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Passive Groundwater Plume Treatment using Sustained-Release Oxidants: Experimental and Modeling Studies

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Agenda

- Technology Description
- Laboratory Experiments
- Pilot-Scale Studies
- Design Tool Development
- Conclusions/Questions

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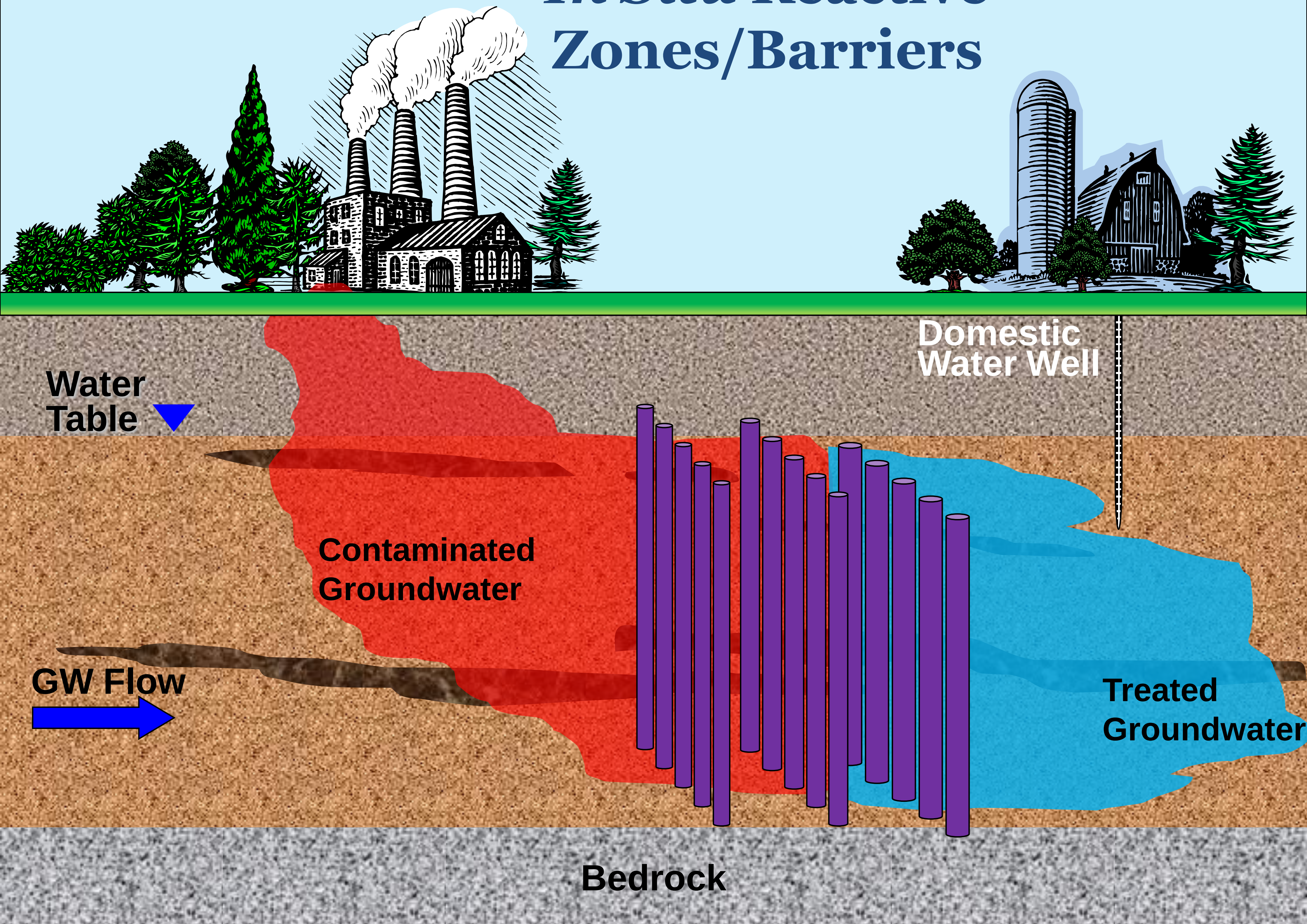
The Challenge...

- All remedial technologies have an impact...
  - Electricity/fossil fuel to power equipment
  - Aboveground treatment of extracted fluids
  - Site disruption/landfill disposal
- Reactive materials used successfully to remove contaminants in soil and groundwater
  - Do not require continued supply of electrical/fossil fuel energies
  - Serve as long-term, low-cost passive treatment

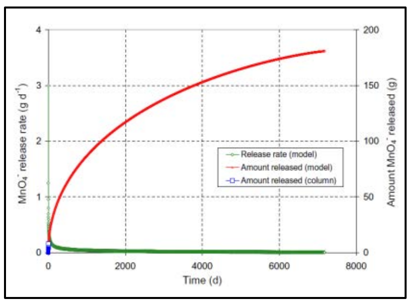
http://www.murraydemolition.com/

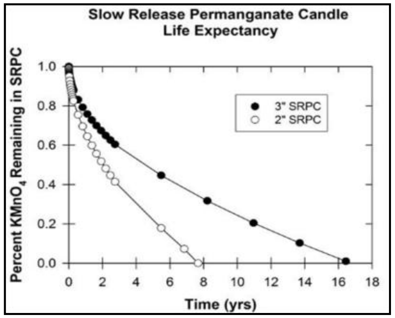
In Situ Reactive Zones/Barriers



Technology Development – Sustained-Release (SR) Oxidants

- Promising slow-release permanganate modeling, lab, pilot-scale field studies (e.g., Ohio State University, Clemson, University of Nebraska)





- 2003 Specialty Earth Sciences-patented methods of encapsulation for sustained-release of reactants
- Variety of reactive materials are possible
  - Oxidants, bio-amendments, oxygen release compounds, activators, chelating agents

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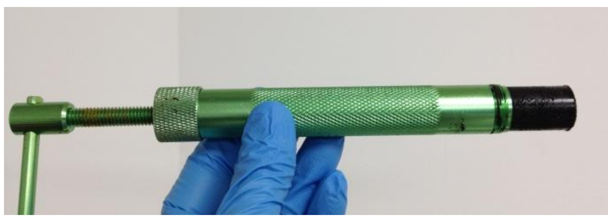
Technology Development – Sustained-Release Oxidants

- Sustained-release permanganate is a $KMnO_4$-based product dispersed in a solid paraffin wax matrix (~80% w/w)



- Sustained-release persulfate is a NaS_2O_8-based product dispersed in a solid paraffin wax matrix (50-80% w/w)

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SR Technology - Versatility in Form

- Solid product formed as cylinder, chipped for trench/barrier applications or small pellets (1-2 mm) for hydro-fracturing into low permeability media/fractured bedrock
  - 1.35 or 2.5 inch diameter
  - 3.4 cm/6.4 cm
  - 18 inches long (46 cm)
  - DPT emplacement or well installation

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Direct Push Installation

- Direct push installation - 2.25 or 3.25 inch tooling and disposable tip
- Lowering cylinders within inner space of rods provides confirmation that cylinder placed at desired depth
- Rods retracted with cylinders remaining in place within the formation

In-Well "Cylinder Holders"

- Cylinders within stainless steel or plastic mesh candle holders secured to flush mount cover with stainless steel wire and clamp

- Cylinders can be removed and weighed for relative comparison against baseline measurements

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SR Technology - Versatility in Treatment of Contaminants

- Applicable to contaminants oxidized by permanganate (Lee and Schwartz, 2007; Christenson et al., 2012)
- Applicable to contaminants oxidized by persulfate (Kambhu et.al., 2012)
- Emerging contaminants (e.g., 1,4-dioxane)
- Can be applied in tandem or following ISCO or other remedial treatments to mitigate back-diffusion and contaminant desorption

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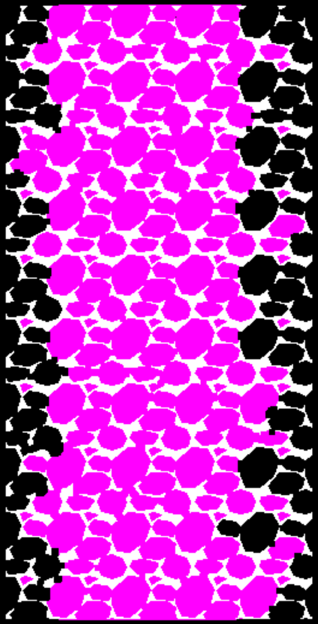
Conceptual Model for Oxidant Release from Paraffin Wax Matrix

