RTDF/NAPL Cleanup Alliance Meeting

Surfactant Enhanced Subsurface Remediation for Source Zone Removal

Surbec Environmental
Norman, Oklahoma

Surbec Environmental, LLC

Developing Real Solutions Through Technology

Source Removal

Surfactant Flushing

Dilute Plume Polishing

Chemical Oxidation
Bioremediation

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Background

- Formed in 1997 as technology transfer company
- Engineers, Hydrogeologists, Chemist, & experienced field implementers
- University researchers

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Primary Clients

- United States Air Force: Hill AFB, Tinker AFB, McClellan AFB, Dover AFB
- United States Navy: Alameda NAS, Office of Naval Research
- Department of Energy: Paducah Gaseous Diffusion Plant
- State Agencies: Michigan DEQ, Oklahoma Corporation Commission, Arkansas DEQ
- Private Industry: Conoco, BP-Amoco, Exxon Mobile, Chevron, Unocal, Waggoner Refinery
- RCRA/CERCLA: US EPA (Spartan Chemical)
- International: Taiwan, Japan

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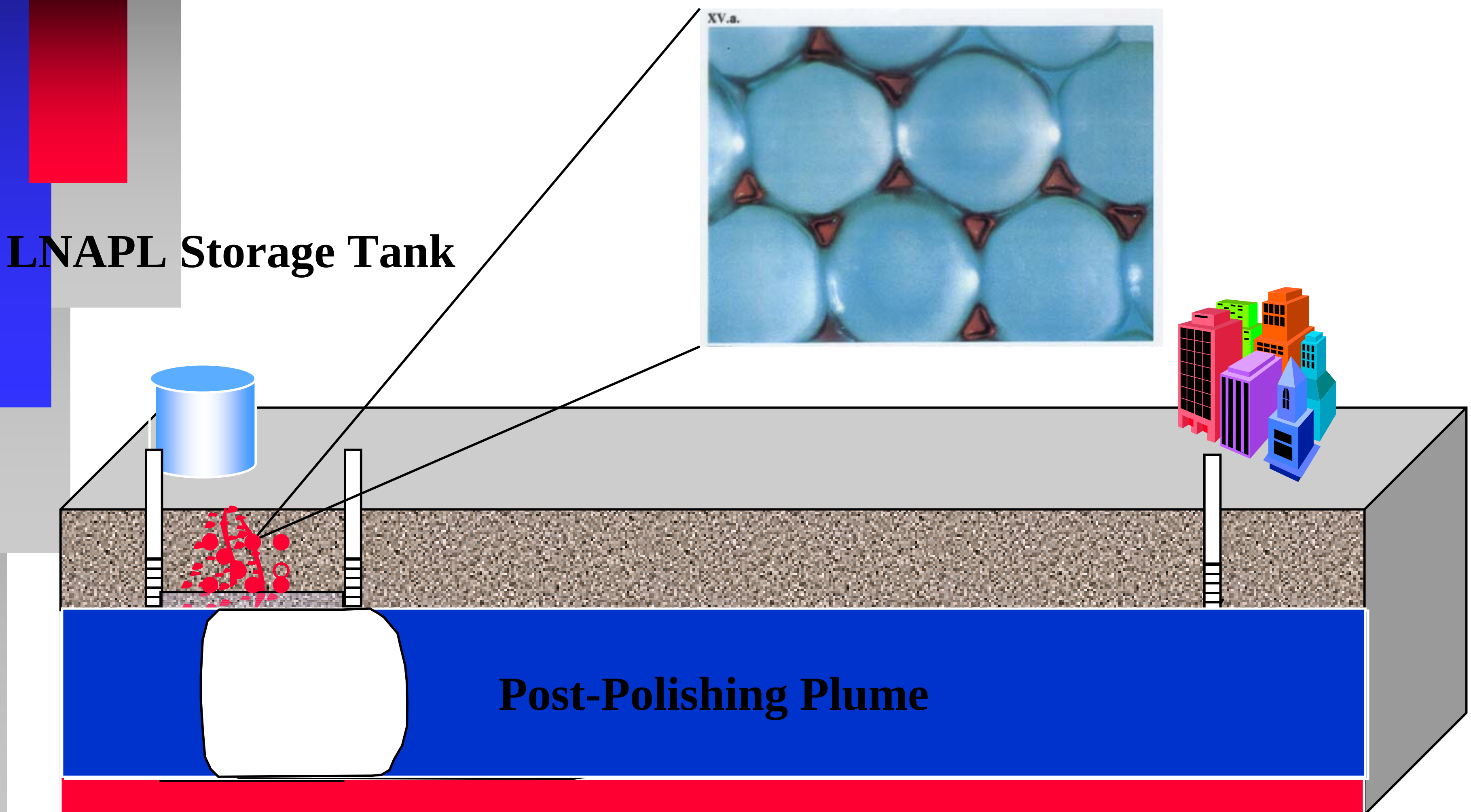
Outline

- Problem Definition / Surfactant Solution
- Field Demonstrations
  - Maximize Extraction Efficiency
  - Integrated Design
  - Low Surfactant Approach
- Economic Factors
- Summary

Problem / Approach



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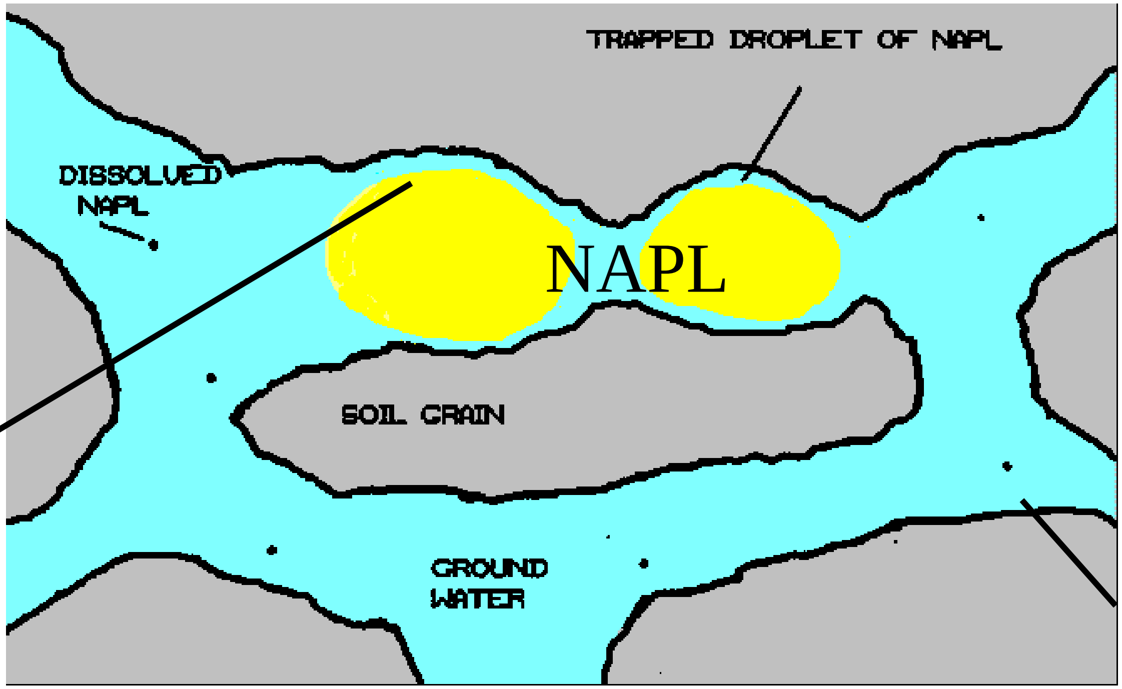
NAPL is Trapped by "Capillary Forces"

High o/w interfacial tension makes the oil immobile.



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

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.

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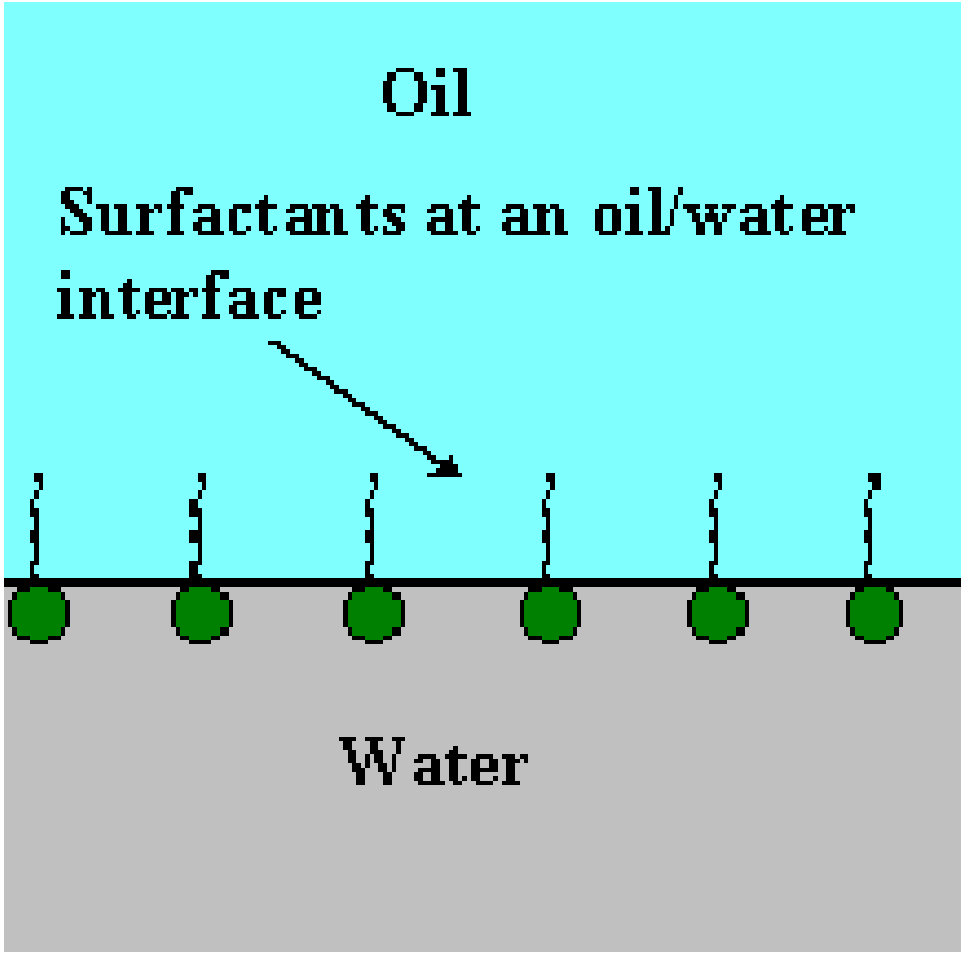
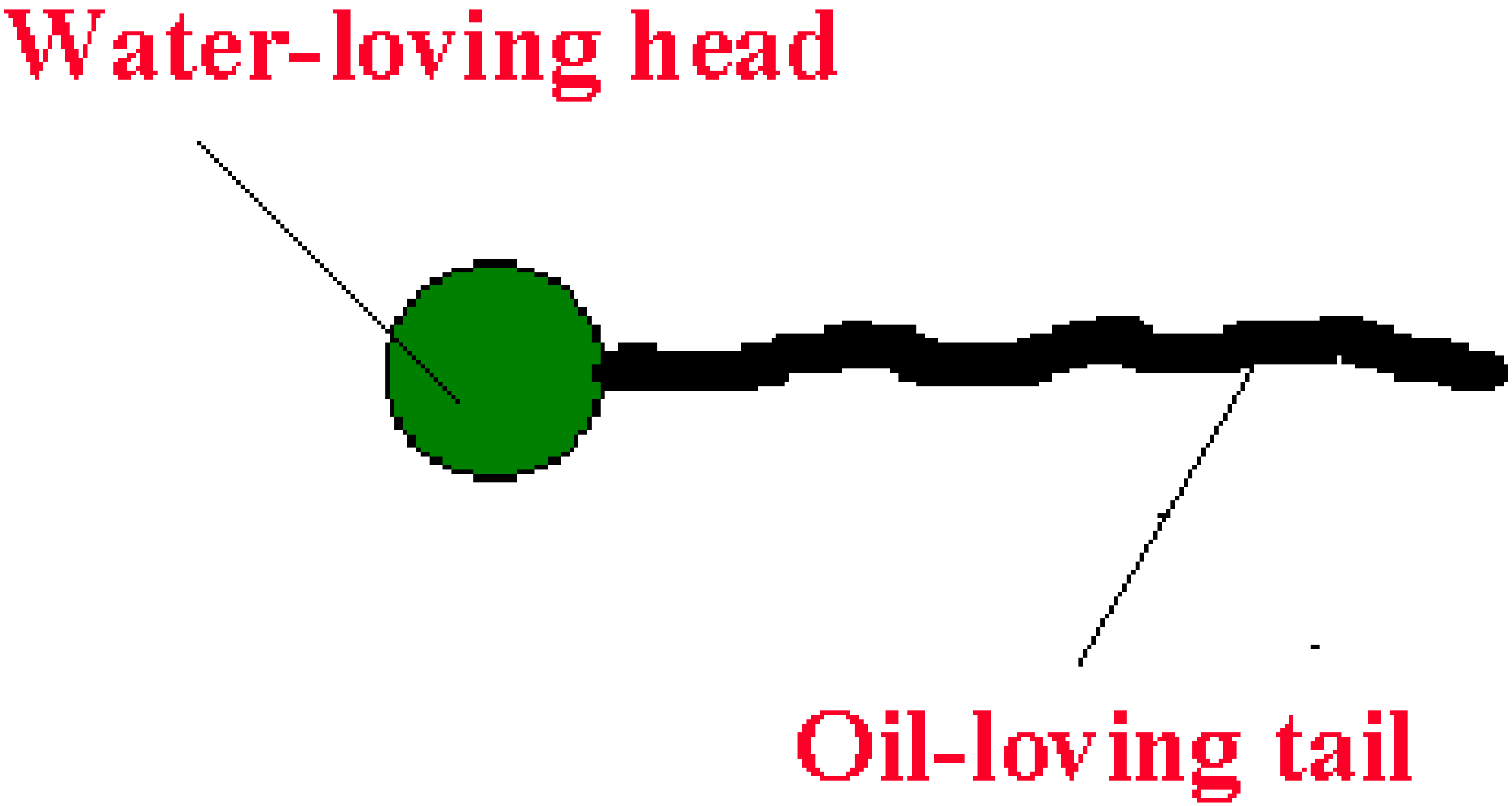
A Surface Active Agent

