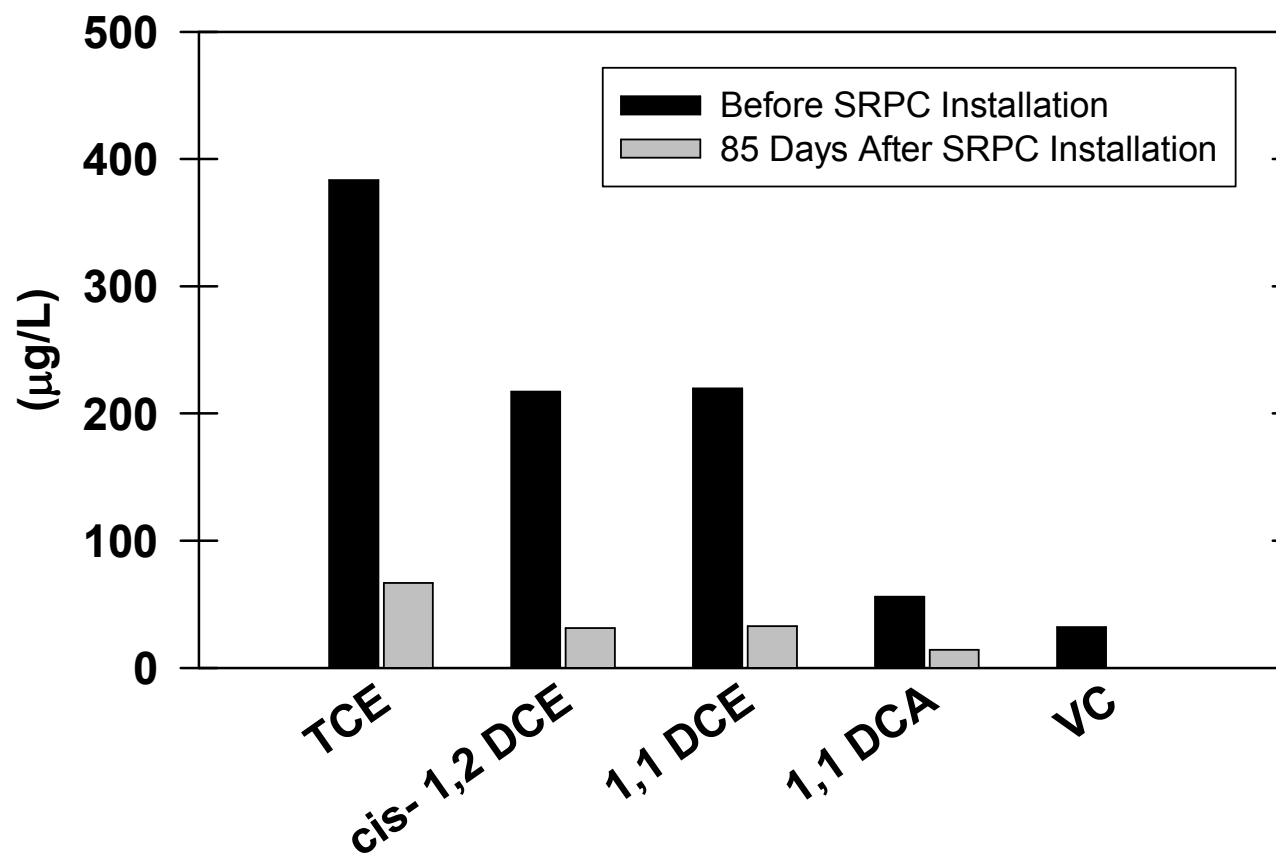


University of Nebraska-Lincoln



Results

Contaminant Concentration in Reactive Barrier
Well MW-8, 11 ft (bgs)



