Surfactant Enhanced Subsurface Remediation

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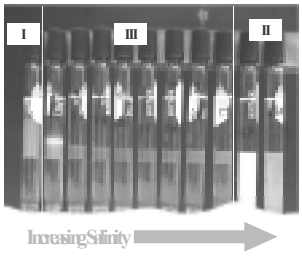

Acknowledgments: IASR Colleagues

- **Chemistry, chemical engineering, environmental engineering**
- **Founded 1986; twenty industrial sponsors** Skey's
- **Fundamental and applied surfactant research – consumer products, environmental technologies, chemical processes**

Colleagues at OU / Surbec

- **Founded in 1996**
- **Dr. Joseph Suflita (Microbiology)**
- **Dr. Robert Knox (Civil Engineering / GW Hyrdology)**
- **Dr. Jeffrey Harwell (Chemical Engineering)**
- **Dr. David Sabatini (Civil / Environmental Engineering)**

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Outline

- Problem / Surfactant Solution
- Surfactant Fundamentals
- Economic Factors
- Design Factors
- Field Results: Overview
- Future Directions

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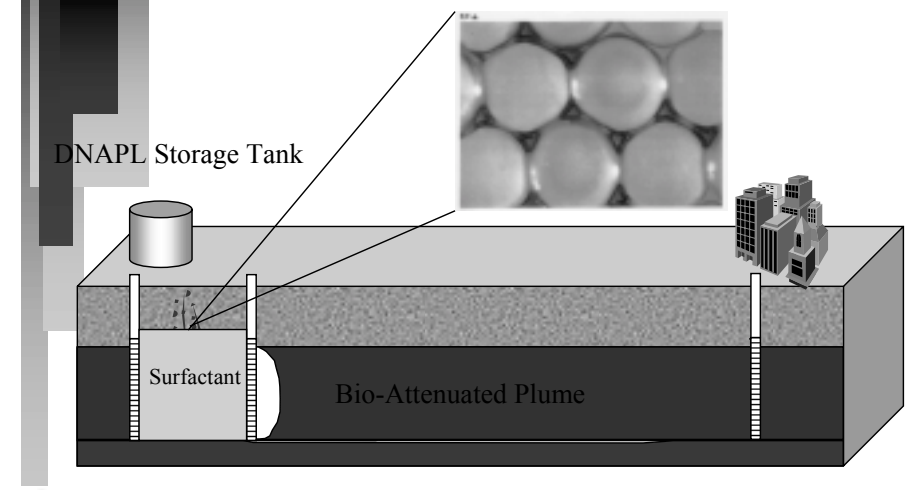
Problem / Approach



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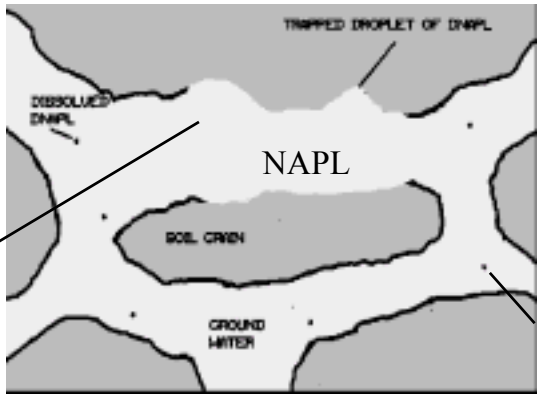
NAPL is Trapped by "Capillary Forces"

High o/w interfacial tension makes the oil immobile.



Low water solubility -- 100s to 1000s of flushings (years) to dissolve oil.