The word SurfActAnt is constructed from the phrase "Surface Active Agent". The word "surfactant" is meant to teach us that a surfactant is a molecule that seeks out and goes to a surface.



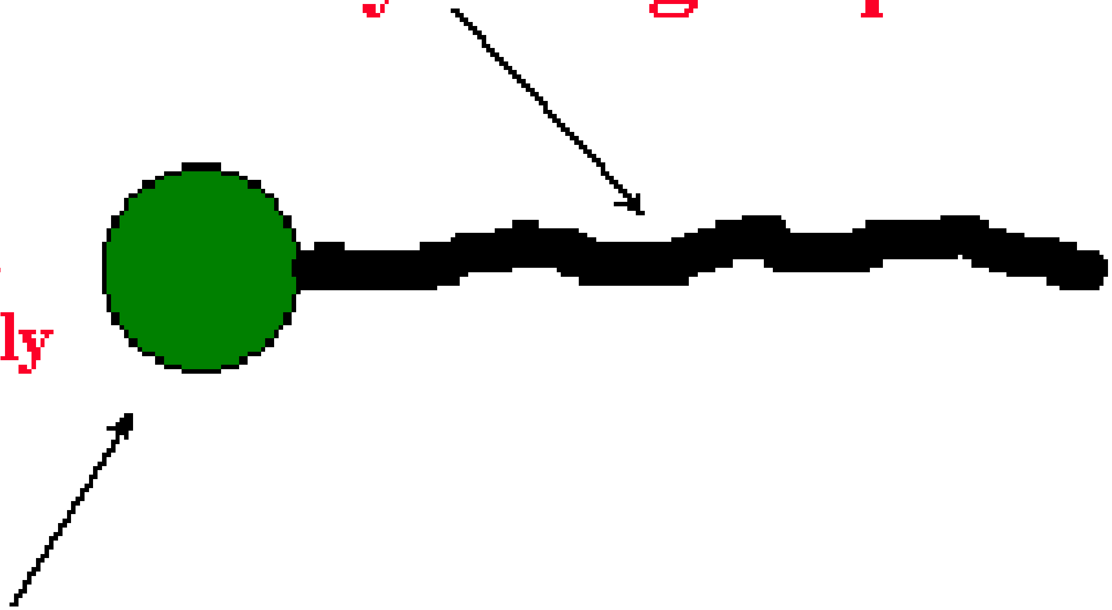
One part loves oil, one part loves water:



Lauric Acid, found in milk and coconut oil, is a naturally occurring surfactant:

Dodecyl tail group--oil loving

Lauric acid is a naturally occurring food lipid.

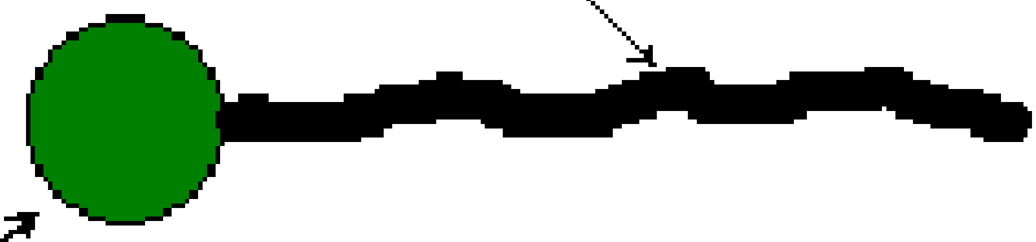


Carboxylic head group--water loving

$HOOC\,CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Sodium Lauryl Sulfate, made from coconut oil, is a good example:

