Coupling Technologies for Enhanced Dense Nonaqueous Phase (DNAPL) Mass Removal

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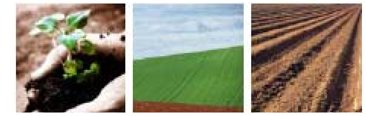
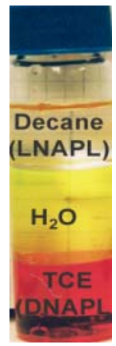
Today’s Agenda

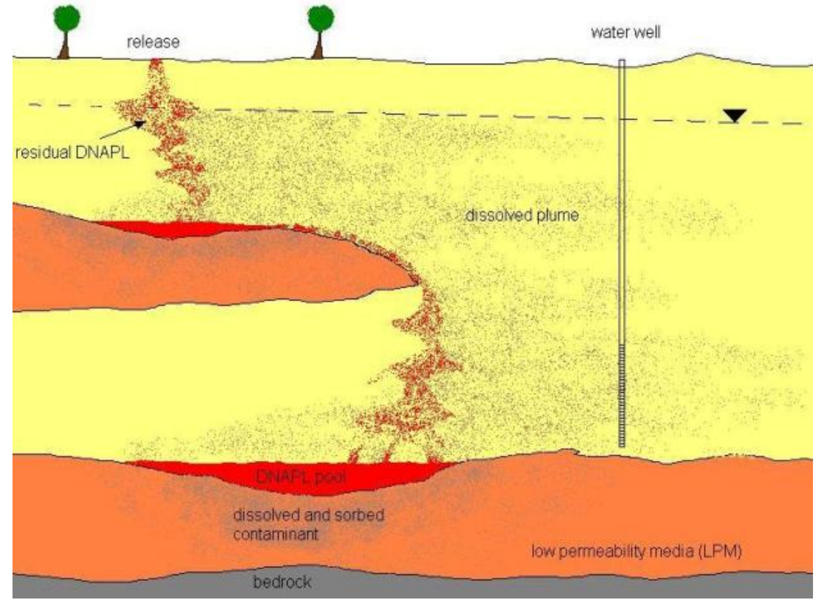
- Motivation and background:
  - The challenge...DNAPL
  - Coupling technologies for expedited DNAPL site clean up
  - Previous research
- Experimental approach and results
- Concluding remarks and questions

The Challenge – Dense Nonaqueous Phase Liquid (DNAPL)



- Global environmental problem...low aqueous solubility, denser than water
    - e.g., trichloroethene (TCE) & perchloroethene (PCE)
    - Degreasers & dry cleaners
    - Toxic and carcinogenic





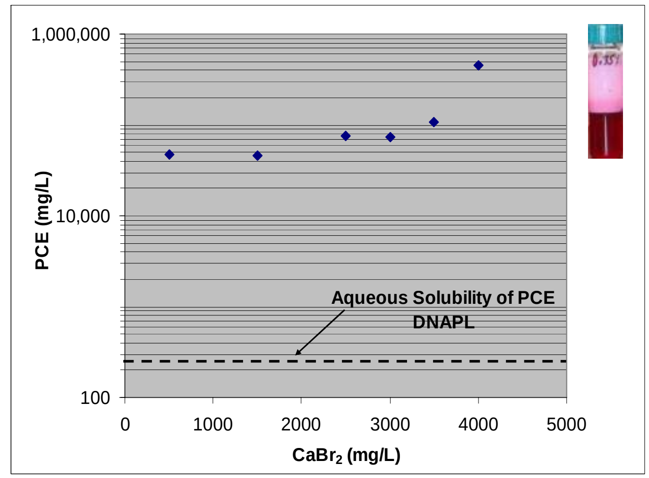
•Pollute *millions of gallons of groundwater* , generate huge plumes, serve as *long-term sources of groundwater contamination* (e.g., *many decades*)

Background – Combined Remedial Technologies

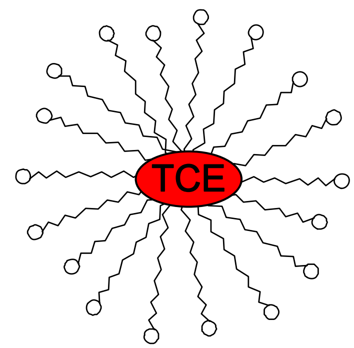
- A single technology is rarely a cost-effective approach for DNAPL site clean-up (EPA 2008)
- Optimal strategies often requires multiple technologies to reach performance goals (i.e., treatment train)
- For example, coupling surfactant-enhanced aquifer remediation (SEAR), with *in situ* chemical oxidation (ISCO) for enhanced DNAPL mass removal

Background – What are Surfactants?

