Project on Brine-Based Remediation of DNAPL-Contaminated Subsurface Systems

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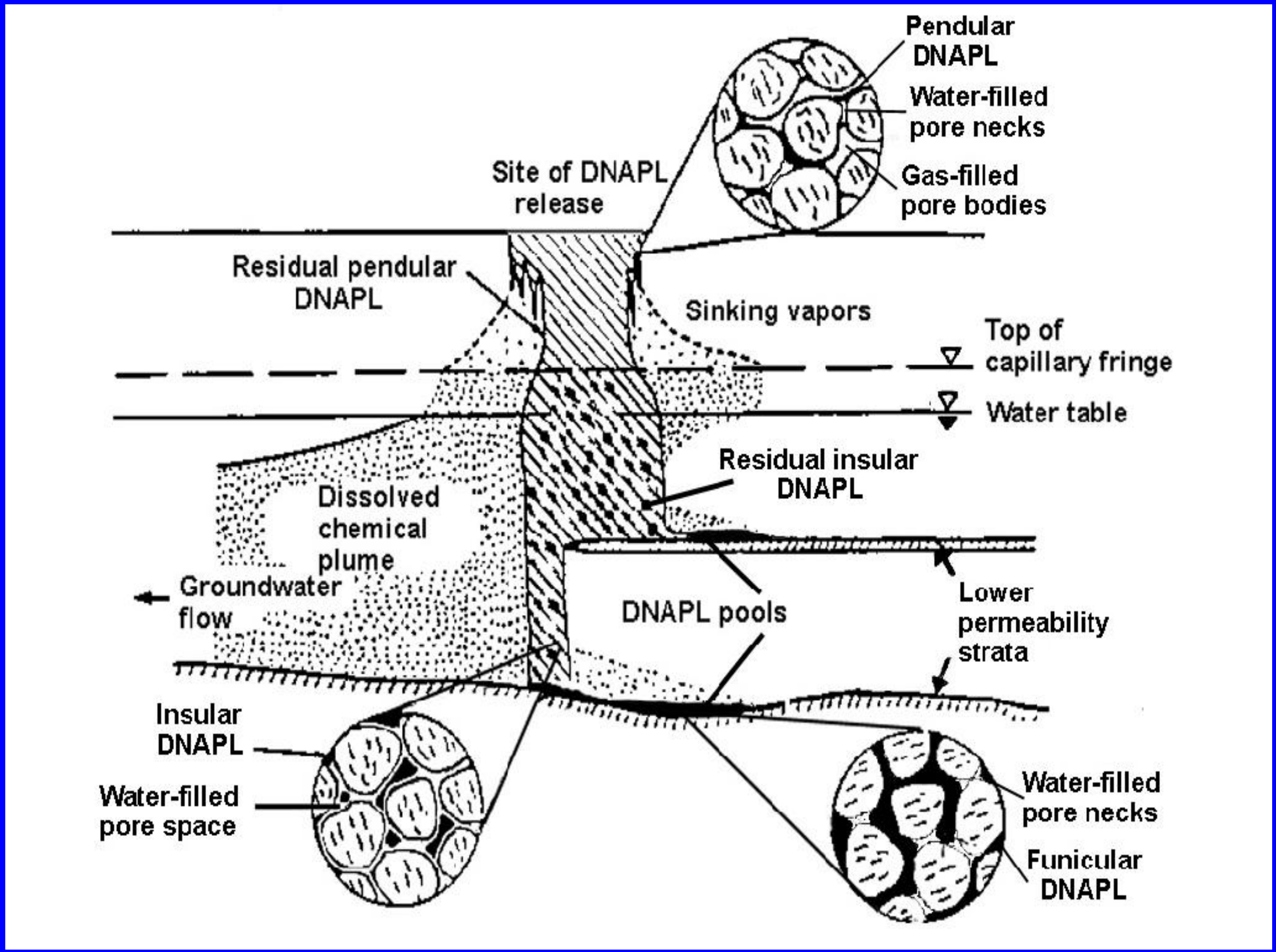
Motivation

- Multiphase systems result from common sources of contamination
- Remediation of such contaminated systems has proven especially difficult
- A wide variety of schemes have been investigated to accomplish such a remediation
- Brine-based remediation methods motivate this project

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

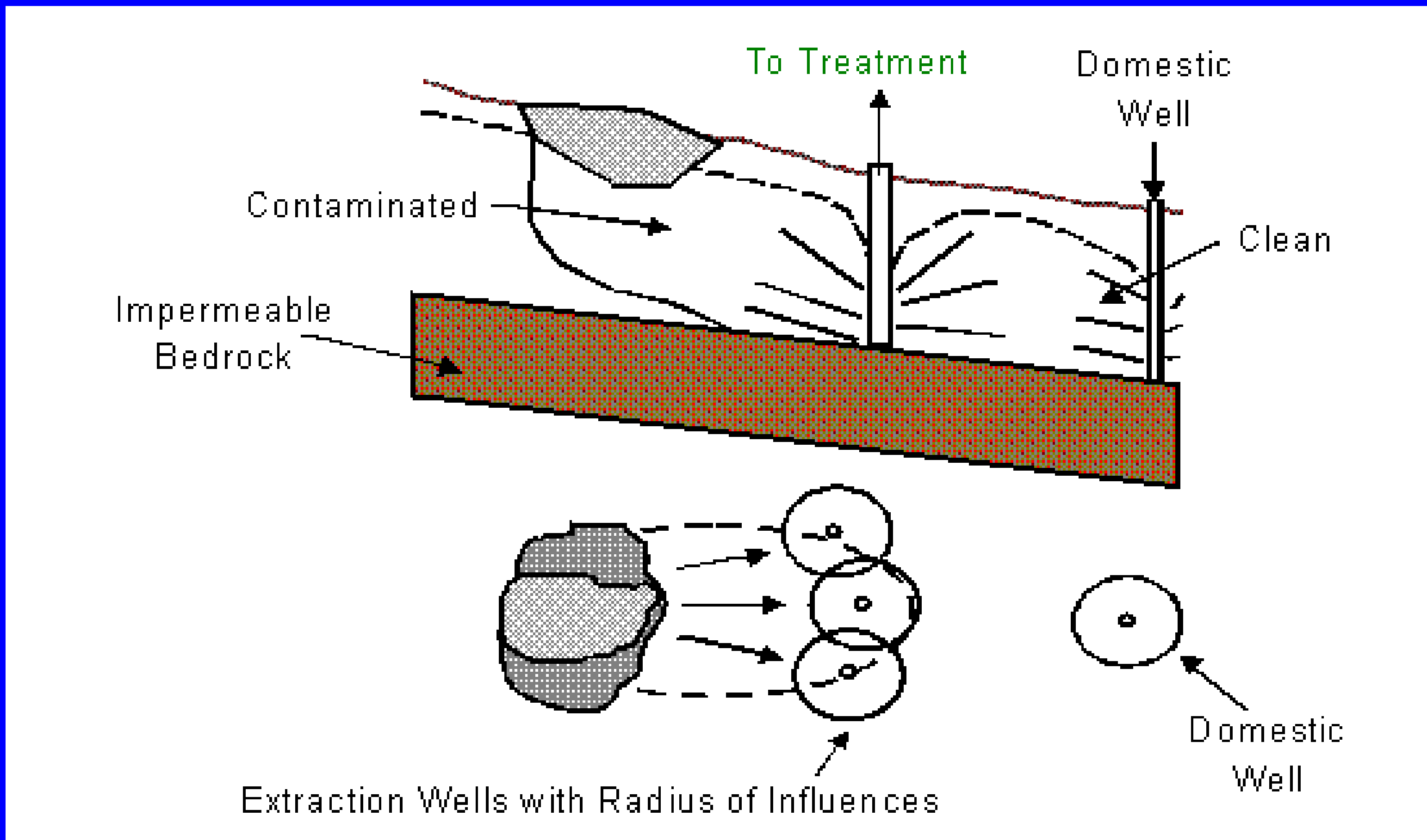
DNAPL Behavior in Heterogeneous Porous Media