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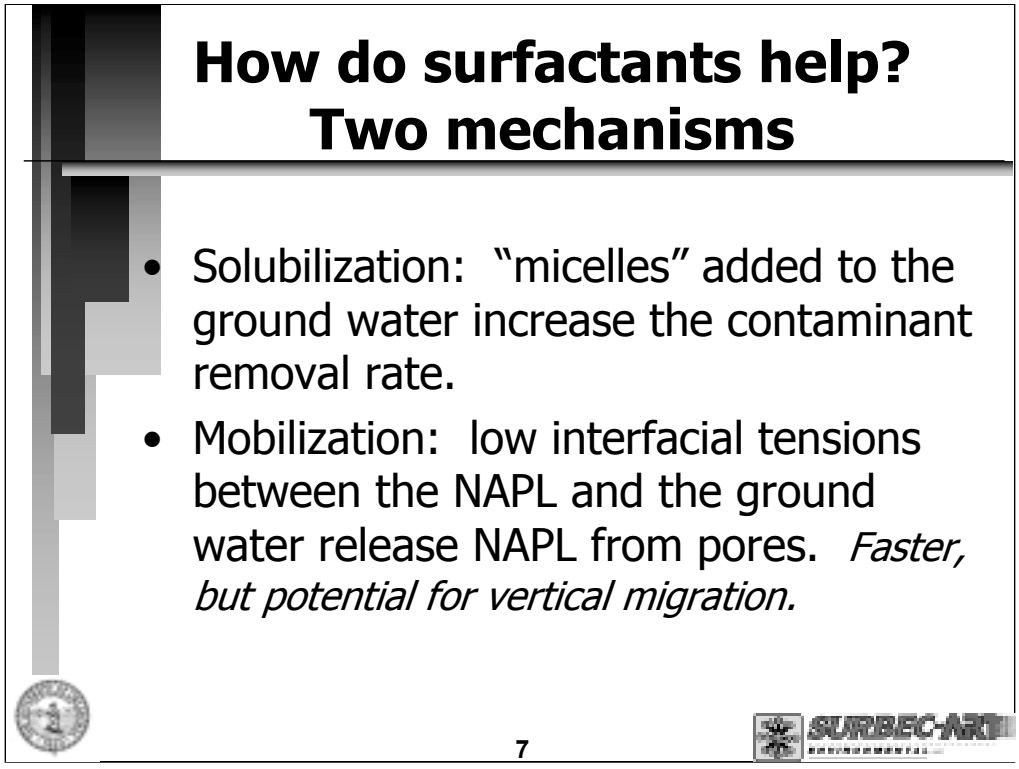
The basic problem in removing nonaqueous phase liquids (NAPLs) from an aquifer is the trapping of the NAPL in the pores of the aquifer matrix by interfacial tension forces. The hydrodynamic forces produced by pumping water through the contaminated zone are too small to cause drops of the NAPL to move from the injection wells toward the recovery wells. So, the level of contaminated liquid is slowly reduced by dissolving it into the ground water as it passes by the droplets. This is a slow, inefficient, and expense process which has been suspended in many places because of depletion of the ground water itself.



The two types of remediation mechanisms possible with surfactants are called solubilization and mobilization. The former enhances the dissolution of the contaminant, the latter un-traps it.

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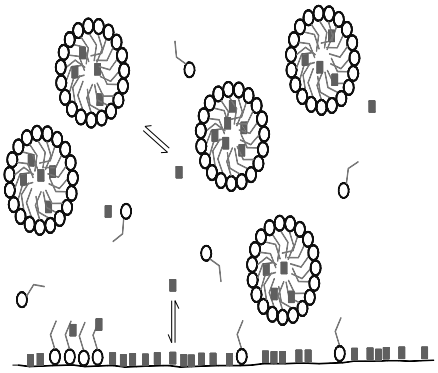
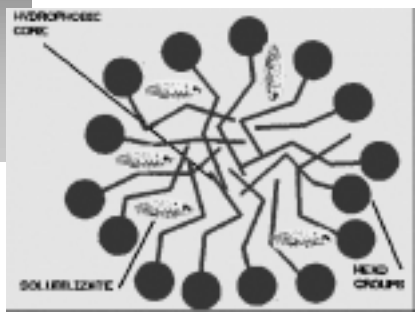
Surfactant Fundamentals

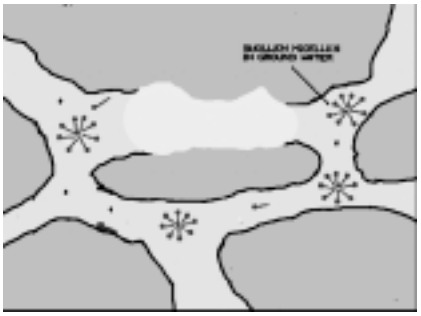
- Surface Active Agent
- Hydrophilic head; hydrophobic tail
- Above CMC form aggregates – micelles