Dodecyl tail group--oil loving

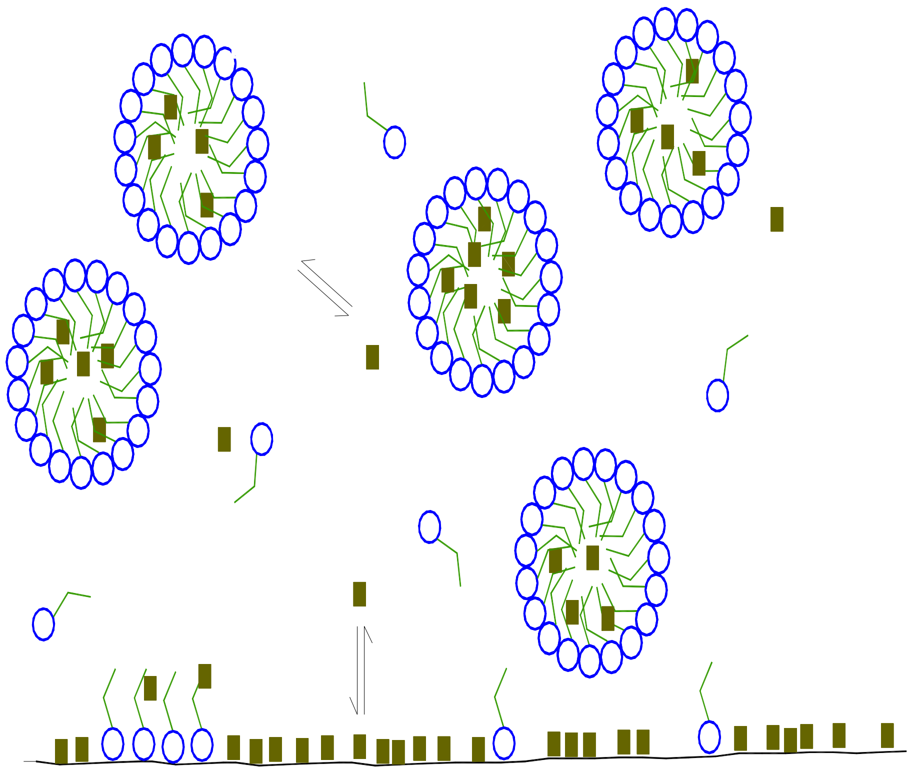


Sodium sulfate head group--water loving

$NaSO_4\ CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

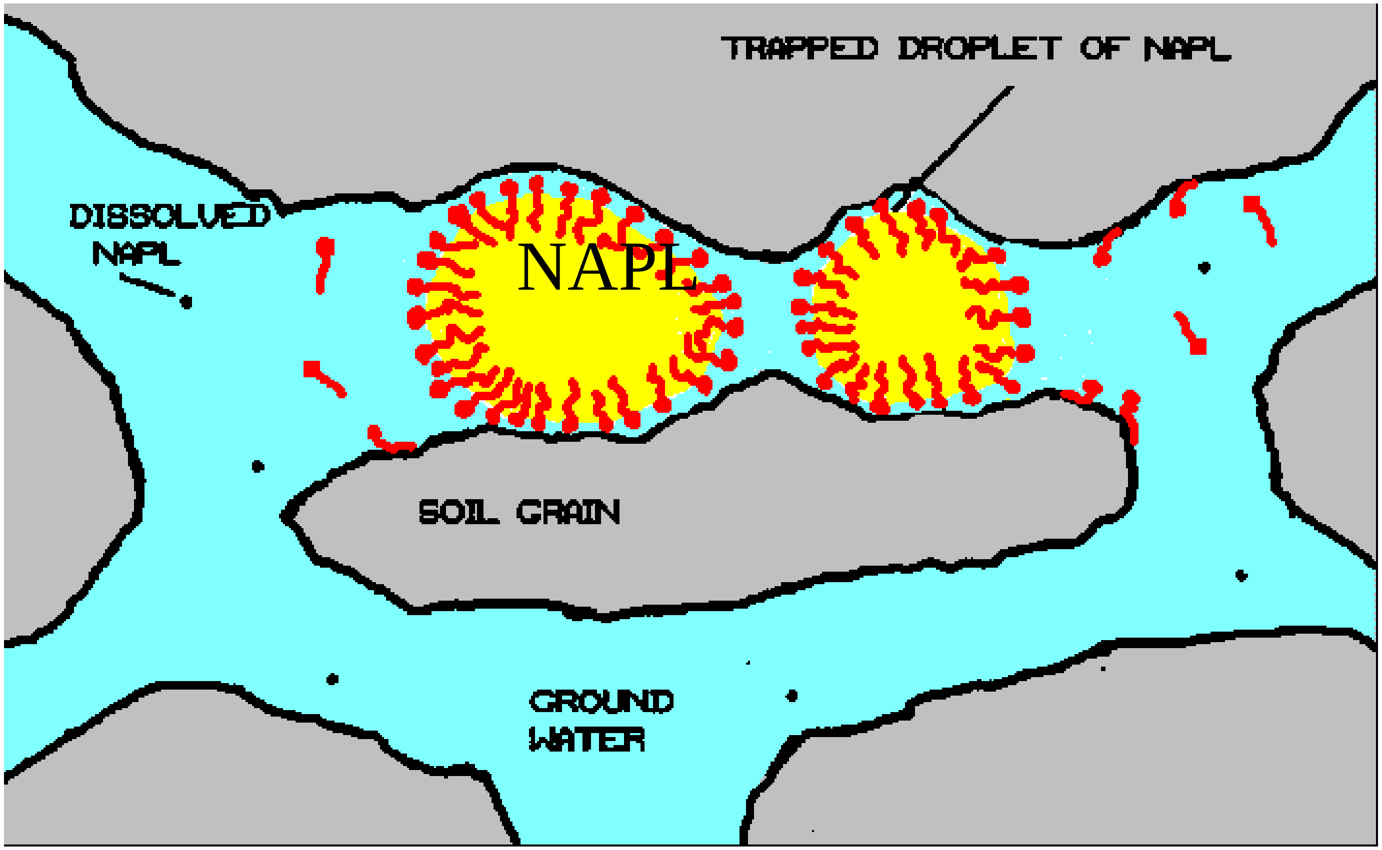
Surfactant Fundamentals

- Above CMC form aggregates – micelles

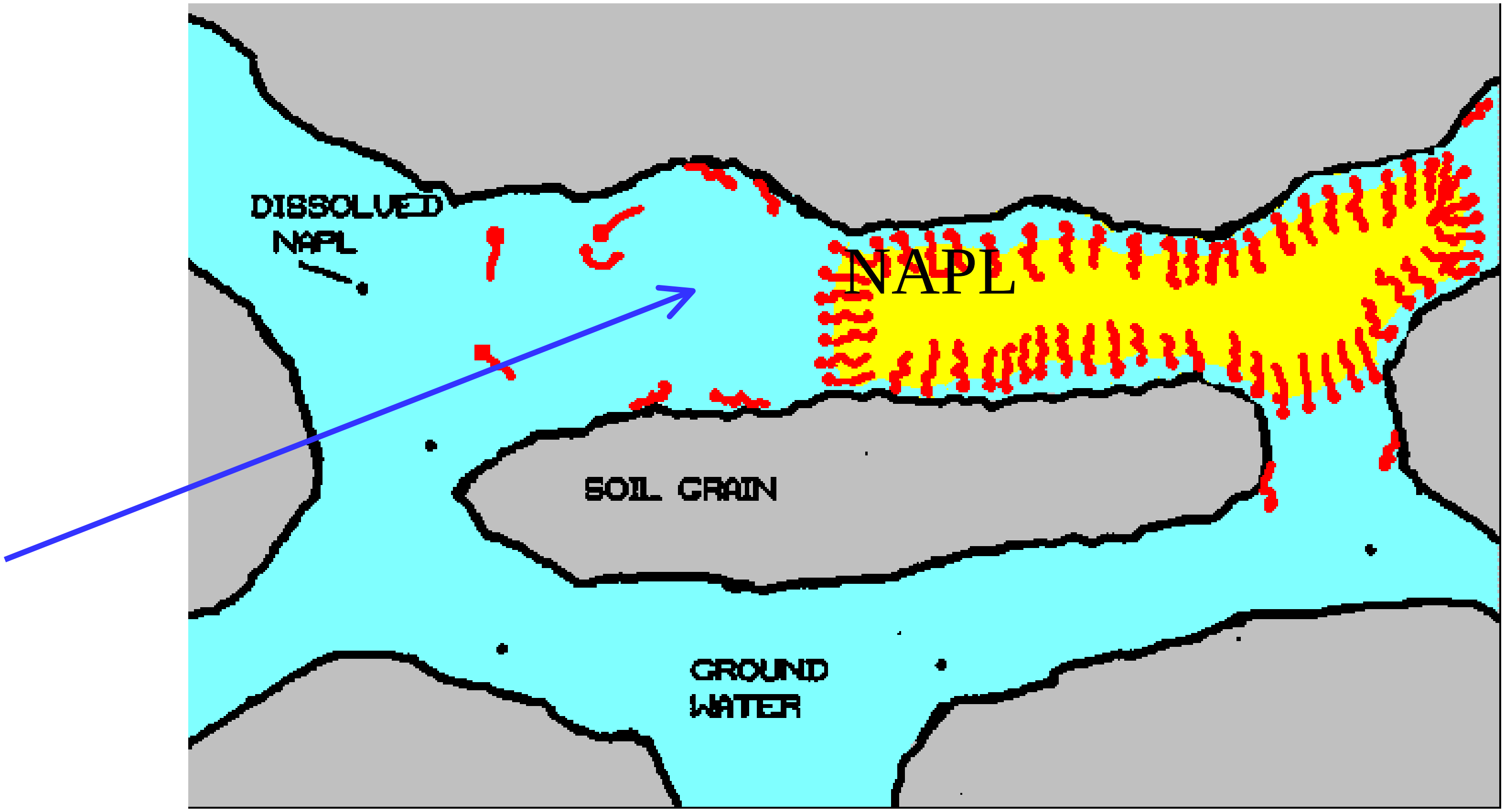


Surfactant adsorption lowers oil/water IFT

Dense monolayer lowers interfacial energy.

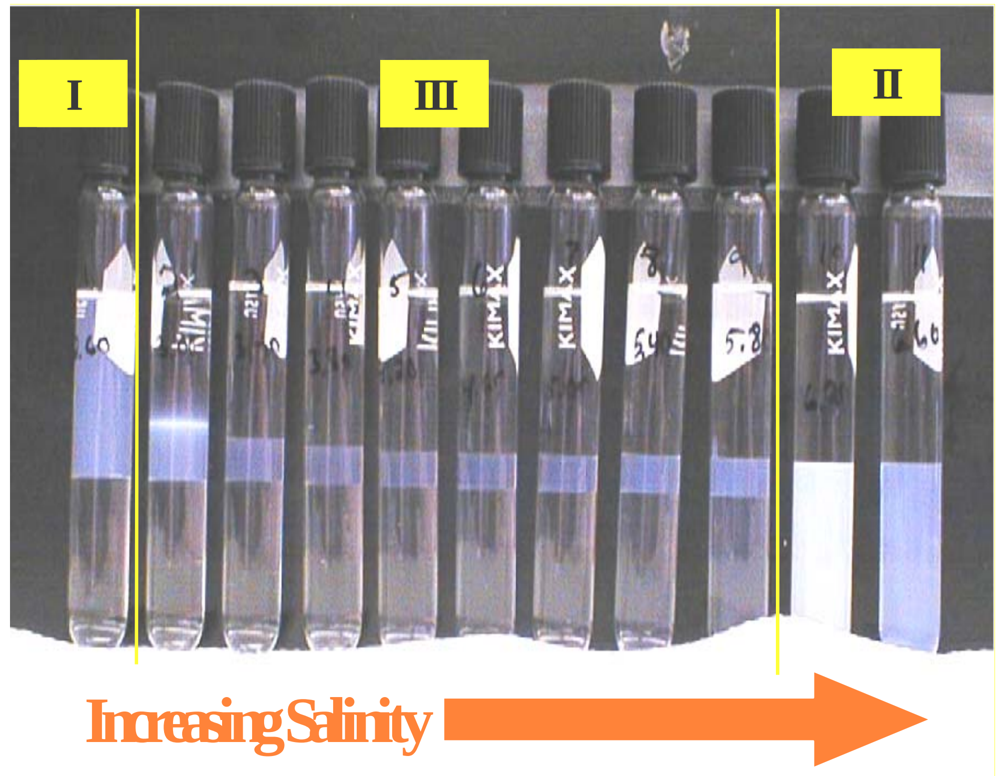


Droplet is mobilized, begins to flow.



Surfactant Fundamentals

- <u>Surf</u>ace <u>Act</u>ive <u>Agent</u>
- Above CMC form aggregates – micelles
- Winsor phase transition
- Surfactants used - Food grade or non-toxic



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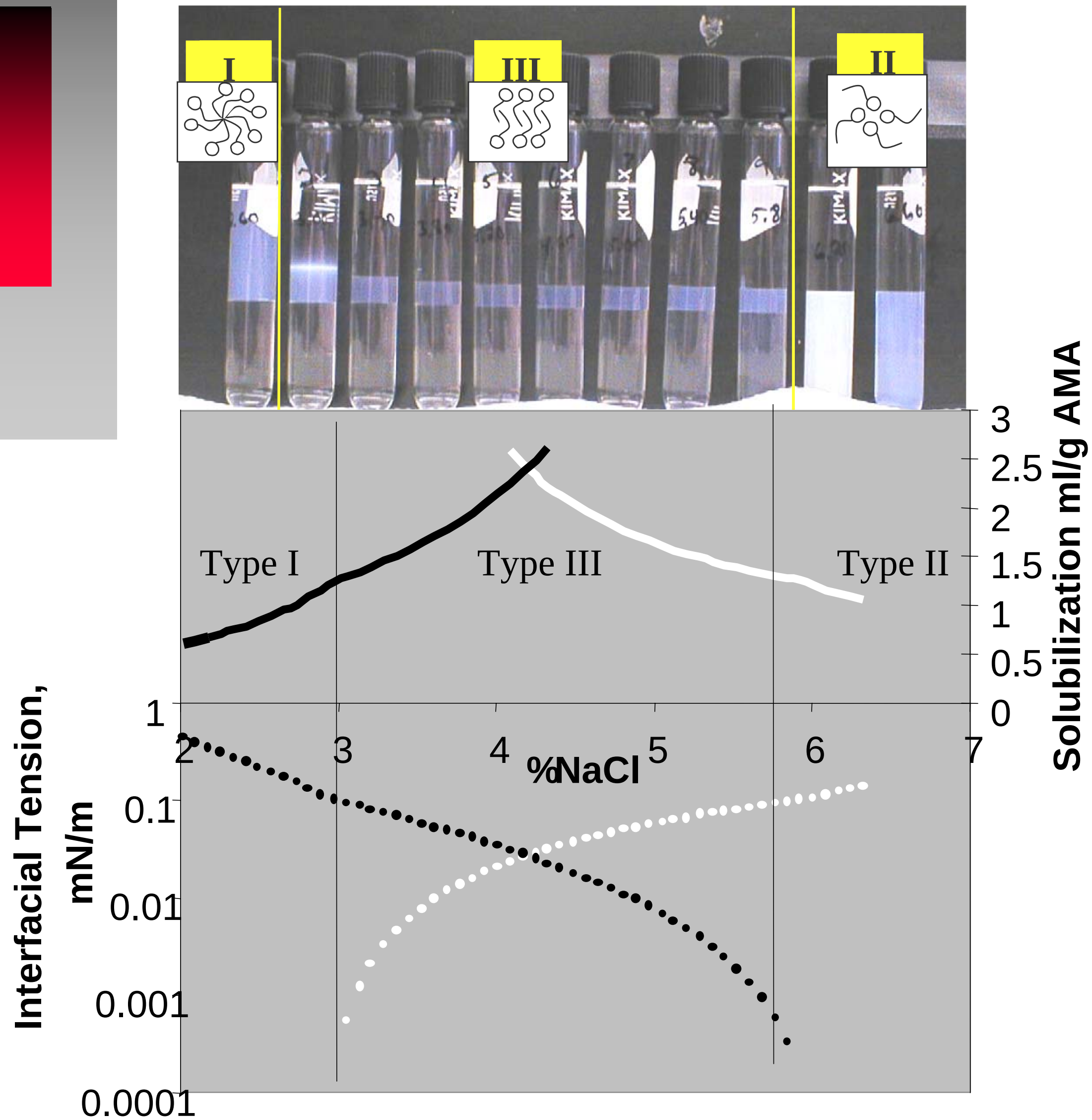
Phase Scan: IFT / Solubilization



- 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"

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Maximize Extraction Efficiency

- **Solubility enhancement increases**
  - **As interfacial tension (IFT) decreases (as described by Chun Huh relationship)**
- **Optimal surfactant system**
  - **Maximizes solubility and mobility while mitigating physical by-passing and/or uncontrolled migration**

