Enhanced Remediation of DNAPL-Contaminated Subsurface Systems

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Overview

- Characteristics of behavior
- Physics of multiphase porous medium systems
- Experimental and modeling results of NAPL behavior
- Current remediation approaches and limitations
- Objectives of effective remediation
- Brine-based remediation methods
- Variants investigated
- Experimental results
- Open issues
- Current efforts

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Physics of Multiphase Porous Medium Systems

- In a multiphase porous medium system, fluids move in response to viscous, capillary, and gravity forces
- This balance of forces is influenced by properties of the medium and the fluids: morphology of the pore space, contact angle, interfacial tensions, densities, and viscosities
- These forces result in very complex patterns of flow and entrapment of residual non-wetting phases
- Entrapment of residual NAPL happens on time scales that are short compared to the life of NAPL contaminants in the environment and which yield complex spatial distributions

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Characteristics of Behavior

- NAPLs leave a state of residual saturation in media through which they pass
- NAPLs follow a complex pattern of flow, which is importantly influenced by media heterogeneity
- LNAPLs accumulate on the top of the water table
- DNAPLs can sink below the water
- NAPLs often reach stable configurations of locally high saturations known as pools
- NAPLs are usually sparingly soluble and DNAPL contaminants usually degrade slowly---thus are long lived in the environment

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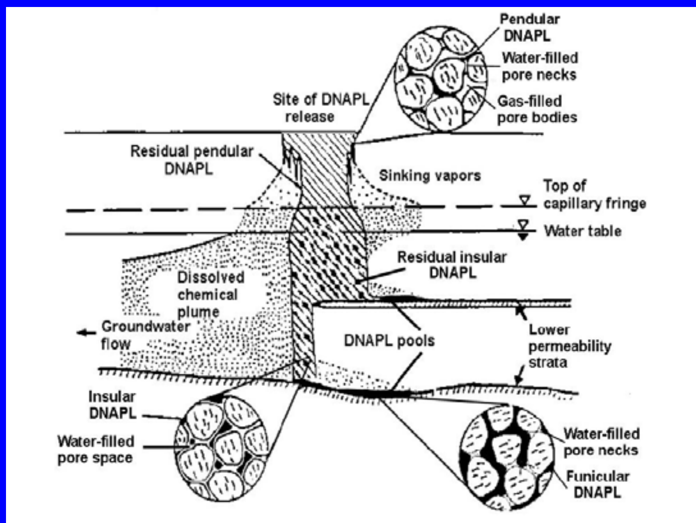
DNAPL Behavior in Heterogeneous Porous Media



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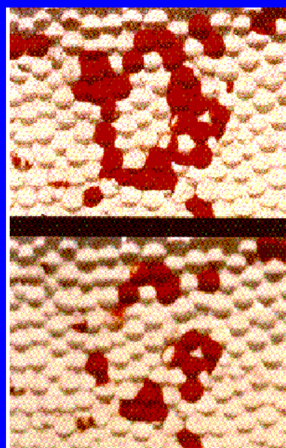
Micromodel TCE Residual



- Two-dimensional glass bead micromodel
- TCE dyed with Oil Red O
- Water saturated followed by DNAPL displacement and then water flushing
- TCE residual saturation results
- Large range of sizes of trapped TCE
- Largest features contain the majority of the TCE mass and are the most difficult to remove

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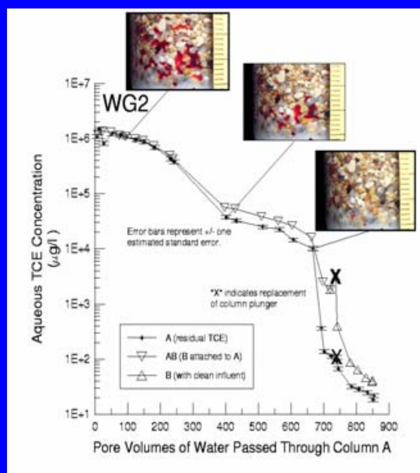
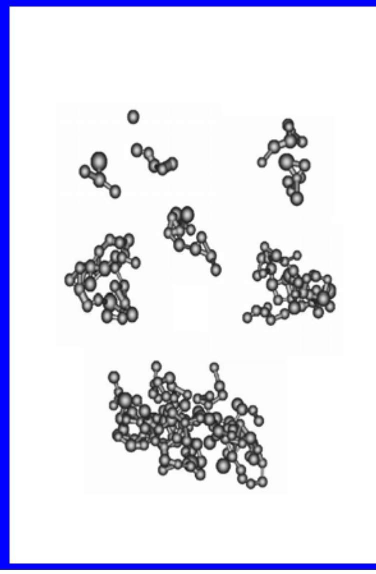
NAPL Dissolution Tailing for TCE



- •Column brought to residual saturation with TCE
- •Water flusing in an attempt to obtain drinking water standard concentrations of TCE
- •Large TCE residual feature determines clean-up time
- •Eventually complex TCE region breaks up and drinking water standards reached
- •Reference: Imhoff et al. [ES&T, 32(16), 1998]

Pore-Scale Network Model of NAPL Entrapment



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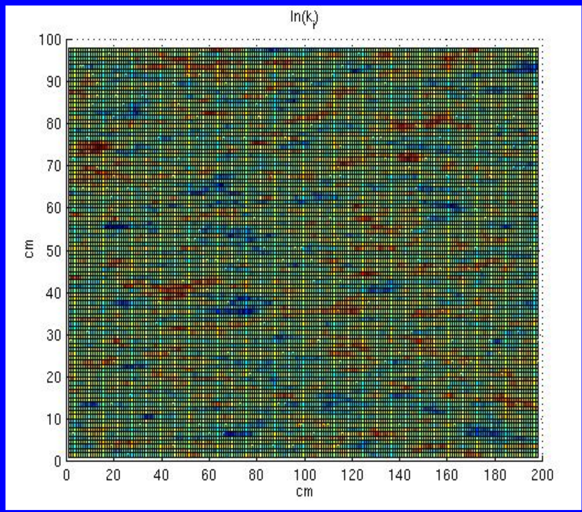
Percolation Simulation: K Field



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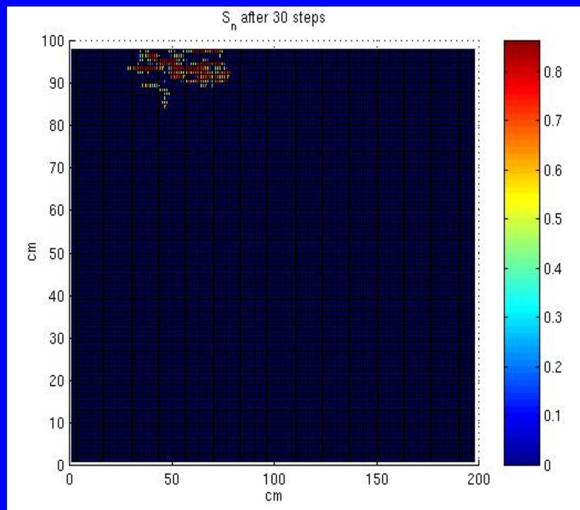
Percolation Simulation of DNAPL



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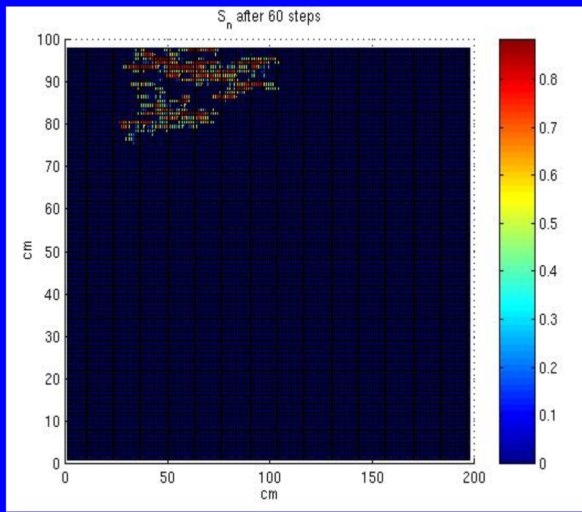
Percolation Simulation of DNAPL



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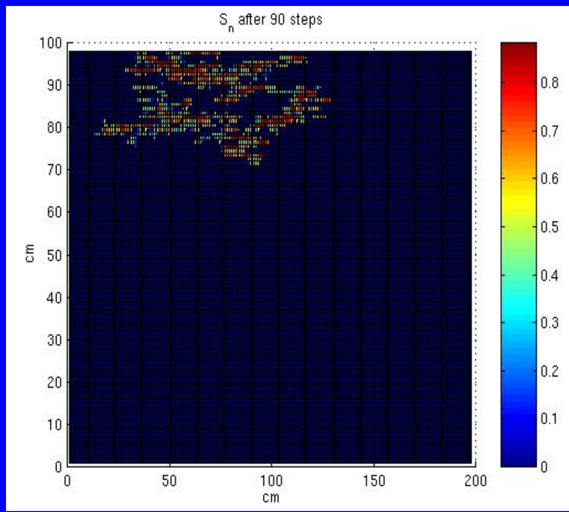
Percolation Simulation of DNAPL



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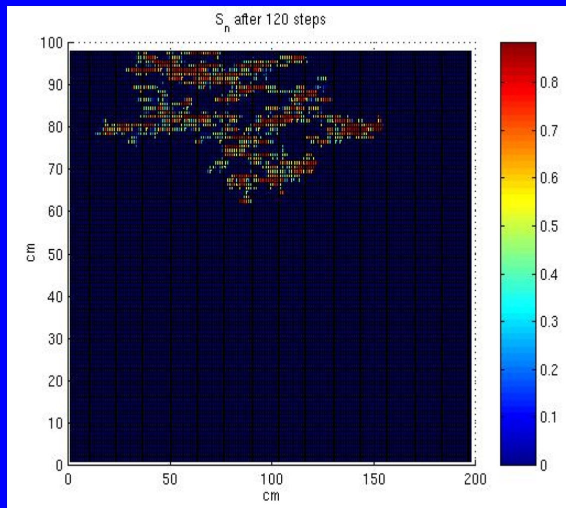
Percolation Simulation of DNAPL