Current Remediation Approaches and Limitations

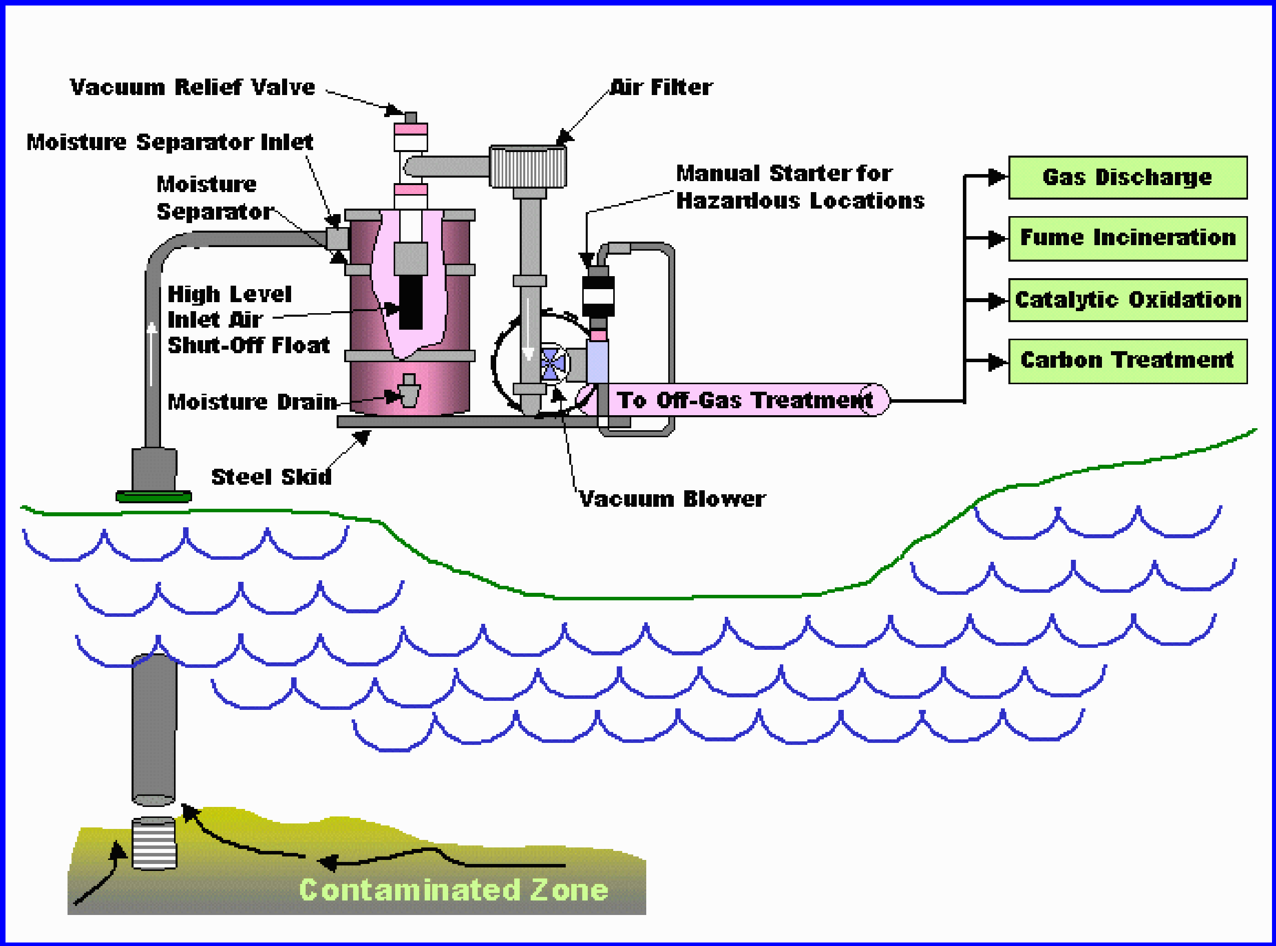
- Pump-and-Treat
- Vapor-Phase Extraction
- Air Sparging
- Cosolvent and Surfactant Flushing
- Thermal Processes
- In Situ Biodegradation

Pump-and-Treat



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

Vapor Extraction



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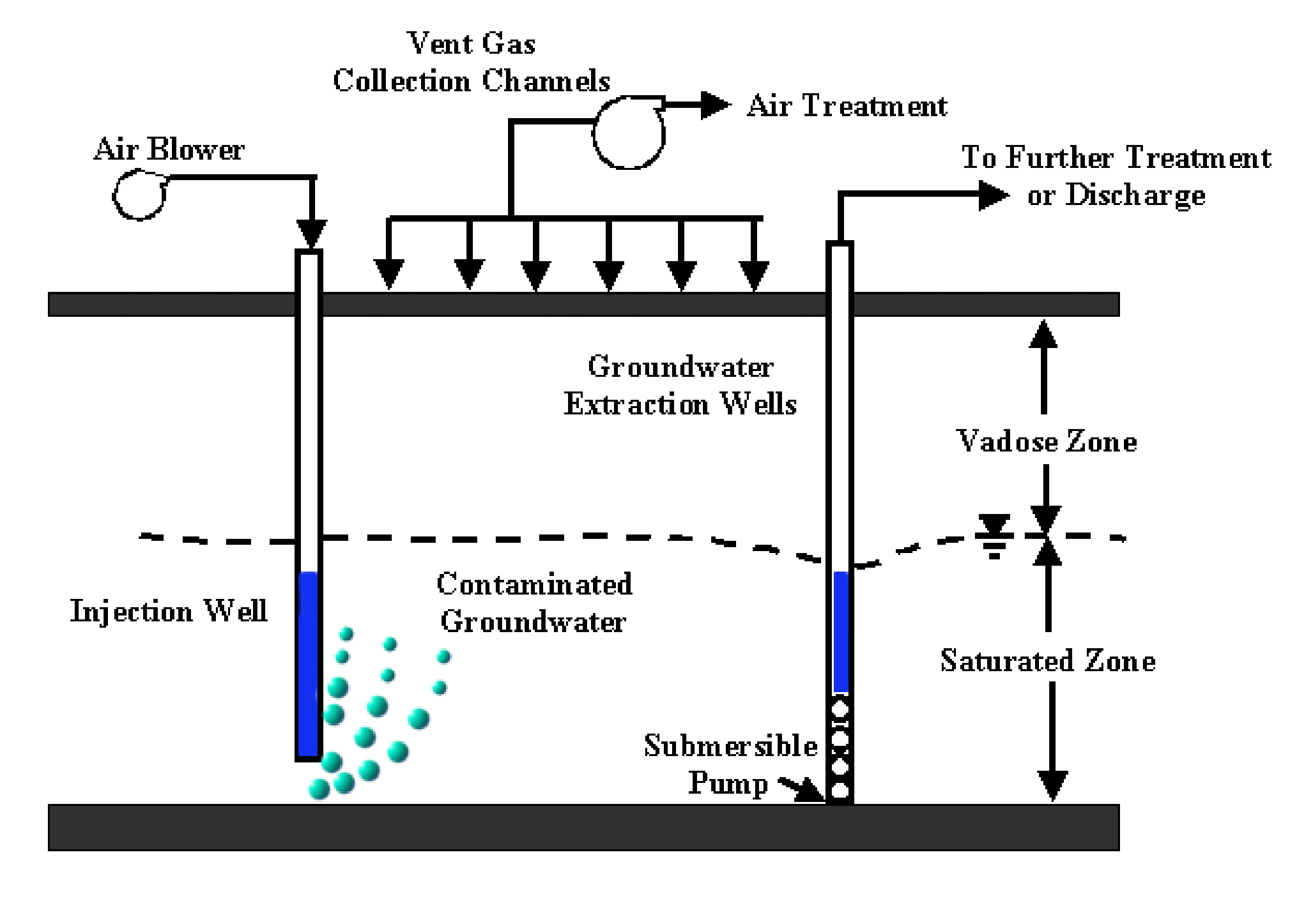
Air Sparging



Federal Remediation Technology:
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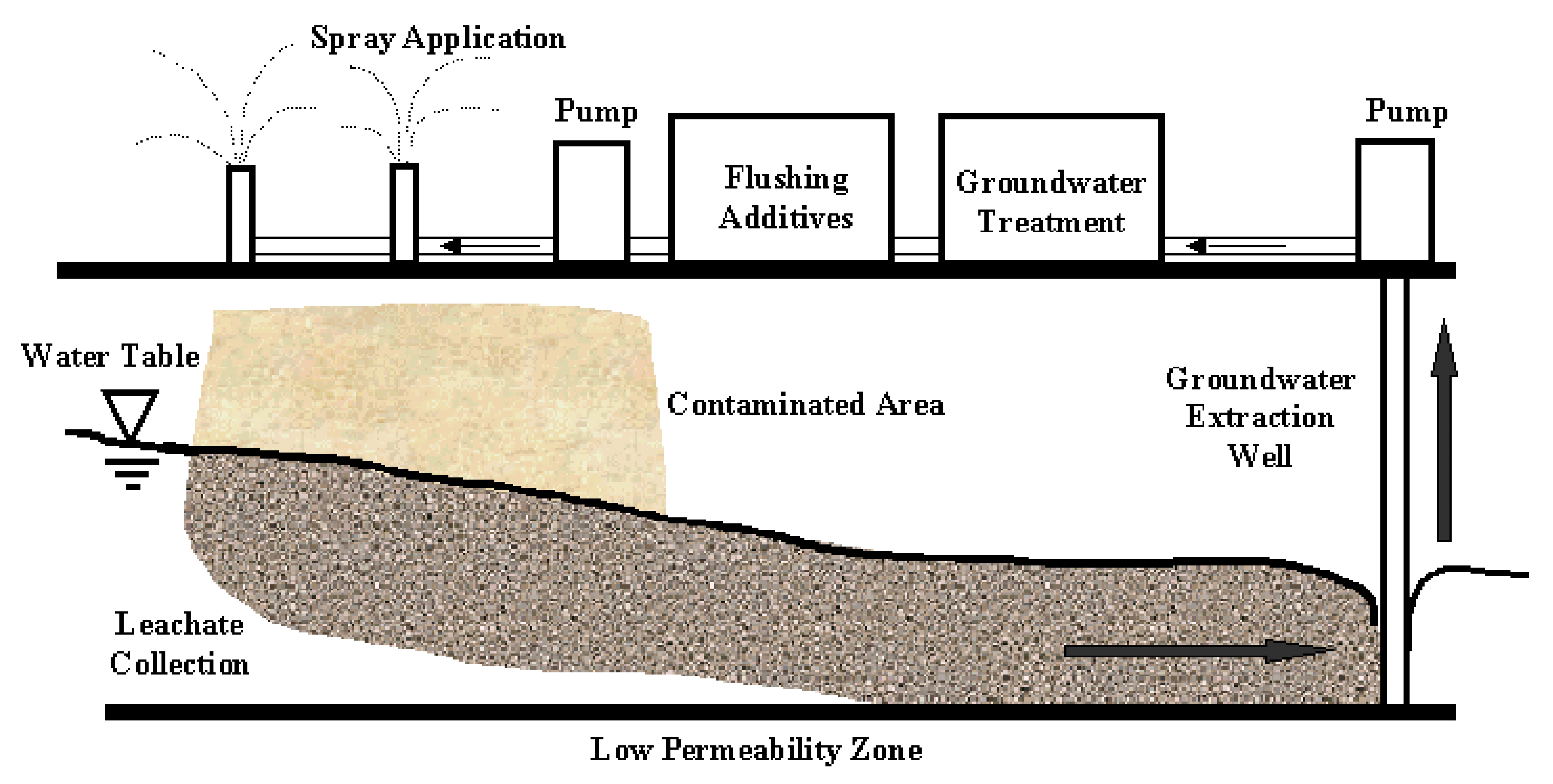
Cosolvent and Surfactant Flushing