- Rosen, M. **Surfactants and Interfacial Phenomena.** 2nd ed. Wiley, 1989.
- Pope, G. and Wade, W. "Lessons from Enhanced Oil Recovery for Surfactant-Enhanced Aquifer Remediation." in Sabatini et al. **Surfactant Enhanced Subsurface Remediation: Emerging Technologies**. ACS Symposium Series 594, 1995.
- Sabatini et al. "Surfactant Selection Criteria for Enhanced Subsurface Remediation." in Brusseau et al. **Innovative Subsurface Remediation.** ACS Symposium Series 725, 1999.

Solubilization Increases NAPL Removal Rate by Water





Surfactant micelles increases oil solubility; more NAPL extracted than possible with water alone

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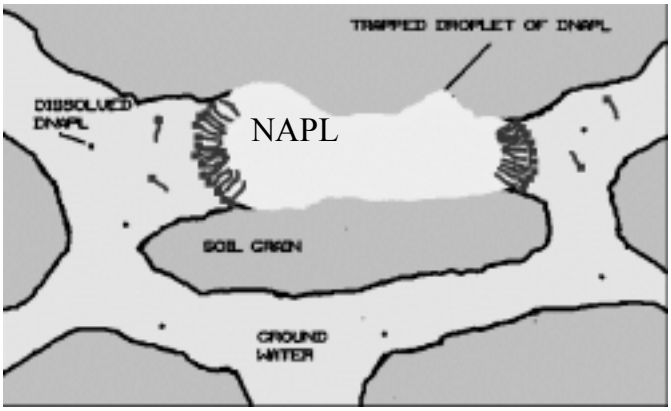
In solubilization micelles of the surfactant increase the concentration of the contaminant in the ground water, speeding the rate at which the contaminant is removed from the subsurface. The increase can be by over an order of magnitude.

Surfactant adsorption lowers oil/water IFT

Dense monolayer lowers interfacial energy.



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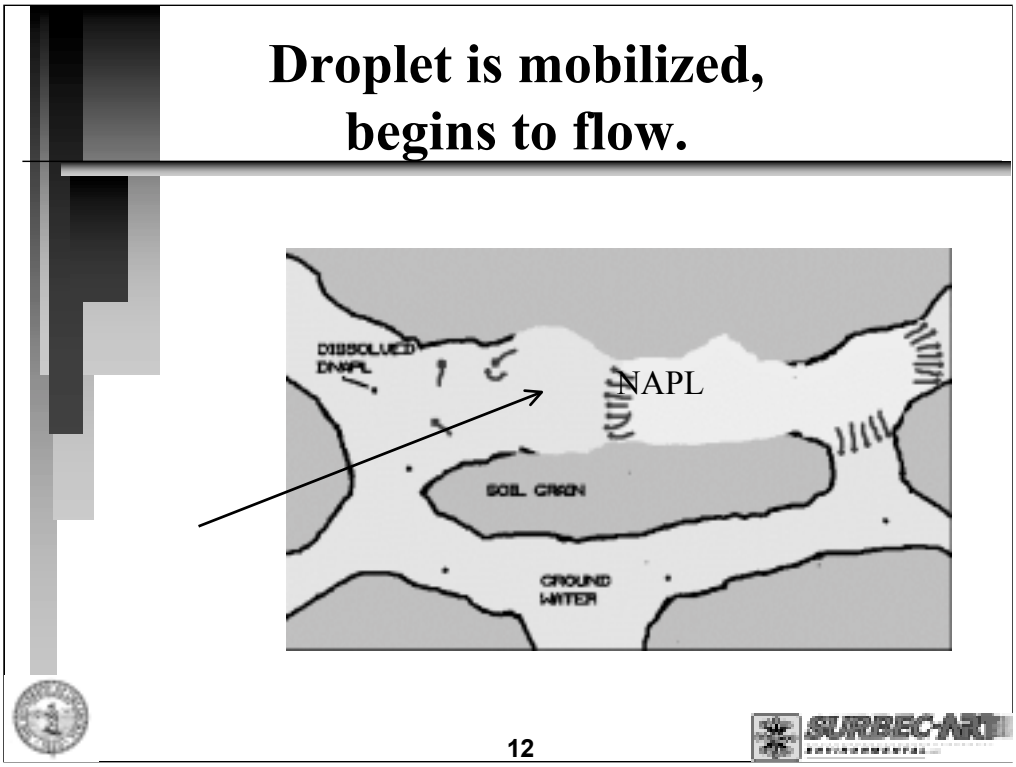
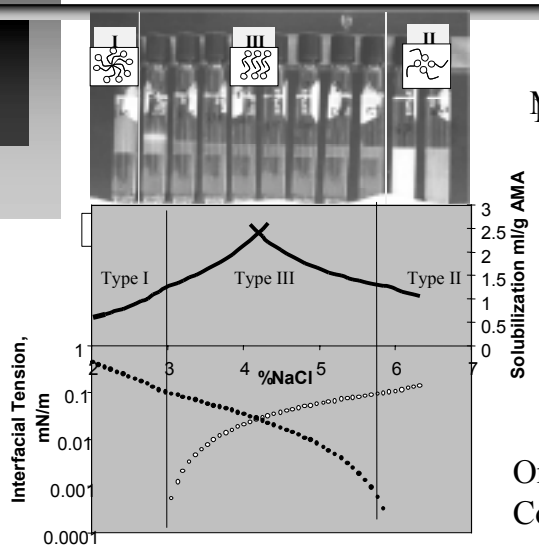
In the mobilization mechanism, the surfactant must adsorb at the interface between the NAPL and the ground water, resulting in the lowering of the interfacial tension between the phases.