Design Factors

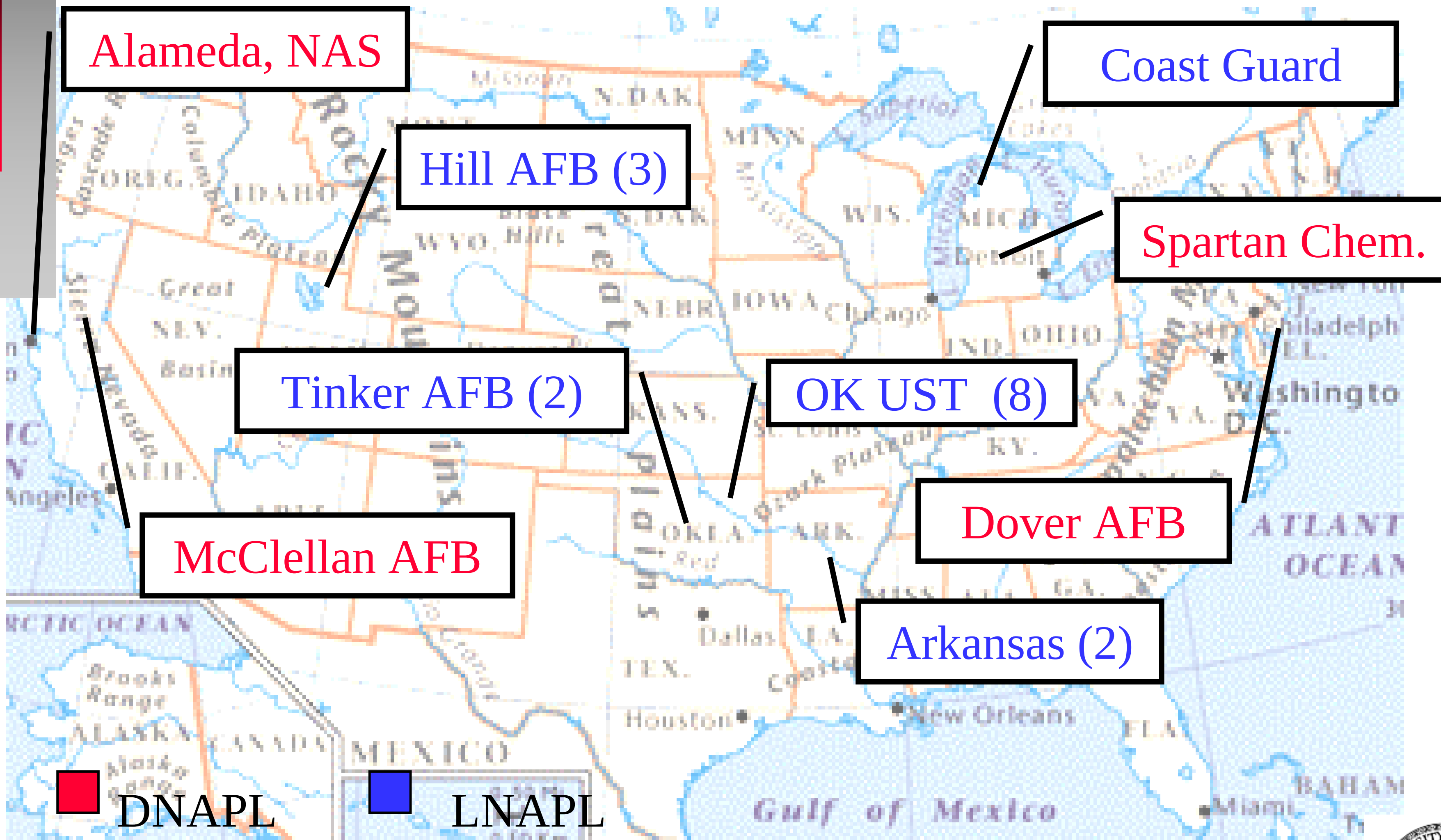
- Contaminant Distribution
- Site Hydrogeology: Heterogeneities, sweep efficiency (polymers, foam)
- Modeling Is Critical
  - How will the system respond
  - Tracer Tests – verification (option)
- Scaleup Approach
  - Batch, column, field scale – tracer test, pilot-scale test

Design Factors

Surfactant Chemistry is Critical!

- Maximize efficiency -- 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!!

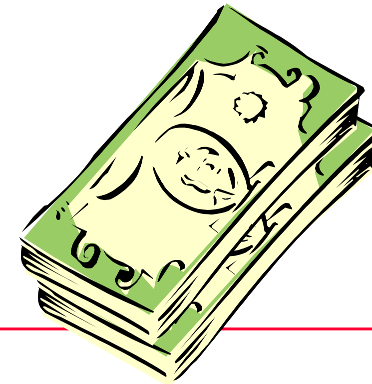
Twenty Field Applications



Surbec's Proprietary Approach Surfactant Flushing Development

- Low Surfactant Concentration
- Integrated Low Surfactant/ Chemical Oxidation and/or Bioamendment for Complete Site Closure

Low Surfactant Concentration



- Most site owners have limited resources for site clean-up efforts
- 0.1 to 1 wt% versus 3 to 8 wt% in earlier Surfactant Flushing projects
- Technical challenges: greater sorption impact, etc

Golden UST Site, OK

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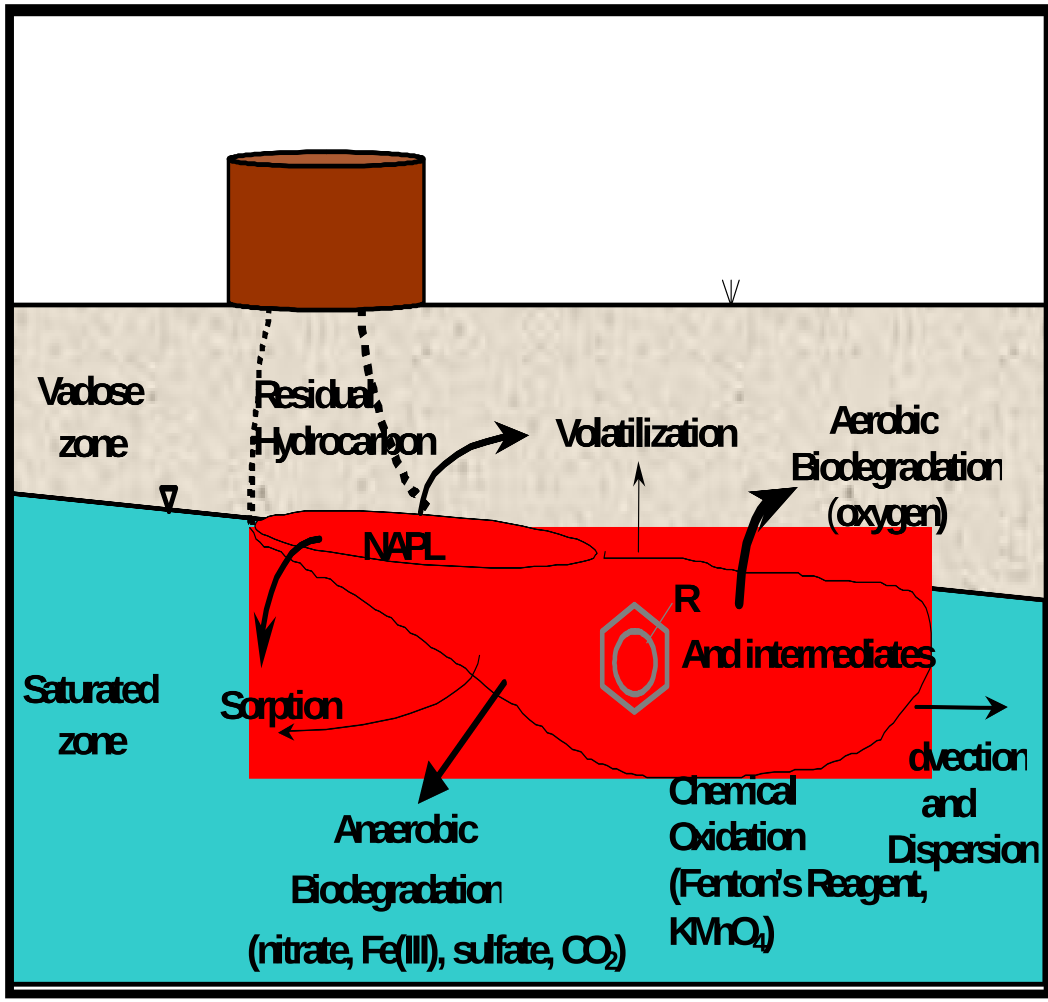
Integrated Low Surfactant/Chemical Oxidation Approach*

- Surfactant flushing is not suitable for dilute plume remediation
- Polishing step: injection of low chemical oxidant (< 1 wt%) and/or bioamendment to polish remaining residual / dilute NAPL plume



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*Surbec U.S. Patent Application No. 20030175081
(PTO Approval Action Date: 03/29/04)

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Oxidation Approach for LNAPL

- Direct attack of chemical bonds and producing CO_2
- Low concentration (< 1 wt% H_2O_2)
- Injection of oxidant after surfactant is recovered
- Optional depending on site goals
- For site closure goal is ppb range

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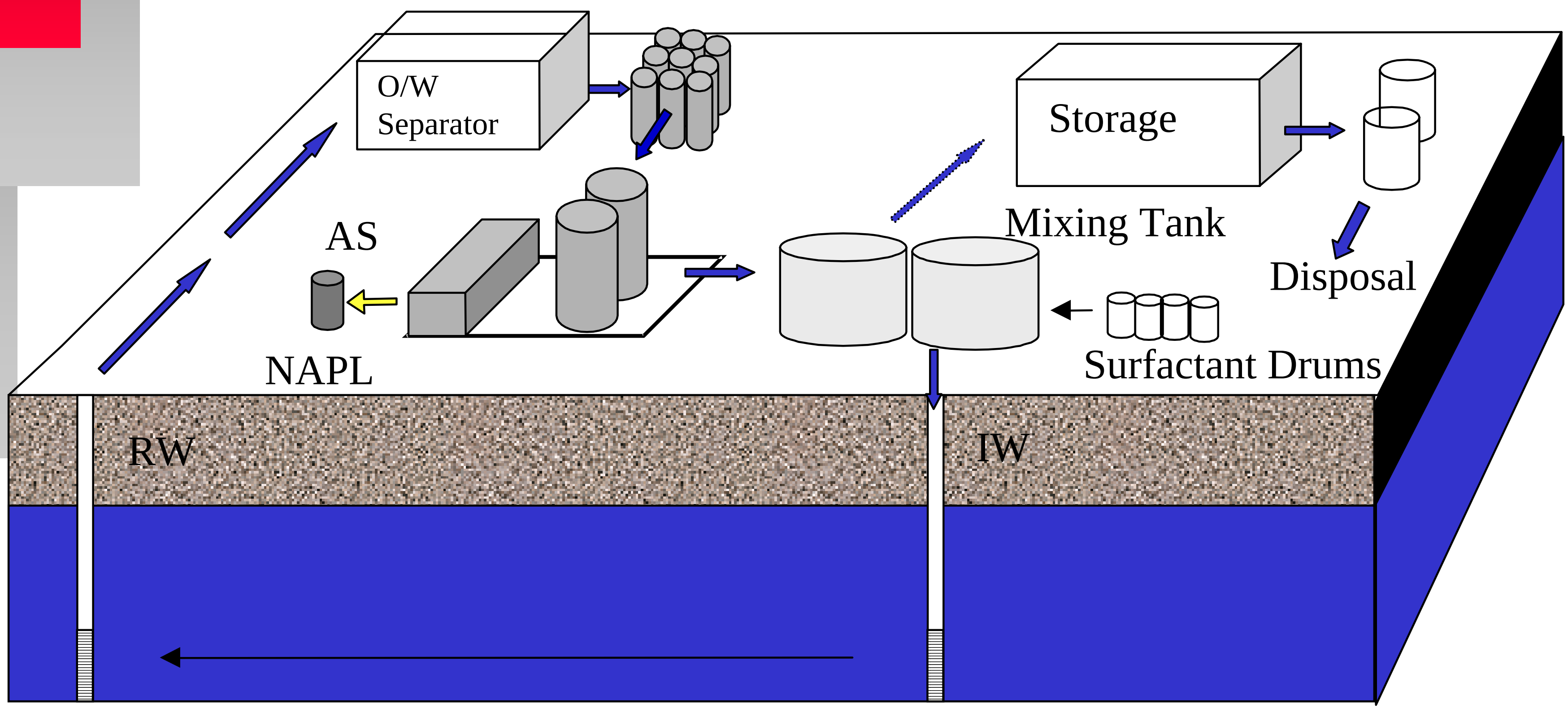
Surfactant Flushing Integrated Process