- Soaps, detergents...<u>surface</u> <u>act</u>ive <u>agents</u>
  - Surfactants greatly enhance DNAPL removal



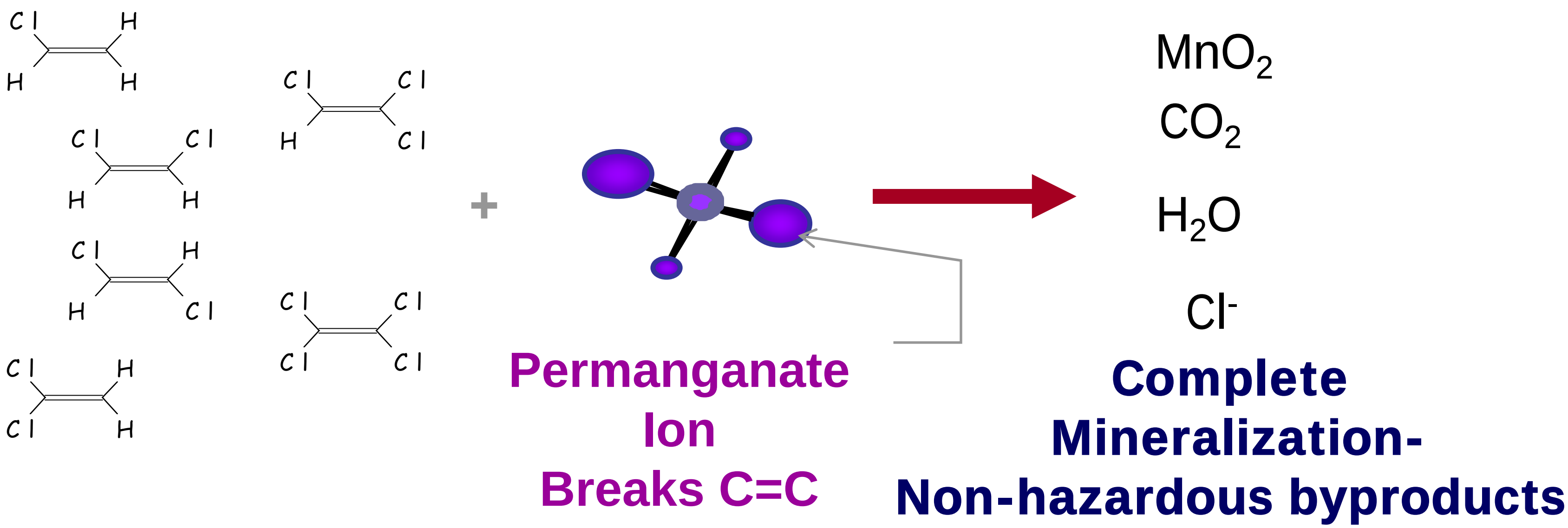
***TCE is a "water-hating" compound**



- However...surfactants ineffective for treating dissolved contaminants only free phase!