- Barrier installed June 2010
- After 85 days 64%-82% TCE reduction



Results

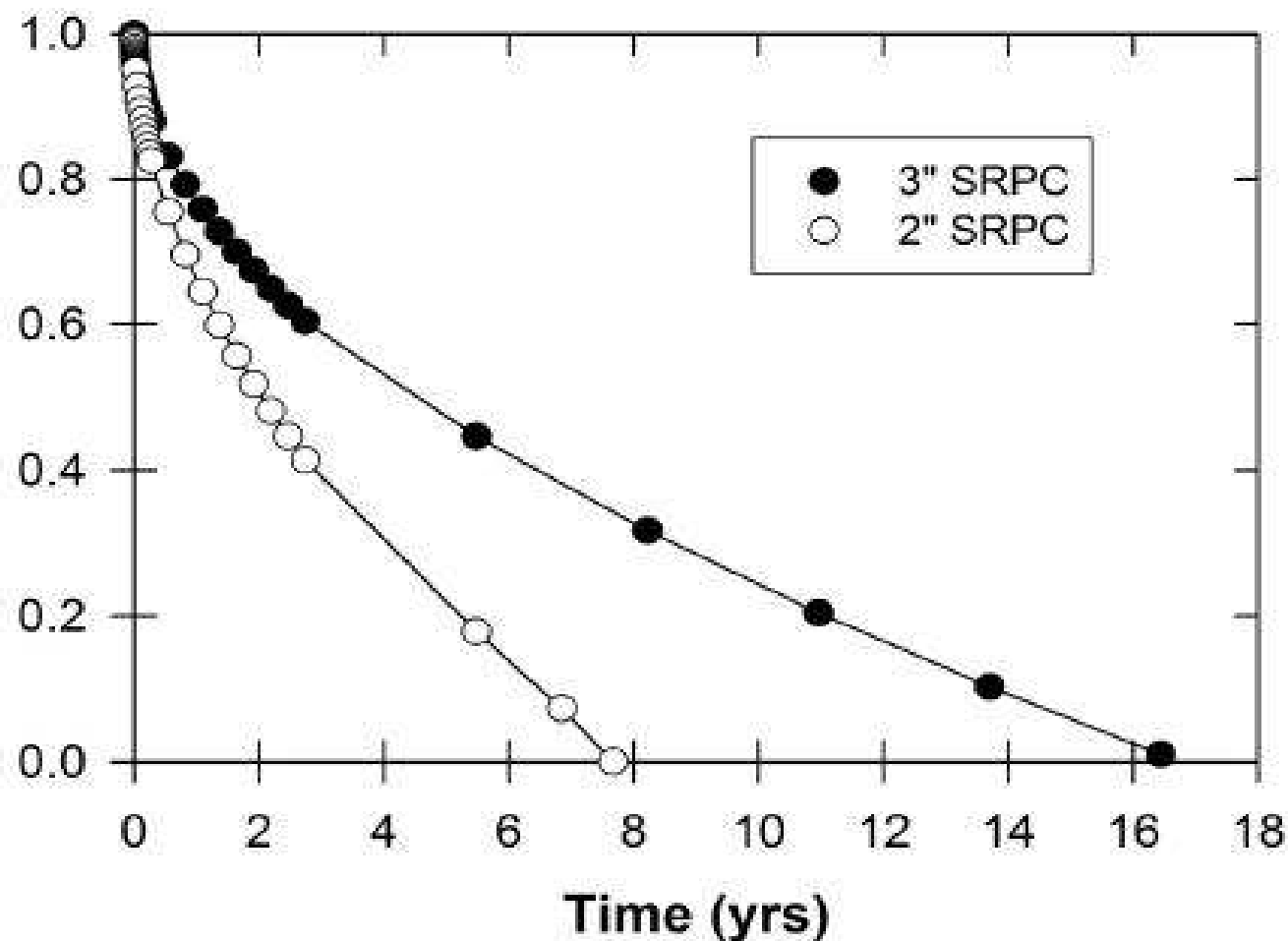
Slow Release Permanganate Candle Life Expectancy

8 year life expectancy for 2" SRPC

16 year life expectancy for 3" SRPC



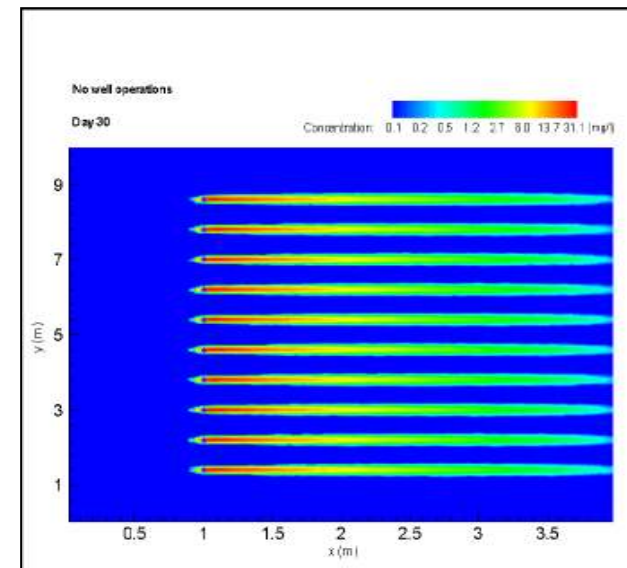
Percent KMnO_4 Remaining in SRPC





Next Steps...Exploring Key Issues

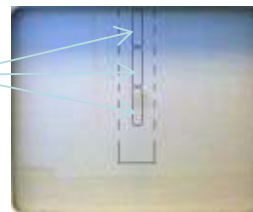
- Slow-release permanganate candles installed in wells (Lee and Schwartz, 2007)
- Lack of lateral dispersion could reduce treatment efficiency
- Requires close spacing of candles
- With wide spacing need ways to provide mixing...