MnO_4^- Release from Wax



- As permanganate solids dissolve void spaces are created

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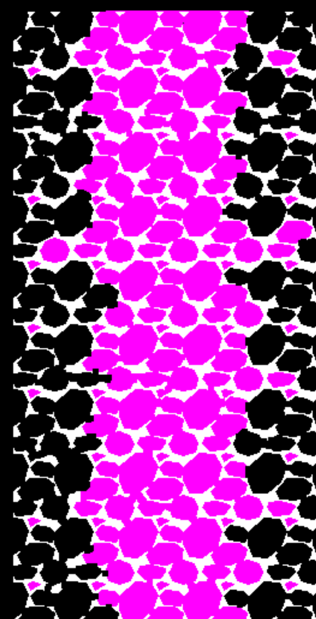
MnO_4^- Release from Wax



- Newly created void spaces expose permanganate solids for dissolution and diffusion
- Process occurs radially from the exterior of the cylinder to the inner core

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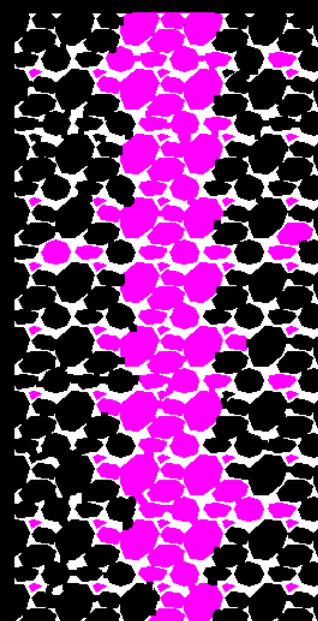
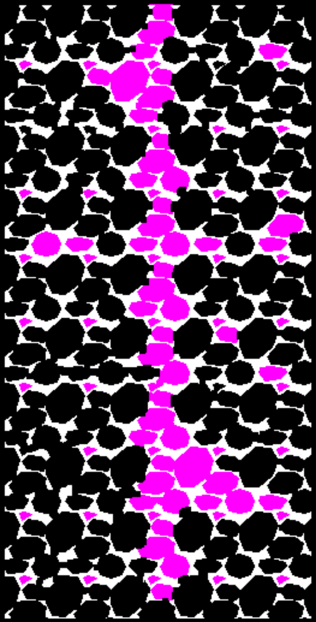
MnO_4^- Release from Wax



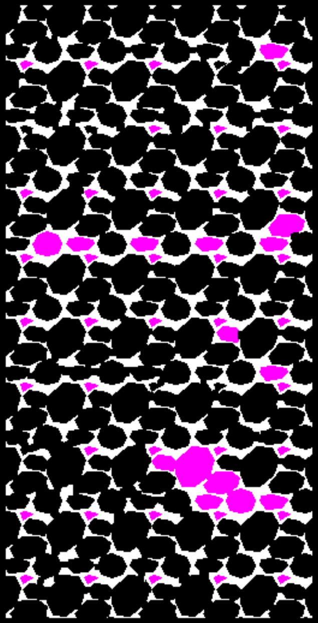
- As permanganate releases/reacts, porosity develops inward to the core of the cylinder
- Diffuses across a greater distance

MnO_4^- Release from Wax



- This is why we see and initial spike of permanganate in early time…

MnO_4^- Release from Wax



- And a significantly slower and lower release of permanganate at later times

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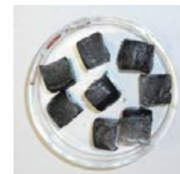
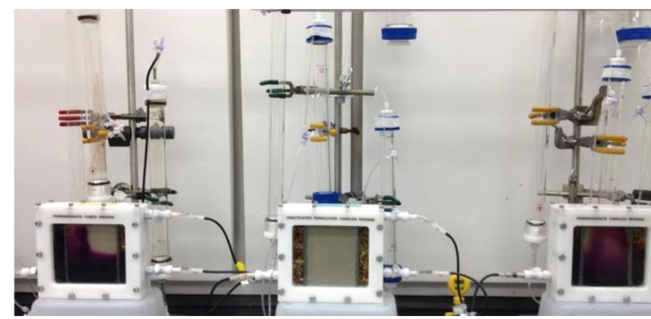
Experimental Approach – 1-D Columns and 2-D Mini-Tanks

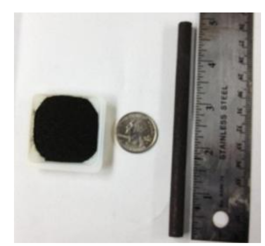
- Columns (30 or 60 cm x 4.8 cm)
  - Cubed material (TCE 0.7-1.5 ppm)
  - ***1.35 inch diameter/1 inch long***
  - ***2.5 inch diameter/1 inch long***
  - Flow rate (0.6 mL/min), 2 ft/day

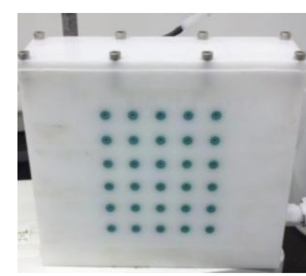


- 2-D mini-tanks (14 x 14 x 2.5 cm)
  - 0.27 inch diameter/5 inch long (DI)
  - Permanganate or persulfate mini-cylinders ***(10 grams of oxidant)***



- Purpose: evaluate oxidant release from SR material (cylinders, cubed, pellets), spatial distribution, and oxidative treatment of contaminants





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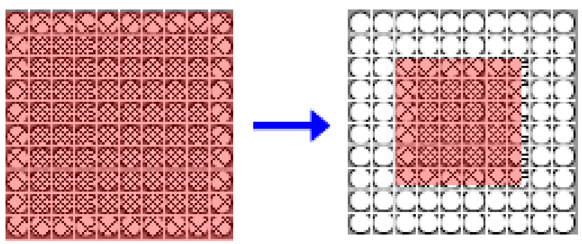
Approach - Sustained-Release Design Tool

- Collect oxidant release rates to support modeling of releases from cylinders, cubes, pellets/pastilles
  - Model adapted after Lee and Schwartz (2007)



Lee and Schwartz, 2007

$$Q = \pi h A(r_o^2 - r^2)$$

$$\frac{r^2}{2} \ln\frac{r}{r_o} + \frac{1}{4}(r_o^2 - r^2) = \frac{C_s D_e t}{A}$$

$$D_{et} = \frac{D_{e\,(t-1)}}{T}$$

- Q’ = quantity of $MnO4^-$ released per unit time
- C_s = $MnO4^-$ solubility
- A = Amount of $MnO4^-$ available for release
- D_e = effective distribution coefficient
- t = time
- h = length of candle
- r_0 = radius of candle
- r = radius $MnO4^-$ diffusion (new porosity development)

