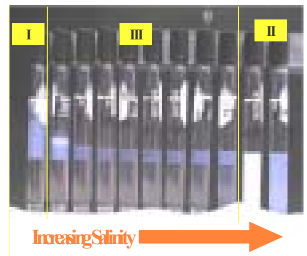
# *Surfactant Enhanced Subsurface Remediation*





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1

# Acknowledgments:  IASR Colleagues

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

2

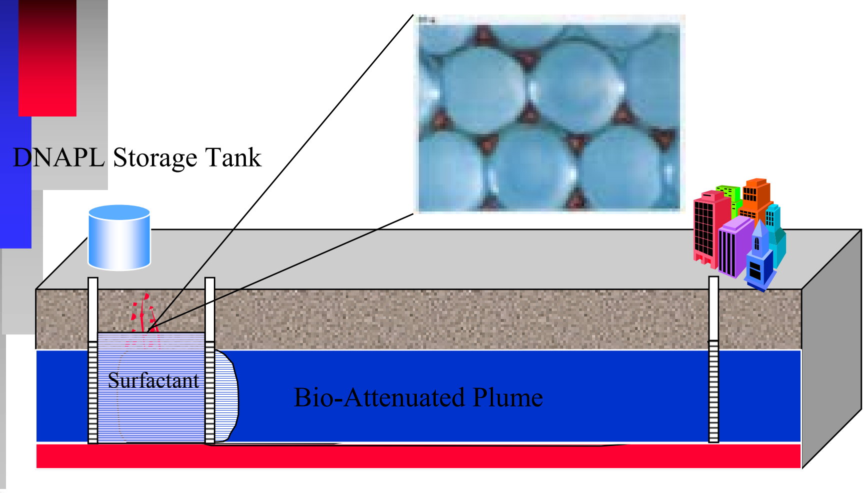
# Colleagues at OU / Surbec

- 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)

# Outline

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

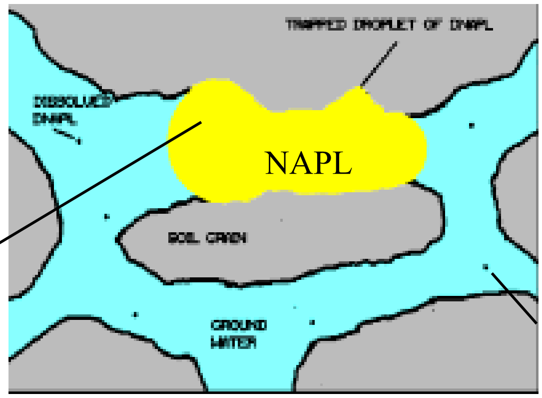
# Problem / Approach




5

# 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.**

6

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.

## How do surfactants help? Two mechanisms

- Solubilization: "micelles" added to the ground water increase the contaminant removal rate.
- Mobilization: low interfacial tensions between the NAPL and the ground water release NAPL from pores. *Faster, but potential for vertical migration.*

7

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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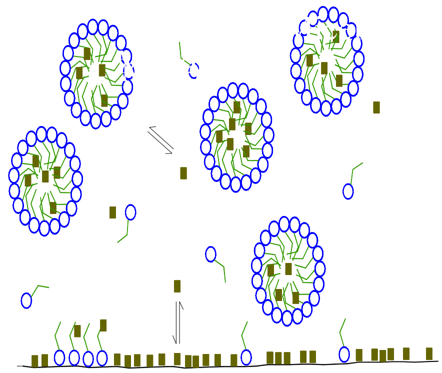
# Surfactant Fundamentals

- 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.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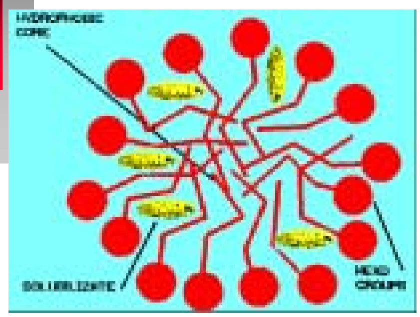
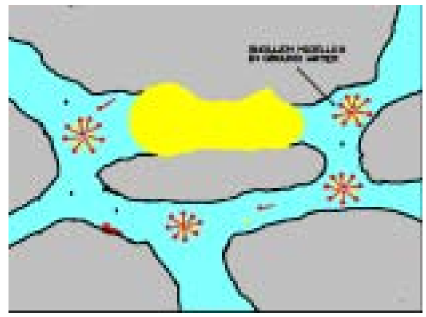
# Solubilization Increases NAPL Removal Rate by Water