Mini-candles in saturated tanks with and without re-circulator



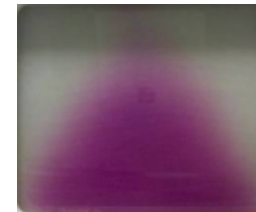
Candle
Location



T = 0



1 day



2 days



3 days

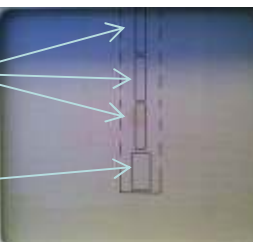


4 days

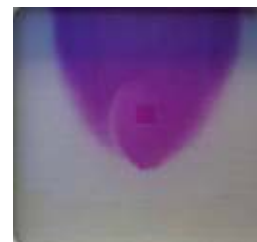


5 days

Candle
Location



T = 0



15 min



30 min



45 min



60 min



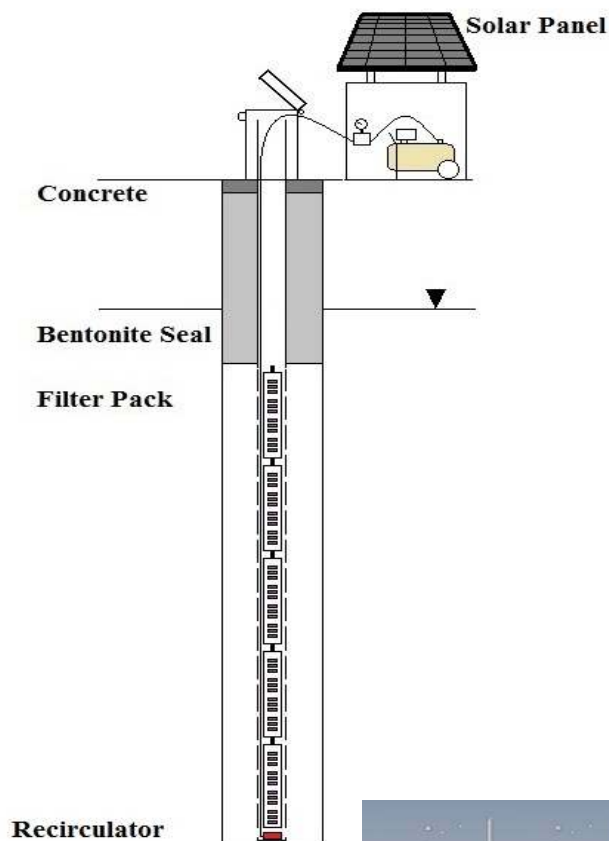
75 min

Re-circulator

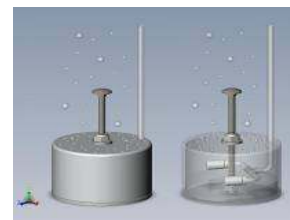
Proposed Modification to Current Treatment



Injection Well Design



Candles with solar-powered recirculator



After inserting the recirculators (and 342 days after candles were installed) there is a 64%-100% reduction in TCE





Specialty Earth Sciences:
Pilot Scale Installation
for
Low Permeability Media Source
Zone Treatment



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Pilot-Scale Sustained-Release Permanganate



- Client seeking remedial solution with potential for cost savings for site in MS with PCE contamination
- Difficult to remediate low permeability soils present
- Site logistics and tenant business operations required:
 - Rapid implementation leaving structures undisturbed
 - Minimized recurrent on-site events



Pilot-Scale Sustained-Release Permanganate



- This site had two vertical zones of PCE impact (shallow and deep zones)
- Groundwater movement in the shallow zone (0-45 bgs)
 - Mississippi blue clays 10^{-9} cm/s
- Groundwater movement in the deeper zone clayey sands (>45 bgs)
 - ranging from 10^{-3} cm/s to 10^{-4} cm/s