Federal Remediation Technology:
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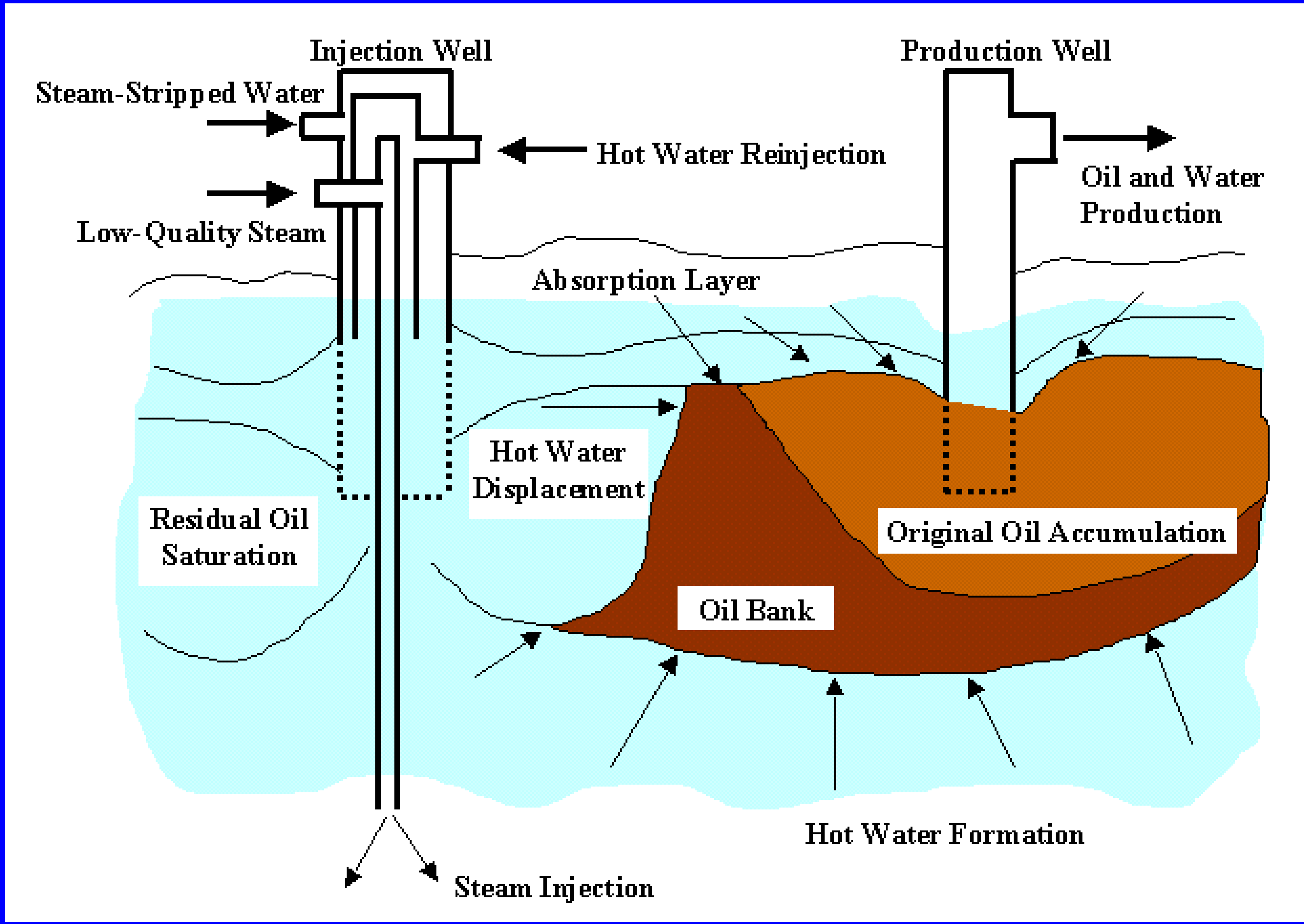
Thermal Processes



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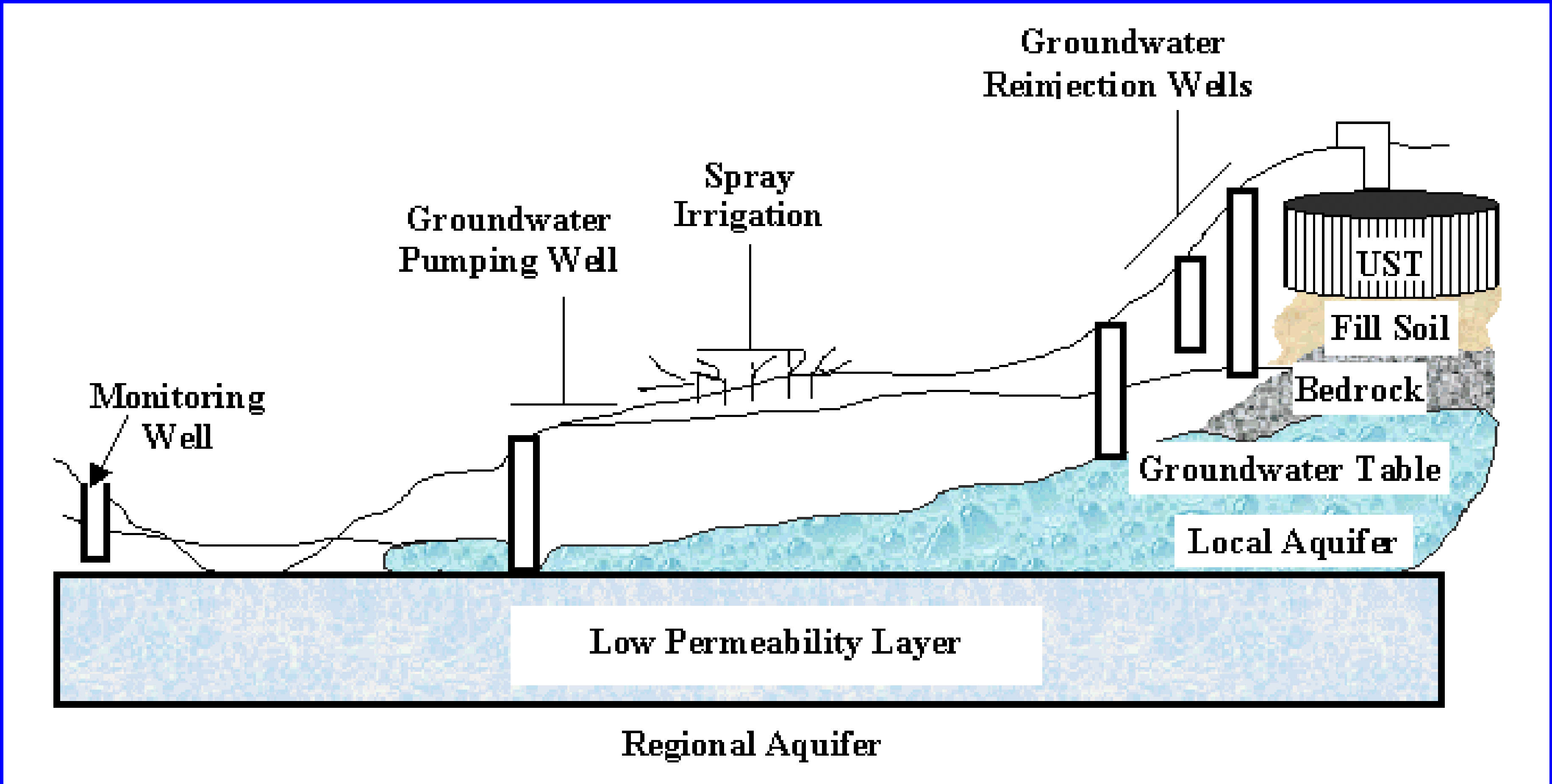
In Situ Biodegradation