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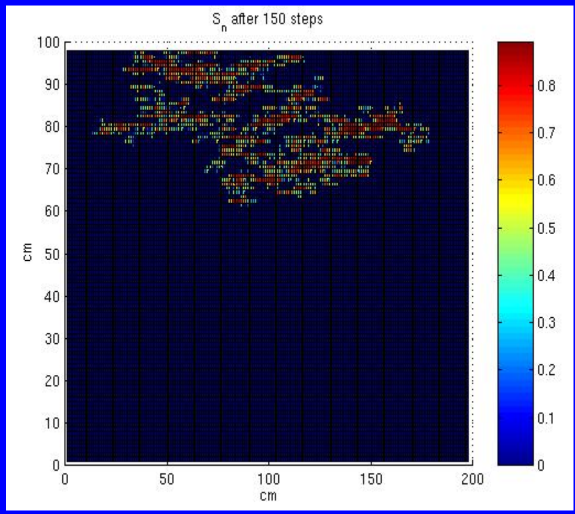
Percolation Simulation of DNAPL



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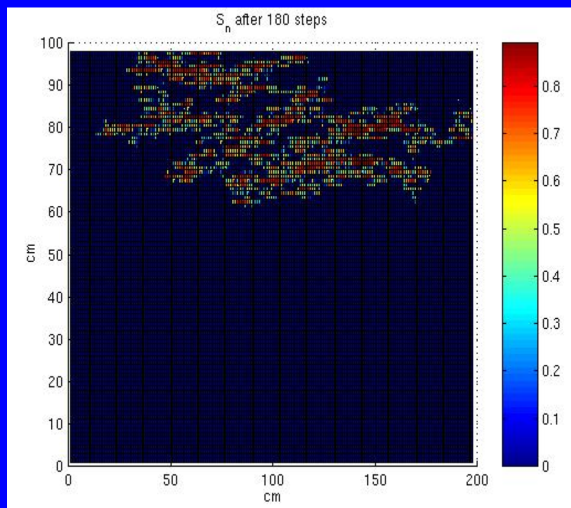
Percolation Simulation of DNAPL



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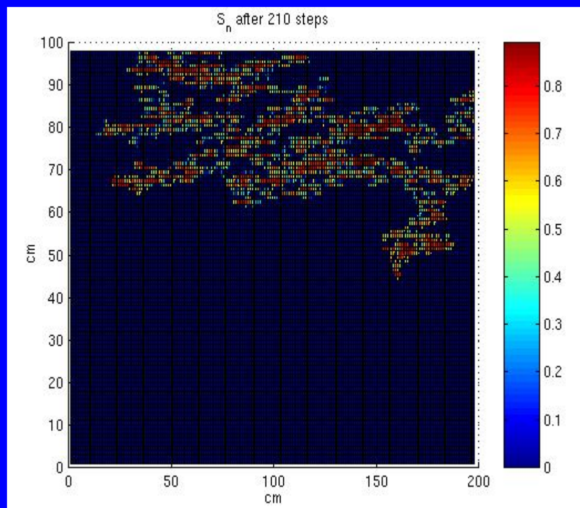
Percolation Simulation of DNAPL



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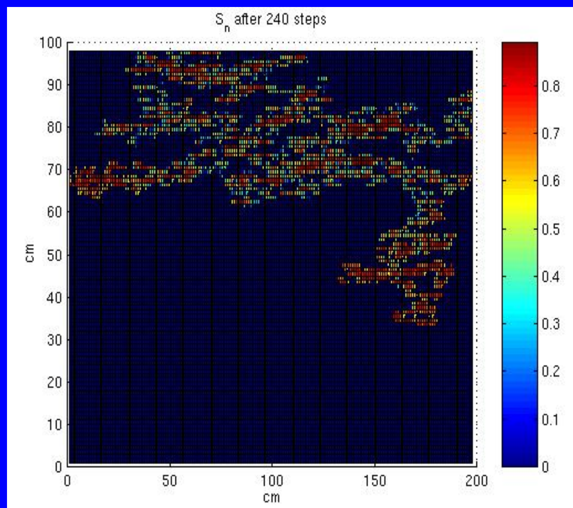
Percolation Simulation of DNAPL



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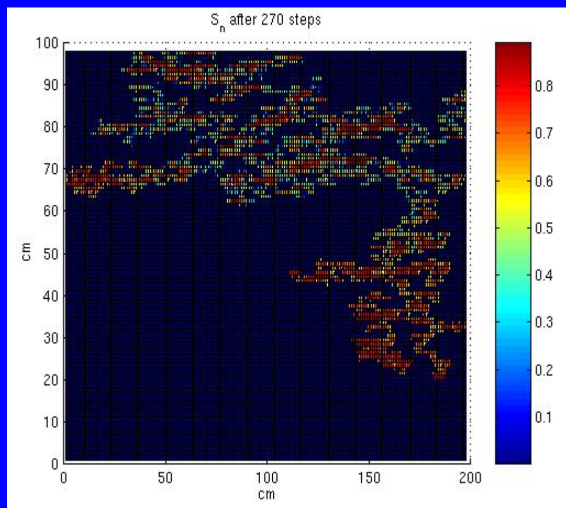
Percolation Simulation of DNAPL



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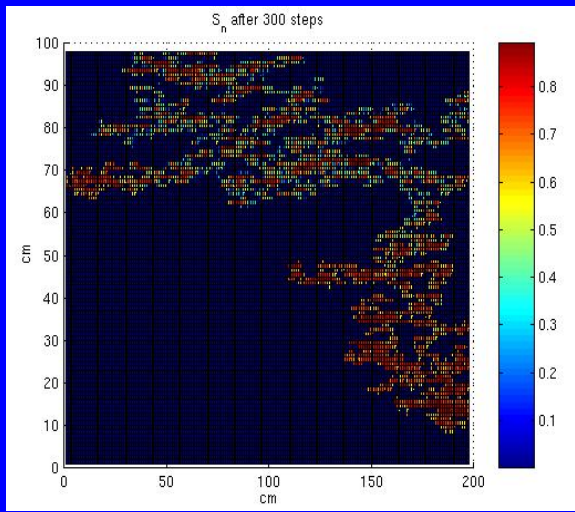
Percolation Simulation of DNAPL



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Current Remediation Approaches and Limitations

- Pump-and-Treat
- Vapor-Phase Extraction
- Air Sparging
- Cosolvent and Surfactant Flushing
- Thermal Processes
- In Situ Biodegradation

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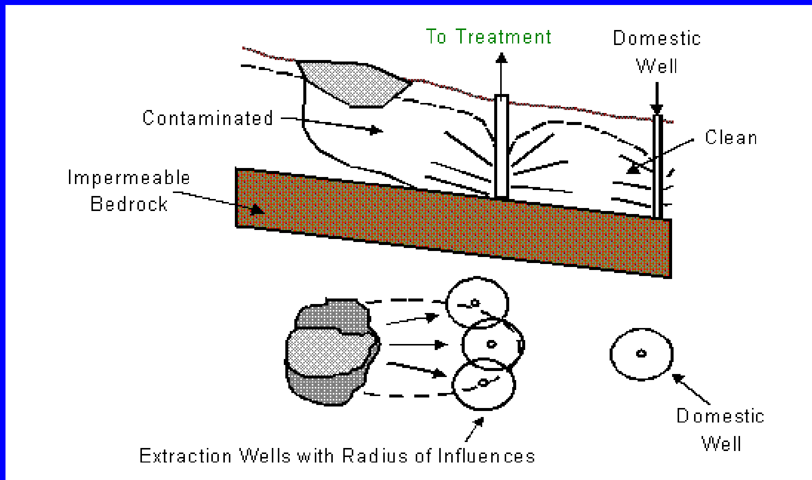
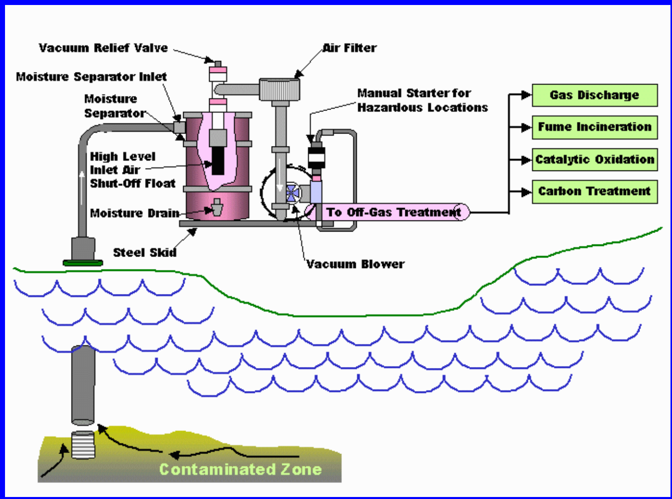
Pump-and-Treat



Federal Remediation Technology:
http://www.frtr.gov/matrix2/section4/D01-4-48.html

Vapor Extraction



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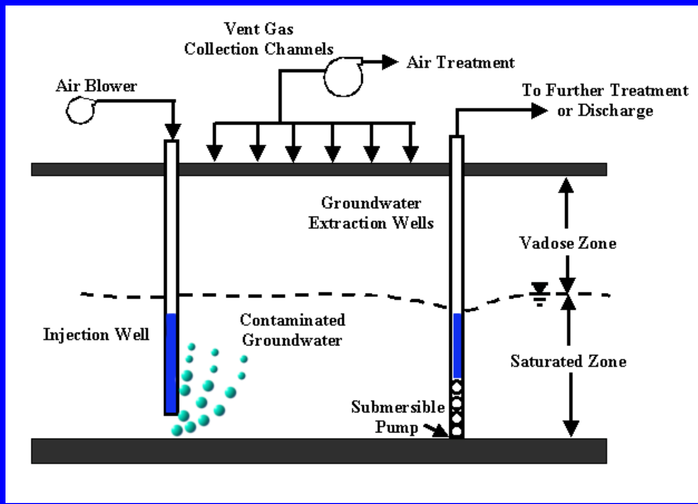
Air Sparging