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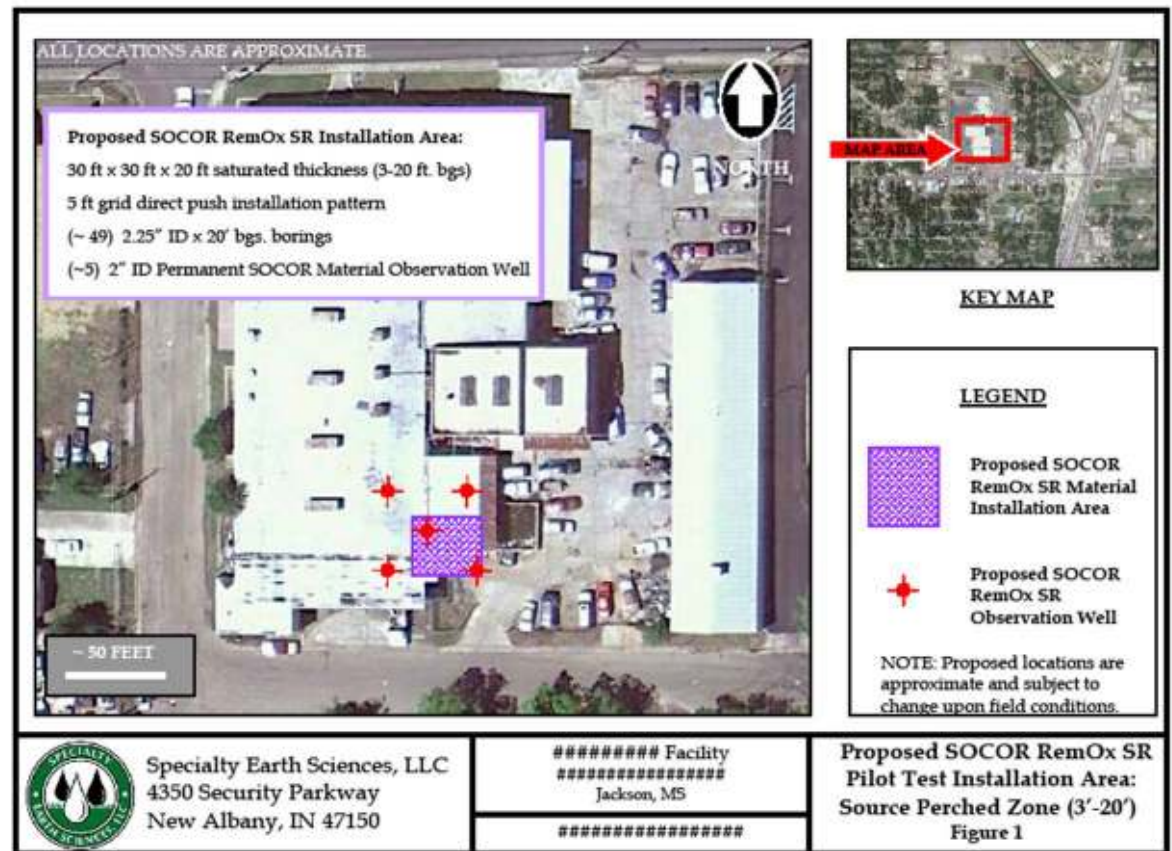
Pilot-Scale Sustained-Release Permanganate



-Shallow zone layout
(3 ft. to 20 ft. below
grade target interval)

-Rectangular grid
DPT installations (5
ft. on center
spacings)