Federal Remediation Technology:
http://www.frtr.gov/matrix2/section4/D01-4-2.gif

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

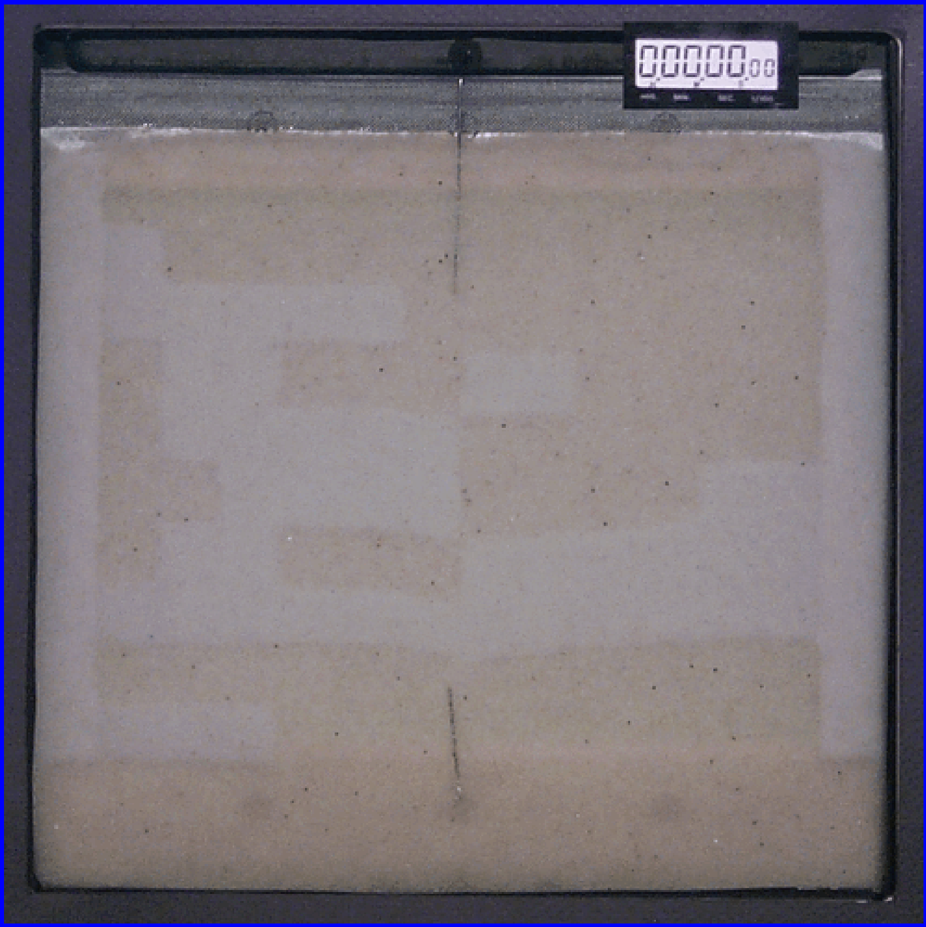
Objectives of Effective Remediation

- 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

Brine-Based Remediation Methods

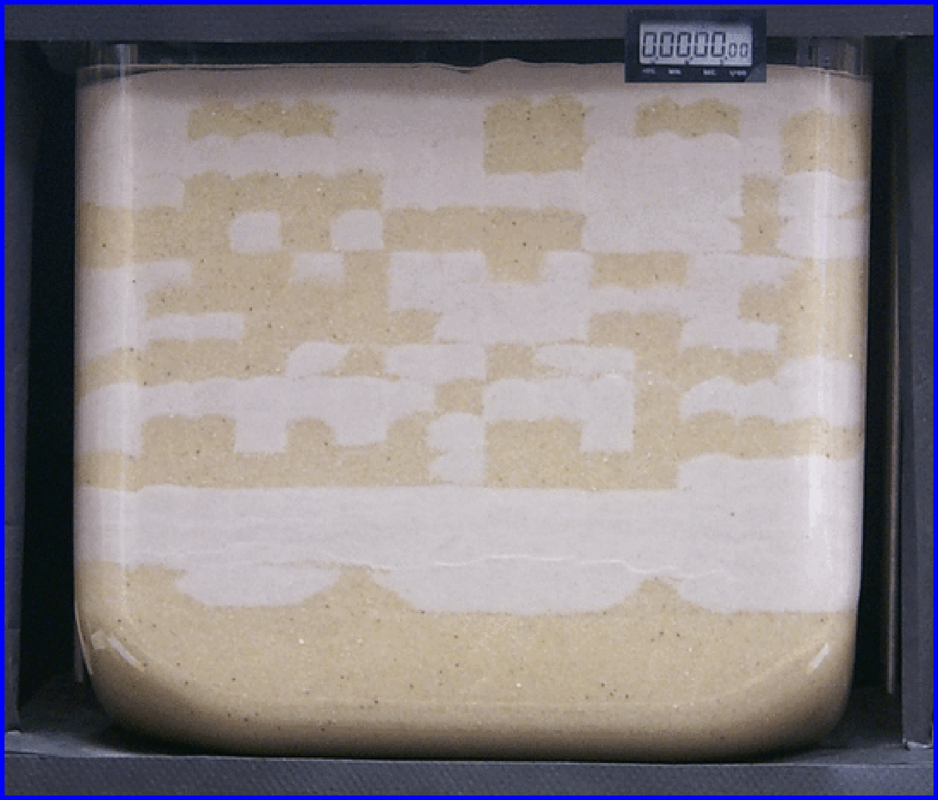
- Manipulate density of aqueous phase to ensure NAPL mobilization is controlled
- Affect balance of forces to free NAPL trapped by capillary forces
- Capture mobilized NAPL as a free phase from the top of the relatively dense aqueous phase
- Use surfactant flushing and vapor extraction to further reduce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

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]

Three-Dimensional Unsaturated Downward Vertical Displacement of TCE



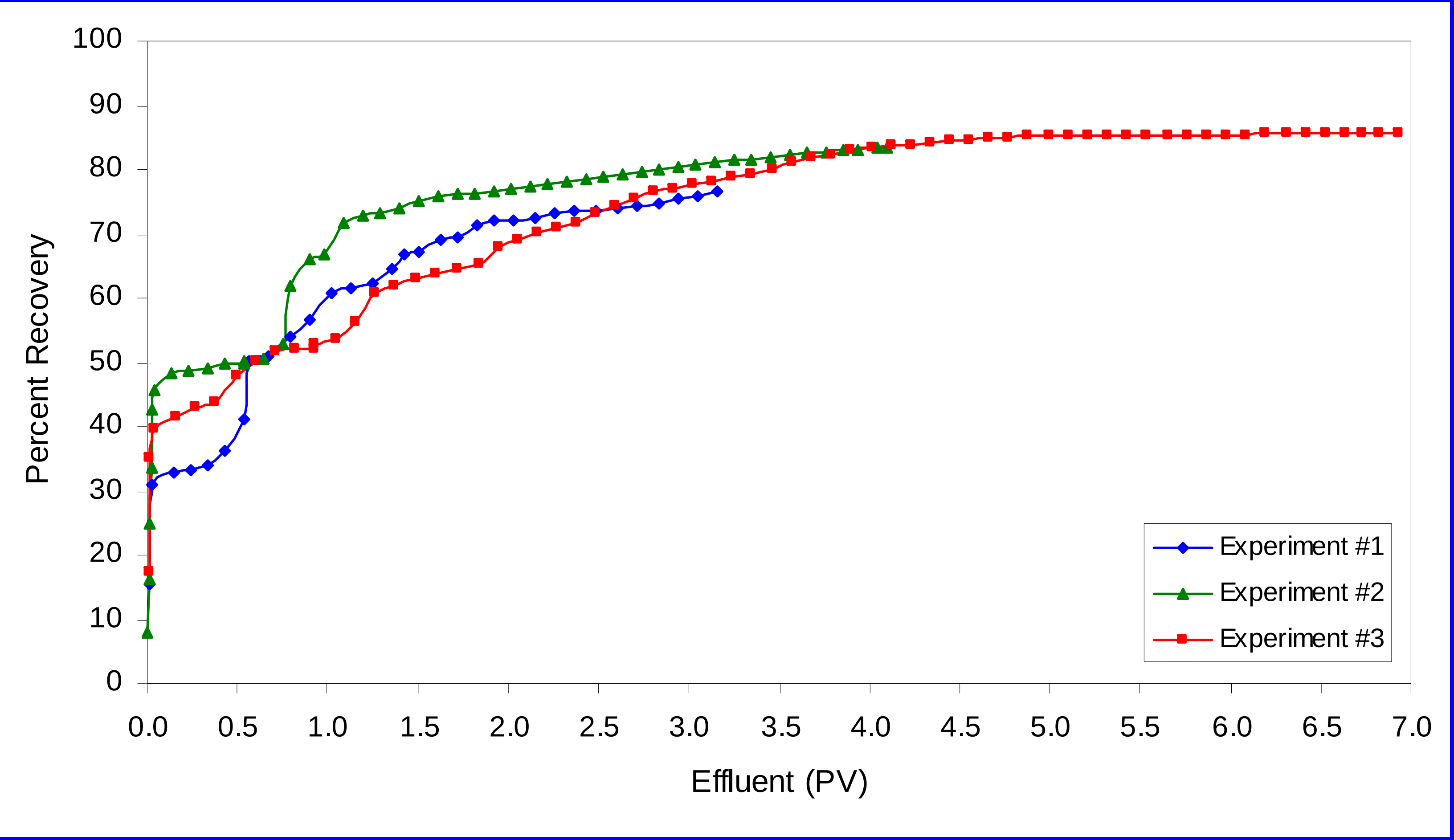
- 22-cm x 24-cm x 16-cm three-dimensional cell
- Pooled TCE established in heterogeneous media
- TCE dyed with Oil Red O for visualization
- Established bottom brine layer
- Drained to unsaturated conditions
- 0.2 pore-volume downward flush with mixture of sulfosuccinate surfantants
- Measured 63.4%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