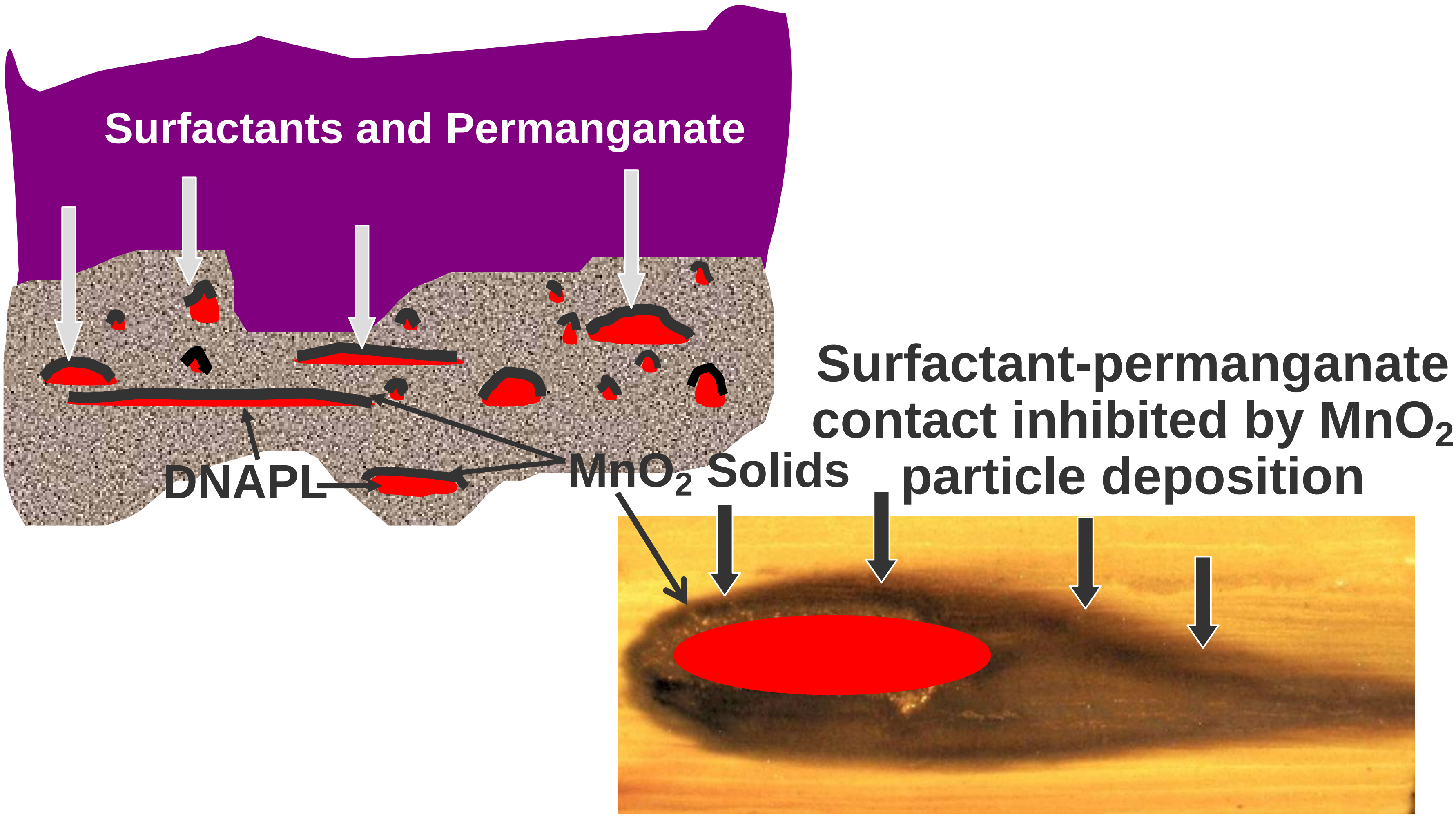
Background – Permanganate ISCO

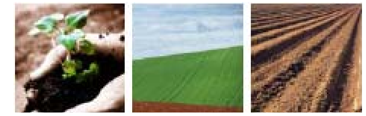
- Converts toxic compounds (e.g., PCE, TCE) to naturally occurring non- hazardous compounds



- Permanganate very effective for treating dissolved phase contaminants...not recommended for DNAPL

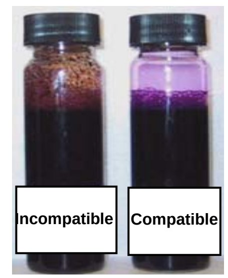
A lot of MnO_2 generated during surfactant-enhanced permanganate oxidation of DNAPL and could challenge *in situ* delivery