-(2) product
consumption
monitoring wells, (3)
performance
monitoring wells

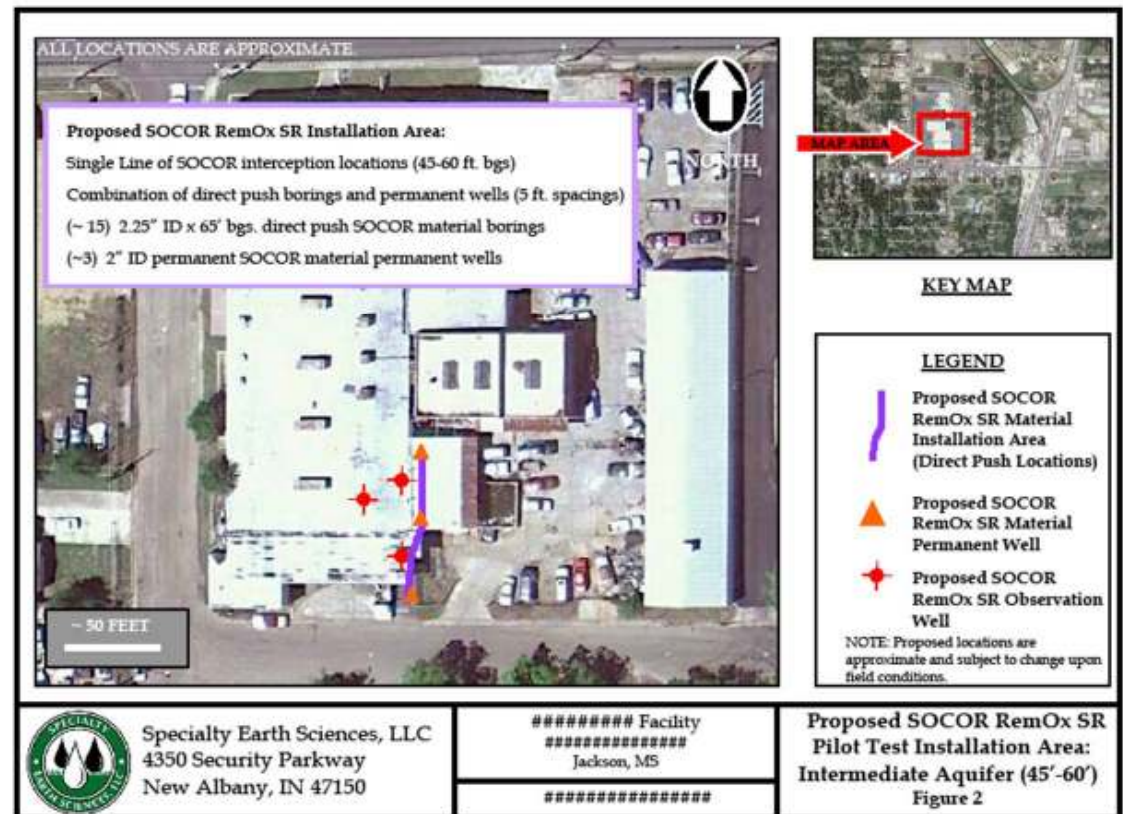




Pilot-Scale Sustained-Release Permanganate



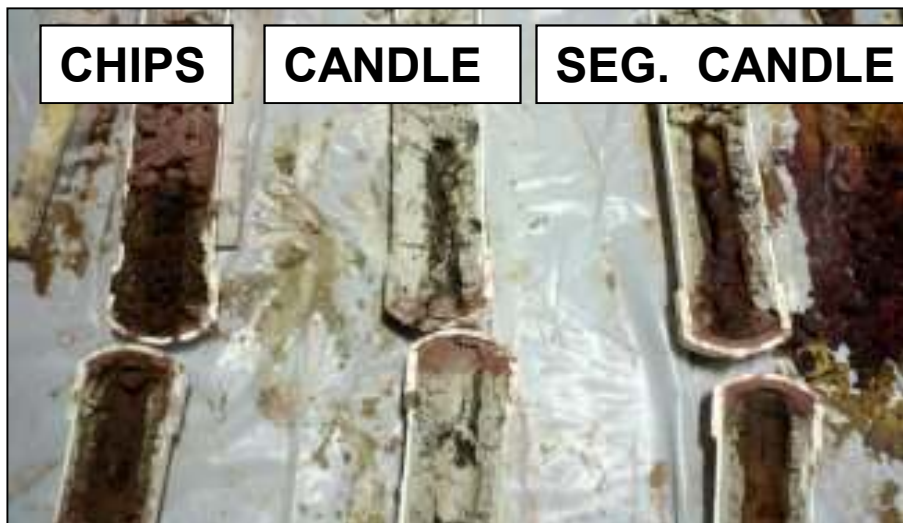
- Deeper transmissive zone
- 45 ft. to 60 ft. below grade target interval.
- Reactive barrier pattern direct push installations (5 ft. on center spacings)
- (3) product consumption monitoring wells (3) performance monitoring wells.



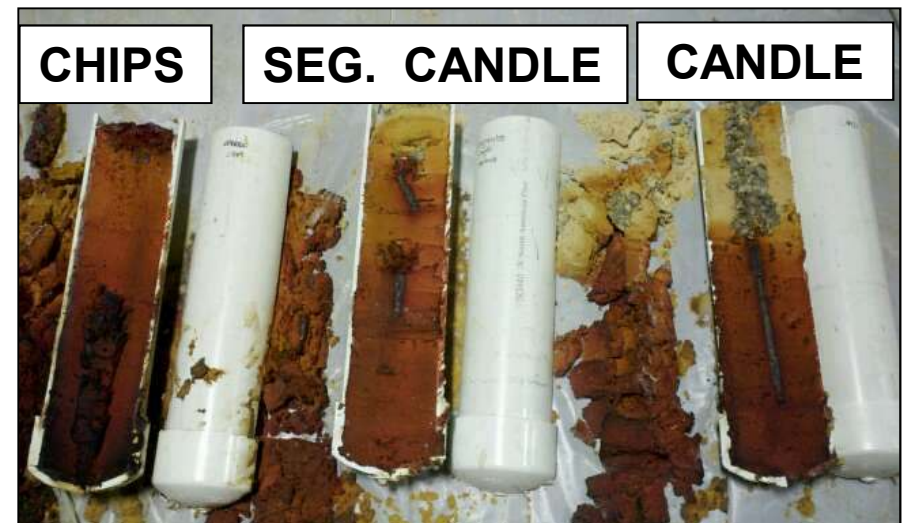
Pilot-Scale Sustained-Release Permanganate