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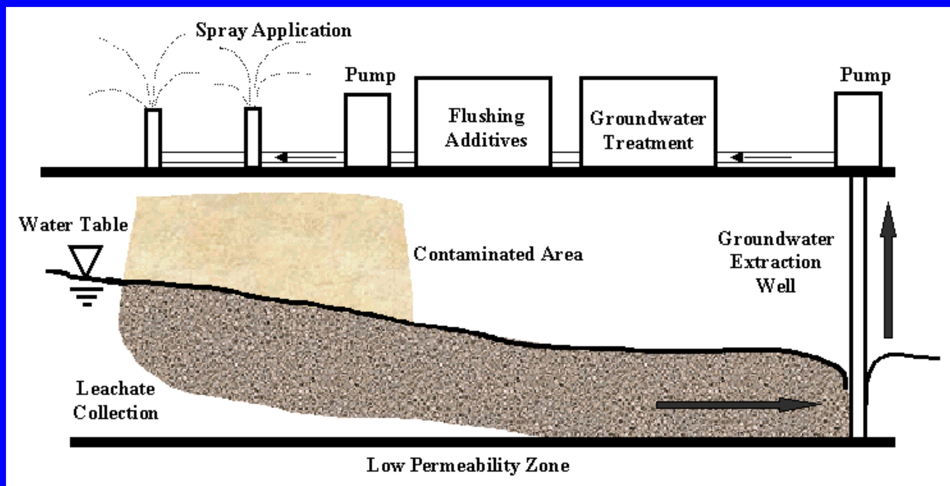
Cosolvent and Surfactant Flushing



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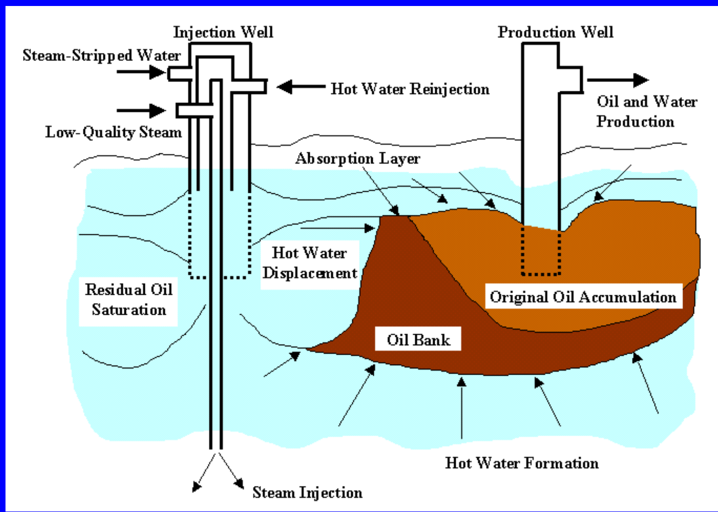
Thermal Processes



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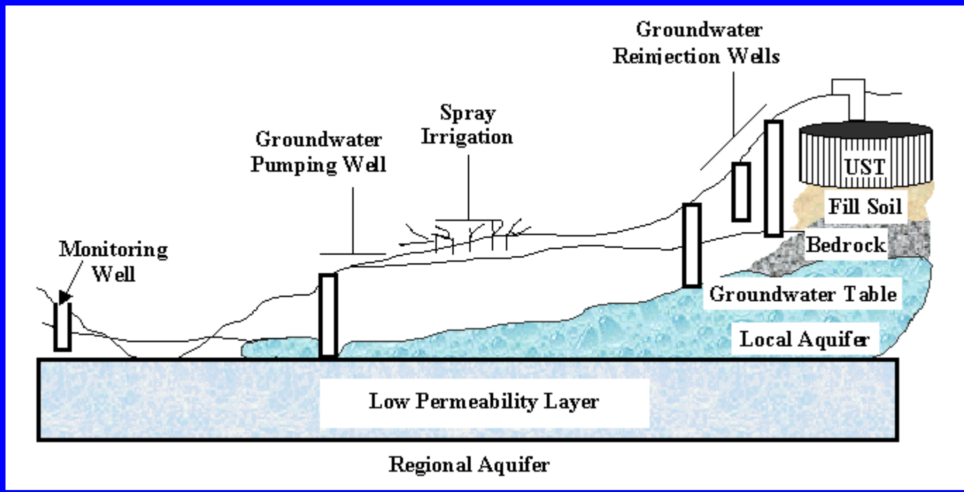
In Situ Biodegradation



Federal Remediation Technology:
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Summary of Current Approaches

- Mass transfer limitations are important for all technologies that do not mobilize the NAPL---leading to long clean-up times
- Technologies that do mobilize the NAPL phase suffer from uncontrolled mobilization that can contaminate previously clean portions of a system
- Invasive techniques can be prohibitively expensive
- In situ removal is a difficult consideration, but effective remediation methods also must solve the waste stream treatment problem
- No silver bullet: no method will be universally the best choice and economics of restoration will be site dependent

Objectives of Effective Remediation

- Remove source zone of long-lived contaminants
- Do not rely on technologies that can be limited by a slow mass transfer process
- Avoid technologies that can spread a contaminant to previously clean portions of a system
- Target approaches that can reduce a sufficient fraction of the source mass in a relatively short period of time
- Consider technologies that have manageable above-ground treatment requirements and allow reuse of flushing solutions

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Density-Based Remediation Methods

- Manipulate density of aqueous phase to ensure NAPL mobilization is controlled
- Affect balance of forces to free NAPL trapped by capillary forces
- Capture mobilized NAPL as a free phase from the top of the relatively dense aqueous phase
- Use surfactant flushing and vapor extraction to further reduce NAPL residual
- Recycle and recover flushing solutions as appropriate
- Treat and separate waste stream with above-ground unit processes

Variants Investigated

- Upward displacement of DNAPL using dense brines
- Downward displacement and collection of DNAPL from the top of a dense brine solution
- Surfactant mobilization of DNAPL downward and simultaneous dewatering of unsaturated zone
- Vapor extraction to remove trapped DNAPL residual after surfactant flush

One-Dimensional Liquid Saturated Upward Vertical Displacement of TCE

- 25-cm long, 2.5-cm diameter column
- Saturations monitored using x-ray attenuation methods
- TCE dyed with Oil Red O for visualization
- DNAPL pool initially in coarse sand layer
- Single pore-volume flush with NaI
- 65.3-74.0% removal, no visible pools
- Reference: Miller et. al. [ES&T, 34(4), 2000]

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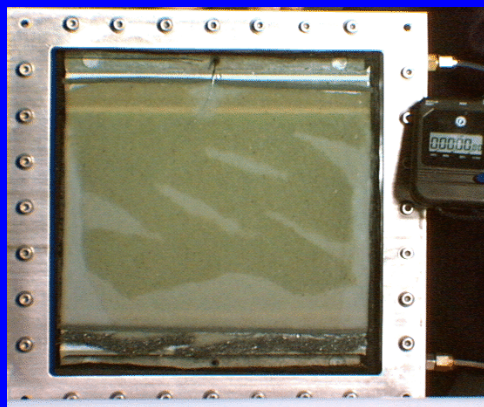
Two-Dimensional Liquid Saturated Upward Vertical Displacement of TCE



- 15-cm x 20-cm two-dimensional cell
- Pooled TCE established
- TCE dyed with Oil Red O for visualization
- Single pore-volume upward flush with NaI maintaining liquid-saturated conditions
- 54.2% removal, no visible pools, but morphology effects important
- Reference: Miller et. al. [ES&T, 34(4), 2000]

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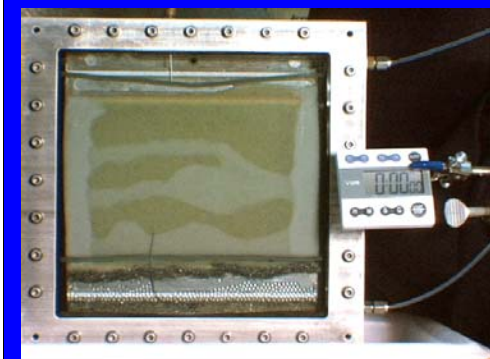
Two-Dimensional Unsaturated Downward Vertical Displacement of TCE



- 15-cm x 20-cm two-dimensional cell
- Pooled TCE established
- TCE dyed with Oil Red O for visualization
- Drainage to partially liquid-saturated conditions with thin brine layer at bottom
- 0.3 pore-volume downward flush with mixture of sulfosuccinate surfactants
- Estimated >90% removal, no visible pools, high gas-phase volume fraction---dry conditions
- Reference: Miller et. al. [ES&T, 34(4), 2000]

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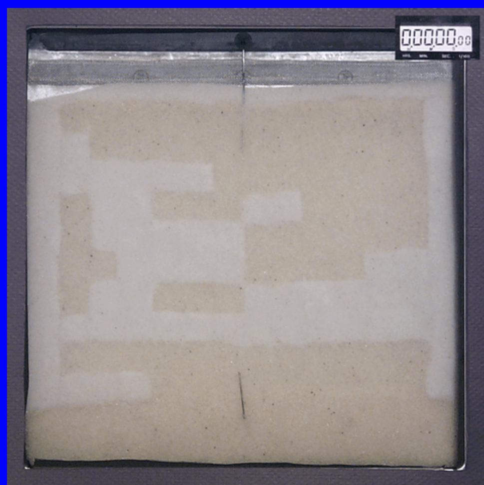
Two-Dimensional Liquid Saturated Downward Vertical Displacement of TCE