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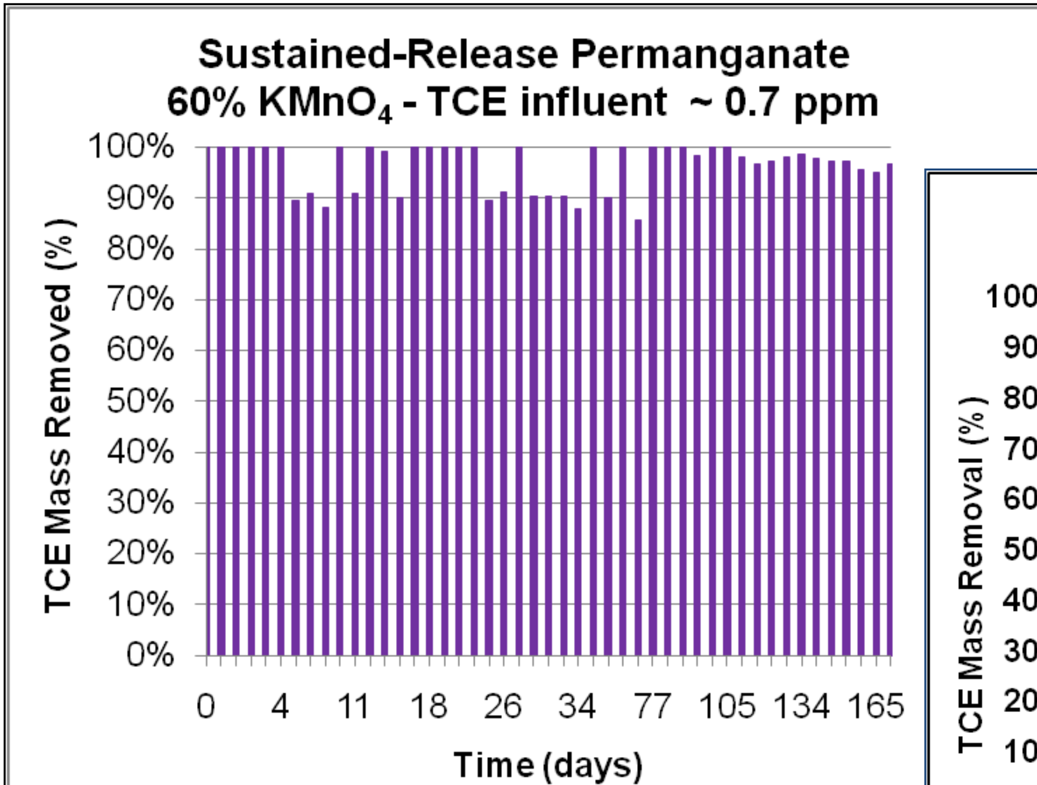
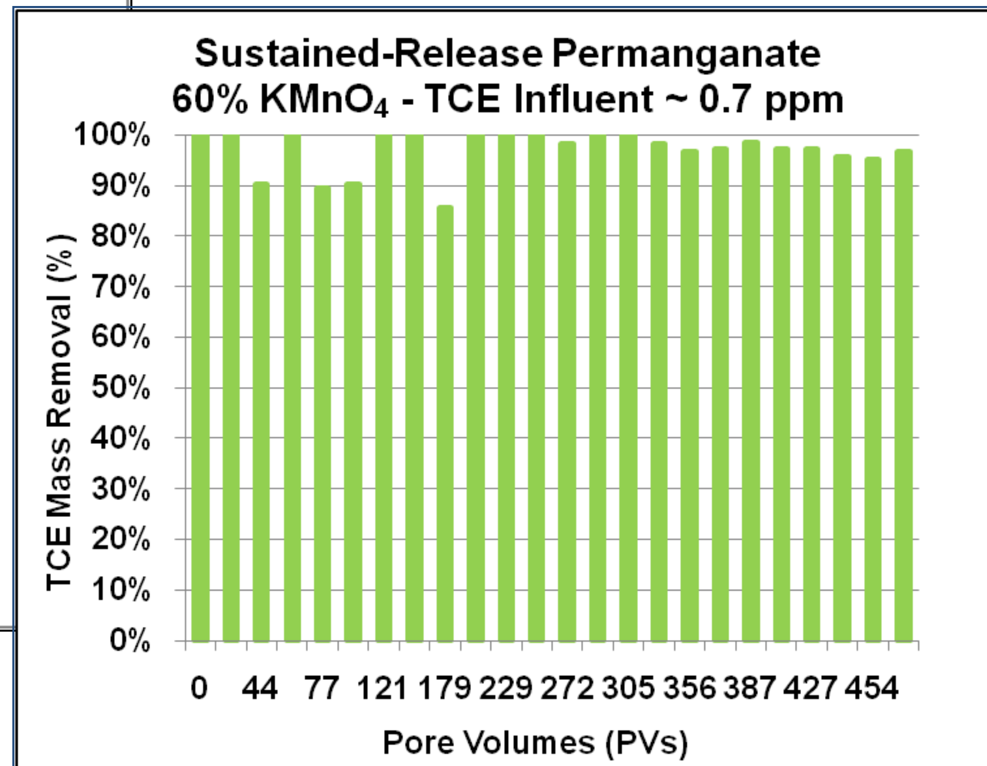
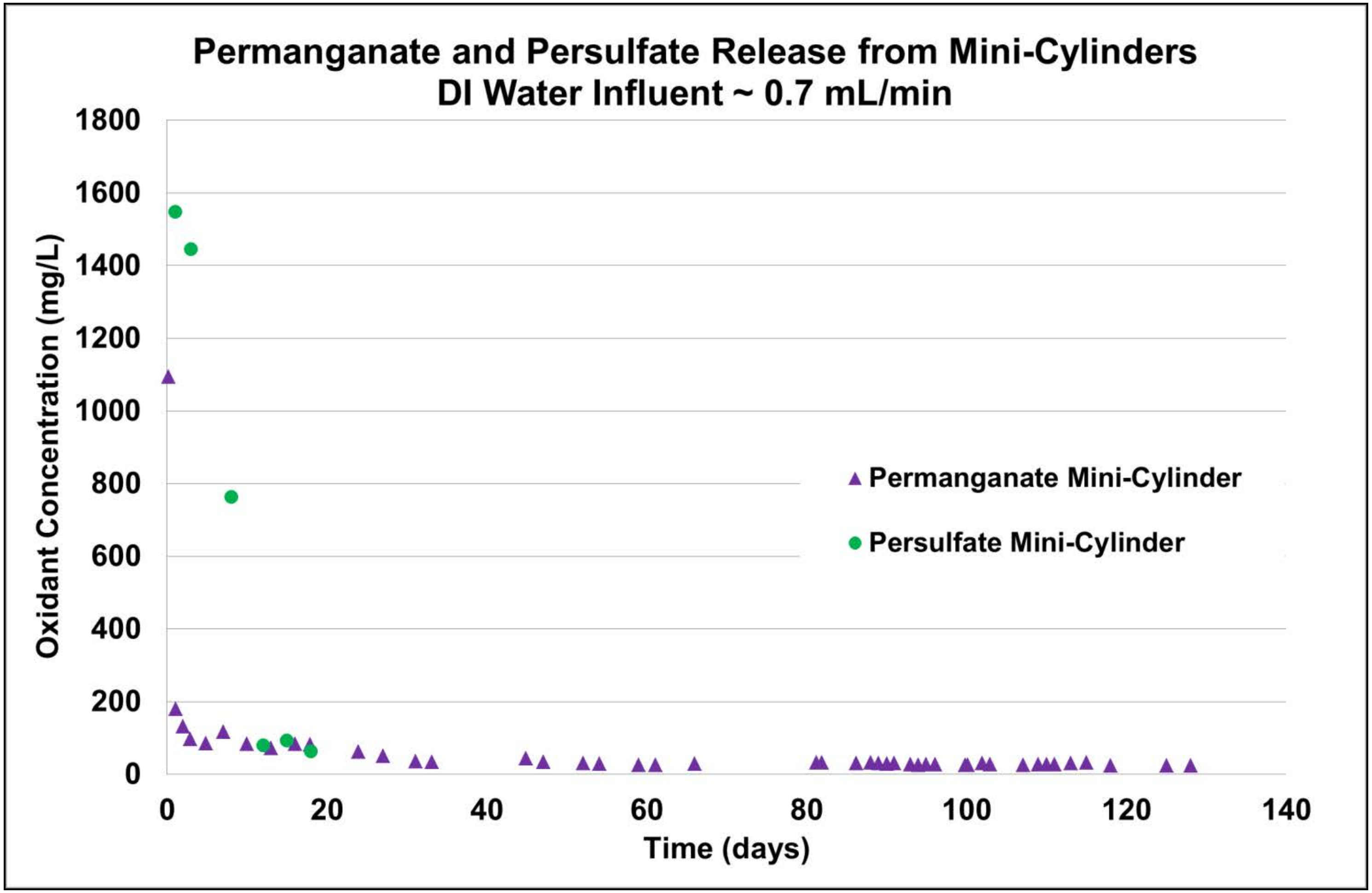
Results – 1D Column with Sustained-Release Cubes