As the interfacial tension becomes ultra low, as is seen in the formation of middle phase microemulsions, the drop becomes mobile. This is the same phenomenon that was proposed for enhanced oil recovery in the late 70s.

Phase Scan: IFT / Solubilization



Winsor Type I, III and II phases

Micelle

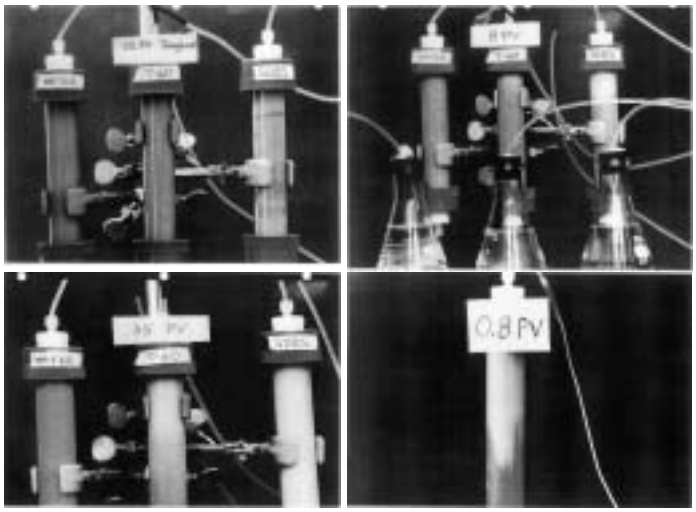
Monomer

Solubilization enhancement maximum, IFT minimum -- Type III

Type I to III boundary – solubility enhanced, IFT reduced versus "micelles"

Organic Contaminant

Column Comparison



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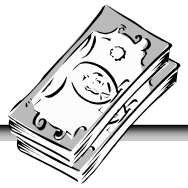
Economics



- **Surfactant costs significant**
  - **At 4 to 8 wt %, likely highest individual cost**
- **Maximize extraction efficiency**
- **Regenerate / reinject surfactant**
  - **When using more than 1.5 to 3 pore volumes**
- **Properly designed, economical**
  - **As low as: $25 - 30 / yd^3 (LNAPL); $60 - 90 / yd^3 (DNAPL)**

Maximize Extraction Efficiency

- **Solubility enhancement increases**
  - As interfacial tension (IFT) decreases (as described by Chun Huh relationship)
- **Vertical migration increases**
  - As IFT decreases (below a critical IFT)
- **Optimal surfactant system**
  - Maximizes solubility while mitigating vertical migration – supersolubilization

Sabatini, Knox, Harwell, and Wu. "Integrated Design of Surfactant Enhanced DNAPL Remediation: Effective Supersolubilization and Gradient Systems." **J. of Contaminant Hydrology.** 45(1), 2000, 99-121.