- •21-cm x 21-cm two-dimensional cell
- •Pooled TCE established
- •TCE dyed with Oil Red O for visualization
- •Established bottom brine layer
- •Maintained liquid saturated conditions
- •1.2 pore-volume downward flush with mixture of sulfosuccinate surfantants
- •Measured 68.1% TCE removal, no visible pools
- •Reference: Hill et. al. [ES&T, 35(14), 2001]

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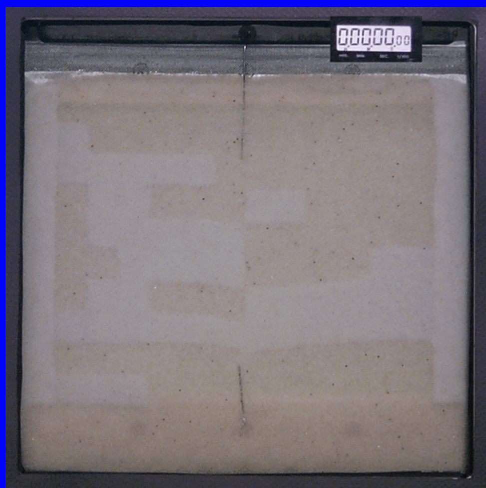
Two-Dimensional Unsaturated Downward Vertical Displacement of TCE



- 21-cm x 21-cm two-dimensional cell
- Pooled TCE established
- TCE dyed with Oil Red O for visualization
- Established bottom brine layer
- Drained to unsaturated conditions
- 0.3 pore-volume downward flush with mixture of sulfosuccinate surfantants
- Measured 80.0% TCE removal, no visible pools
- Reference: Hill et. al. [ES&T, 35(14), 2001]

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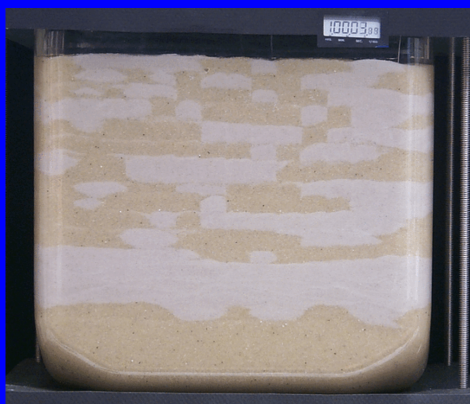
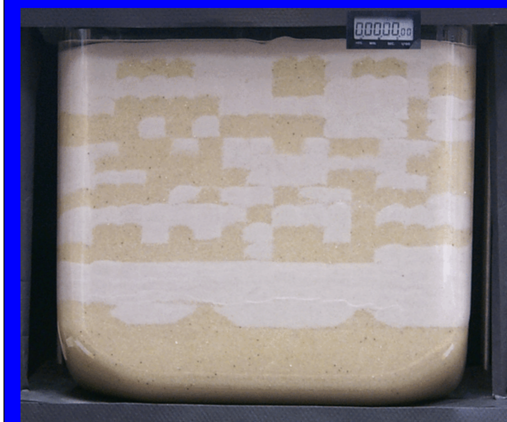
Three-Dimensional Liquid Saturated Downward Vertical Displacement of TCE



- 22-cm x 24-cm x 16-cm three-dimensional cell
- Pooled TCE established in heterogeneous media
- TCE dyed with Oil Red O for visualization
- Established bottom brine layer
- Maintained liquid saturated conditions
- 0.6 pore-volume downward flush with mixture of sulfosuccinate surfantants
- Measured 68.2% TCE removal, no visible pools
- Reference: Hill et. al. [ES&T, 35(14), 2001]

Three-Dimensional Unsaturated Downward Vertical Displacement of TCE



- •22-cm x 24-cm x 16-cm three-dimensional cell
- •Pooled TCE established in heterogeneous media
- •TCE dyed with Oil Red O for visualization
- •Established bottom brine layer
- •Drained to unsaturated conditions
- •0.2 pore-volume downward flush with mixture of sulfosuccinate surfantants
- •Measured 63.4% TCE removal, no visible pools
- •Reference: Hill et. al. [ES&T, 35(14), 2001]

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Three-Dimensional Density-Motivated Mobilization Experiments

Properties of Fluids and Porous Media

Property	$CaBr_2$ Solution	TCE w/ ORO[a]	Surfactant Solution[a]
Density @20°C (g/cm^3)	1.75± 0.01	1.4639 ± 0.0002	0.9987 ± 0.0002
Viscosity @20°C (mPa-s)	6.652± 0.033	0.577 ± 0.004[b]	0.989 ± 0.007@26°C[c]

[a] Data from Environmental Science & Technology, 35(14): 3031-3039, 2001, unless otherwise referenced.
[b] CRC Handbook of Chemistry and Physics, 1997.
[c] Environmental Science & Technology, 33(14): 2440-2446, 1999.

	Accusand[d]				A.F.S. Silica	U.S. Silica
Property	A12/20	A20/30	A30/40	A40/50	A50/70	F125
d_{50}(mm)	1.105	0.713	0.532	0.359	0.212	0.109
Uniformity Coefficient (d_{60}/d_{10})	1.231	1.190	1.207	1.200	1.047	1.500
Particle Density (g/m^3)	2.665	2.664	2.665	2.663	2.664	2.664
Hydraulic Conductivity (cm/s)	5.03×10^{-1}	2.50×10^{-1}	1.49×10^{-1}	7.20×10^{-2}		2.10×10^{-3}
Air Entry Pressure (cm H_2O)	5.8	8.7	11.6	16.8		80.2

[d] Data for Accusand was taken from Soil Science of America Journal, 60 (5): 1331-1339, 1996.

Three-Dimensional Density-Motivated Mobilization Experiments

Setup

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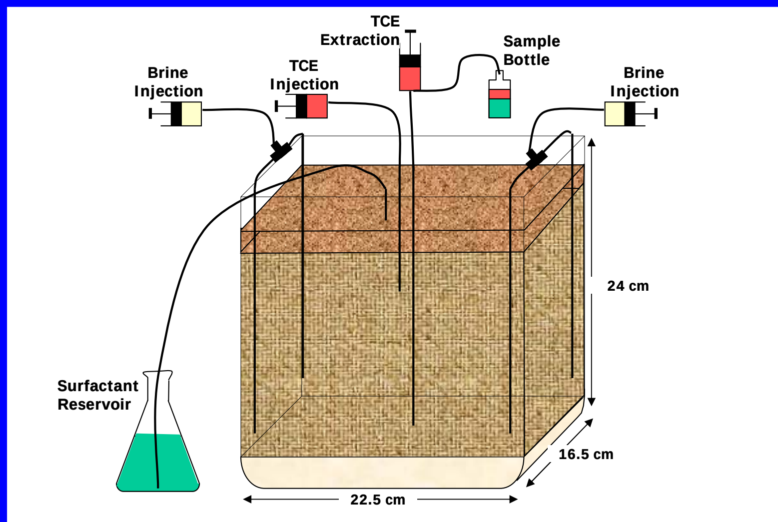
Three-Dimensional Density-Motivated Mobilization Experiments

Cell Schematic



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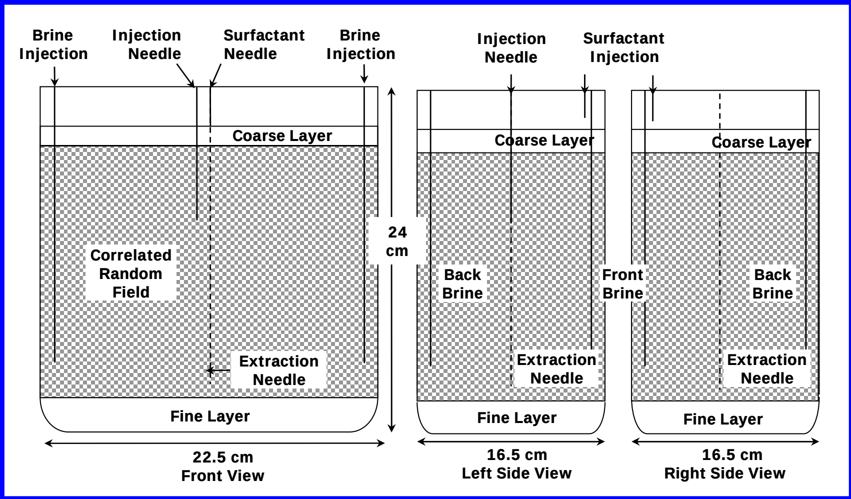
Three-Dimensional Density-Motivated Mobilization Experiments

Cell Layout



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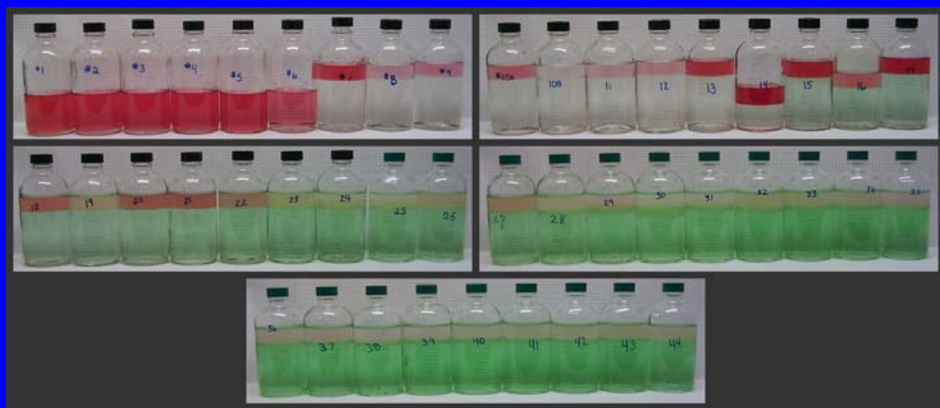
Three-Dimensional Density-Motivated Mobilization Experiments