In Situ Surfactant Flushing: Case Studies

Important Note

- For case studies – site specific goals not limited to free product removal
- In all cases goal was site closure
- Total cost in all cases are site closure & include Surbec profit
- This is not an experimental process – it is a operation which we are currently making money

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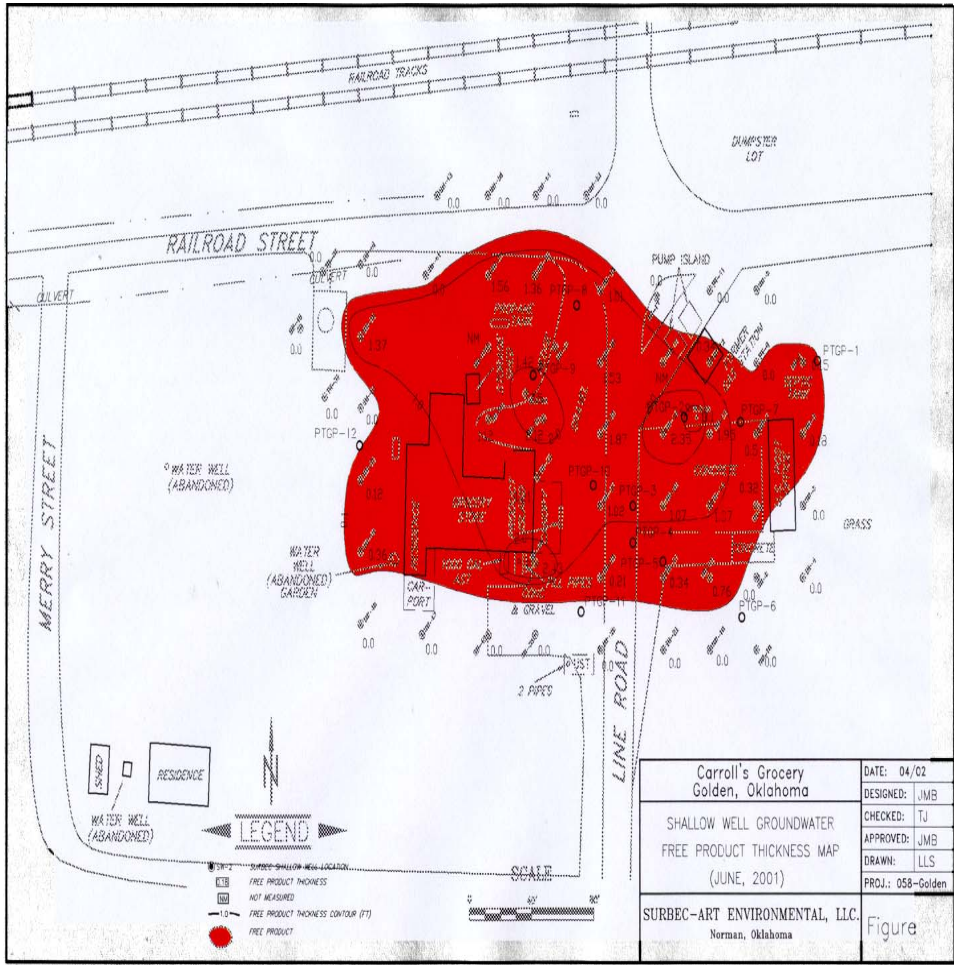
Golden, OK UST Site
Starting Point (LNAPL)-- 2-acre site

- Gasoline free phase: thickness on water table 2.7 to 3.3 ft
- Shallow zone (< 15 ft) - silt:benzene, 2,000 to 36,000 µg/L in GW; TPH, non-detect to 345 mg/L
- Deep zone - sand/gravel: benzene, 50 to 3,000 µg/L; TPH, non-detect to 30 mg/L
- Surfactant Flushing Zone: 1.5 acres



Golden Free Product Map

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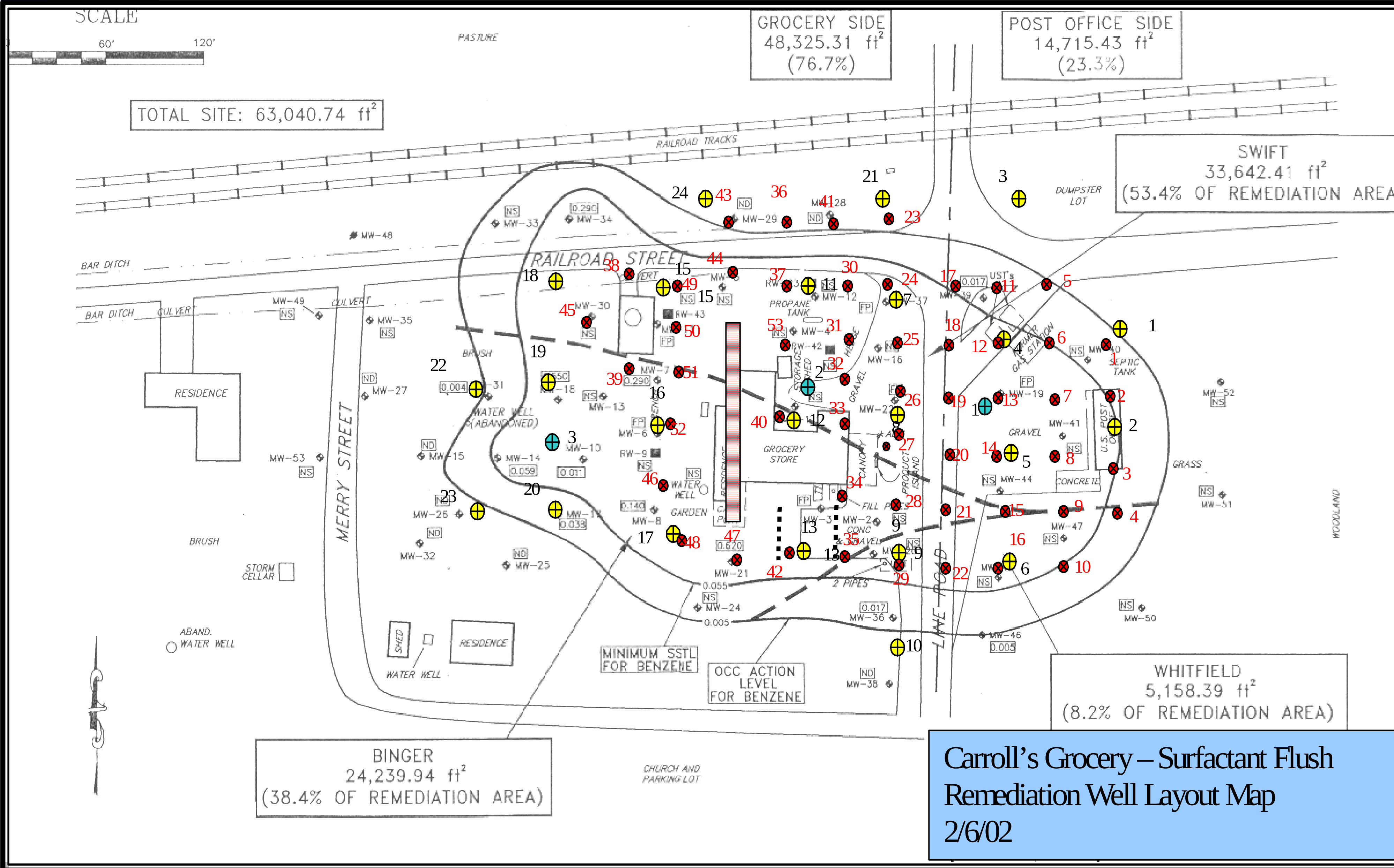

Carroll's Grocery – Surfactant Flush Remediation Well Layout Map 2/6/02

Legend

Deep Well (DW)
Shallow Well (SW)
Horizontal Wells
MLS

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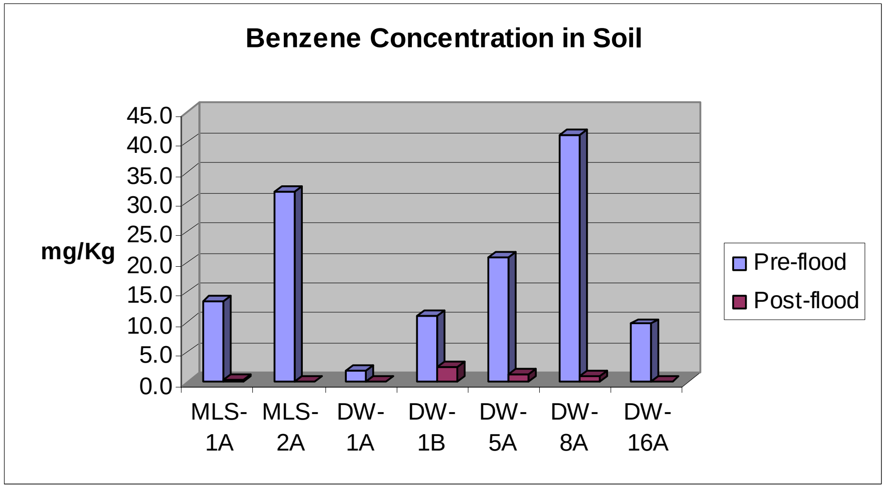
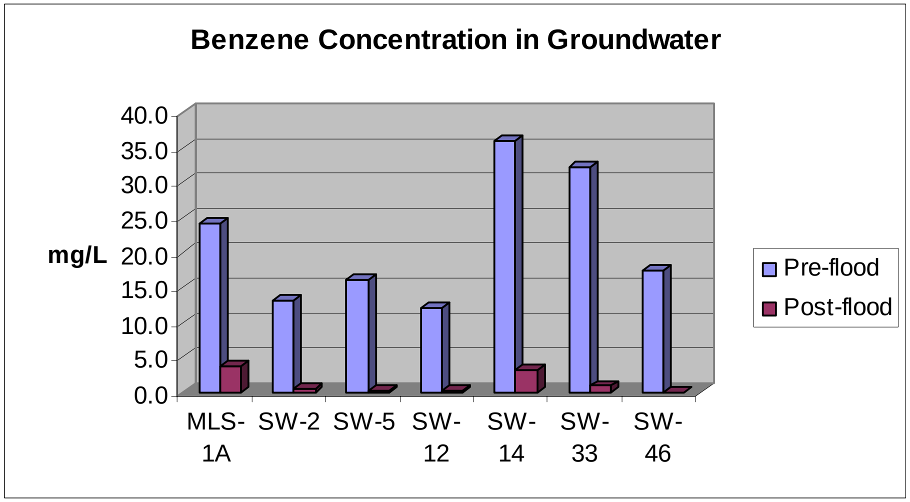
Golden, OK UST Site Approach / Results

- Low level (< 1 wt%) surfactant/cosurfactant mixture
- 1 PV (190,000 gallons) – 60 days flushing
- Polishing: shallow -- low level chemical oxidation; deep – bioammendments (Phase I); chemical oxidation (Phase II)
- Soil and ground water concentrations reduced by one to three orders of magnitude