Three-Dimensional Density-Motivated Mobilization Experiments

Setup

Three-Dimensional Density-Motivated Mobilization Experiments

Cumulative Recovery of TCE

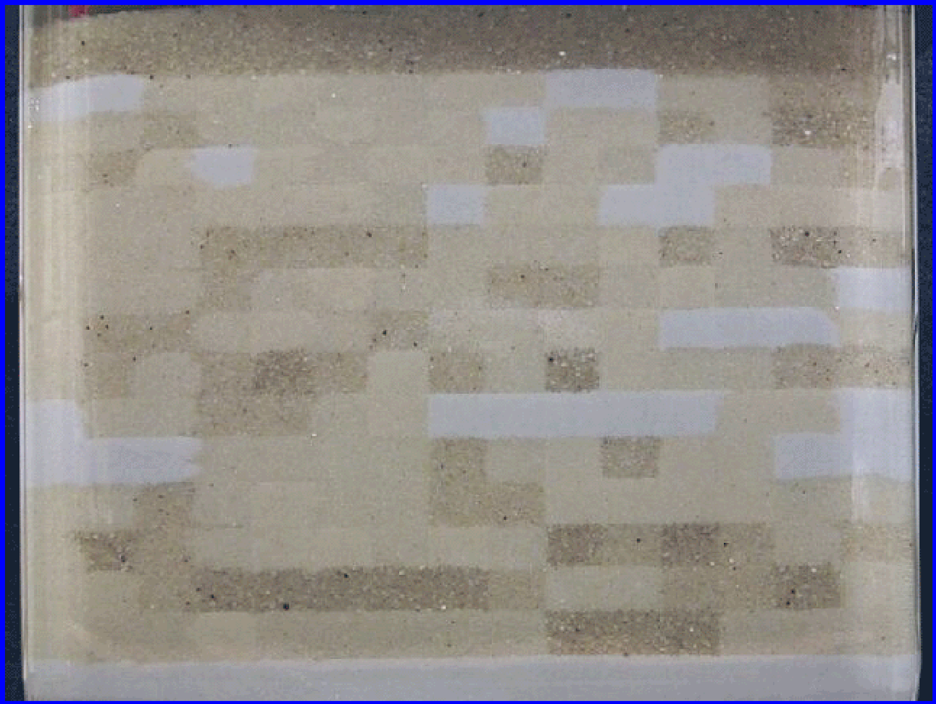


Three-Dimensional Density-Motivated Mobilization Experiments

Properties and Recovery

	No. Extraction Wells	Pore Volume (L)	Surfactant (PV)	TCE Recovery (%) Well Extraction	Vapor Extraction	Soil Extraction	Mass Balance (%)
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

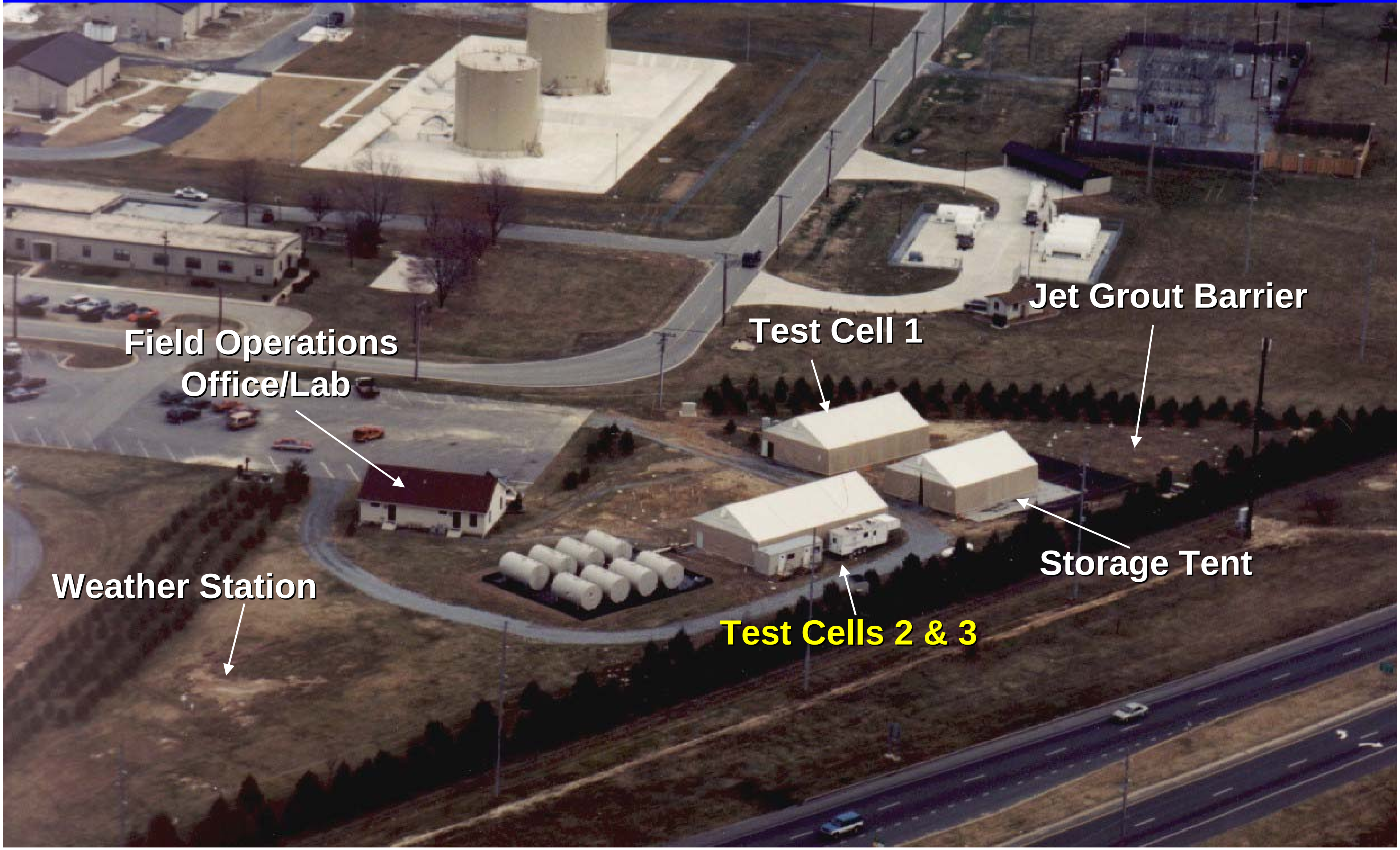


- 22-cm x 24-cm x 16-cm three-dimensional cell
- Pooled TCE established in heterogeneous media
- TCE dyed with Oil Red O for visualization
- Established bottom brine layer
- Drained to unsaturated conditions
- 3.2 pore-volume downward flush with mixture of sulfosuccinate surfantants followed by vapor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