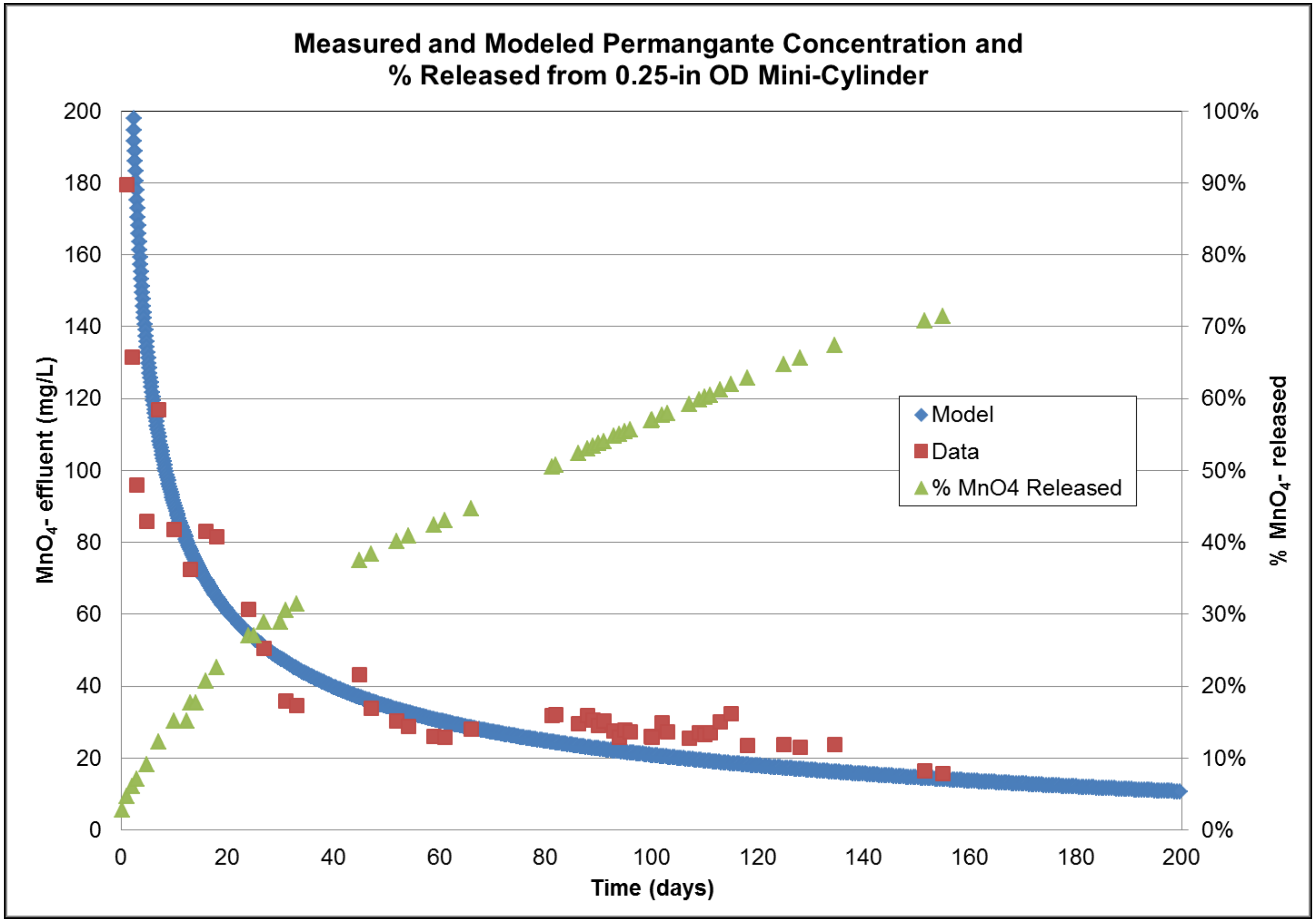


TCE mass removal 86% - 100% over 170 days or > 470 PVs

Results – 2-D Tanks (Influent-DI Water)



Results – 2D Tank (Influent-DI Water)