Samples



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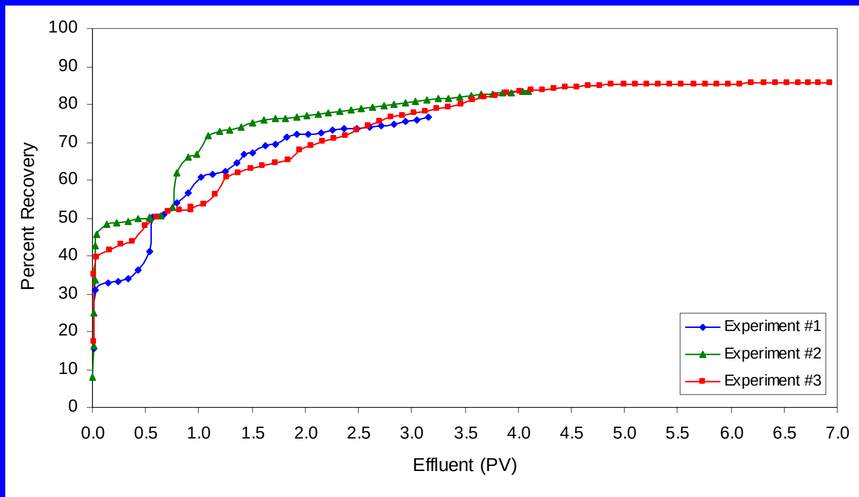
Three-Dimensional Density-Motivated Mobilization Experiments

Cumulative Recovery of TCE



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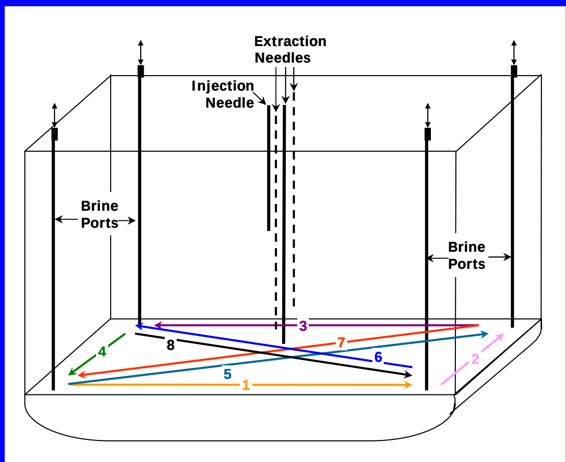
Three-Dimensional Density-Motivated Mobilization Experiments

Vapor Extraction Nitrogen Flow Paths



- Vapor extraction was performed in Experiments 2 & 3.
- Nitrogen was circulated counterclockwise through adjacent ports (1-4) and opposing ports (5-8).
- Dotted lines are additional extraction needles in Experiment #3

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Three-Dimensional Density-Motivated Mobilization Experiments

Vapor Extraction

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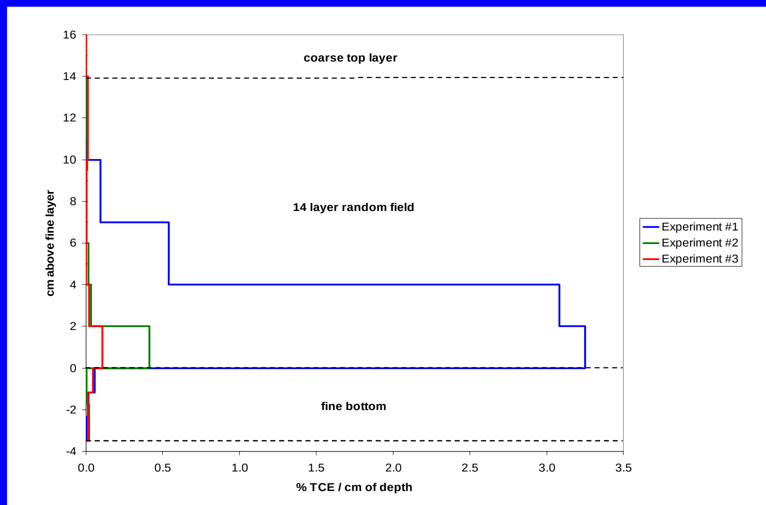
Three-Dimensional Density-Motivated Mobilization Experiments

Soil Extraction



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Three-Dimensional Density-Motivated Mobilization Experiments

Properties and Recovery

	No. Extraction Wells	Pore Volume (L)	Surfactant (PV)	TCE Recovery (%)			Mass Balance (%)
				Well Extraction	Vapor Extraction	Soil Extraction	
Experiment #1	1	1.3	1.8	76.5	n/a	14.7	91.2
Experiment #2	1	1.5	2.6	83.5	5.7	1.0	90.2
Experiment #3	3	1.4	5.3	86.2	8.2	0.4	94.8

Three-Dimensional Unsaturated Downward Vertical Displacement of TCE

- •22-cm x 24-cm x 16-cm three-dimensional cell
- •Pooled TCE established in heterogeneous media
- •TCE dyed with Oil Red O for visualization
- •Established bottom brine layer
- •Drained to unsaturated conditions
- •3.2 pore-volume downward flush with mixture of sulfosuccinate surfantants followed by vapor extraction
- •Measured 99% TCE removal of recovered TCE
- •Reference: Johnson et. al. [ES&T, 38(19), 2004]

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Open Issues

- Scale up
- Brine density control and recovery
- Surfactant selection
- Geochemical stability
- Waste-stream separation and process treatment design and pilot testing
- Mathematical model development and application
- Development of optimal design strategies
- Economical analysis

Dover Air Force Base

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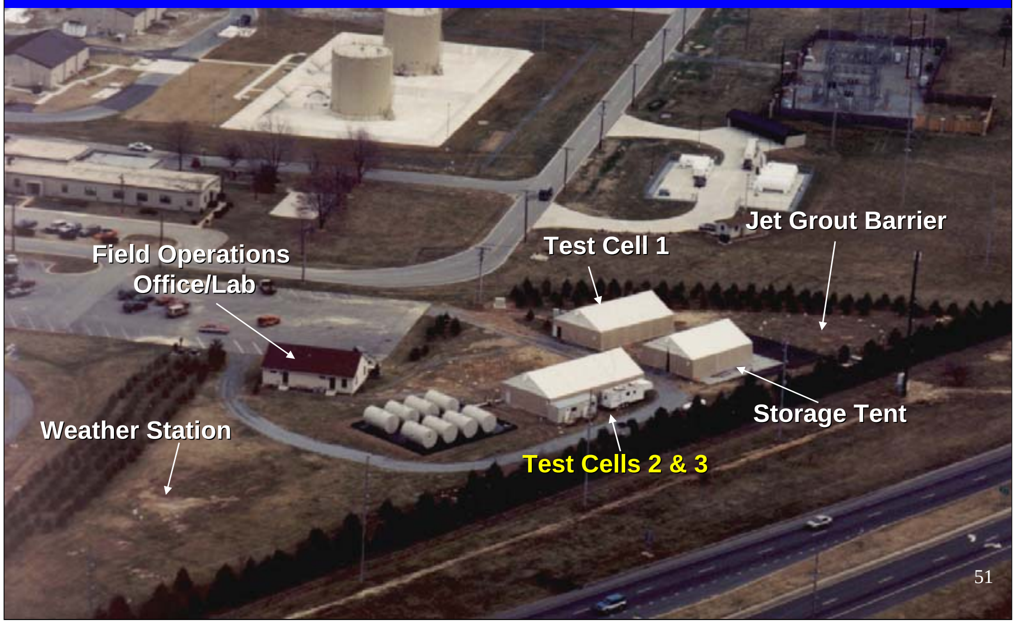
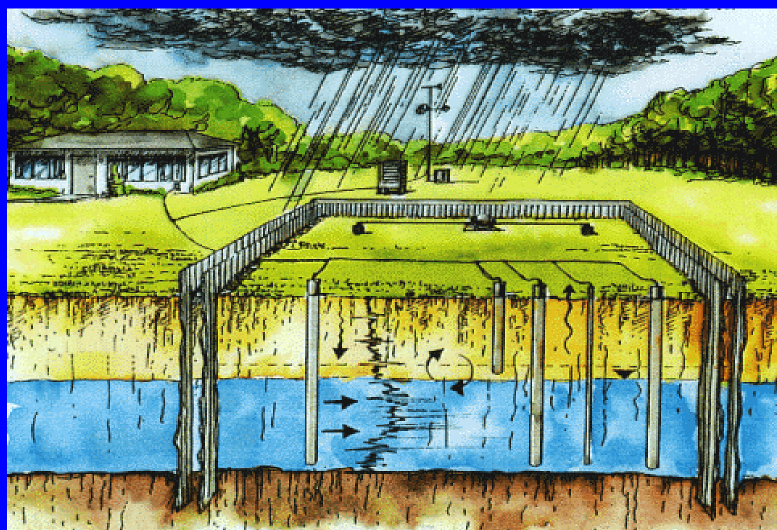
Dover National Test Site



The DNTS supports technology demonstrations anywhere on DAFB, however the focus of research is conducted on this 3.5 acre plot surrounded by pine trees, located in the NW corner of DAFB. Commonly referred to as the GRFL, the site consists of an office, laboratory, weather station, tank farm, and test plots. Three of these test plots are actually sealed test cells situated within in the Columbia Aquifer. This particular portion of the aquifer was considered to be a clean, pristine area when the facility was established in 1995. Also available to research projects are established utilities, a cone penetrometer test (CPT) rig for drilling and investigative work, and analytical equipment.