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

10

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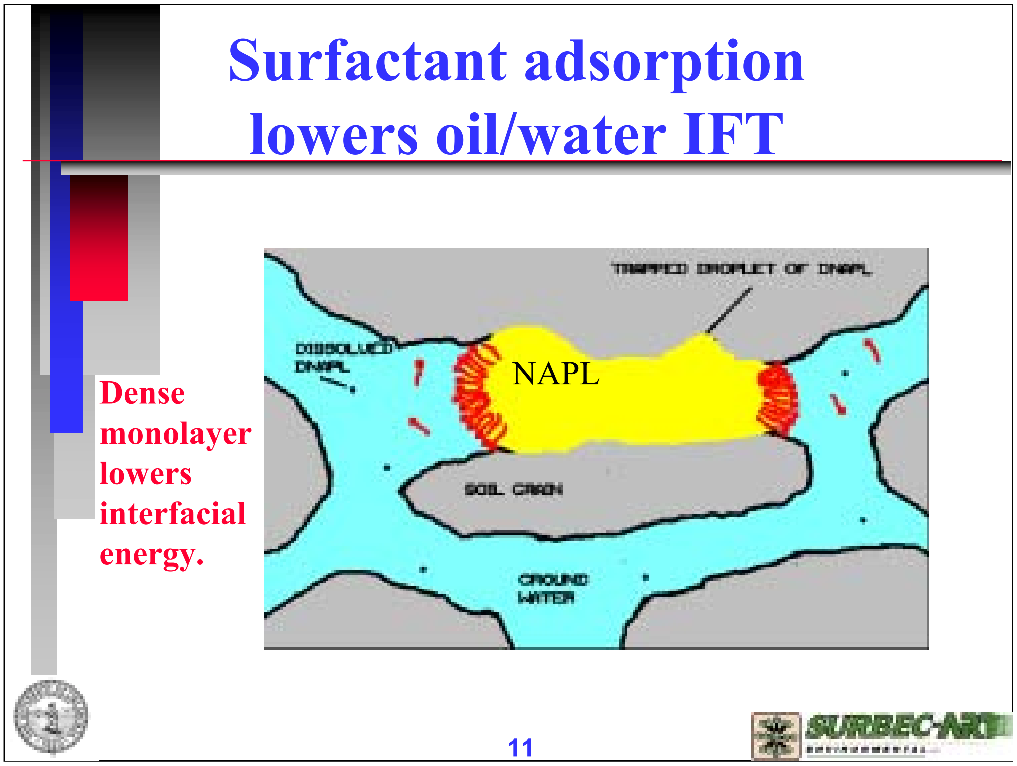
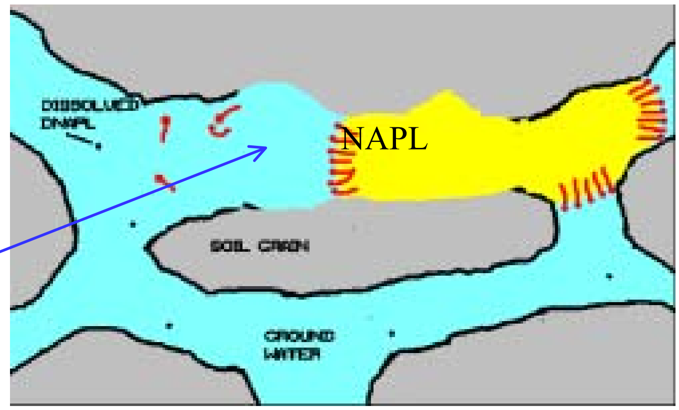
In solubilization micelles of the surfactant increase the concentration of the contaminant in the ground water, speeding the rate at which the contaminant is removed from the subsurface. The increase can be by over an order of magnitude.




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.

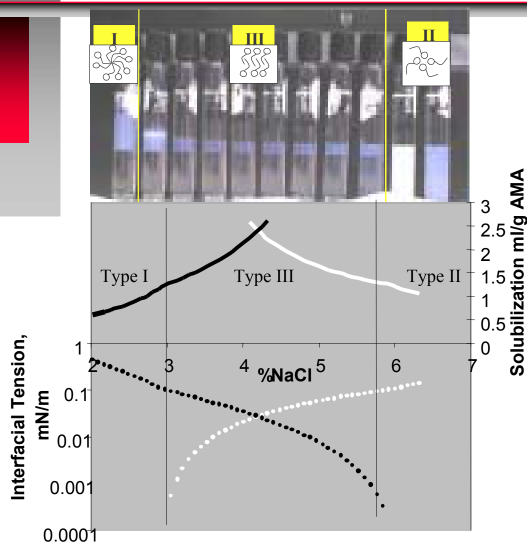
# Droplet is mobilized, begins to flow.