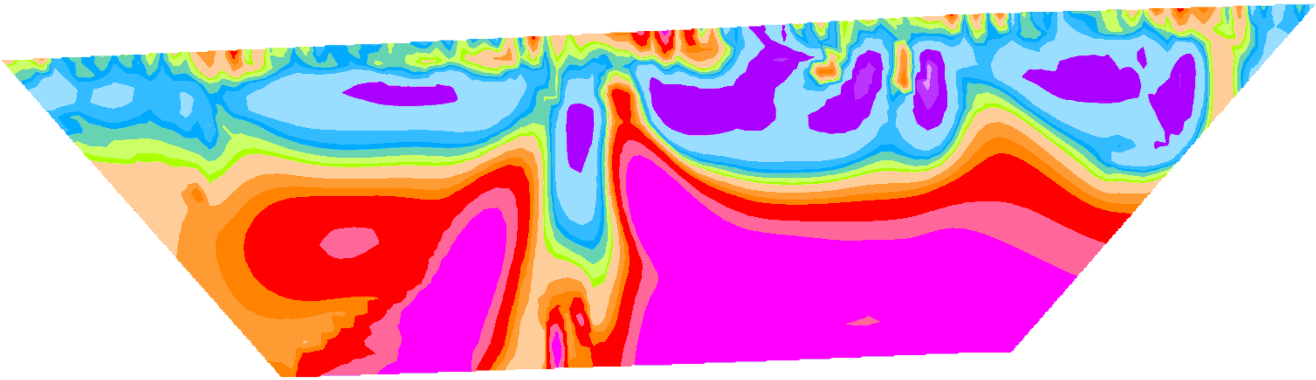


School of Natural Resources

Cozad Former Solid Waste Disposal Site

University of Nebraska

Dr. Steve Comfort

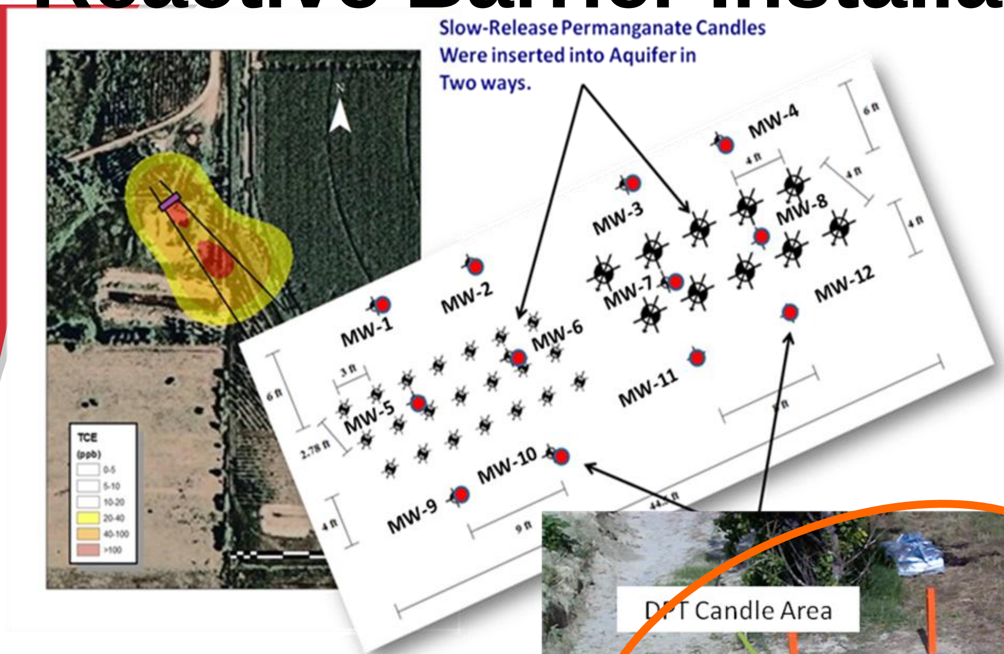


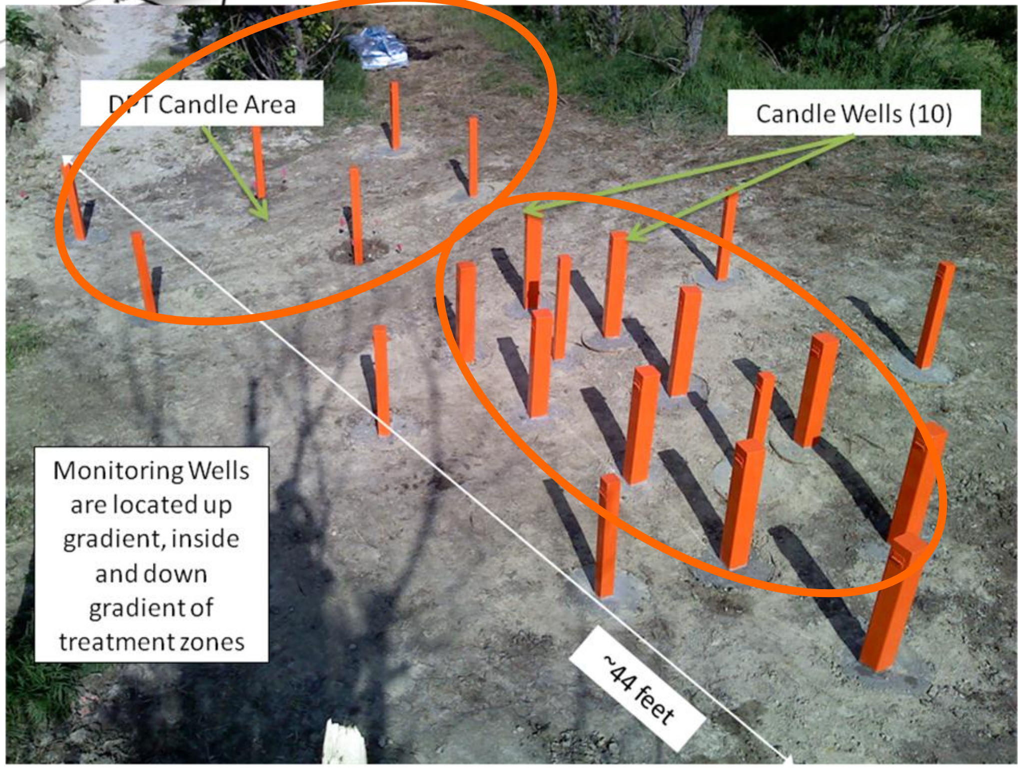
University of Nebraska–Lincoln

Slow-Release Permanganate Reactive Barrier Installation

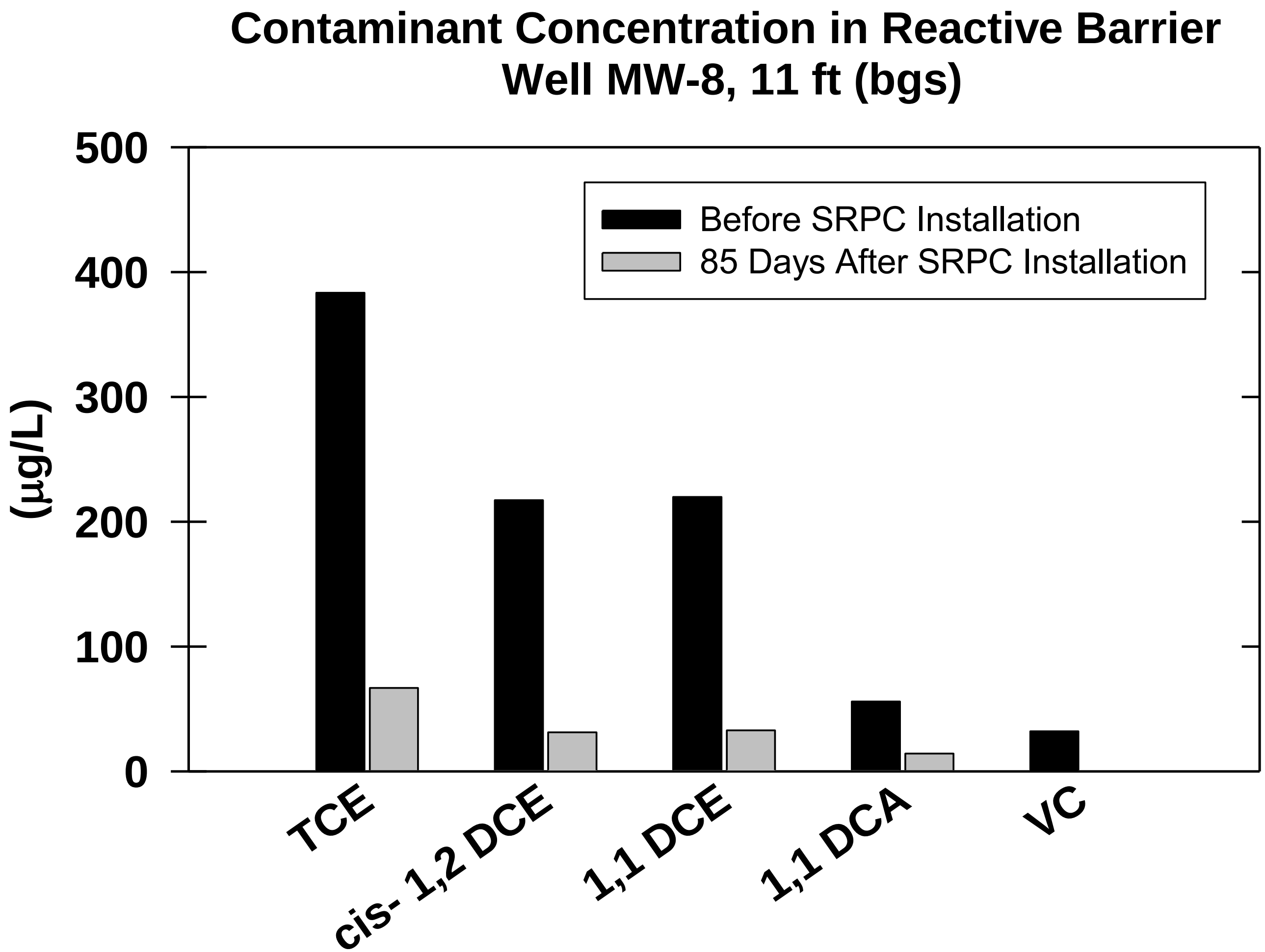
105 two inch DPT SRPCs

50 three inch injection well SRPCs





Results



- **Barrier installed June 2010**
- **After 85 days 64%-82% TCE reduction (Christenson et al., 2012)**

Evaluating Oxidant Transport and Release Kinetics

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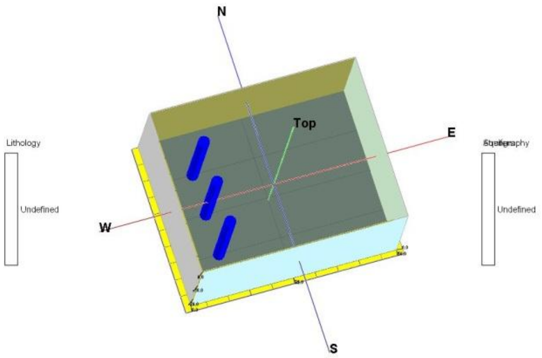
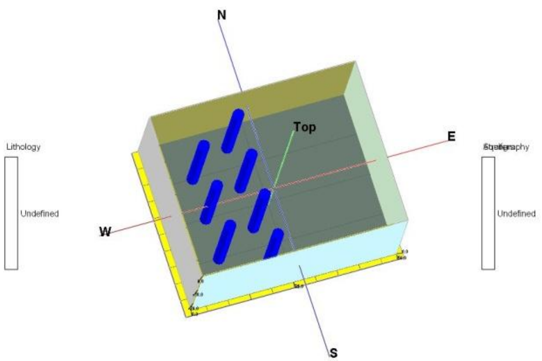
Sustained-Release Design Tool





- 1D column, 2D and 3-D tank data to develop sustained-release design tool
- Key processes
  - Oxidant release (source)
    - Oxidant type, candle dimensions
  - Oxidant reaction and transport
    - 2^{nd} order NOD
    - 1-D transport with reaction and dispersion
  - Contaminant reaction and transport
    - 2^{nd} order rate constants for TCE, dioxane and co-contaminant(s)
- Output: oxidant and contaminant distribution
  - Can optimize for number and spacing of candles
  - Conceptual design cost estimate

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Sustained-Release Design Tool

Design Tool Input

Slow Release Oxidant - release, reaction, and transport

Project:
Date:
Prepared by:

Basic project information

Oxidant Release Parameters

Oxidant:
Candle diameter (cm):
Oxidant solubility (mg/'
Effective diffusion
Amount of ava'
Treatmen'
Treat'
...per row):

Dropdown menus

(will autofill)
(will autofill)
(will autofill)

Auto-fill parameters

Factors affecting oxidant release rate and resulting concentration

Si... aracteristics*

Primary contaminant:
Concentration (mg/L):
Secondary contaminant:
Concentration (mg/L):
Longidudinal dispersivity:
Transverse dispersivity:
Vertical dispersivity:
Natural oxidant demand (NOD) (mg/kg):
NOD rate (2nd order; $M^{-1}s^{-1}$):
Hydraulic conductivity (cm/s):
Hydraulic gradient (dh/dl):
Porosity:
*guidance provided in 'site characteristics guidance' tab

Dropdown menus

Contaminant characteristics
Dispersion parameters
Oxidant demand – rate and extent
Flow properties

Simulation

Simulation time:
Simulation or compliance
distance downgradient:

Simulation **time and distance** of interest

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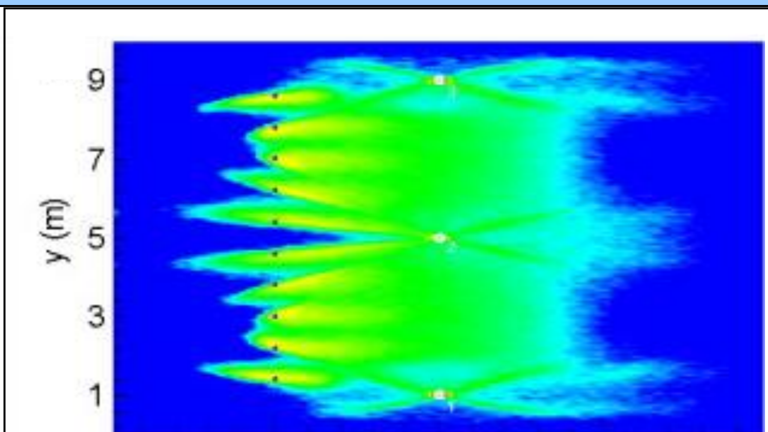
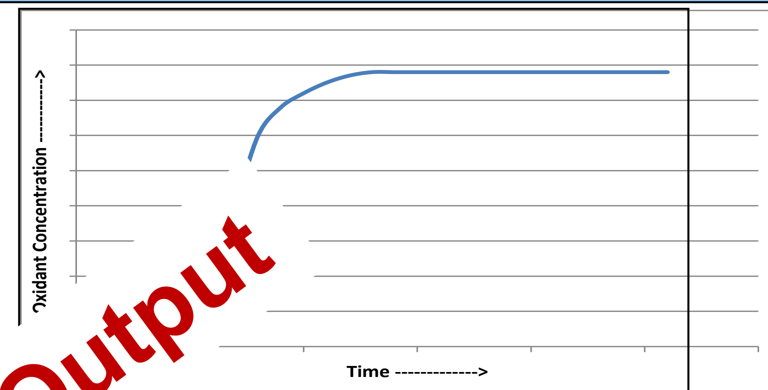
Sustained-Release Design Tool

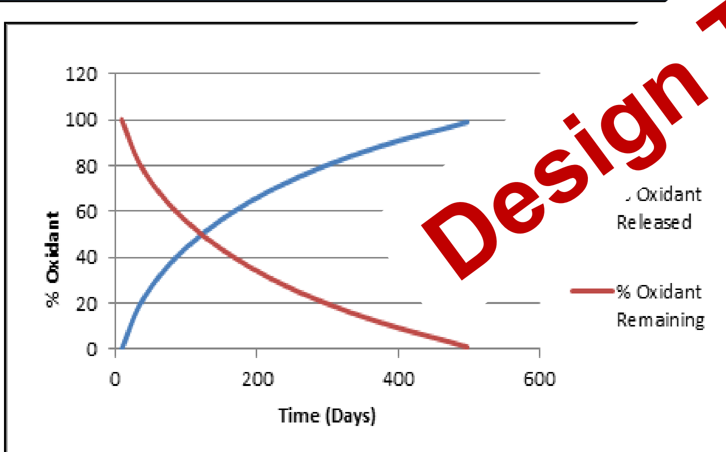
Oxidant concentrations vs. distance at a given time



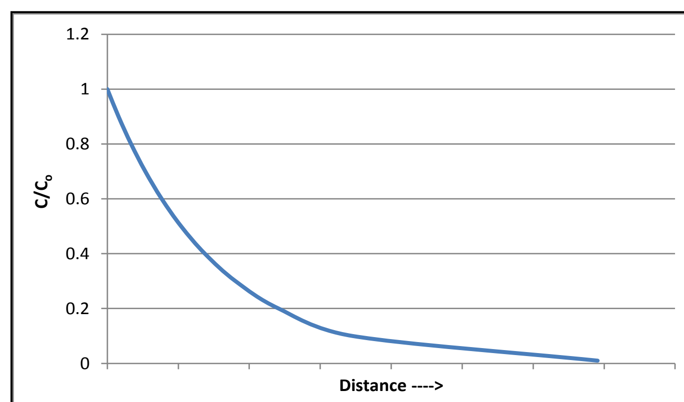
Oxidant concentrations at a given point over time



Oxidant release from cylinders



Contaminant concentrations vs. distance at a given time



Design Tool Output

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Sustained-Release Design Tool

Scenario 1 - minimum required mass flux of MnO4 required - mg/day (based on 1gTCE:1.8gMnO4 * 10 SF)							
	COC (mg/L)						
Vgw (feet/day)	0.01	0.05	0.1	0.5	1	5	10
0.01	**0.046**	**0.229**	**0.459**	**2.294**	**4.587**	**22.937**	**45.873**
0.05	**0.229**	**1.147**	**2.294**	**11.468**	**22.937**	114.683	229.366
0.1	**0.459**	**2.294**	**4.587**	**22.937**	**45.873**	229.366	458.733
0.5	**2.294**	**11.468**	**22.937**	114.683	229.366	1146.832	2293.665
1	**4.587**	**22.937**	**45.873**	229.366	458.733	2293.665	4587.329
5	**22.937**	114.683	229.366	1146.832	2293.665	11468.323	22936.646
10	**45.873**	229.366	458.733	2293.665	4587.329	22936.646	45873.291

Scenario 2 - minimum required mass flux of MnO4 required - mg/day (based on 1gTCE:1.8gMnO4 * 10 SF)							
	COC (mg/L)						
Vgw (feet/day)	0.01	0.05	0.1	0.5	1	5	10
0.01	**0.092**	**0.459**	**0.917**	**4.587**	**9.175**	**45.873**	91.747
0.05	**0.459**	**2.294**	**4.587**	**22.937**	**45.873**	229.366	458.733
0.1	**0.917**	**4.587**	**9.175**	**45.873**	91.747	458.733	917.466
0.5	**4.587**	**22.937**	**45.873**	229.366	458.733	2293.665	4587.329
1	**9.175**	**45.873**	91.747	458.733	917.466	4587.329	9174.658
5	**45.873**	229.366	458.733	2293.665	4587.329	22936.646	45873.291
10	91.747	458.733	917.466	4587.329	9174.658	45873.291	91746.583