DNTS Concept



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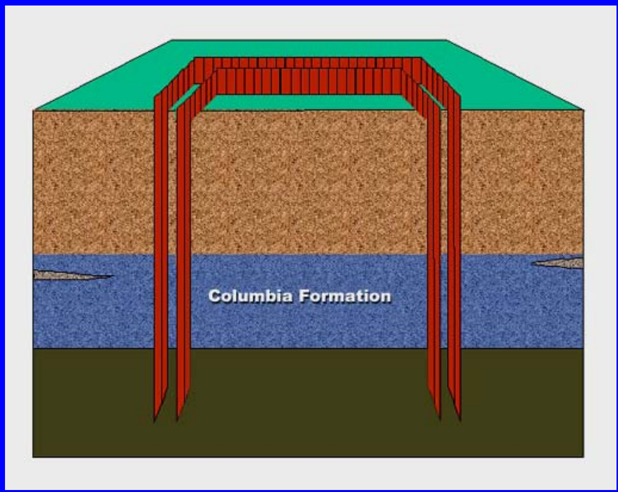
One of the difficulties in evaluating innovative technology effectiveness lies in the inability to accurately quantify the mass of contaminant in the ground prior to treatment. To simplify this factor, the DNTS would install sealed test cells enabling a very accurate mass balance. We know how much DNAPL goes in; how much comes out; and the mass that's remaining.

Dover National Test Site



- Depth to the water table is approximately 28 feet.
- Aquifer depth is approximately 12 feet.
- Test cells are double-walled sheet piles driven into the subsurface.
- Sheet piles are keyed into a confining aquitard approximately 45 feet below the surface.

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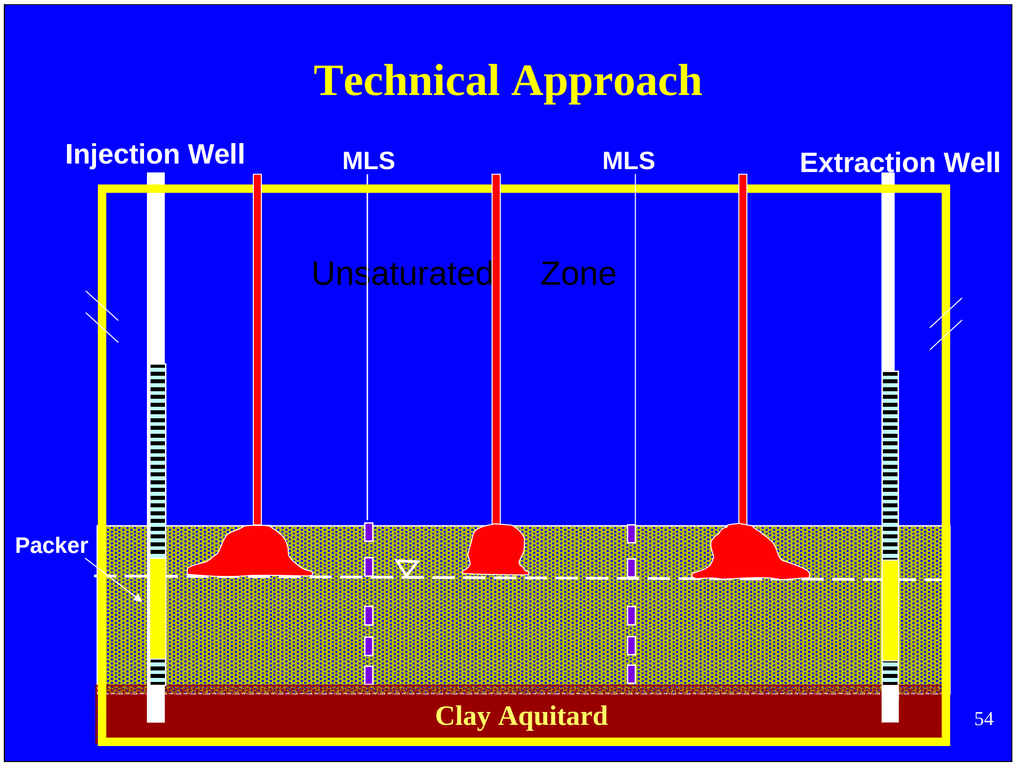

DNAPL injections are conducted by pumping pure PCE into stainless steel tubes. The water level in the cell is adjusted to a point just below the openings of the CIPs. PCE is pumped in at the maximum rate limited by formation. The PCE hits the water interface and tends to spread laterally. Once the injection is complete, the water level is lowered to a point about 1-foot above the clay, and then raised back up – essentially creating a smear zone of residual DNAPL.

Test Cells 2 & 3

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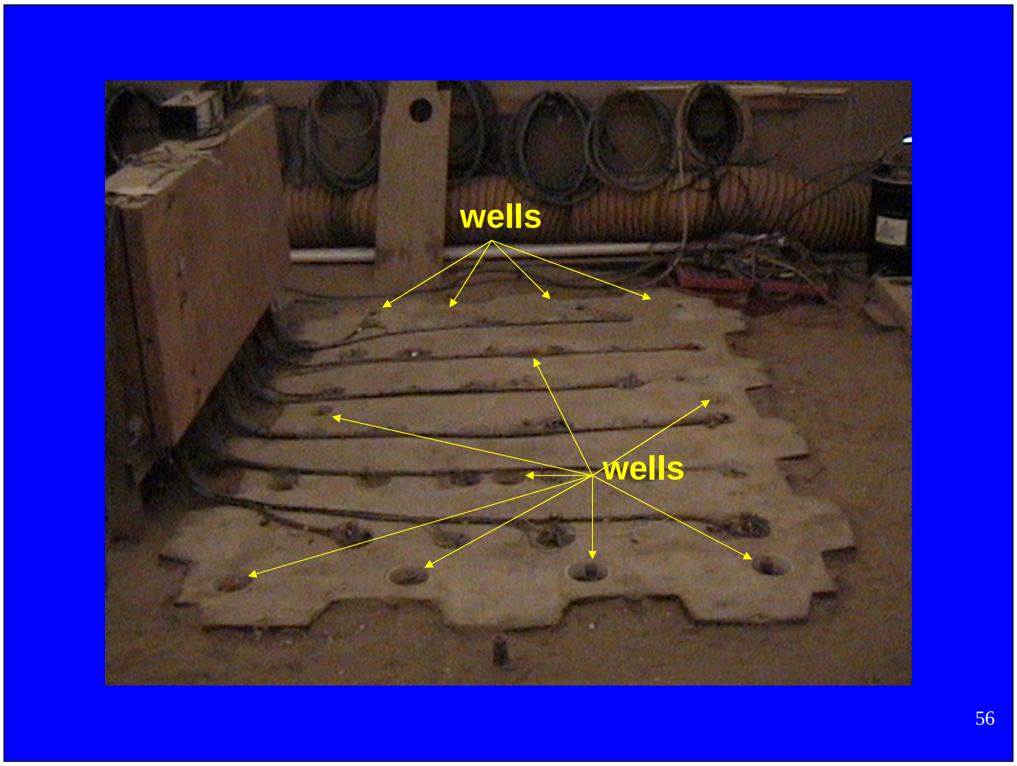
To date, EPA is completing the 5th and final demonstration.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wells
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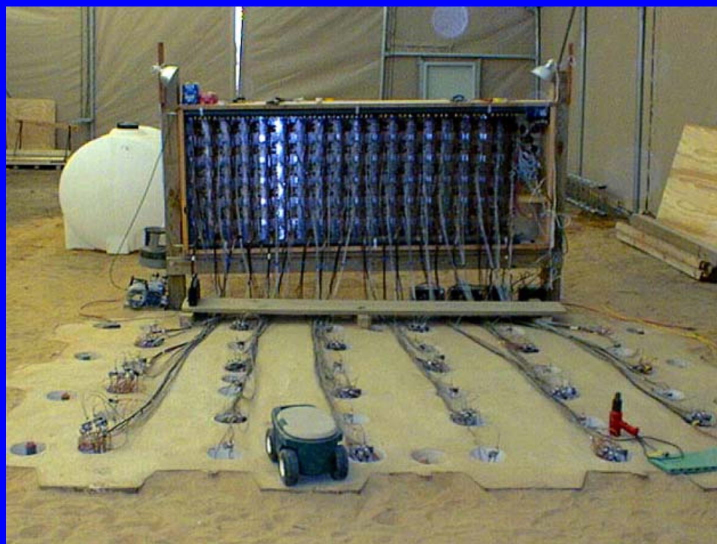
DNTS Test Cell 3



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Multi-level samplers
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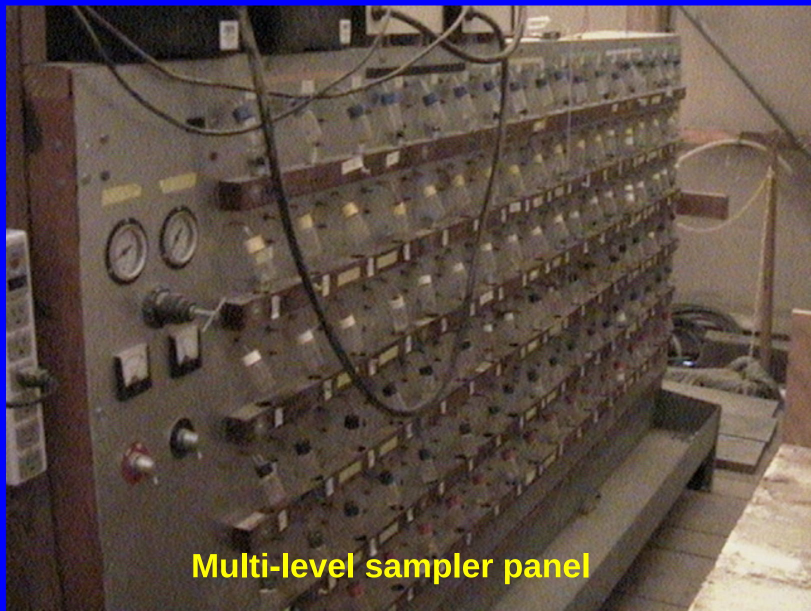

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Piping manifold
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CPT Rig