12

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.

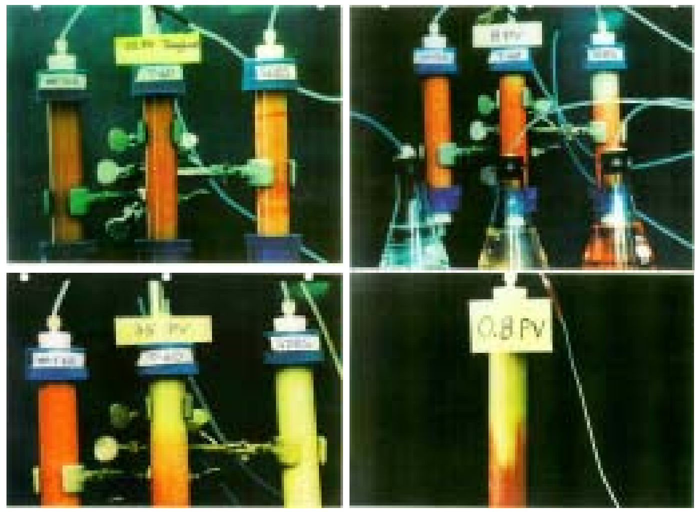
# Phase Scan: IFT / Solubilization




- Winsor Type I, III and II phases
- Solubilization enhancement maximum, IFT minimum -- Type III
- Type I to III boundary – solubility enhanced, IFT reduced versus "micelles"

13

# Column Comparison



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15

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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)

16

# 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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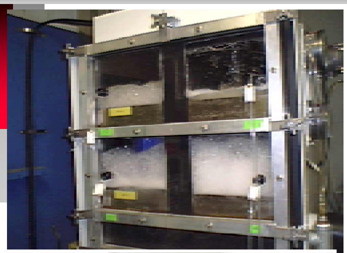
# Surfactant Regeneration / Reuse



- 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 Surfactant-Enhanced Subsurface Remediation: Results of a Field Demonstration." Journal of Membrane Science. 151(1), 1998, 89-100.

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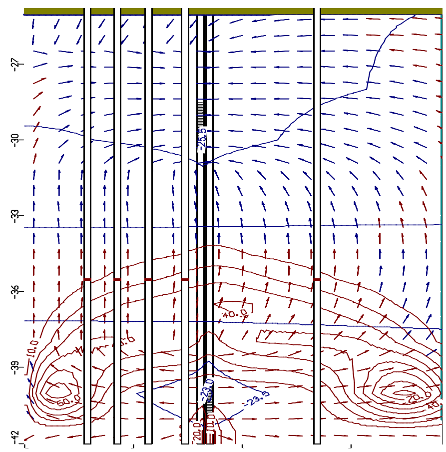
# Design Factors

- 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

20

# Site Modeling (Dover AFB)

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



21

# 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.

22

# 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 |

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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  EPA: www.
- Future Directions

24

# 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%)

25

# SEAR Field Demonstrations

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

CPGE

Gary Pope, University of Texas

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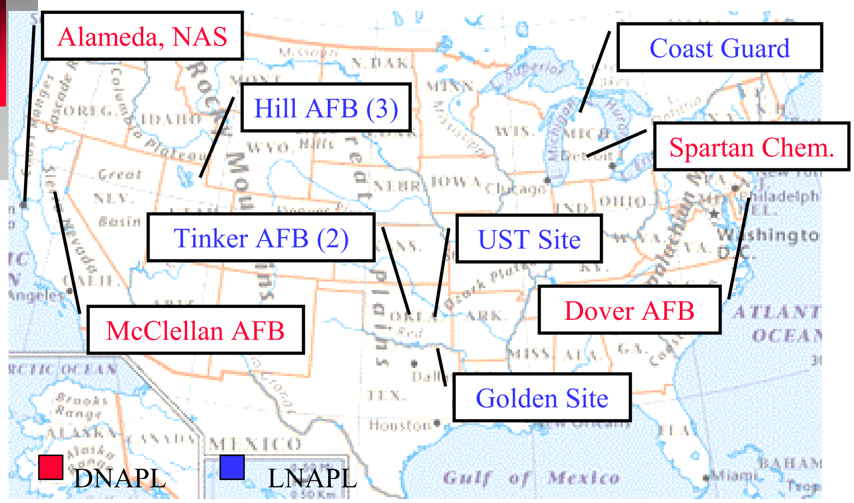
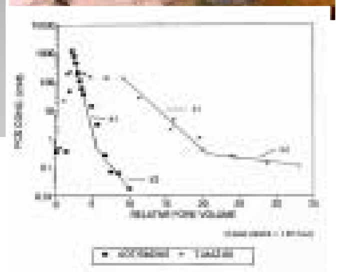
26