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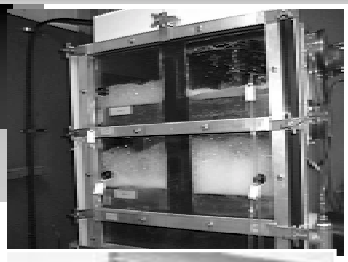
Surfactant Regeneration / Reuse



- **Surfactant hindrances –**
  - **Foaming, emulsions**
- **Hydraulic control**
  - **Over-pumping / dilution – MEUF reconcentration**

Surfactant-reduced partitioning / stripping

Regeneration / reuse can be critical to surfactant selection

Sabatini, Harwell, Hasegawa, and Knox. "Membrane Processes and Surfacant-Enhanced Subsurface Remediation: Results of a Field Demonstration." Journal of Membrane Science. 151(1), 1998, 89-100.

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Design Factors

- Contaminant Distribution
- Site Hydrogeology: Heterogeneities, sweep efficiency (polymers, foam)
- Modeling Is Critical
  - How will the system respond
  - Tracer Tests -- verification
- Scaleup Approach
  - Batch, column, sand tank (?), field scale – tracer test, pilot-scale test

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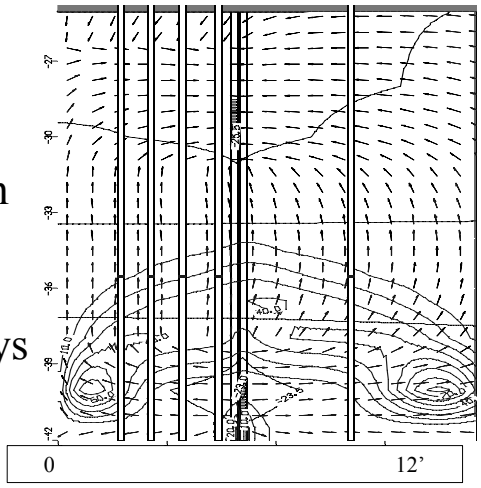
Site Modeling (Dover AFB)

- Low permeability soils, interbedded silts and sands
- Vertical circulation → by line drive
- Recirculated surfactant -- 34 days
- AMA/IPA surfactant



Design Factors

Surfactant Chemistry is Critical!

- **Maximize efficiency / regeneration -- economics**
- **Avoid formation of precipitate, coacervate, liquid crystals – phase separation (salinity / temperature)**
- **Avoid significant sorption (geology, gw chemistry)**
- **Avoid super-high viscosities**
- **Avoid density gradients**
- **Consider environmental factors: biodegradability, metabolites, aquatic toxicity**
- **AVOID FAILURE!!**

Sabatini, Knox, Harwell, and Wu. "Integrated Design of Surfactant Enhanced DNAPL Remediation: Effective Supersolubilization and Gradient Systems." **J. of Contaminant Hydrology.** 45(1), 2000, 99-121.

Design Factors

- **Optimizing surfactant formulation**
  - **Maximize efficiency while optimizing viscosity / density / interfacial tension**
  - **Tradeoff between parameters**
  - **Temperature, salinity, geology sensitive**

Tween (%)	AMA (%)	IPA (%)	Cont. Solub.(ppm)	Viscosity (cp)	Density (g/ml)	IFT (mN/m)
2.5	2.5	0	140,000	5.6	1.1	0.02
2.5	2.5	2.5	70,000	2.8	1.01	0.05
0	8	4	69,000	2.47	1.01	1.9
0	5	4	70,000	2.2	1.03	0.4

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  EPA: www.
- **Future Directions**

EPA Summary -- Sites

- Summary of 46 sites (to be posted at www.cluin.org in several months)
  - **Funding**: 2/3 federal, 1/3 state
  - **Contaminant**: 1/3 chlorinated, 1/3 fuel hydrocarbons, 1/6 mixed
  - **Flushing agent**: 3/4 used surfactants
  - **Depth**: 1/4 – 10 to 25 ft; 1/2 – 25 to 50 ft
  - **Size**: < 1,000 ft^3 – 17%; 1,000 to 3,000 ft^3 – 26%; 3,000 to 10,000 ft^3 – 13%, > 10,000 ft^3 – 13% (not specified – 30%)