Cone penetrometer data
Soil sampling
Well installations

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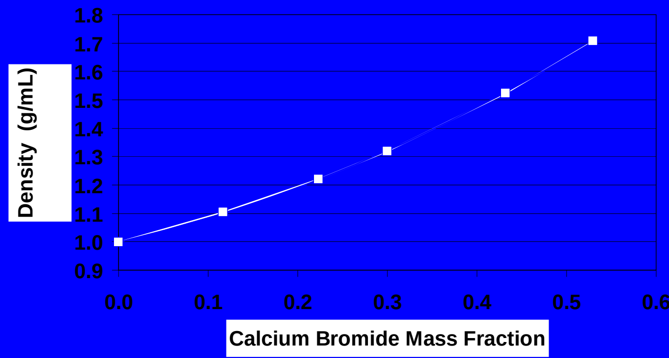
DNTS Previous Studies

Study	Conducted by	Test Cell	Started	Recovery
Cosolvent Solubilization	EPA/ U of FL	3	1998	~64%
Air Sparging/ Soil Vapor Extraction	EPA/ MTU	2	1999	~88%
Surfactant Solubilization	EPA/ U of OK	3	2000	~65%
Bioremediation	NFESC	1	2001	On-going
Cosolvent Mobilization	EPA/ Clemson	2	2001	~78%
Complex Sugar Flushing	EPA/ U of AZ	3	2001	~48%

Brine Density



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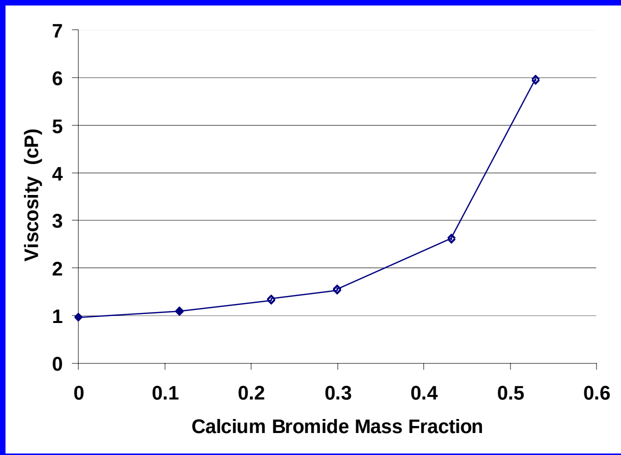
Brine Viscosity



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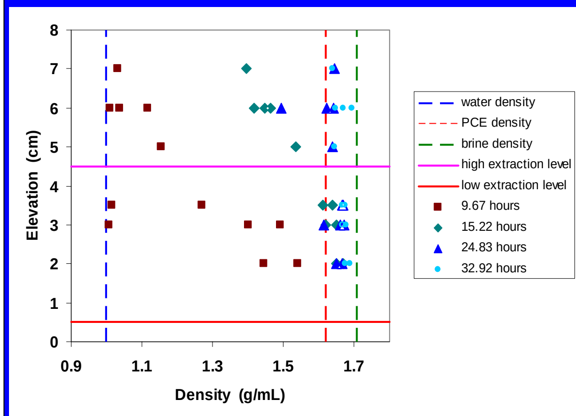
Formation of Brine Layer



- Three-dimensional experiment
- Dover-like sand
- Brine injected from bottom
- Density monitored throughout the system and with time
- Density of the brine layer exceeds the density of PCE after about 33 hours

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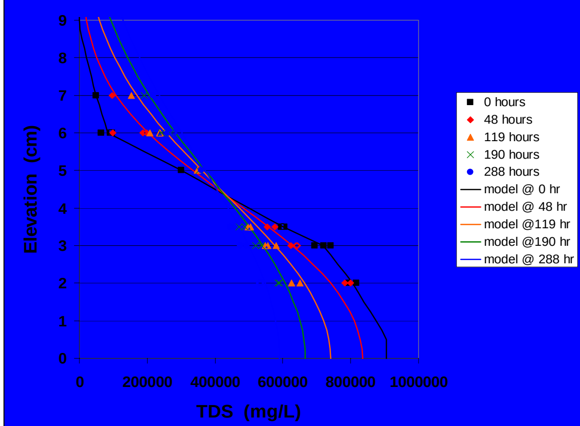
Diffusion of Brine



- Diffusion of brine about sharp interface observed in space and time
- Density of 1.7 g/mL corresponds to a TDS of 900,000 mg/L
- PCE density 1.62 g/mL corresponded to a TDS of 780,000 mg/L
- Brine barrier is stable and long-lived in presence of diffusion alone

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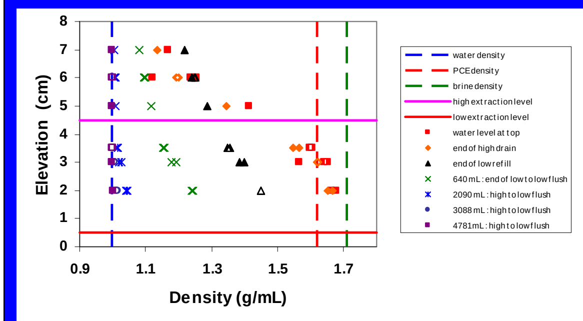
Recovery of Brine



- Brine removed by drainage from upper, then lower, ports
- After drainage, horizontal flushing performed
- Water table reduced further as flushing continued

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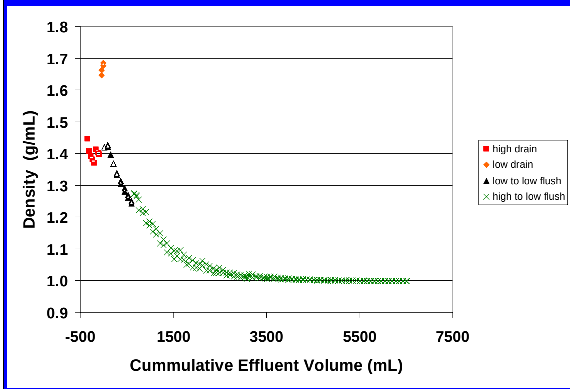
Effluent Density During Recovery



- Three-dimensional cell
- Dover-like sand
- Drained first from top of brine layer
- Drainage from within brine layer
- Horizontal flushing to observe brine residual removal

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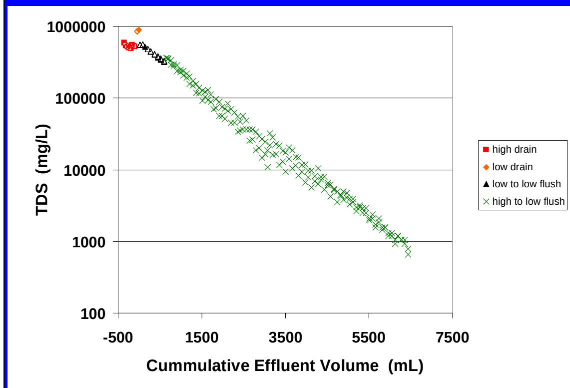
Effluent Brine Concentration During Recovery



- Three-dimensional cell
- Dover-like sand
- Drained first from top of brine layer
- Drainage from within brine layer
- Horizontal flushing to observe brine residual removal

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Surfactant Properties

Surfactant (Molecular Formula)	Composition (% by wt)	Density @20°C (g/cm^3)	HLB	CMC (mM)
Anionic				
Aerosol AY-100 ($C_{14}H_{25}O_7NaS$)	>97% Sodium diamyl sulfosuccinate	1.2	NA	28
Aerosol MA 80-I ($C_{16}H_{29}O_7NaS$)	78-80% Sodium dihexyl sulfosuccinate 5.0% isopropanol	1.12 @ 25°C	NA	24
Aerosol OT-100 ($C_{20}H_{37}O_7NaS$)	>97% Sodium dioctyl sulfosuccinate	1.1	NA	1.12
Nonionic				
Triton X-45 ($C_{14}H_{22}O(C_2H_4O)_n$; n=4-5)	>97% Polyethylene glycol octylphenyl ether <3.0% Polyethylene glycol	1.037	9.8	0.11
Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$; n=9-10)	>97% Polyethylene glycol octylphenyl ether <3.0% Polyethylene glycol	1.067	13.5	0.24
Triton X-114 ($C_{14}H_{22}O(C_2H_4O)_n$; n=7-8)	>97% Polyethylene glycol octylphenyl ether <3.0% Polyethylene glycol	1.058	12.3	0.21
Tween 80 ($C_{64}H_{124}O_{26}$)	90-100% Polyoxyethylene (20) sorbitan monooleate <3.0% Polyethylene glycol	1.075	15.4	0.12

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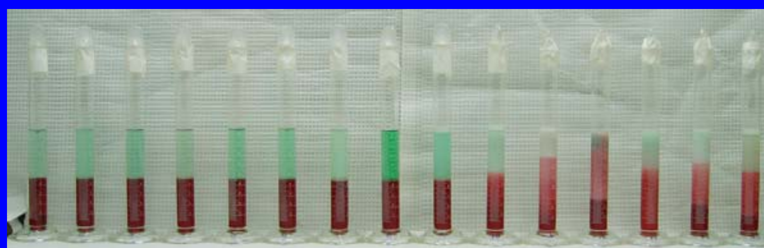
Surfactant Screening

- Optimal Surfactant
  - Does NOT precipitate out of solution in the presence of brine
  - Does NOT form a stable macroemulsion
  - Has a relatively short equilibration time (<24 hours)
  - Low microemulsion viscosity and interfacial tension with PCE
  - Avoids Winsor Type II microemulsion, which serves as a surfactant sink



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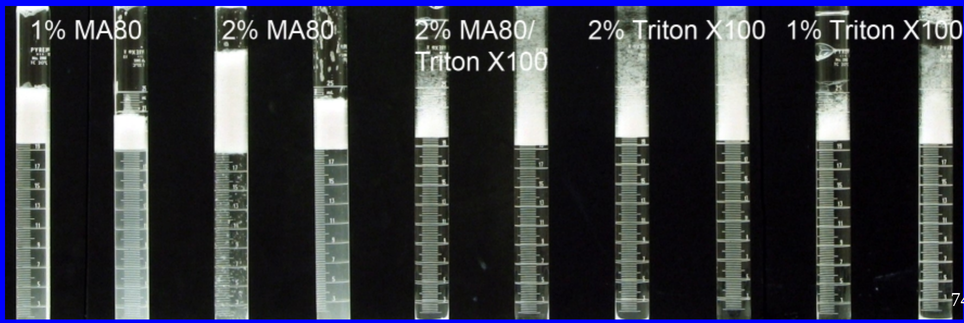
Movie shows a combination of surfactants, with some equilibrating in a short period of time, others forming a stable macroemulsion.