# Twelve Field Studies




27

# 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

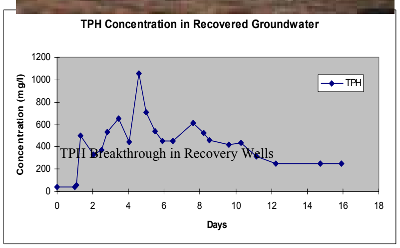
Mobilization: 6.6 PVs of AOT (2.2 wt%), Tween 80 (2.1 wt%), $CaCl_2$ (0.43 wt%) – MPM / Supersolubilization

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.

28

# 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 Surfactant-Enhanced Subsurface Remediation: Results of a Field Demonstration." Journal of Membrane Science. 151(1), 1998, 89-100.

# Tinker AFB -- Unit Dimensions

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

30

# Alameda Point NAS – Supersolubilization

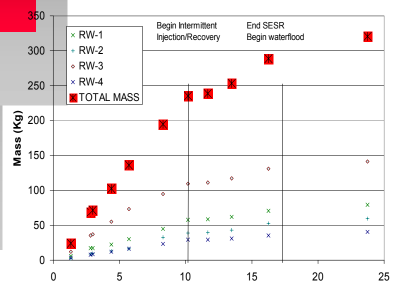
Alameda site

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

31

# 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

32

# 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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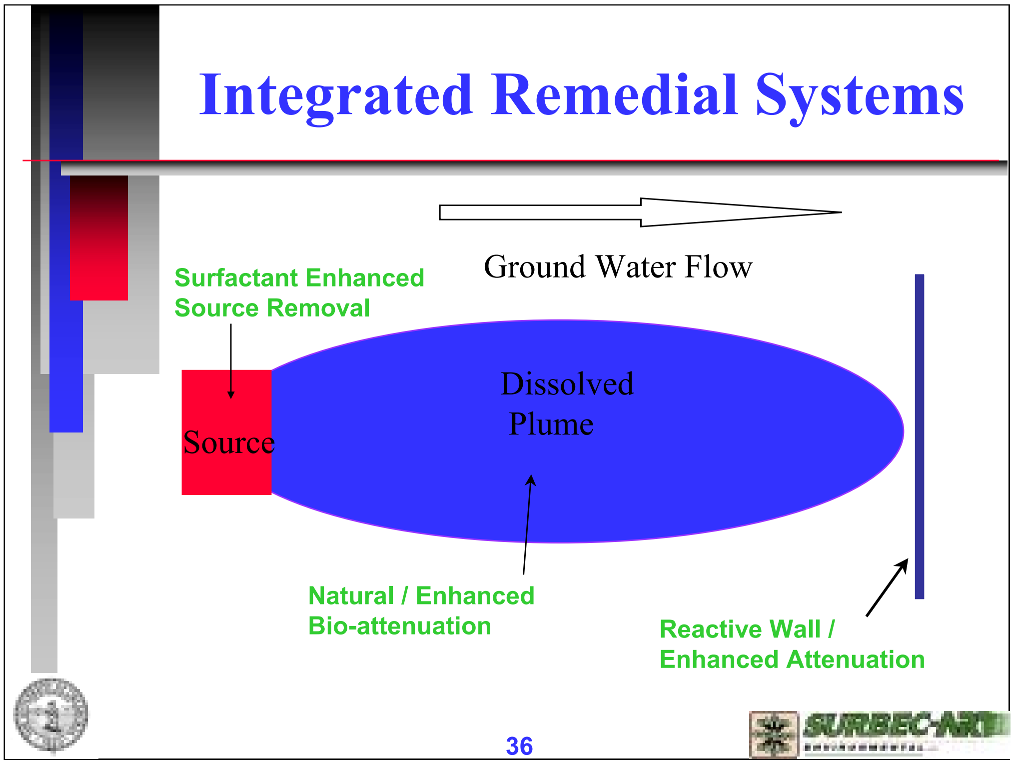
# Future Directions

- 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

35


Integrated Remedial Systems
Ground Water Flow
Surfactant Enhanced
Source Removal
Source
Dissolved
Plume
Natural / Enhanced
Bio-attenuation
Reactive Wall /
Enhanced Attenuation
36

# Surfactant-Based Risk Mitigation

*Questions?*

37