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SEAR Field Demonstrations

Location (year)	NAPL Composition	Swept Pore Volume (m^3)	Reduction in NAPL Mass (%)	NAPLSaturation (%) After Surfactant
Borden, Ontario 14 PV 2% surfactant (1991)	PCE	9.1	77	0.2
L'Assomption, Quebec 0.9 PV surfactant (1994)	Multicomponent DNAPL	6.1	86	0.45
Hill AFB OU1 9.5 PV 3% surfactant (1996)	Multicomponent LNAPL	4.5	86	0.8
Hill AFB OU2 2.4 PV 8% surfactant (1996)	Multicomponent DNAPL, 70% TCE	57	99	0.03
Hill AFB OU 2 4% surfactant + foam (1997)	Multicomponent DNAPL, 70% TCE	31	90	0.03
Camp Lejeune 5 PV 4% surfactant (1999)	PCE DNAPL	18	72	0.5
Alameda Point 6 PV 7% surfactant (1999)	DNAPL, TCA, TCE	32	98	0.03
Pearl Harbor 10 PV 8% surfactant (1999)	Naval Special Fuel Oil, 1000 cp	7.5	86	0.35
Hill AFB OU2 2.4 PV 4% surfactant (2000)	Multicomponent DNAPL	188	94	0.07

CPGE

Gary Pope, University of Texas

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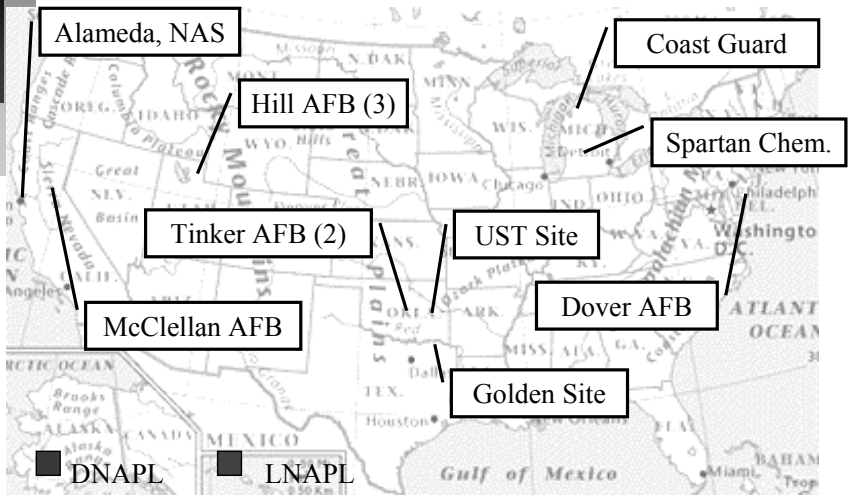
Twelve Field Studies



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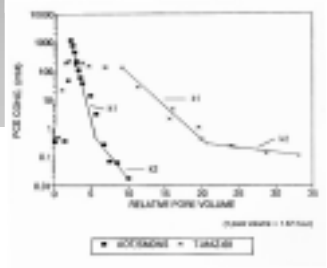
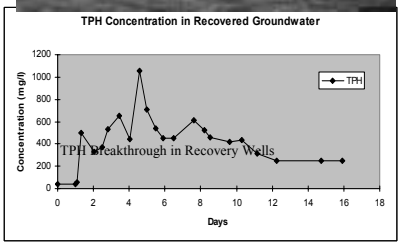
Hill AFB – Solubilization / Mobilization



- Sandy gravel formation; jet fuel / chemical disposal pits
- Solubilization: 10 PVs of Dowfax 8390 (4.3 wt%); > 95% surfactant recovery
- 40 to 50 % contaminant removal
- Mobilization: 6.6 PVs of AOT (2.2 wt%), Tween 80 (2.1 wt%), CaCl2 (0.43 wt%) – MPM / Supersolubilization
- 85 to 95% contaminant removal

Knox et al. "Field Demonstration of Surfactant Enhanced Solubilization and Mobilization at Hill Air Force Base, UT." In **Innovative Subsurface Remediation.** Brusseau et al., eds. ACS Symposium Series 725, 1999, 49-63.