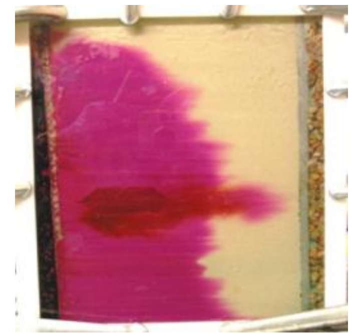




Background –
Coupling ISCO Permanganate

- Previous research evaluated coupling surfactants with permanganate ***to dissolve-destroy DNAPL <u>in one step</u>*** (Dugan et al. 2010)





- Previous lab/field work coupled the polymer sodium hexametaphosphate (SHMP) with permanganate ***<u>for MnO_2 particle stabilization-mobilization</u>*** (Crimi et al. 2010)

A Solution – Coupling Surfactants and SHMP with Permanganate ISCO

- Incorporate SHMP into surfactant-enhanced permanganate to ***keep MnO_2 solids stabilized for effective contact***
  - Stability = inhibition of particle aggregation that leads to settling, and/or deposition
  - Stabilized particles remain dissolved/suspended in solution (i.e., groundwater)
  - Achieved through the processes of electrostatic repulsion, sequestration of ions that promote particle aggregation, and/or steric hindrance

Experimental Approach

- Column tests with surfactants-permanganate-SHMP
- Purpose:
  - Clean-up goal >90% TCE DNAPL removal
  - Effect of SHMP on MnO_2 particle deposition
- Four column studies:
  1. Water
  2. Permanganate
  3. Surfactants-Permanganate
  4. Surfactants-SHMP-Permanganate
- TCE, chloride, MnO_4^-, and Mn as MnO_2

Experimental Approach

Parameter	Column 1	Column 2	Column 3	Column 4
Delivery Method	Water Flush	Permanganate Flush	Coinjection of Surfactants with Permanganate	Coinjection of Surfactants, SHMP with Permanganate
Composition of Flushing Solutions	Deionized Nanopure Water	0.5 wt% $NaMnO_4$	1.0 wt% Aerosol OT + 1.0 wt% SDS + 0.5 wt% $NaMnO_4$	1.0 wt% Aerosol OT + 1.0 wt% SDS + 0.5 wt% SHMP + 0.5 wt% $NaMnO_4$
Column Pore Volume (PV) (mL)	115	123	105	107
Initial TCE DNAPL Saturation (S_N)	2%			
Flushing Flow Rate (mL/min)	3			
PVs Flushed	0.75			