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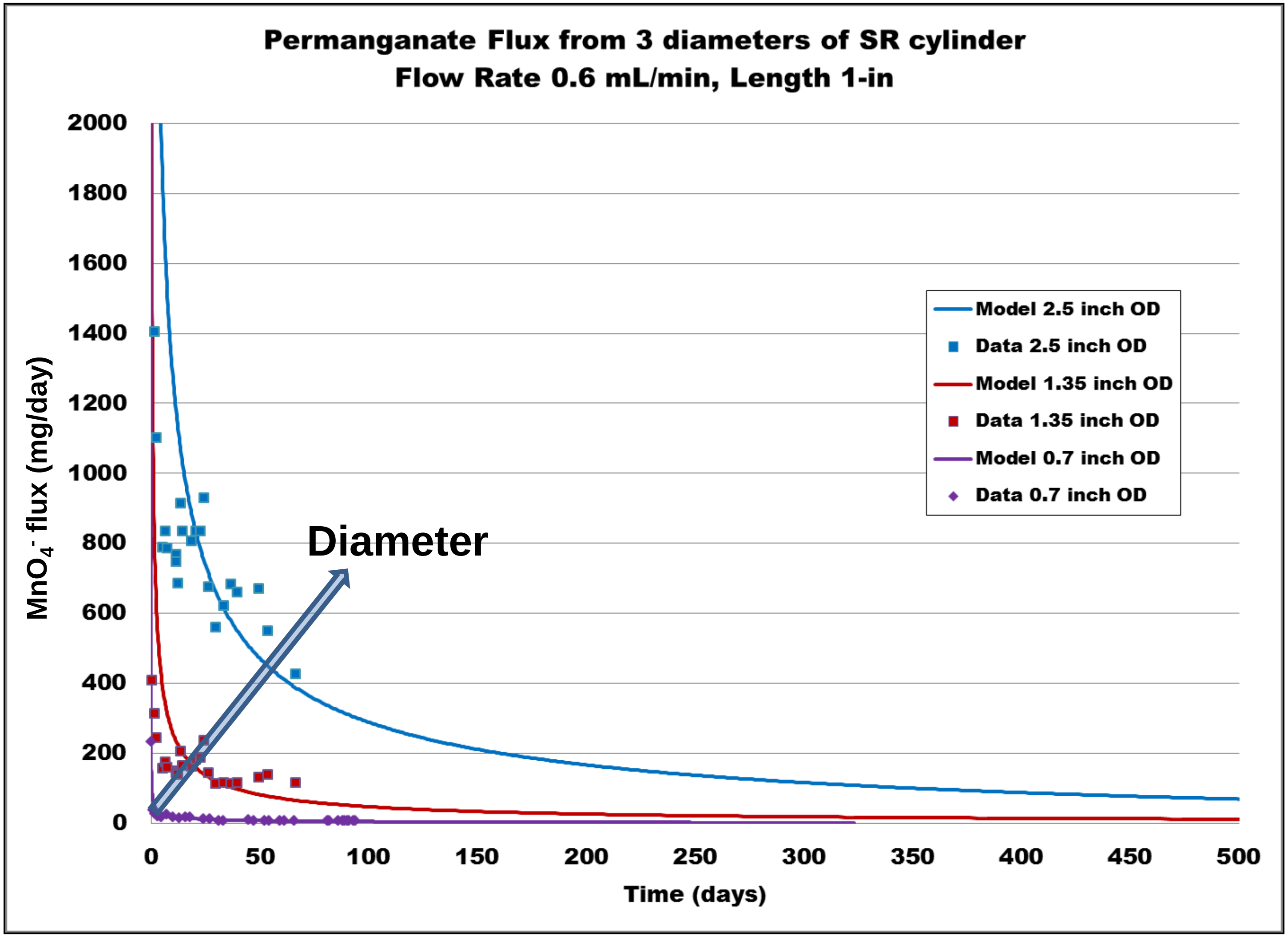
Model Results – 1-in Sections Mini-SRPC, 1.35-in, 2.5-in



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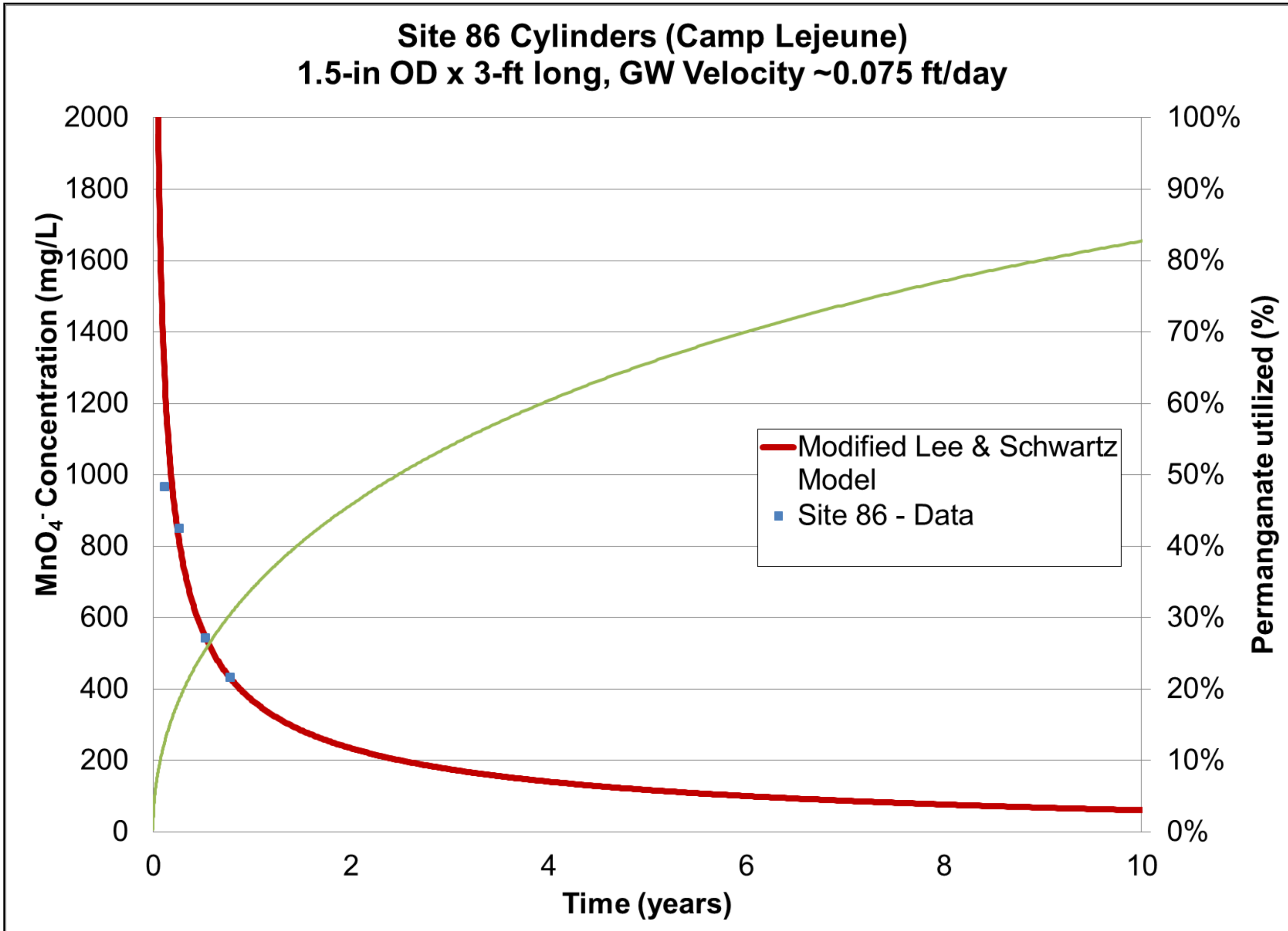
Model Results – Preliminary Field Data



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Exploring the Possibilities…

1. Minimal aboveground infrastructure (and site disruption) so can implement quickly at an active site
   - No tanks, water needs, dust, pressurized injection