- Simulations with candles and chipped material in medium to fine sands and in clay
- Enhanced permanganate release in clay was seen with chipped material (better contact between SR material and the borehole wall aiding in improved diffusion into LPM)



CLAYS



SANDS

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Pilot-Scale Sustained-Release Permanganate



- 348 candles* emplaced with direct push (*approx 40% in chipped form)
- 27 candles installed in stainless steel candle holders



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Direct Push Installation



- Direct push installation - 2.25 inch tooling and disposable tip
- Lowering candles within inner space of rods provides confirmation that candle has been placed at desired vertical depth
- String and “removable eye hook” assembly are removed and rods retracted with candles remaining in place within the formation



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Pilot-Scale Sustained-Release Permanganate



- Candles within stainless steel candle holders secured to flush mount cover with stainless steel wire and clamp
- Candles can be removed and weighed for relative comparison against baseline measurements
- In-well candle consumption rates can be utilized to infer overall consumption within the target area



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Field Implementation Cost Savings (Candles vs Liquid Injection)



- Mississippi Site (Sustained-Release Candles) (shallow interval treatment):
- Conductivity: 10^{-9} cm/sec
- Target interval: 3-20 ft bgs
- Total pounds of permanganate: 1053 lbs
- On-site labor: 2 field professionals + Geoprobe for 4 days (approx \$12,000)
\$11.40 in field labor per lb of permanganate applied
- Northern KY Site (Liquid Permanganate Injection):
- Conductivity: 10^{-6} to 10^{-7} cm/sec
- Target interval: 2-8 ft bgs
- Total pounds of permanganate: 440 lbs
- On-site labor: 2 field professionals + Geo-prober for 4 days (approx \$12,000)
\$27.27 in field labor per lb of permanganate applied

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RemOx[®] SR Possibilities

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1. Minimal aboveground infrastructure required for applications



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1. Minimal aboveground infrastructure required for applications
 - No Tanks, Water needs, Dust, Pressurized injection
 - Very good health and safety profile