Results

Permanganate Flush

Figure 4a: 0.5 PVs

Figure 4b: 0.75 PVs

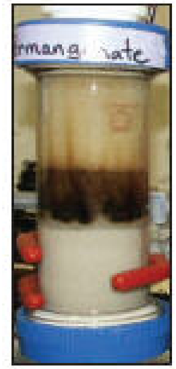


Figure 4c: End

Surfactant Permanganate

Figure 5a: 0.5 PVs

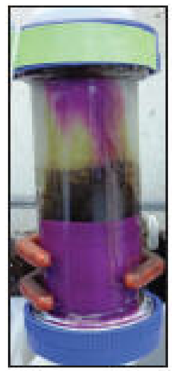


Figure 5b: 0.75 PVs

Figure 5c: End

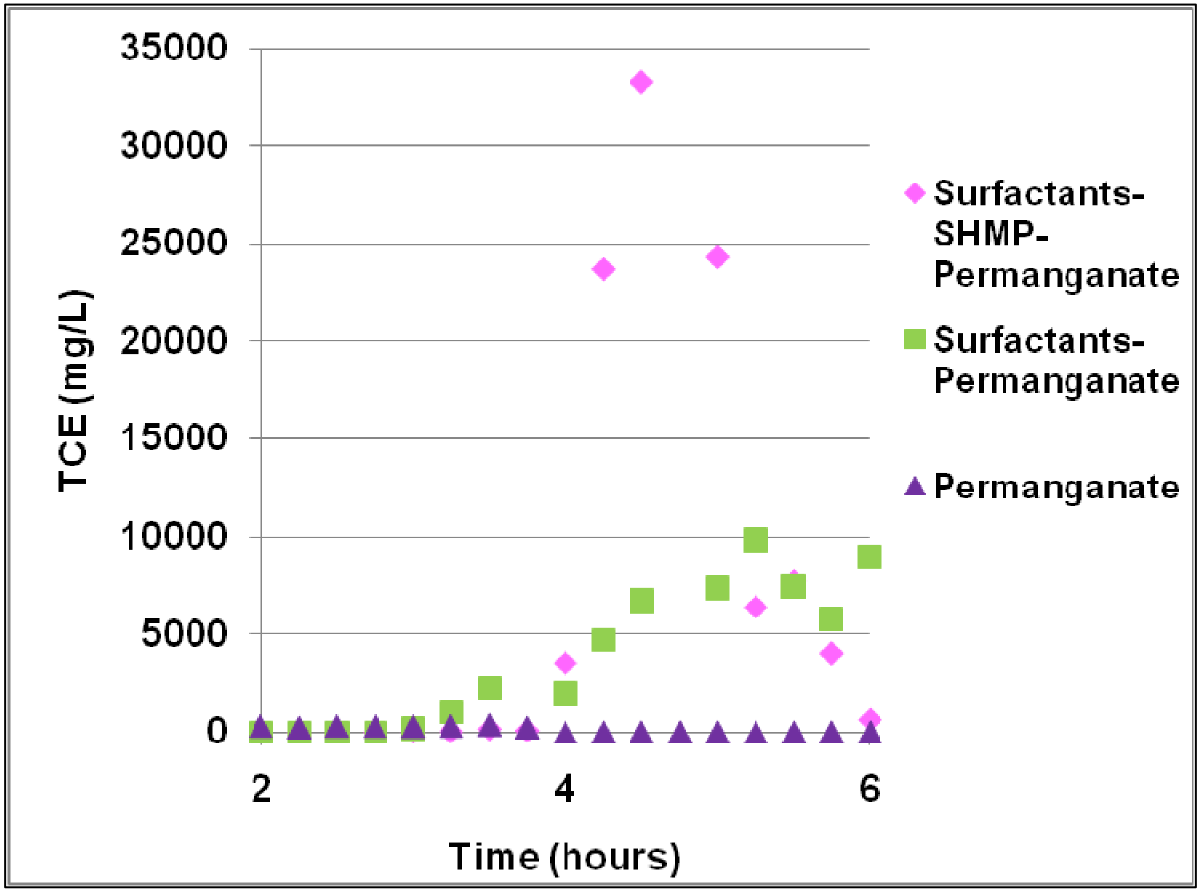
Surfactant and SHMP with Permanganate