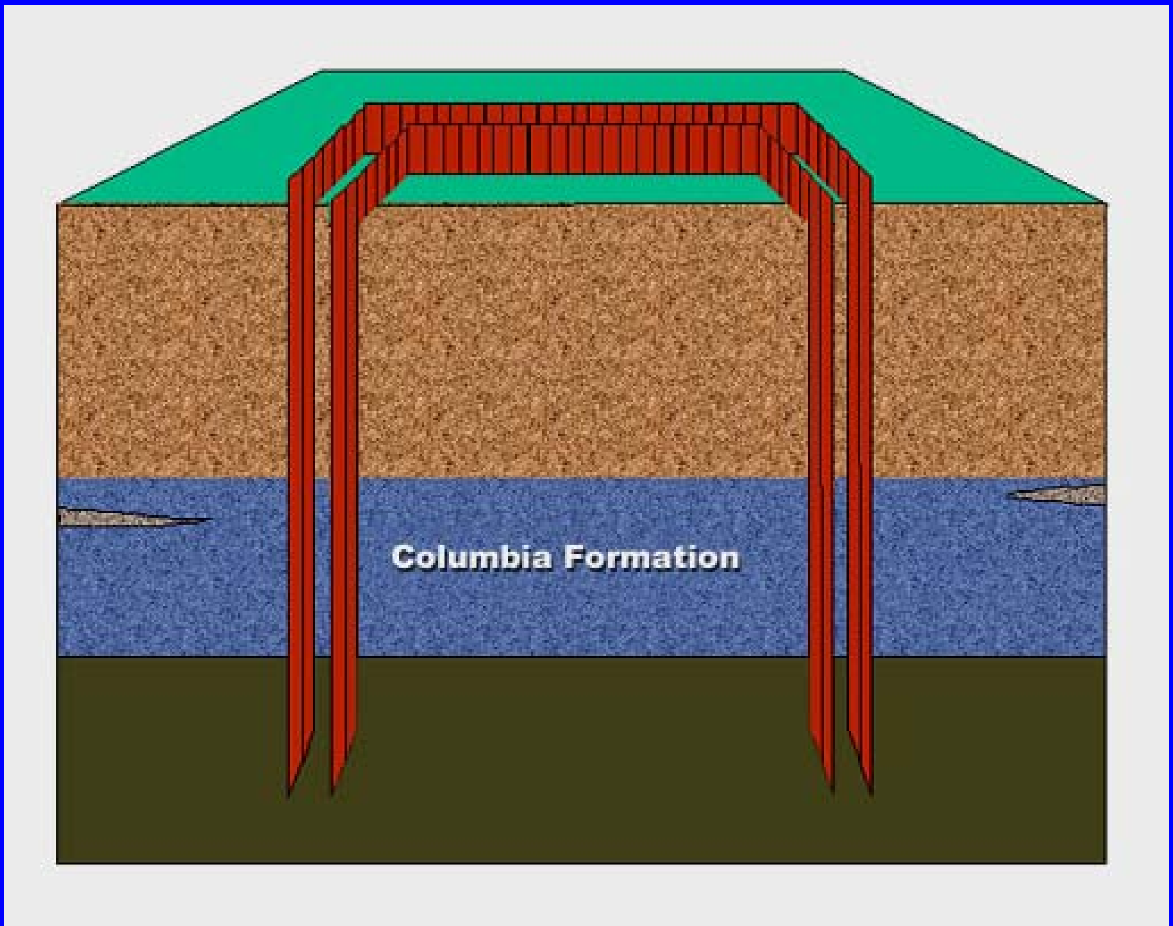
Open Issues

- 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 National Test Site

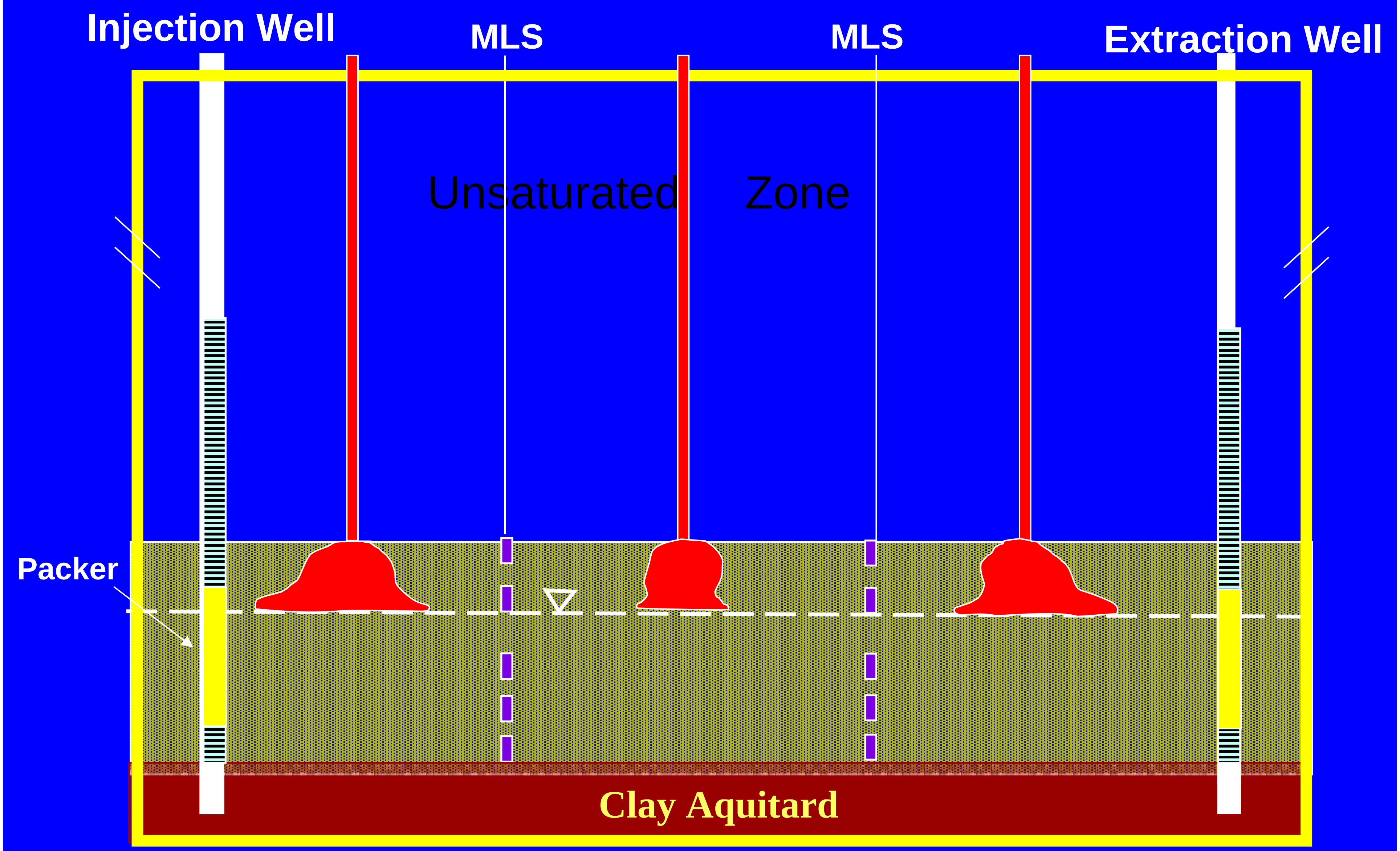


Dover National Test Site

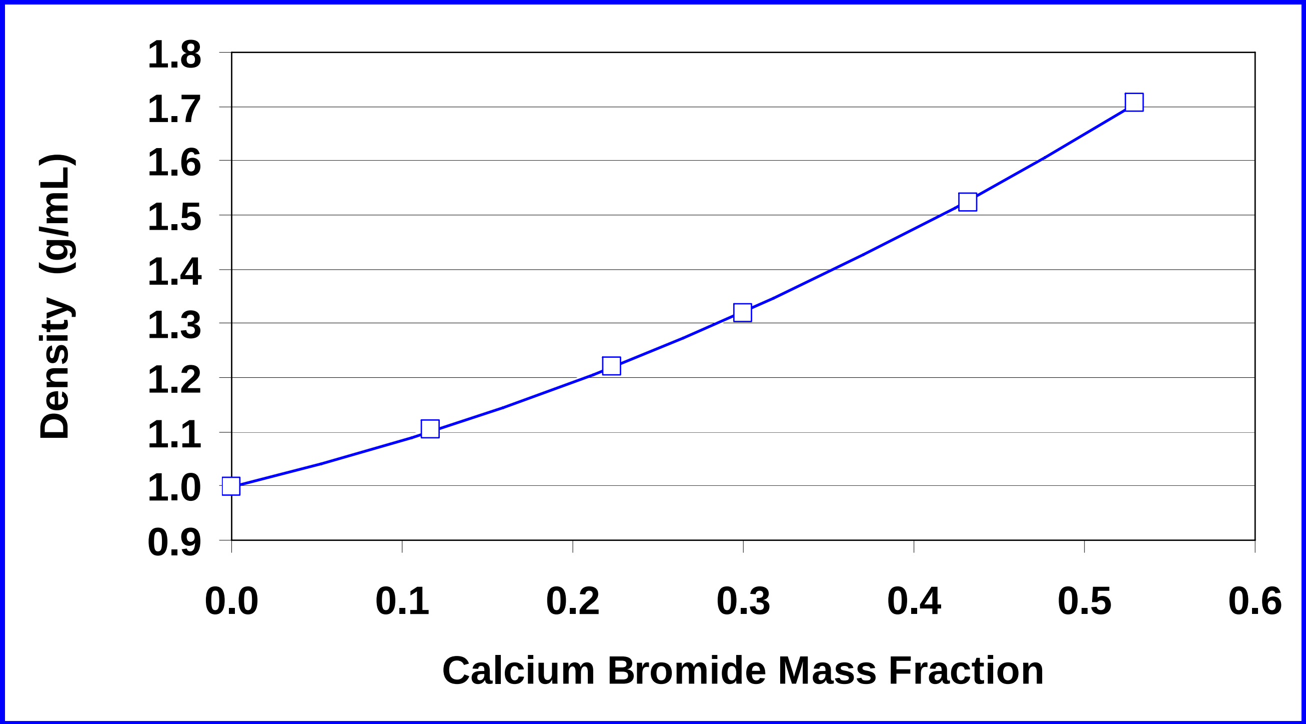


- Depth to the water table is approximately 28 feet.
- Aquifer depth is approximately 12 feet.
- Test cells are double-walled sheet piles driven into the subsurface.
- Sheet piles are keyed into a confining aquitard approximately 45 feet below the surface.