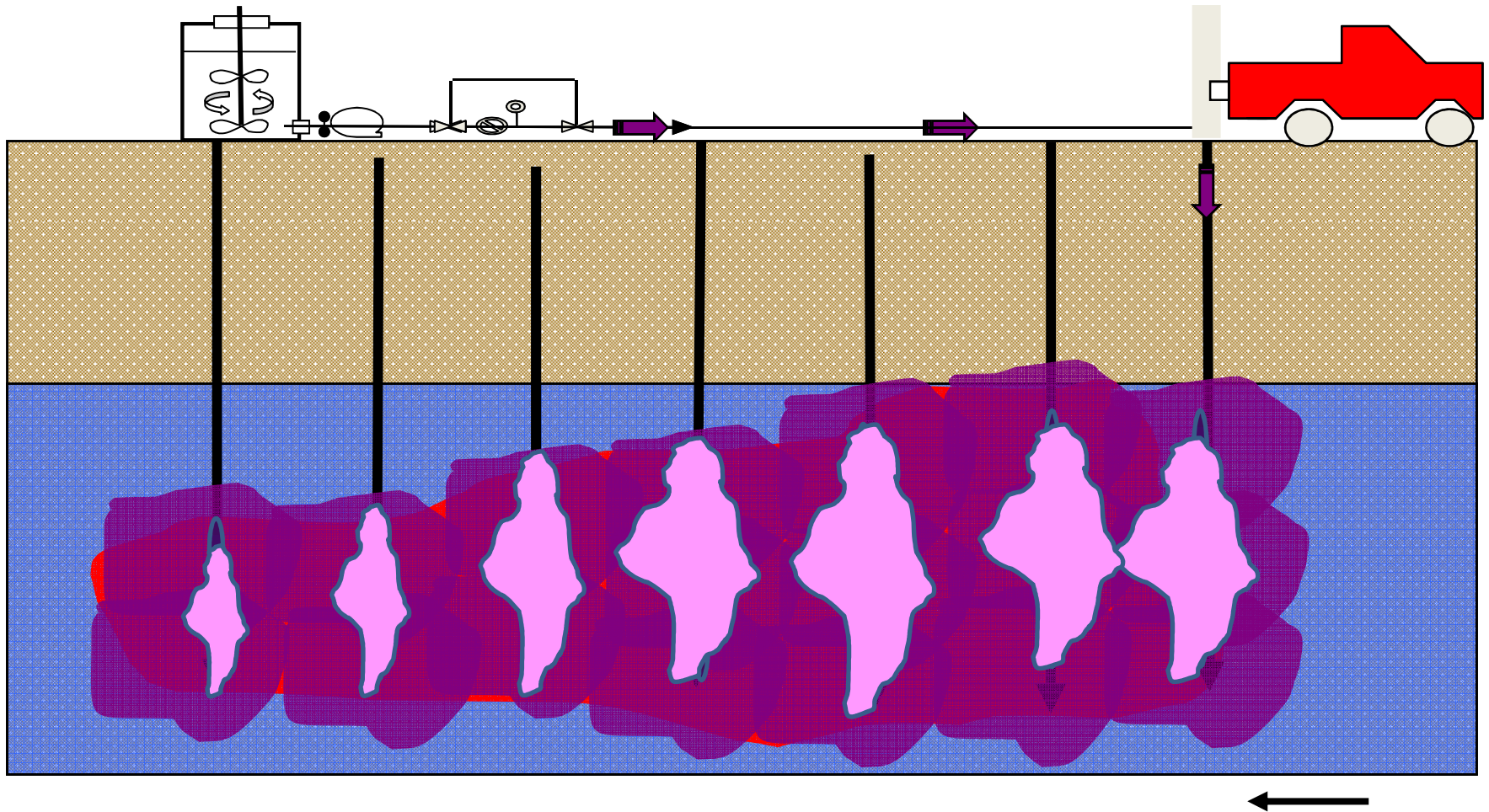


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2. Get two injections for the price of one
 - Long term treatment of residual absorbed material



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3. No liquid. No surfacing of liquids

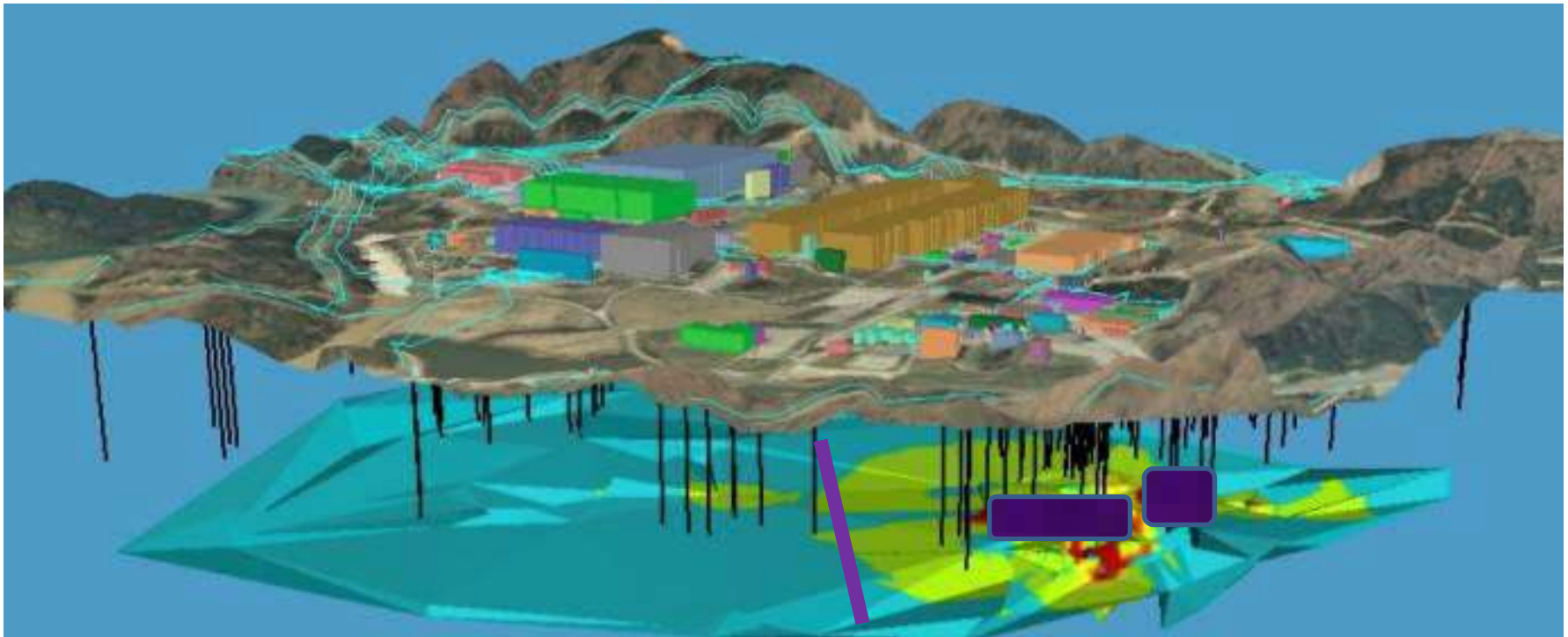


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4. Ability to approach ISCO in an active stepped manner



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4. Ability to approach ISCO with some economic flexibility
 - Get more sites under active remediation with the same budget in a fiscal year
 - One of the financial negatives of ISCO is the speed that it works and the effect on cash flow.
 - If you do a full site for \$200K you will have to pay that in a fiscal year. With RemOx SR you can spread the cost out over more time to improve cash flow or allow use at more sites
 - One prime example is orphaned dry cleaning sites
 - Active facilities with risk
 - Not well funded
 - Large volume
 - For the cost of remediating one site (\$200K) you could get 10 sites with active hot spot treatment with little impact to business and expand over time to complete remediation.