Figure 6a: 0.5 PVs

Figure 6b: 0.75 PVs

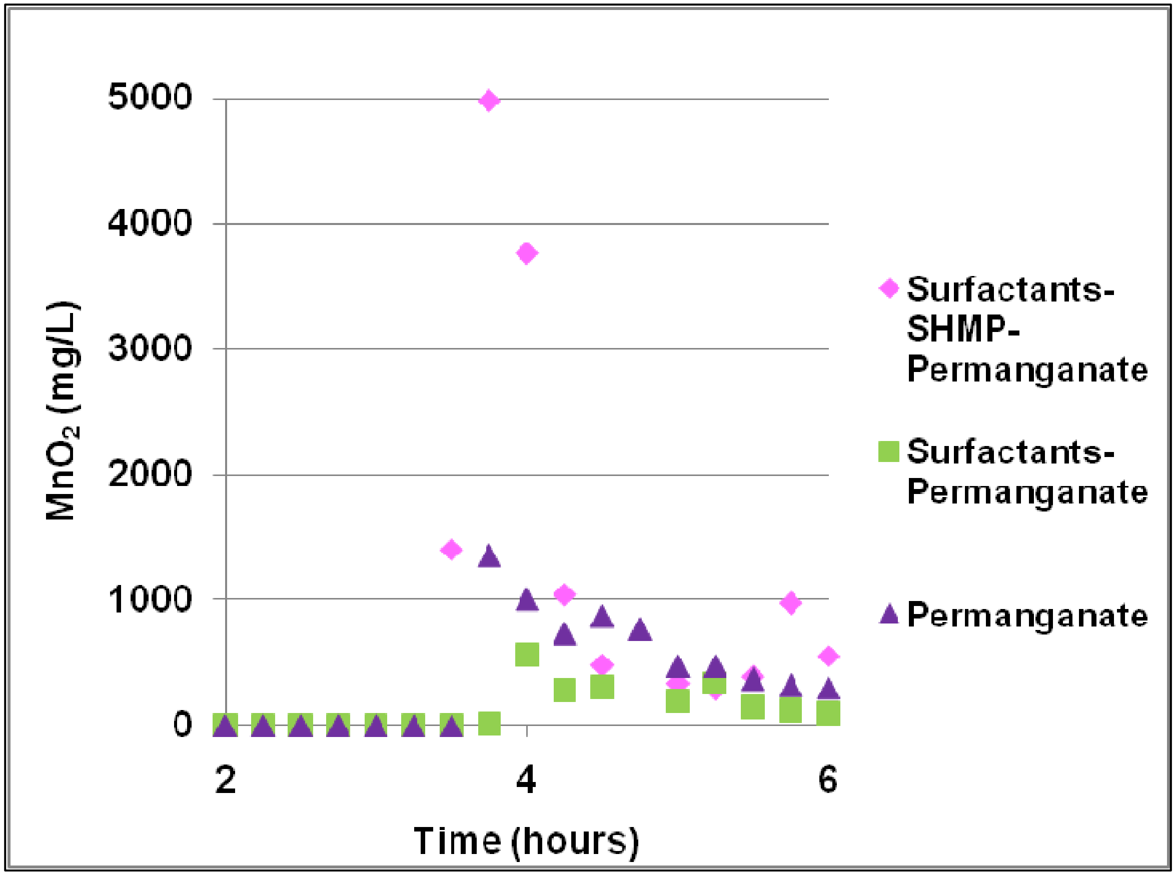
Figure 6c: End

Results – Column Studies



- Increased DNAPL mass transfer in the surfactant-SHMP-permanganate column due to less MnO_2 film formation

Results –
Column Studies



- Enhanced mobility of MnO_2 solids due to the addition of the sequestering reagent SHMP