Data collected on 06/27/02

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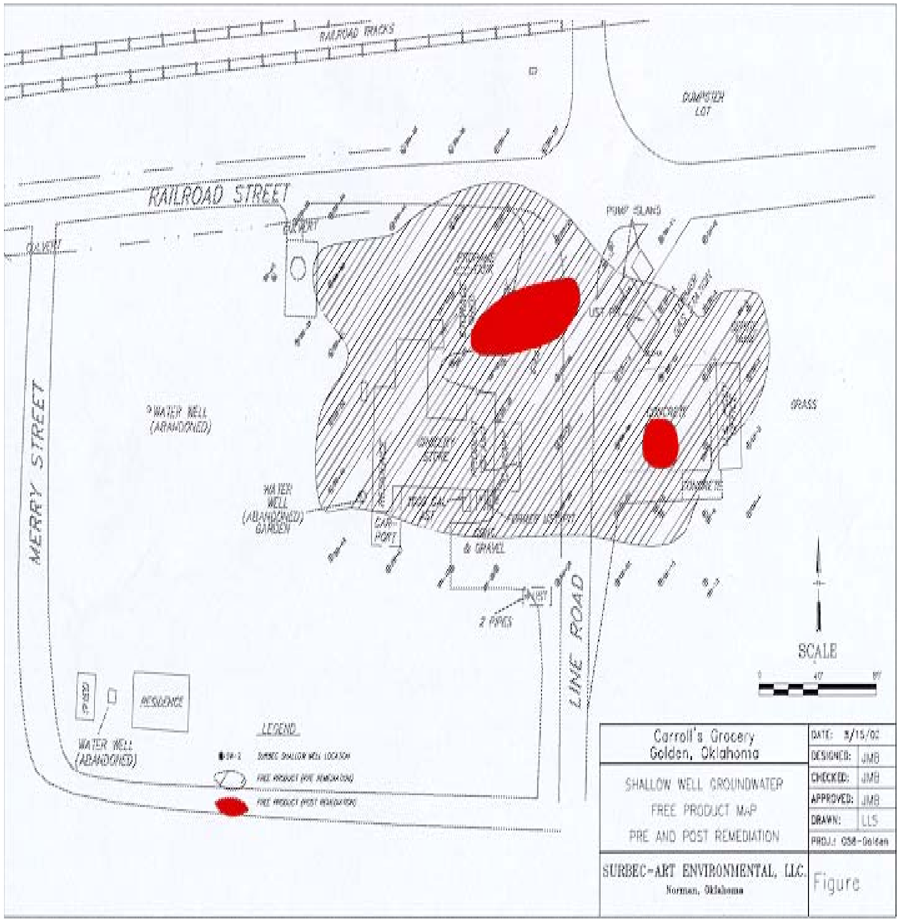
Golden, OK UST Site
Results vs Goals

- Primary: no visible or instrumental evidence of free phase gasoline in 22 wells after three-month shut-down (3 had trace levels of NAPL)
- > 6,500 gallons gasoline extracted



Post Flush Free Product Map
(06/02 data collected)

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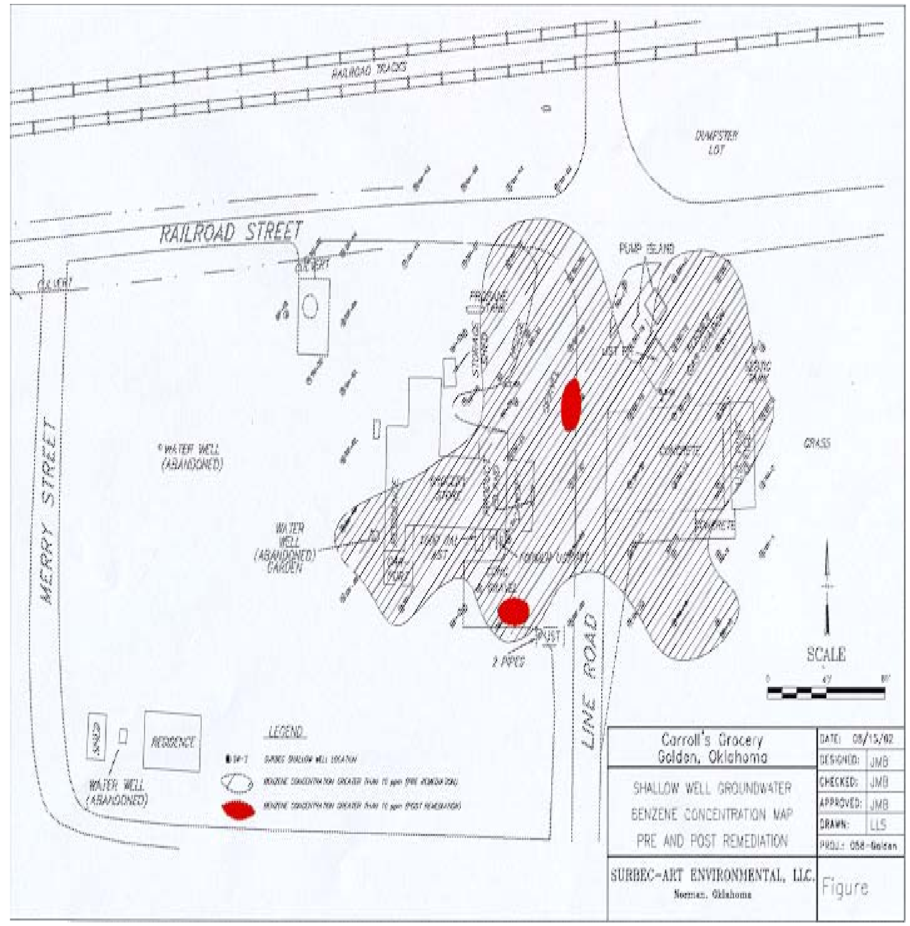
Golden, OK UST Site Results (cont.)

- Secondary: Groundwater 70% to 99% reduction in benzene concentration
- Final Polishing (Chem. Oxid.) to approach MCL



Post Flush Benzene Map
(06/02 data collected)

Tinker North Tank, Tinker AFB, OK (LNAPL)

Tinker North Tank

Goal: Removal of free phase No. 2 heating oil

Approach: 1.7 PV low surfactant (1 wt%) flushing+polymer drive

> 6,400 gallons free product recovered during 22-day surfactant flushing

634% increase in NAPL recovery rate compared to pre-existing dual phase extraction

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Bixby UST Site, Bixby, OK (LNAPL)

- NAPL: mixed gasoline and kerosene
- Geology: fine sand
- Free product: 0.5 to 2.2 ft in MWs, extent 120 ft x 85 ft
- Surfactant flushing: Mobilization, 0.94 wt%, 120,000 gallons (1.5 PV) over 13 days
- Polishing: 0.4 wt% Fenton's Reagent, 130,000 gallons over 6 days

Bixby UST Site

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Bixby UST Site (cont.)

- No free product was observed after surfactant flushing
- Post surfactant flushing: GW Benzene conc. 50 ug/L to 20 mg/L
- Post chem ox polishing: GW Benzene conc. ND to 1.8 mg/L (SSTL 5.6 mg/L)
- Project completed in 2.5 months

Well #	Middle (Post surfactant-pre FW) Benzene µg/L	Post-chem ox Benzene µg/L
EW-3 (1.7)*	17,200**	165
EW-10 (1.69)	13,400**	217
SMW-3 (2.3)	2,670**	198

*() pre-flushing free phase thickness, ft

**most contaminated locations

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Tank Pits Flushing

- **Pollution Prevention**:
  - Free phase removal (gasoline & diesel pits)
  - Love’s Country Store (OKC, Completed--10/02)

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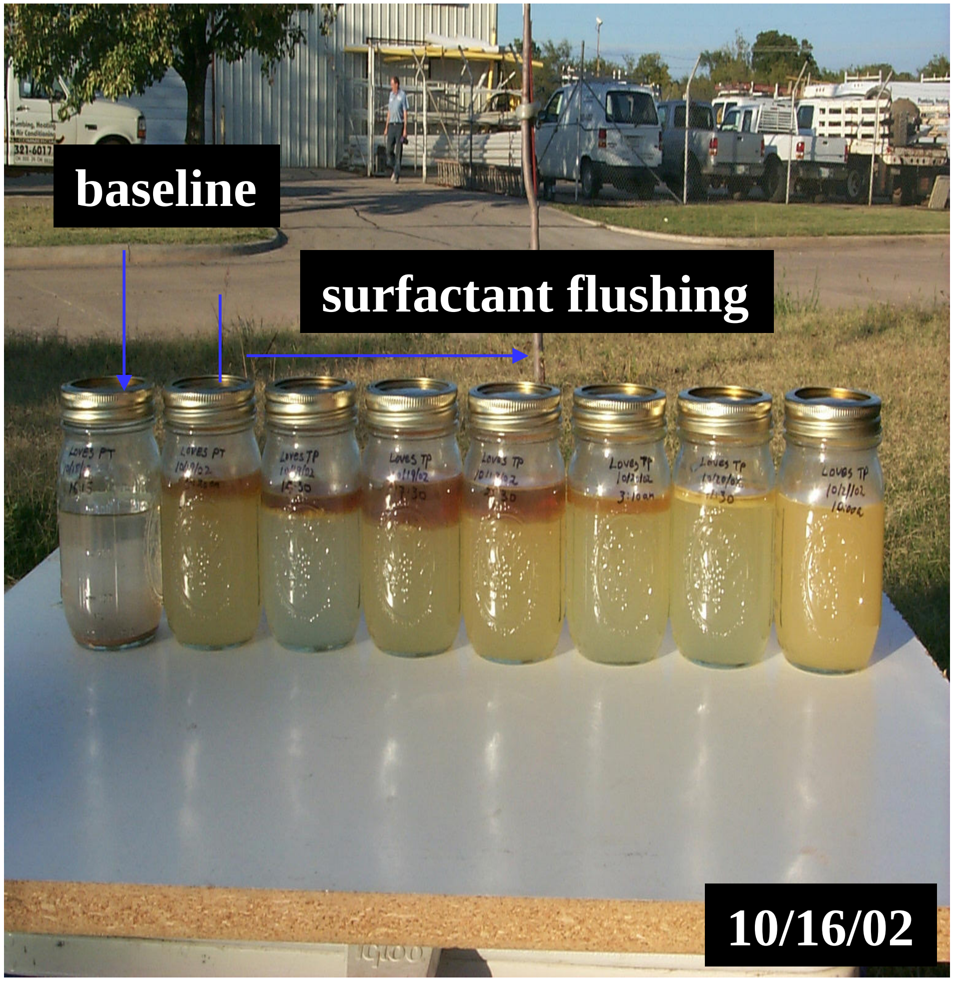
Tank Pits Flushing (cont.)

- Approach: low surfactant conc. (1PV)
- Different surfactant systems for gasoline and diesel pits
- Low cost ($ 20K)
- Recycling/ reuse of recovered water
- Compact design without interrupting the routine activity



Tank Pit Effluent

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Surfactant Enhanced Source Removal Summary

- Surfactant Flushing is technically and economically viable and very competitive with other technologies
- Significant NAPL mass removal can be achieved by low surfactant concentration approach
- Treatment-train approach -- combination of Surfactant Flushing (source removal) with Chemical Oxidation and/or Bioamendments (contaminant plume polishing) will expedite site closure

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Next Generation Process Modification

- Significant cost saving possible
- Low cost, low dose, low pore volume possible
- Improved surfactant technology
- Large site – cost reduction by
  - Marching approach
  - Optimize system operation
  - Optimize flushing pore volume (reduce by trial and error on first few sub-plots)

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Cost Summary for First Generation Technology

UST contract value		yd^3 remediated	$/yd^3$*
• Golden	$560 K	15,550	36
• Bixby	$275 K	5,400	51**
• Cobb Creek	$296 K	7,415	40**
• Spencer	$335 K	7,400	45

- Total project costs for Golden = $36 / yd^3 for source zone;

(48,000 yd^3 including diluted plume zones area treated with chem oxid = $15 / yd^3)

- Properly designed, economical

  As low as: $25 / yd^3 (LNAPL); $60 / yd^3 (DNAPL)

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*Not direct cost, but is total cost included profit