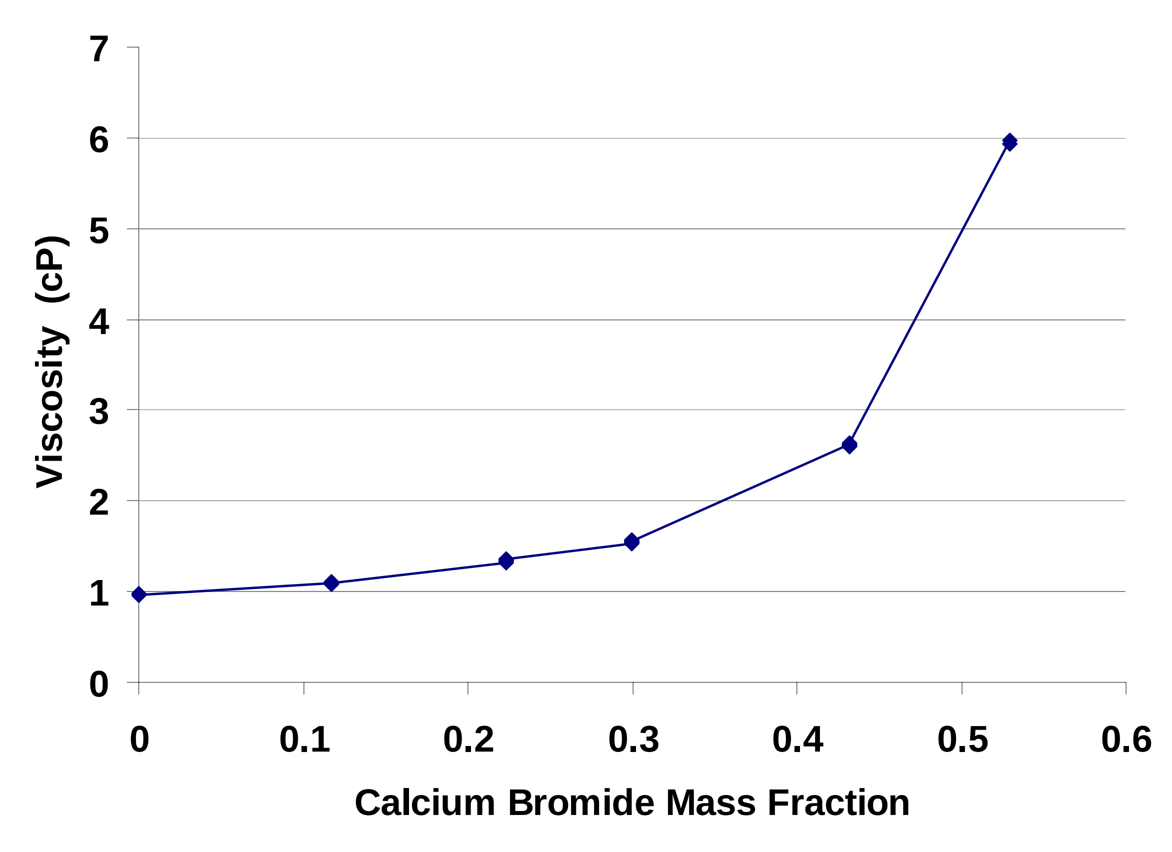
Technical Approach



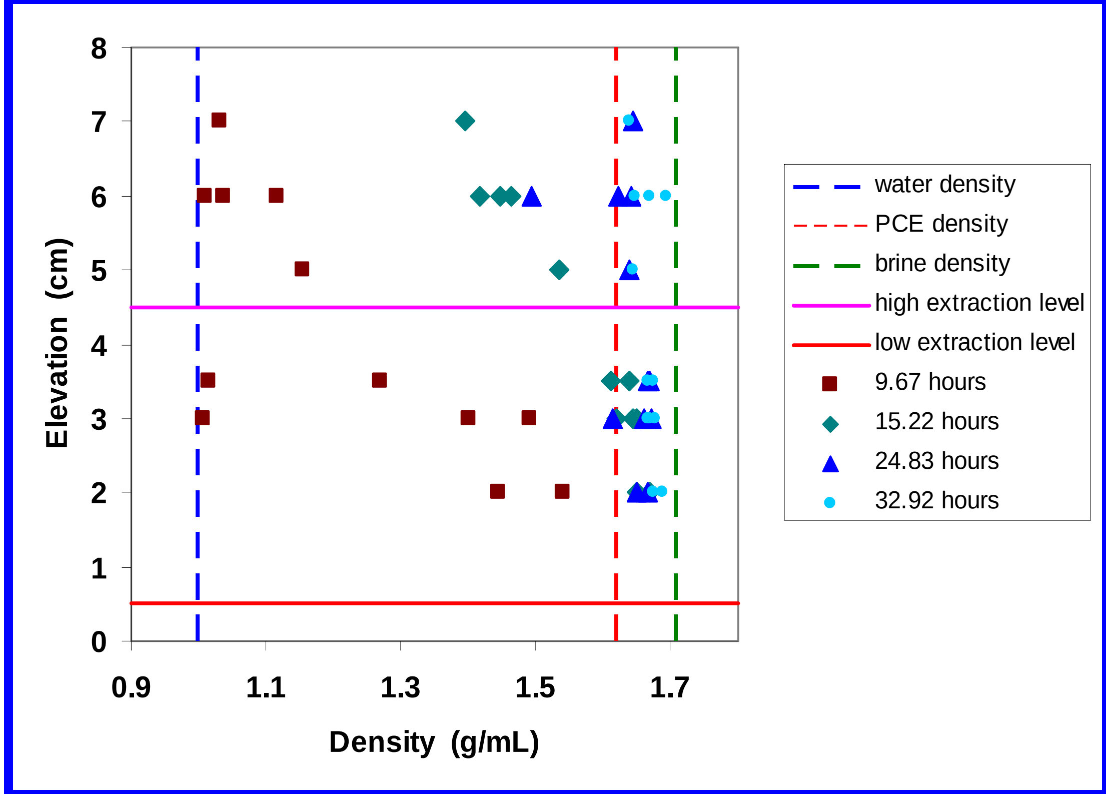
Brine Density



Brine Viscosity

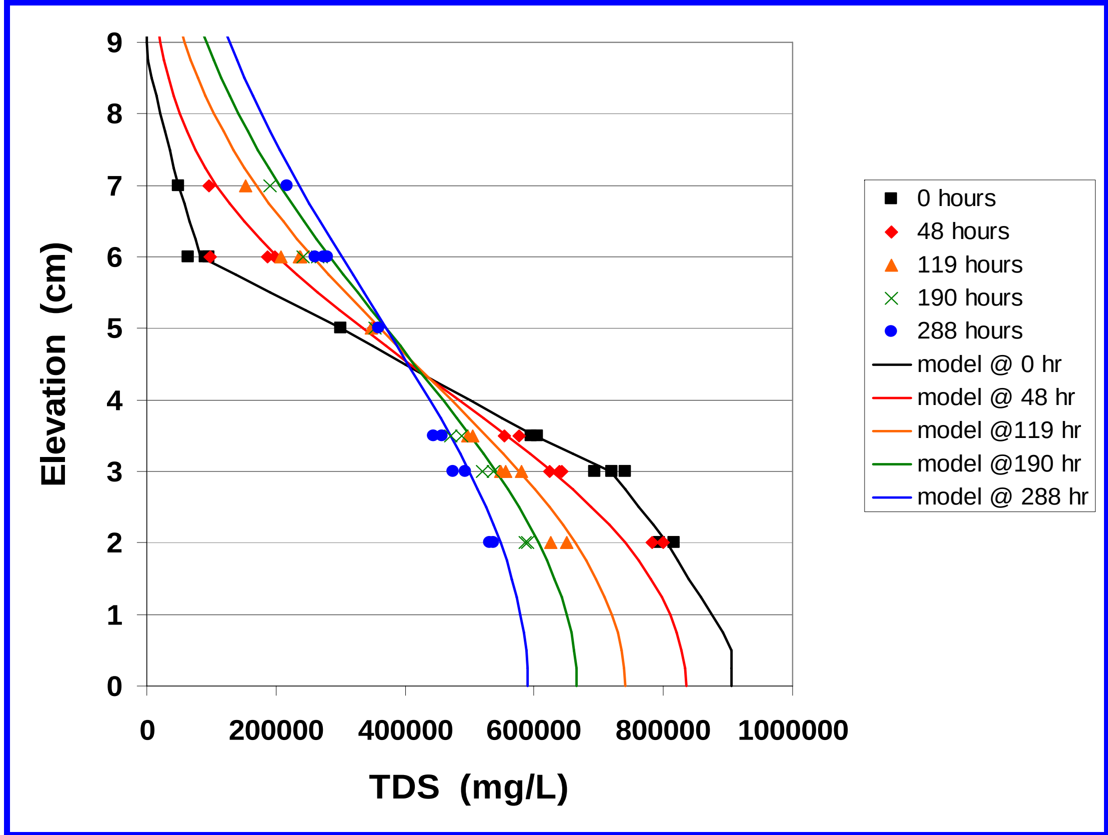


Formation of Brine Layer



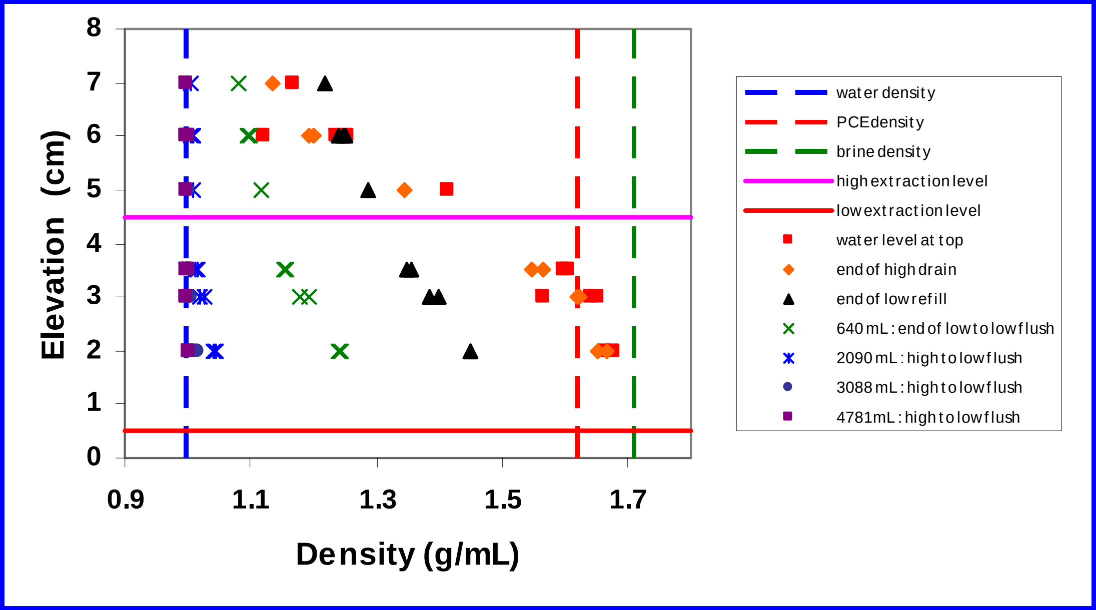
- Three-dimensional experiment
- Dover-like sand
- Brine injected from bottom
- Density monitored throughout the system and with time
- Density of the brine layer exceeds the density of PCE after about 33 hours

Diffusion of Brine



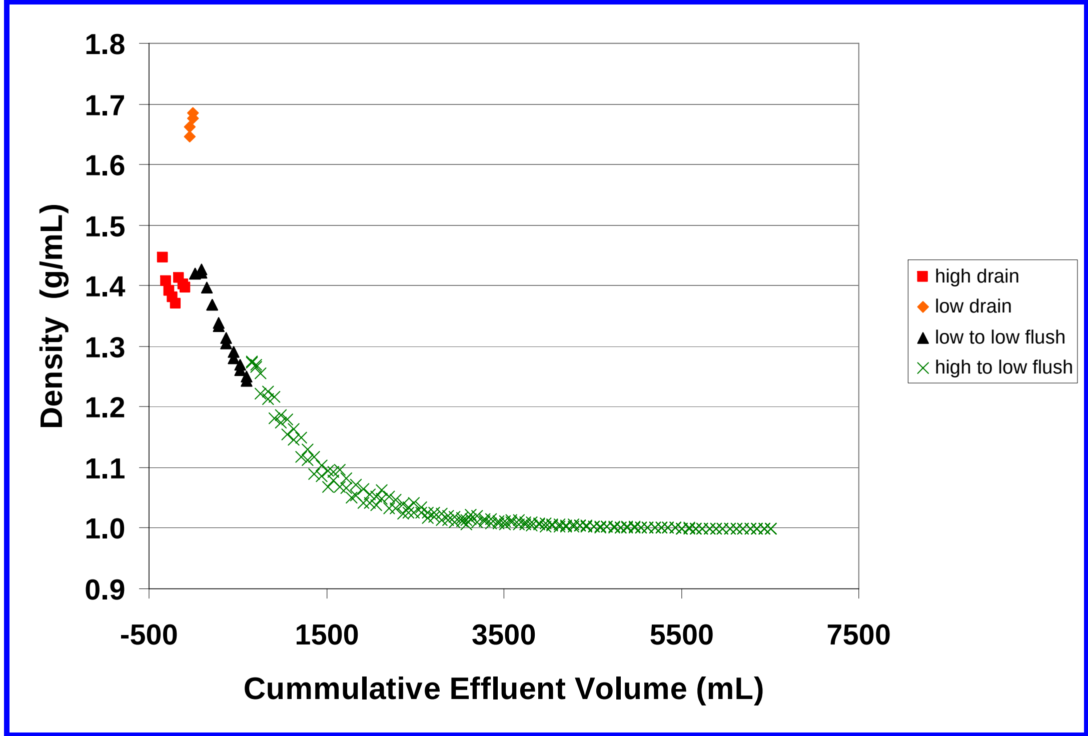
- Diffusion of brine about sharp interface observed in space and time
- Density of 1.7 g/mL corresponds to a TDS of 900,000 mg/L