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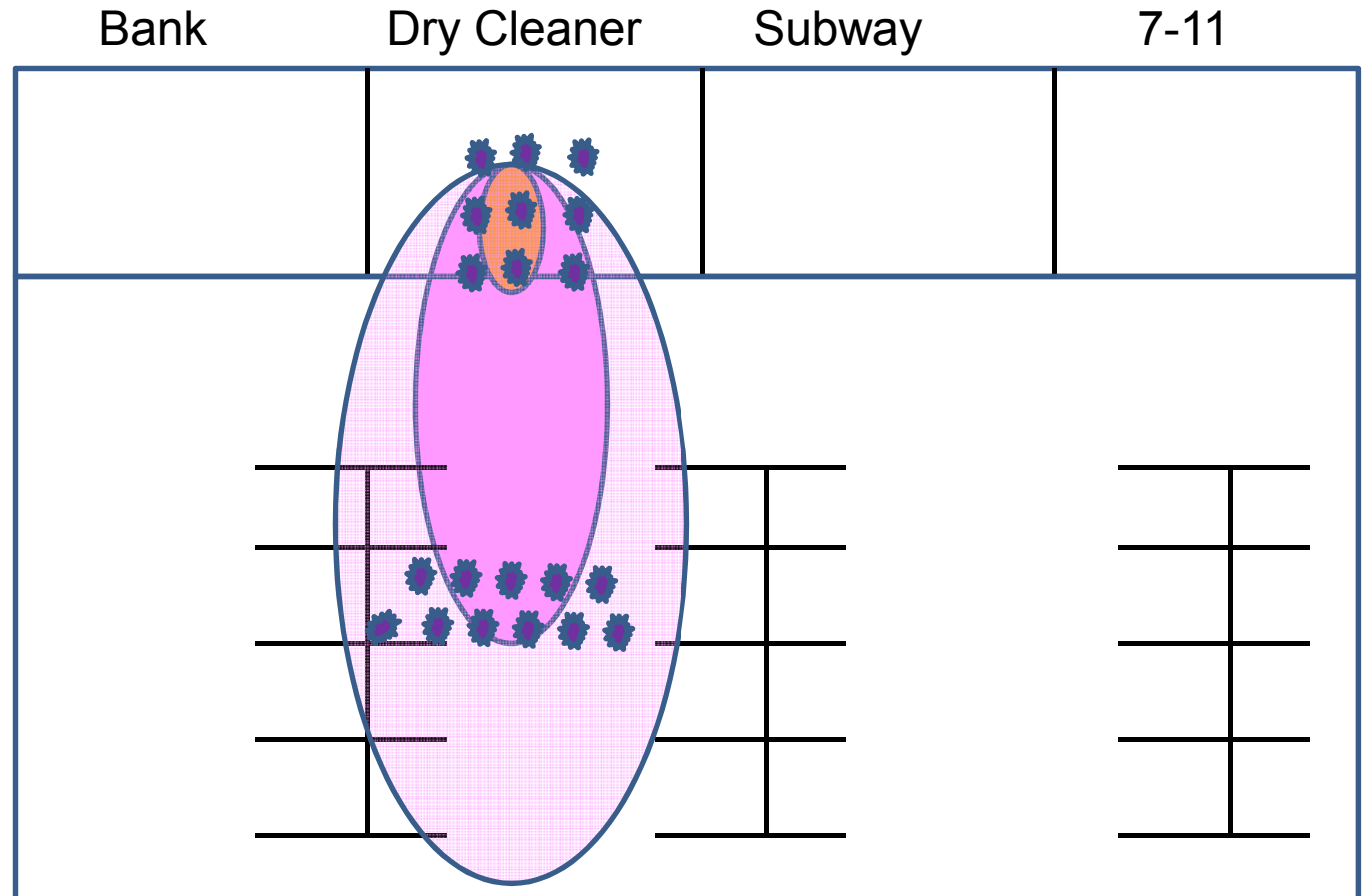
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\$200K Full Scale

- Close Store and disruption to businesses

\$30K With RemOxSR

- 2 nights with Geoprobe = \$2,800
- 2 techs 16 hrs each @ \$125/hr = \$4,000
- 20 RemOx SR candles = \$8,000



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Questions?