**Cost included Oxidation

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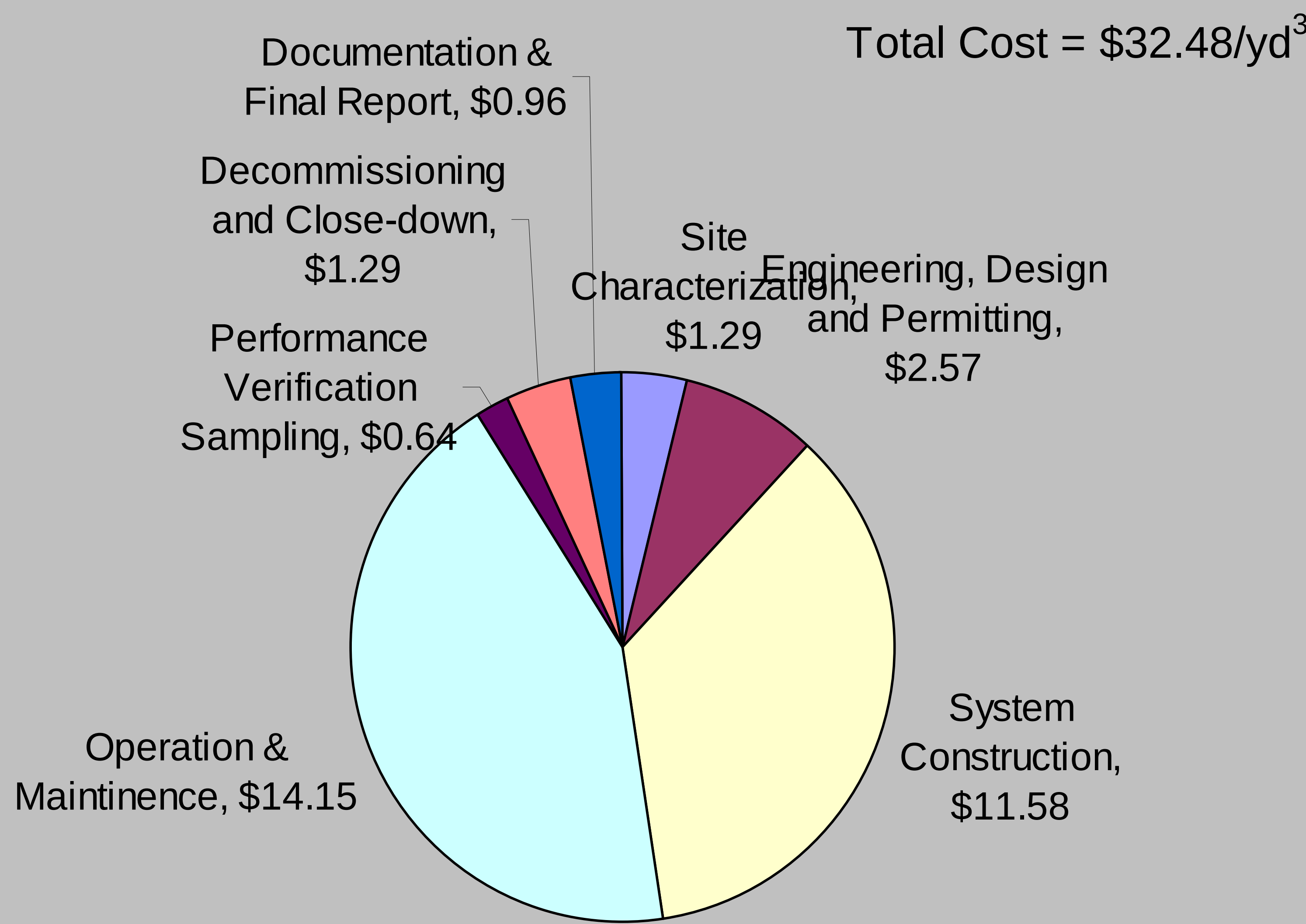
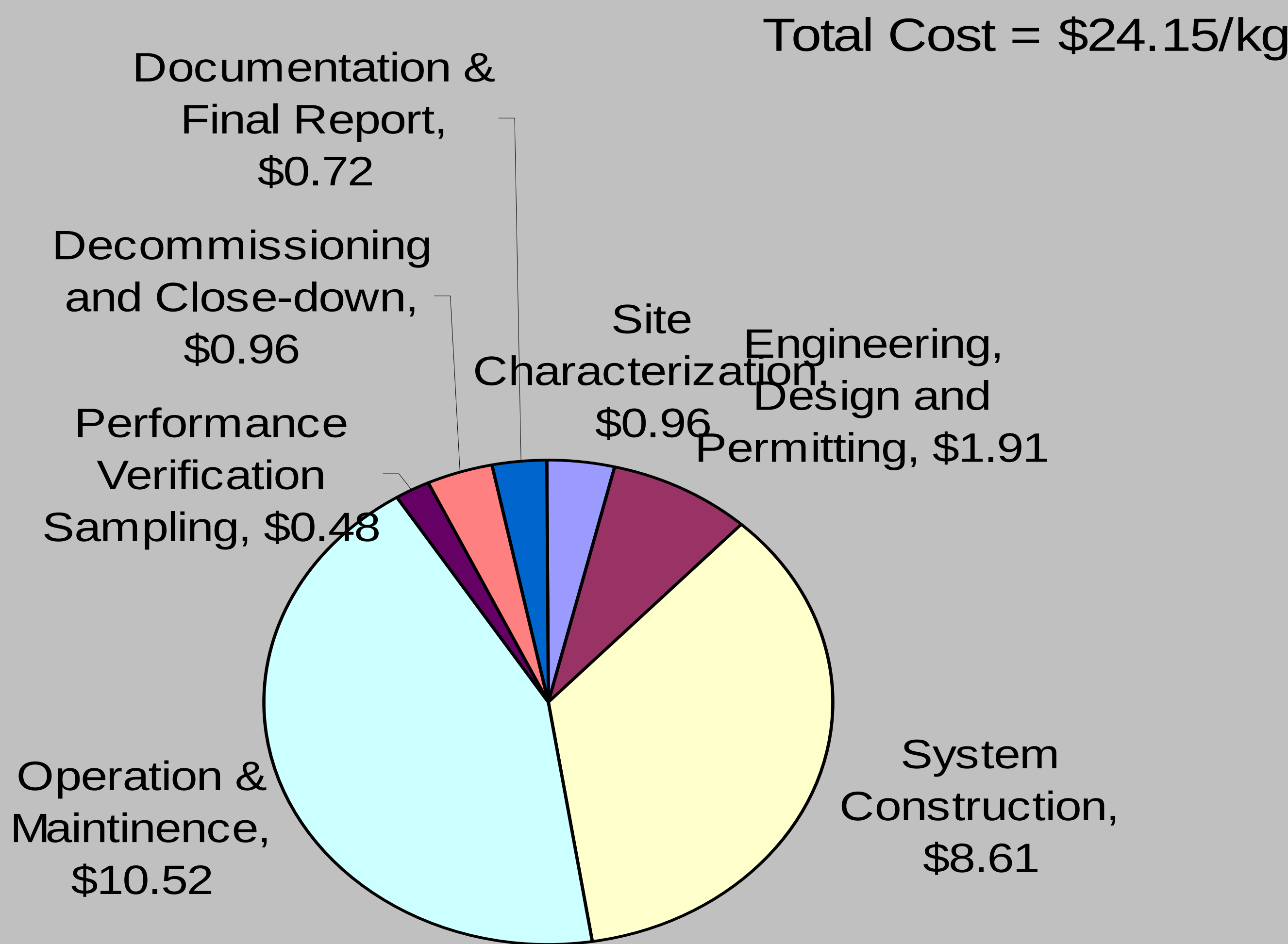
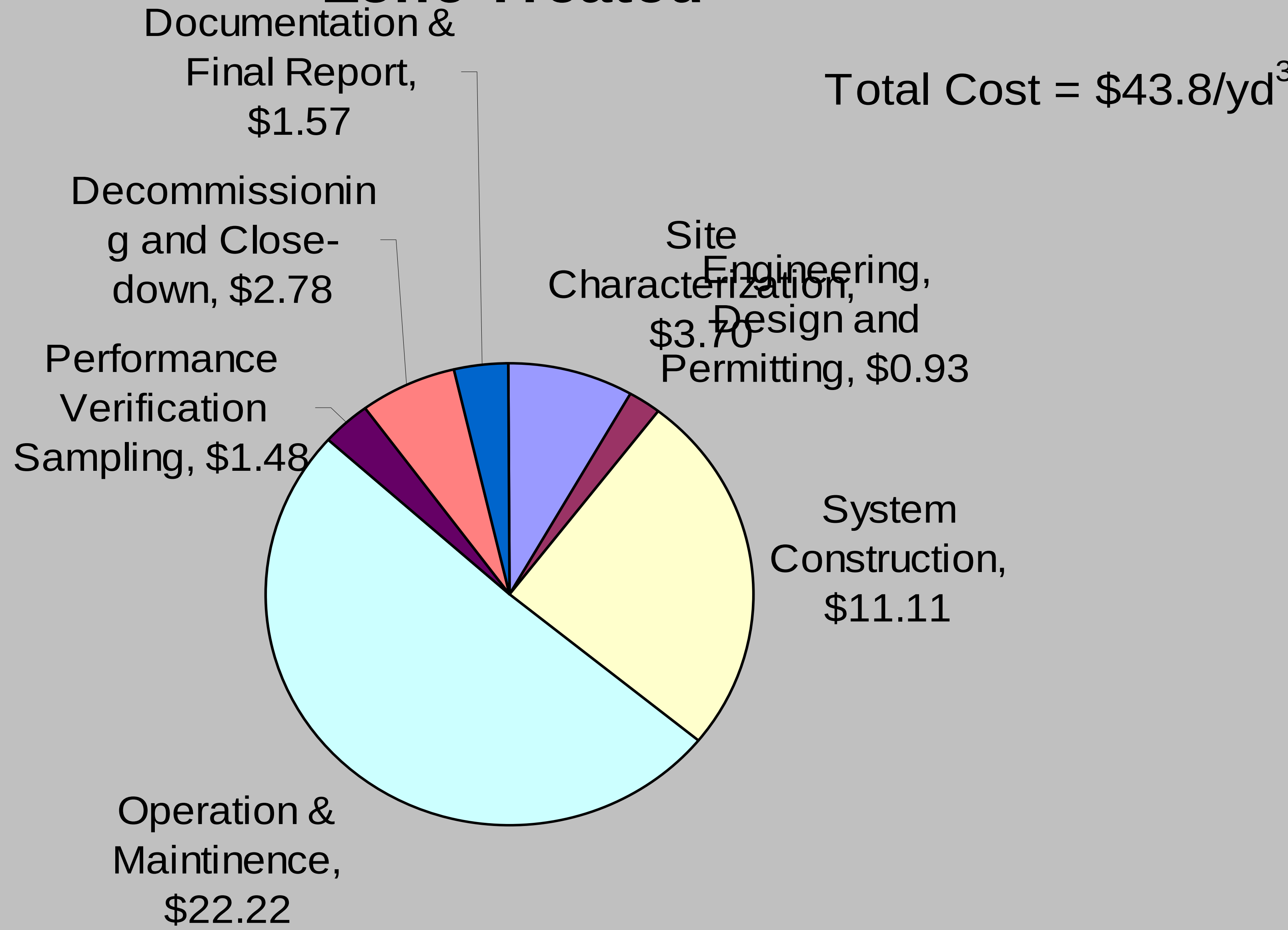
Golden UST Cost per Cubic Yard of Smear Zone Treated