- PCE density 1.62 g/mL corresponded to a TDS of 780,000 mg/L
- Brine barrier is stable and long-lived in presence of diffusion alone

Recovery of Brine



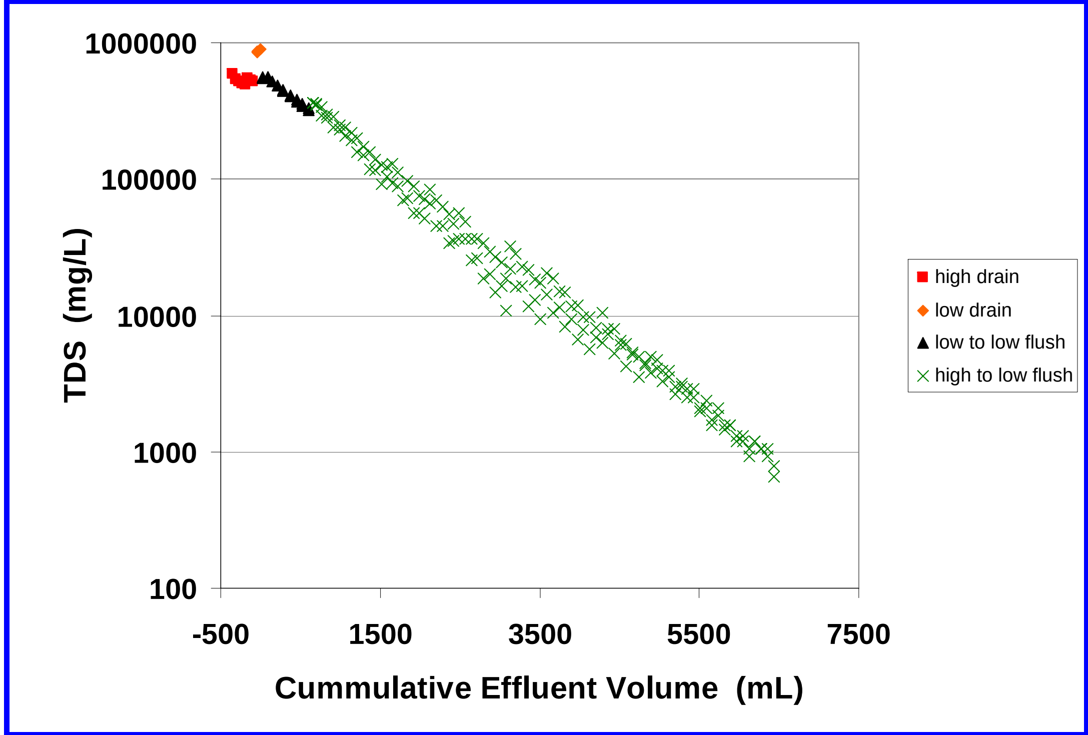
- Brine removed by drainage from upper, then lower, ports
- After drainage, horizontal flushing performed
- Water table reduced further as flushing continued

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

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

Project

- Focus on brine emplacement and removal aspects of brine-based technology
- Investigate effects of viscous and gravity instabilities
- Investigate effects of media heterogeneity and learn about homogenization-based upscaling methods