Results – Performance Assessment

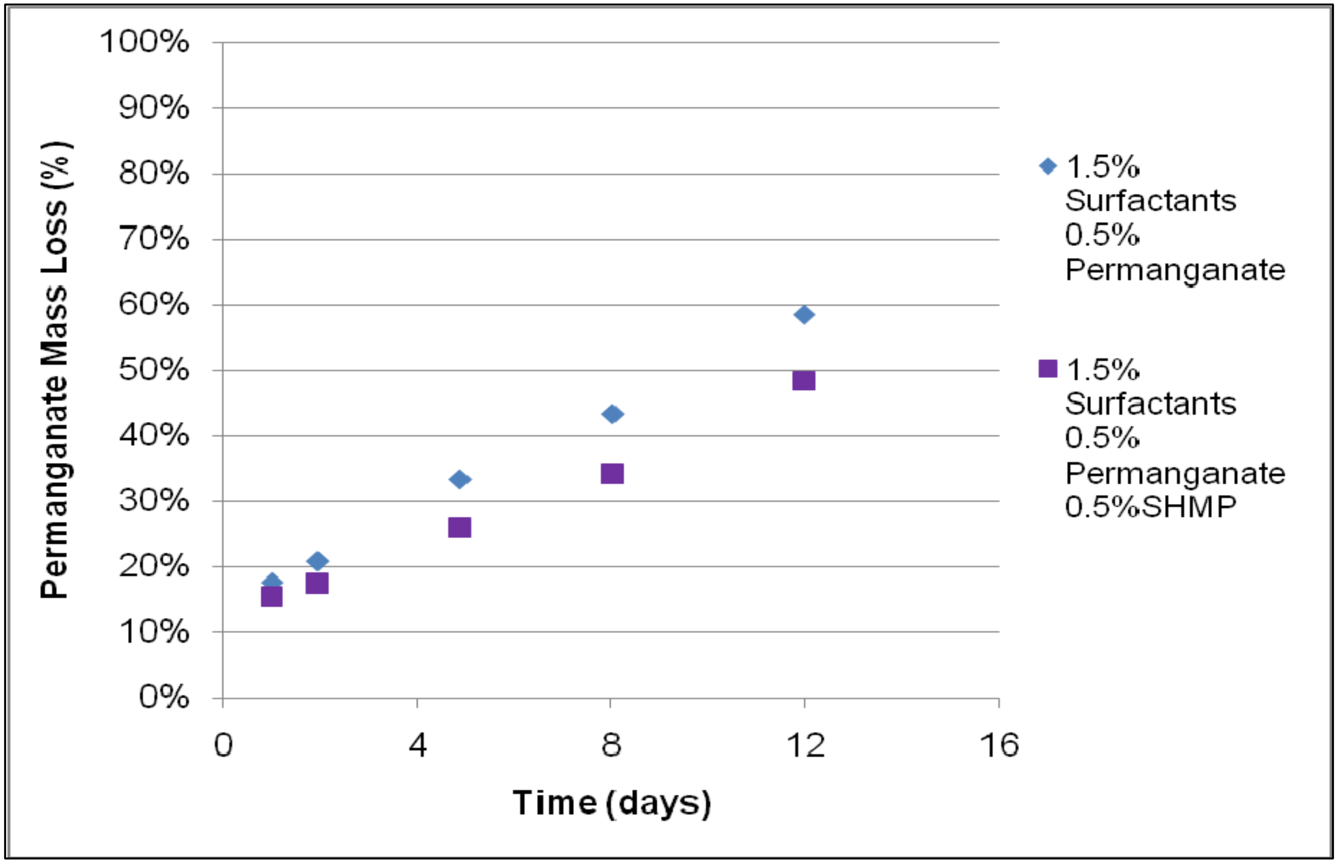
Parameter	Column 1	Column 2	Column 3	Column 4
Delivery Method	Water Flush	Permanganate flush	Coinjection of Surfactants with Permanganate	Coinjection of Surfactants, SHMP with Permanganate
TCE removed (%)	58%	73%	94%	>99%

Column	MnO_2 in effluent (g)	MnO_2 extracted from sand (g)
Permanganate Flush	0.05	0.061
Surfactant-Permanganate Flush	0.017	0.228
Surfactant-SHMP-Permanganate Flush	0.109	0.069

85% more MnO_2 in the surfactant-SHMP permanganate effluent

80% more MnO_2 retained in the surfactant-permanganate column

Results – Column Studies



- Reduced permanganate demand through addition of SHMP

Modeling Interphase Mass Flux Between PCE and Permanganate in the Presence of Surfactants

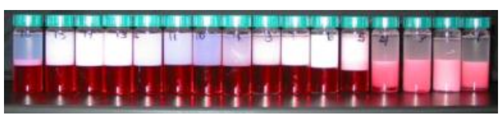
Mark Julian, Advisor—Michelle Crimi

In Situ Chemical Oxidation

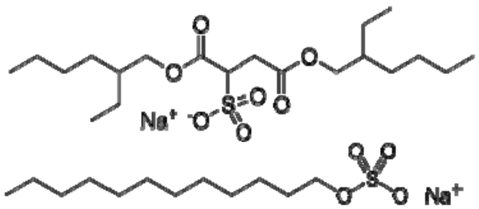
This technology offers remediation for soil and groundwater polluted with dense non-aqueous phase liquids (DNAPL) such as chlorinated solvents.

ISCO Can Be Enhanced With Surfactant Molecules Present

Organic perchloroethylene (PCE) is immiscible with the aqueous phase permanganate, making the oxidation limited by the mass transfer of the PCE into the MnO_4^- solution.