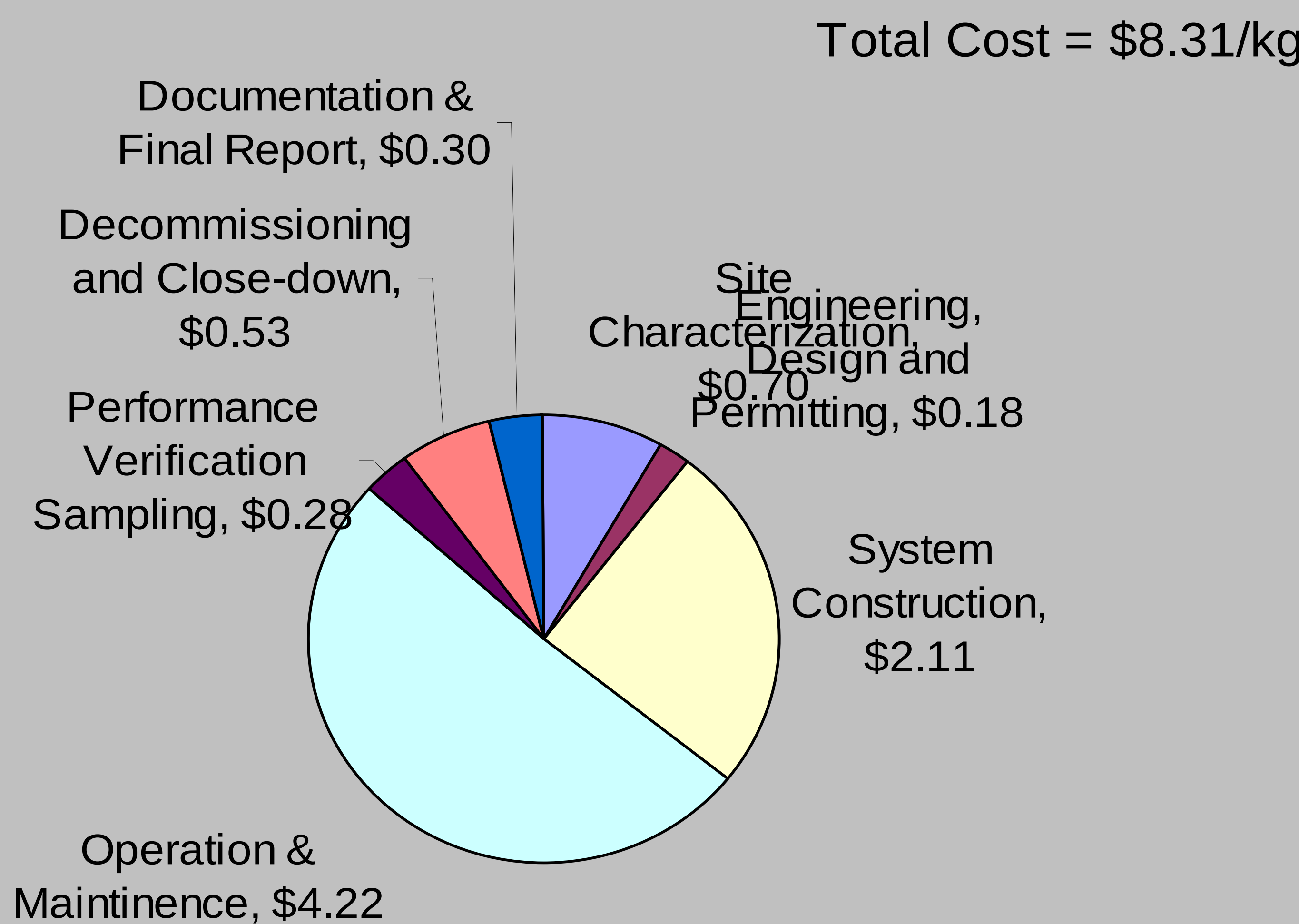
Golden UST Cost per Kilogram of Contaminant Removed



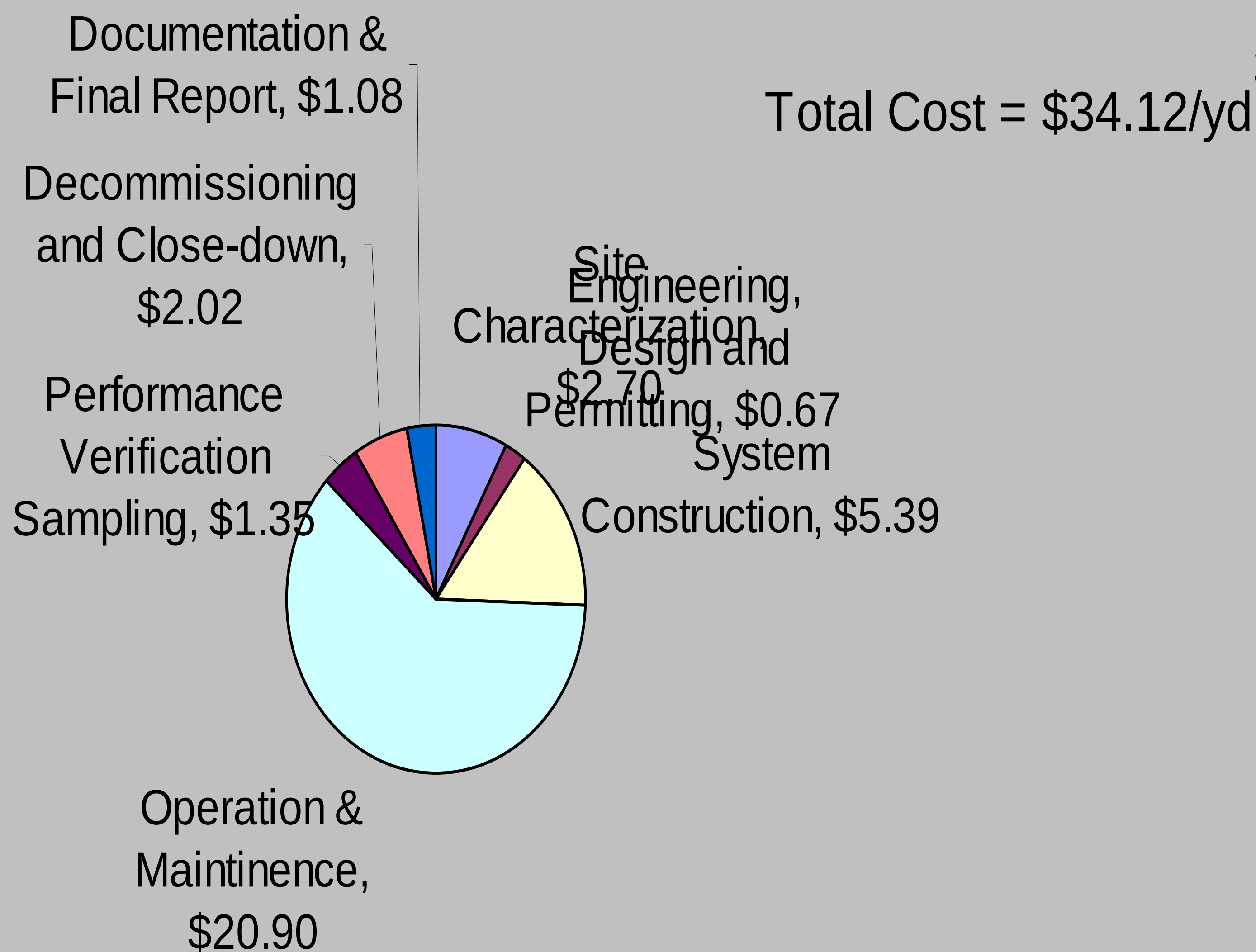
Bixby UST Cost per Cubic Yard of Smear Zone Treated



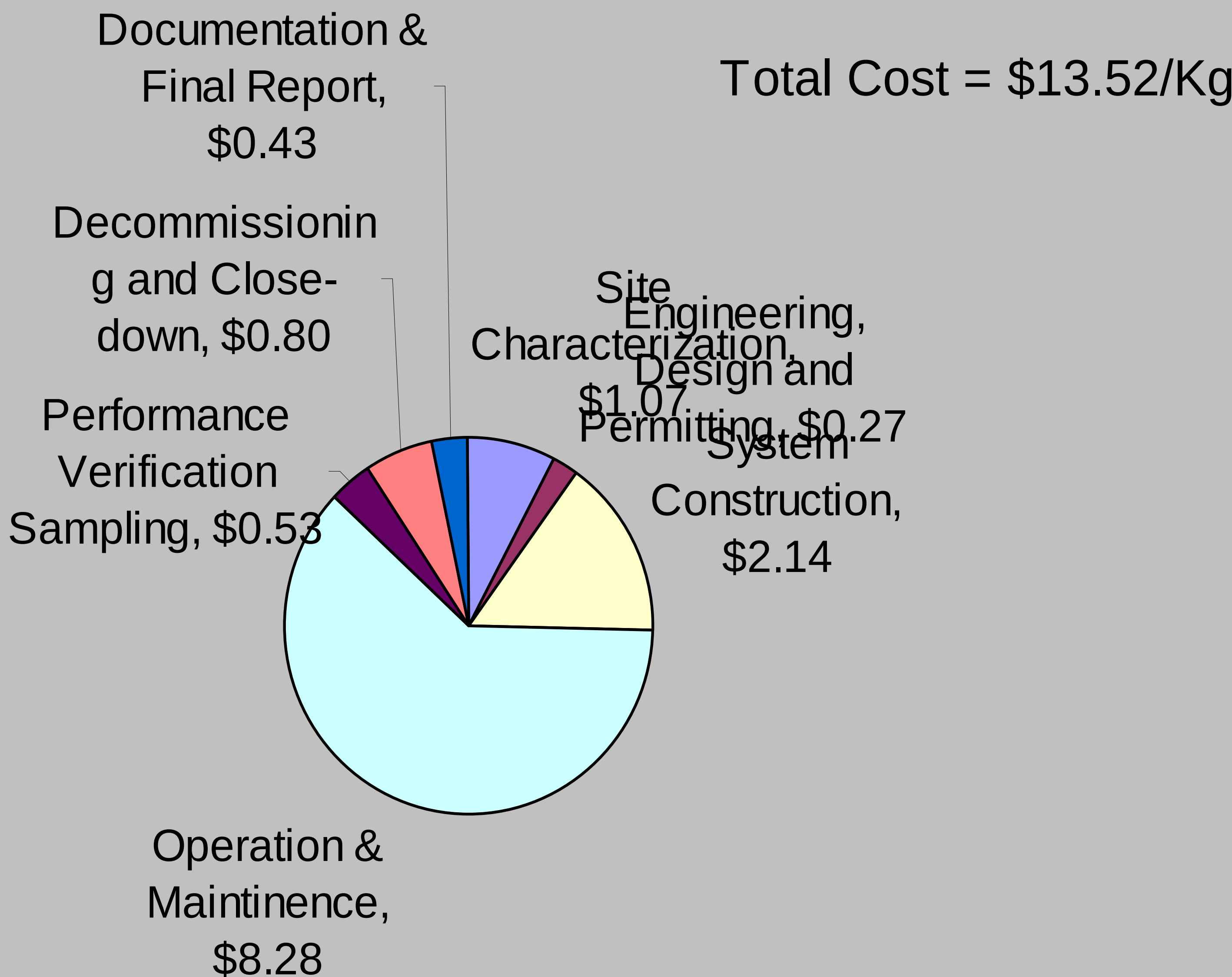
Bixby UST Cost per Kilogram of Contaminant Removed



Cobb Creek UST Cost per Cubic Yard of Smear Zone Treated



Cobb Creek UST Cost per Kilogram of Contaminant Removed



Cost Estimate for Pilot Test Site in Gasper, Wyoming

- Cost estimate assumptions:
  - 2-acre lot x 9 ft thickness smear zone
  - Targeted zone: 3 ft below water table, 6 ft above water table
  - Coarse sand and homogeneous
  - Easy access for wells and pipes installation (including trenching)
  - NAPL disposal fees not included
  - Average porosity = 0.38, oil saturation = 0.05 (based on site data provided)

Cost Estimate (cont.)

- Estimated total project cost = $870,000
- Unit volume treated cost = $30 / yd^3 (total treated volume = 29,000 yd^3)
- Unit contaminant mass removed cost = $2.54 / kg (total oil recovered = 106,000 gallons = 343,000 kg based on 95% contaminant removal after surfactant flushing)

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Conclusion

- SESR is already a commercial process – we're already making money
- Extensive field experience has identified cost reduction optimization for next generation
- Proven at most difficult sites – all failed with conventional technologies (SVE/Air Sparging)

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