Surfactant Particle Behavior

- Surfactant solutions with various concentration of surfactants, 3% isopropanol, 1.7% $CaCl_2$. In each set, right image also has 6% $CaBr_2$.
- Due to the presence of brine, anionic surfactants used in remediation of systems with PCE have resulted in precipitation of surfactant out of solution as with Aerosol MA.
- However, mixtures containing nonionic solutions such as Triton X-100 do not precipitate out.



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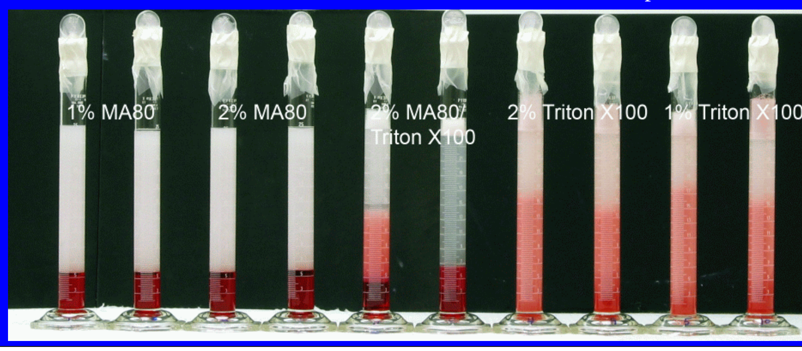
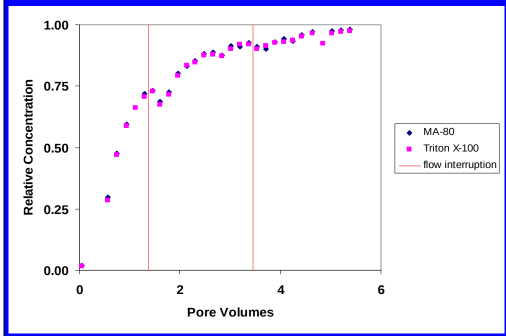
Surfactant Phase Behavior

- Phase behavior experiments resulted in highly stable macroemulsions forming with solutions containing only Triton X-100
- MA80 solutions equilibrated quickly but resulted in a Winsor II microemulsion, which serves as a surfactant sink
- Mixture of MA80/Triton did not precipitate, equilibrated rapidly, and formed a high solubilization Winsor III emulsion, with low interfacial tensions capable of mobilization



Sorption of Surfactant



- Dover sand
- Surfactant mixture of 1% MA 80-I, 1% Triton X-100, 3% IPA, and 1.7% $CaCl_2$
- Triton X-100 included to prevent precipitation of the MA 80-I in the presence brine
- MA 80-I and Triton X-100 do not separate due to sorption during transport through the Dover sand.
- Rate limited sorption observed
- Retardation factors of 1.28 and 1.30 for MA 80-I and Triton X-100, respectively

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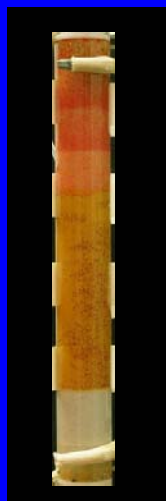
Mobilization and Solubilization



- Dover sand
- PCE dyed red
- Surfactant mixtures of 1% MA 80-I, 1% Triton X-100, 3% IPA, and 1.7% $CaCl_2$
- Clean PCE mobilization front
- PCE front followed by microemulsion phase containing residual PCE

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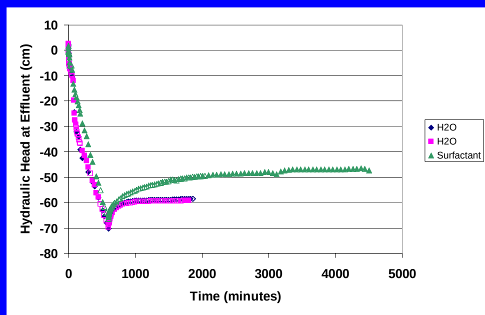
Effect of Surfactant on Drainage



- Dover sand
- Drainage rate to mimic a water table dropping at about 2 ft/day
- Rate of 3 mL/hr for water and 4 mL/hr for surfactant
- Surfactant flush had a smaller pressure gradient and more extensive rebound due to changes in IFT and drainage

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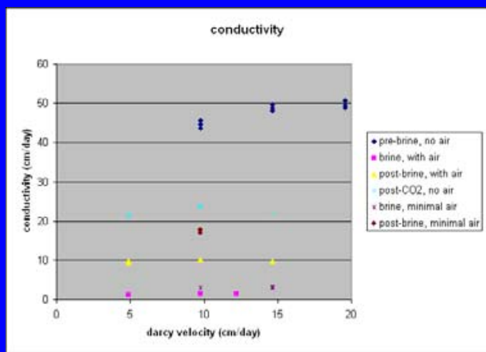
Effect of Brine on Clay Hydraulic Conductivity



- Dover clay material, dried, hand packed
- De-aired, de-ionized water and calcium bromide brine
- Gas bubbles formed during brine portion of experiments
- Brine reduced effective hydraulic conductivity
- Hydraulic conductivity values are significantly greater than reported by Dames & Moore---due to clay preparation

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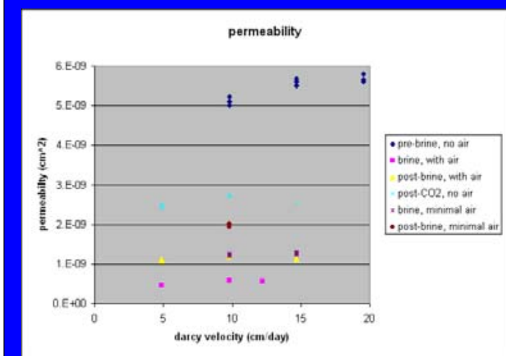
Effect of Brine on Clay Permeability



- Dover clay material, dried, hand packed
- De-aired, de-ionized water and calcium bromide brine
- Gas bubbles formed during brine portion of experiment
- Brine reduced effective intrinsic permeability
- Intrinsic permeability values are significantly greater than reported by Dames & Moore---due to clay preparation

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Conclusions

- Standard remediation approaches are influenced by slow mass transfer and/or uncontrolled mobilization
- Brine-barrier methods have been found to overcome these limitations
- High fractions of removal have been observed in a wide range of laboratory studies
- Field-scale testing is underway
- Open issues remain to be resolved

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Students, Associates, and Collaborators

- Ed Hill III
- Morris Arthur
- Jose Alfaro
- Rick Bond
- Deona Johnson
- Huina Li
- Marylene Moutier
- Paul Imhoff
- Matthew Farthing
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- Emmie Granbery
- Patrick Sanderson
- Lauren Murphy
- Pam Birak
- Stephanie Knight
- Dottie Schmitt
- Randy Kabrick
- Yossef Gohary
- And several others...

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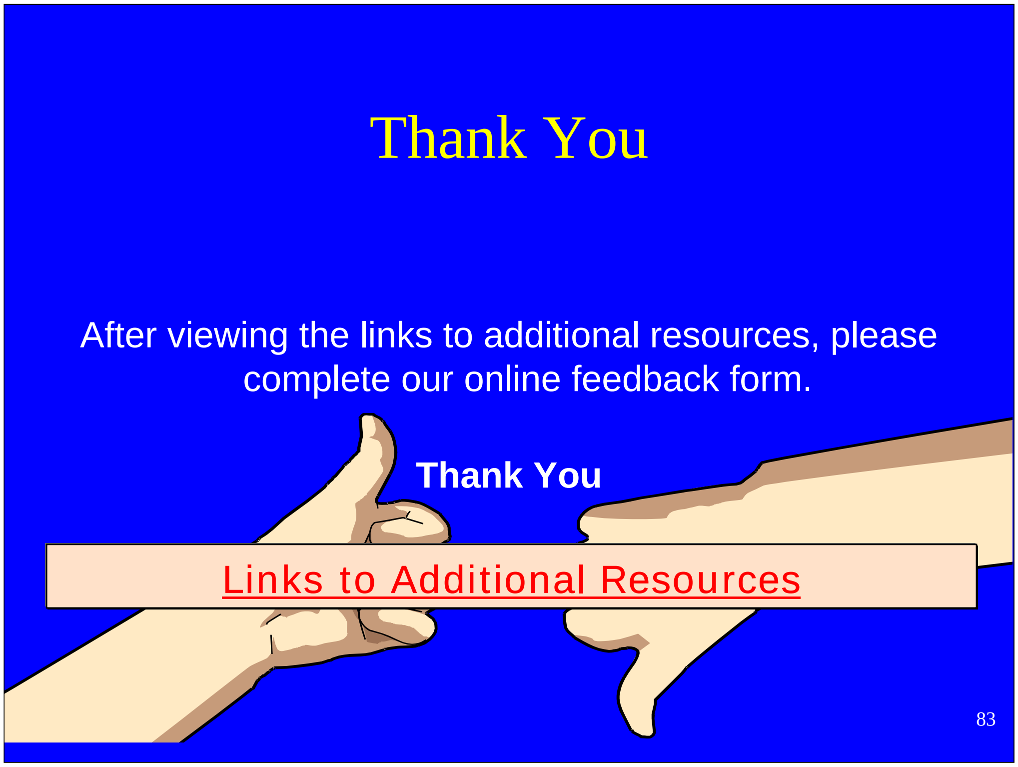
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