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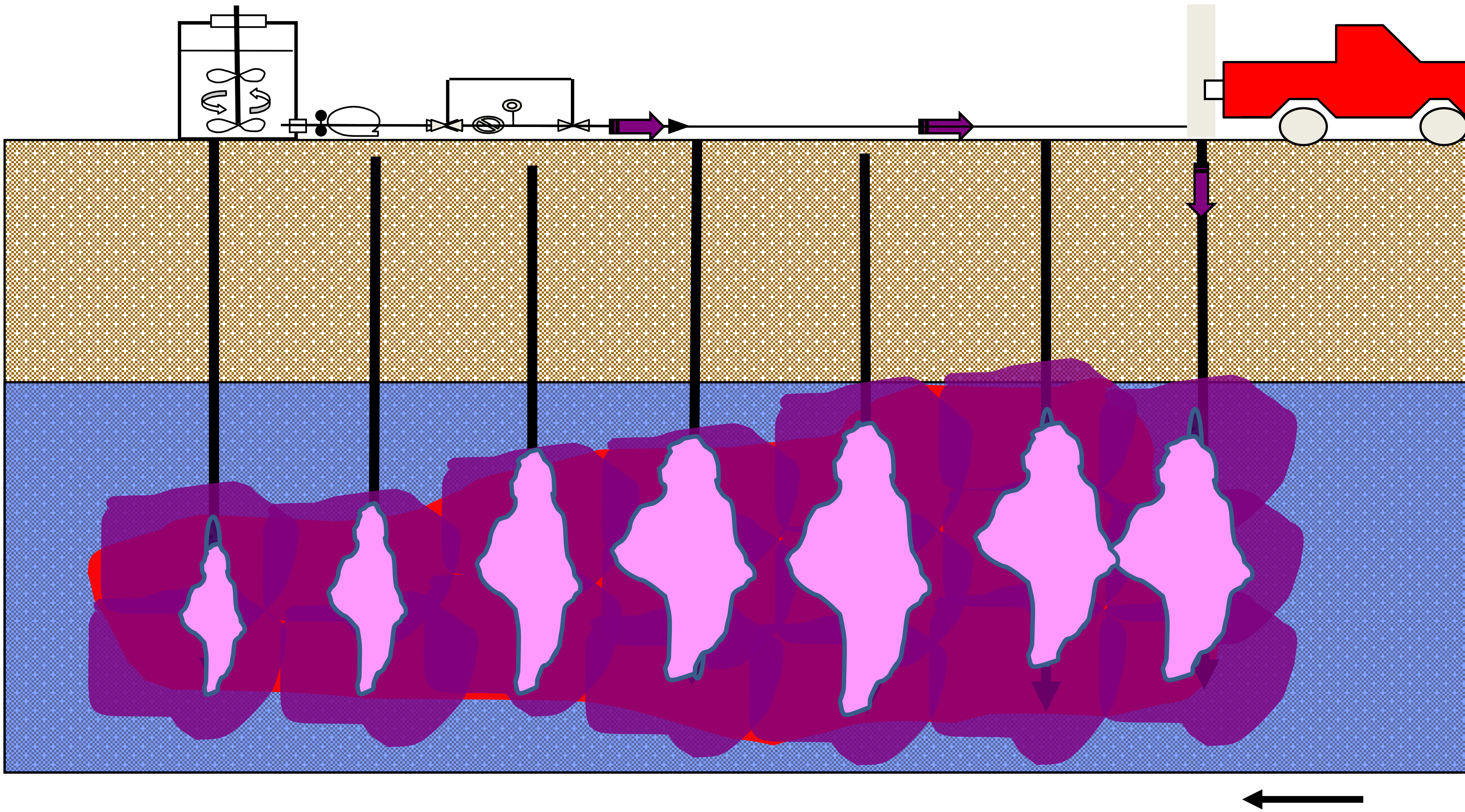
Exploring the Possibilities…

2. Get two injections for the price of one

- Long term treatment of residual absorbed material in clay (back diffusion)



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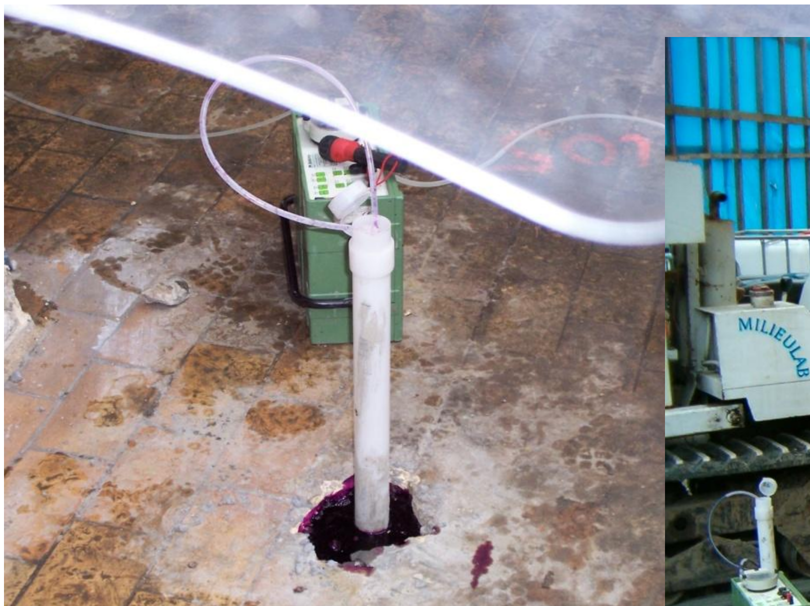
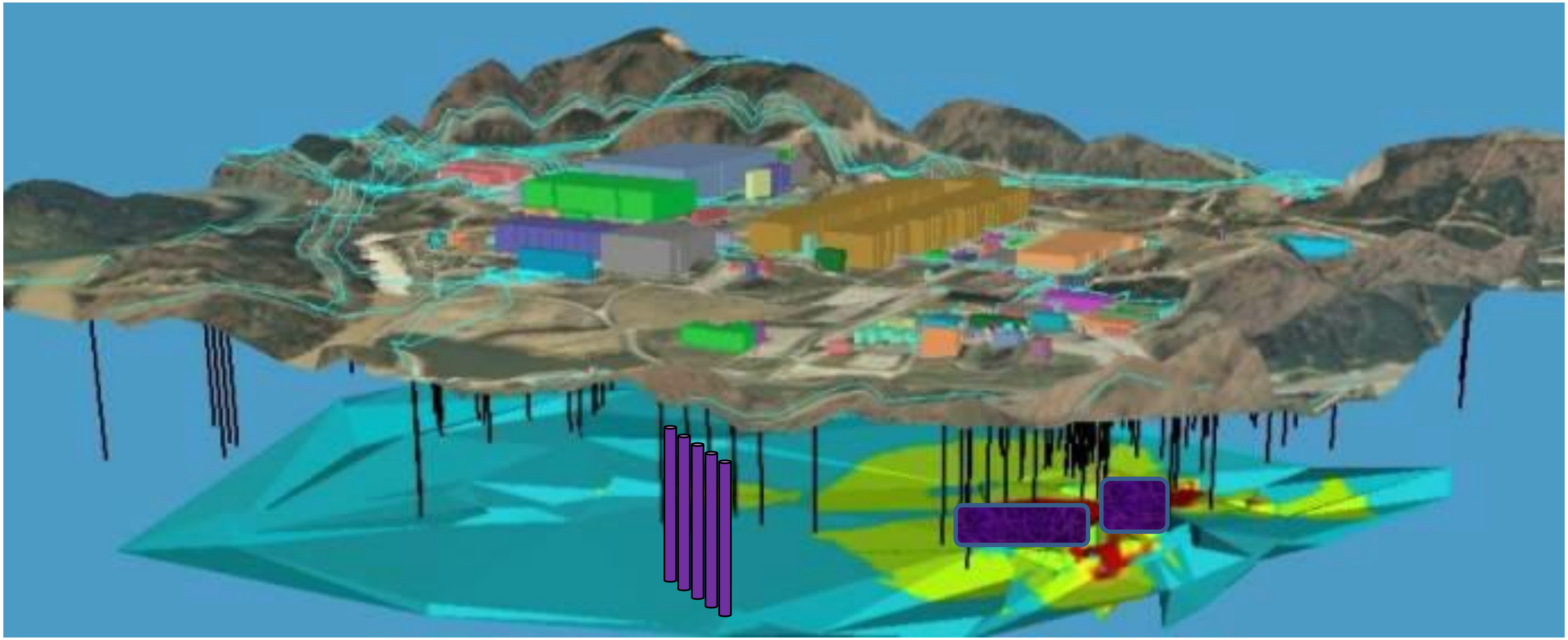
Exploring the Possibilities…

3. No surfacing of liquids



Exploring the Possibilities…

4. Ability to approach ISCO in an active stepped manner



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Take Home Message

- 5 pilot-scale sites (US), 2 pending (US and Brazil) Canada?
- Direct push/in-well applications for treatment that may last years
  - Potential for application in low permeability soils and fractured bedrock
  - Address "rebound" and back diffusion
  - Active industrial and commercial facilities: passive *in situ* treatment without above ground equipment/infrastructure
- Cost savings realized with direct push delivery


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Questions?
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