Tinker AFB – Separations



- Integrated SESR / above ground treatment – reuse
- LNAPL: Toluene, TPH
- Formation permeability less than 1 ft/d (0.15 gpm/well)
- 8 PVs of 4 wt% Dowfax 8390
- Demonstrated surfactant recovery and "regeneration" for reinjection

Sabatini, Harwell, Hasegawa, and Knox. "Membrane Processes and Surfacant-Enhanced Subsurface Remediation: Results of a Field Demonstration." Journal of Membrane Science. 151(1), 1998, 89-100.

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Tinker AFB -- Unit Dimensions

Unit	Dimension	Media
Air Stripper - Packed Tower	0.66 ft ID 8.0 ft tall	1 in Polyethylene Flexirings
Air Stripper - Hollow Fiber	0.33 ft ID 2.5 ft tall	Celgar X 30; 0.24 mm ID, 30 nm pores fibers
Ultrafilter	2.0 ft long 0.5 ft ID	10,000 MWCO

Alameda Point NAS – Supersolubilization

Alameda site

DNAPL: TCA, TCE, DCE, DCA

- **Supersolubilization – 6 PVs of 5% Dowfax 8390, 2% AMA**
- **Test goal: >95% removal**
- **Cores: pre – 40,000 ppm**
- **Recycled and reinjected surfactant**

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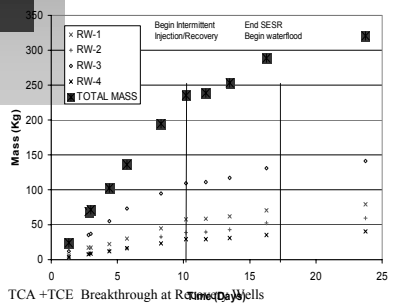
Alameda Point (cont)



TCA +TCE Breakthrough at Recovery Wells

- 98% DNAPL removal (pre- versus post- cores / PITTs)
- 50-80% reduction in groundwater concentrations
- Levels achieved in 6 pore volume or 18 days
- Surfactant regenerated and reinjected
- Predicted full scale (60,000 ft^2) cost 1/3 P&T

Subsurface Remediation

- Can optimize surfactant system
  - Maximize extraction efficiency
- Can reuse surfactant systems
  - Regeneration, re-concentration, approval
- System can be economically viable
  - Mass removals of 90 – 99%; economically competitive

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Future Directions

- **Coupling technologies**
  - Biopolishing, chemical oxidation
- **Low surfactant approach**
  - Especially LNAPLs – mobilization
- **Surfactant alternatives**
  - More efficient, robust, economical systems
- **Higher EACN oils (e.g., coal tar)**
  - Surfactant branching, temperature

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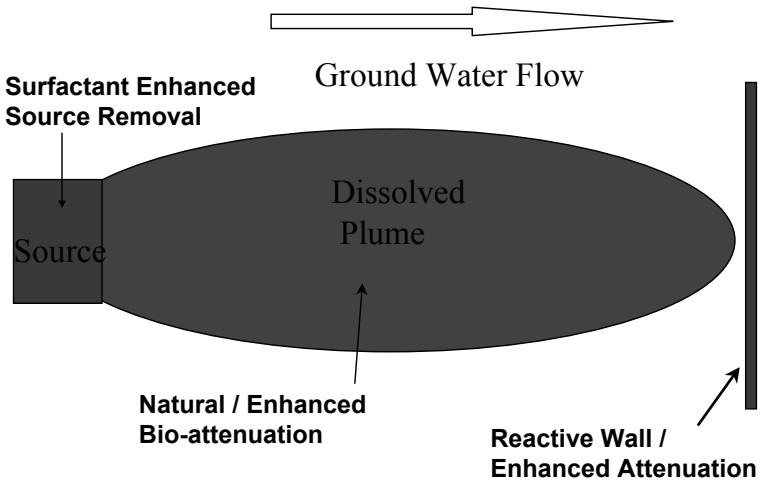
Integrated Remedial Systems



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Surfactant-Based Risk Mitigation

Questions?

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