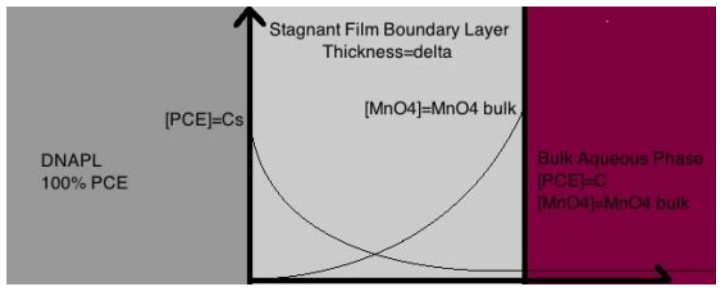
Combinations of sodium dioctyl sulfosuccinate and sodium dodecyl sulfate help facilitate interphase mass flux of PCE for efficient oxidation.



The Objective is to Determine if an Existing Diffusion Model Works

$$3C_2Cl_4(l) + 4MnO_4^-(aq) + 4H_2O(l) \rightarrow 4MnO_2(s) + 6CO_2(g) + 8H^+(aq) + 12Cl^-(aq)$$

Can the mass flux of PCE be determined from an existing reactive diffusion model, given the above oxidation in the presence of surfactant molecules? The existing conceptual[1] and mathematical[2] models may apply if the reaction rate constant, PCE solubility limit, and molecular diffusion coefficients can be modified for the surfactant solution. These parameters must be determined experimentally.



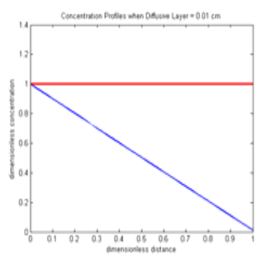
$$D_A \frac{d^2C_A}{dx^2} - 3kC_AC_B = 0$$

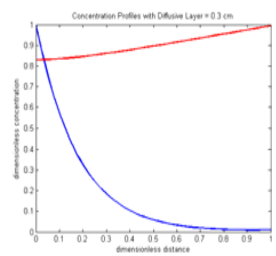
$$D_B \frac{d^2C_B}{dx^2} - 4kC_AC_B = 0$$

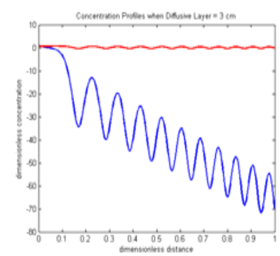
$$C_A(0) = C_S, \frac{dC_A}{dx}(\delta) = 0, C_B(\delta) = C_b, \frac{dC_B}{dx}(0) = 0$$

Shooting Methods Provide a Solution for the Concentration Profiles

Through MATLAB's ode45 algorithm, the concentration profiles can be obtained when a reasonable estimate of delta is assumed. Insufficiently small deltas yield linear profiles, while extremely large delta values result in model breakdown. The following concentration profiles were generated using available parameters for a system with no surfactants present.







The PCE mass flux values can then be obtained from Fick's Law

$$J = -D_A \frac{dC_A}{dx}\bigg|_{x=0}$$

These values can be compared to experimental values to assess the model's capability.

References

1 Urynowicz, M.A., Siegrist, R.L., 2005. *Journal of Contaminant Hydrology*. vol 80, 93-106.
2 Cussler, E.L., 1997. Diffusion: mass transfer in fluid systems. Cambridge University Press.

Concluding Remarks

- Despite the growing toolbox of DNAPL technologies the use of a single remedial technology for cleanup to typical regulatory criteria is a rare occurrence
- The combined SEAR-SHMP and permanganate-ISCO remedy aims to improve the efficiency and cost-effectiveness of DNAPL destruction by:
- Reducing time-on-site requirements
- Amendment costs
- Infrastructure costs

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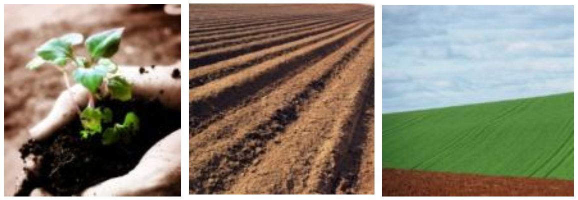

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