Webinar Series: Integrating Surfactants in Remediation Technologies and Avoiding Contaminant Rebound

Second Webinar in Series: Enabling NAPL Removal Through Surfactant and Oxidant Technologies

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EthicalChem

A division of Ethical Solutions LLC

Enabling NAPL Removal Through Surfactants and Oxidants

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Green Chemical Solutions for Environmental Remediation

ETHICALCHEM BACKGROUND

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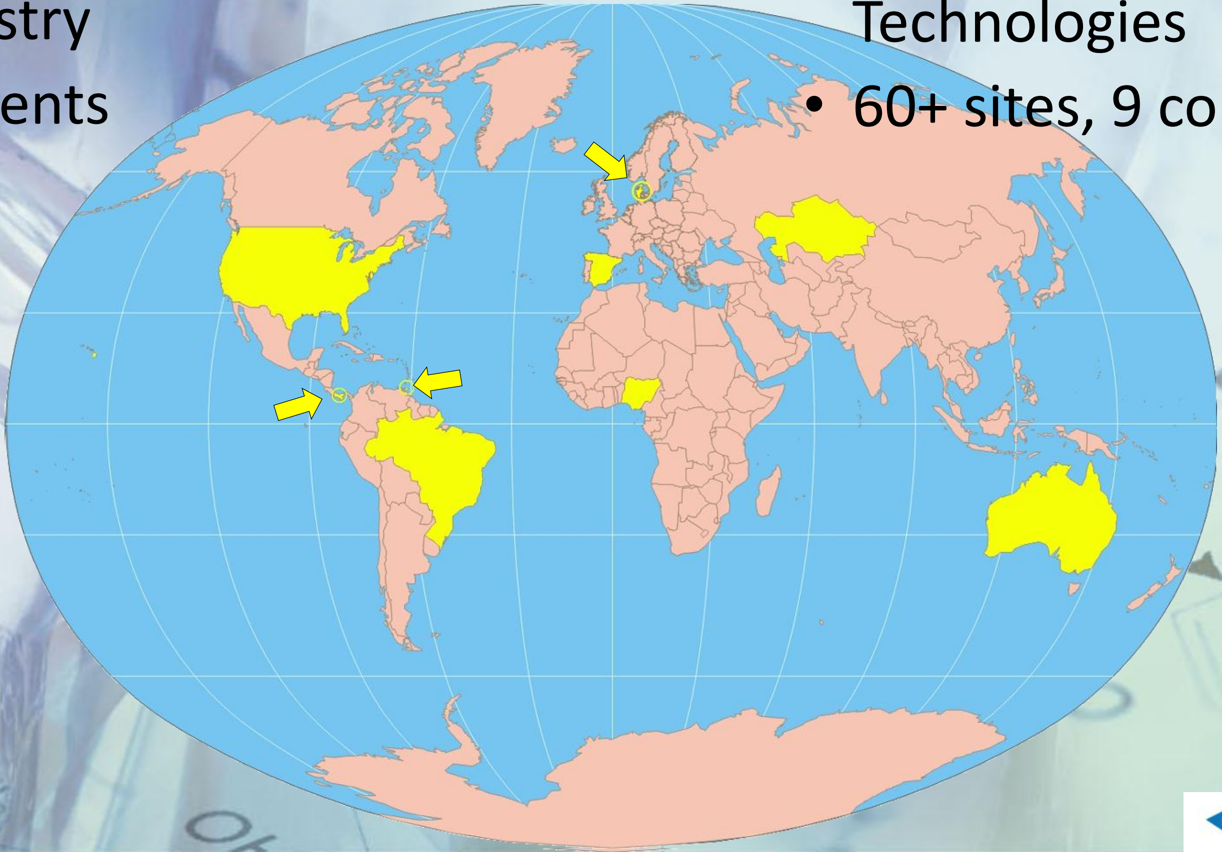
EthicalChem Background

- Formulate high performance chemicals for remediation and oil industries
- Specialize in plant-based chemistry
- 14 patents
- Flexible business model
  - Chemicals alone / full implementation
- Acquired IP from VeruTEK Technologies
- 60+ sites, 9 countries



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EthicalChem Background

Optimized plant-based surfactants for enhanced in situ remediation technologies

Surfactant Enhanced Product Recovery (SEPR)	Surfactant-enhanced In Situ Chemical Oxidation (S-ISCO)
Bulk free phase removal – creosote, DNAPL, LNAPL Surfactants with low doses of hydrogen peroxide	Oxidation of heavy hydrocarbon contamination on soil Surfactant with persulfate or peroxide

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NON-AQUEOUS PHASE LIQUID

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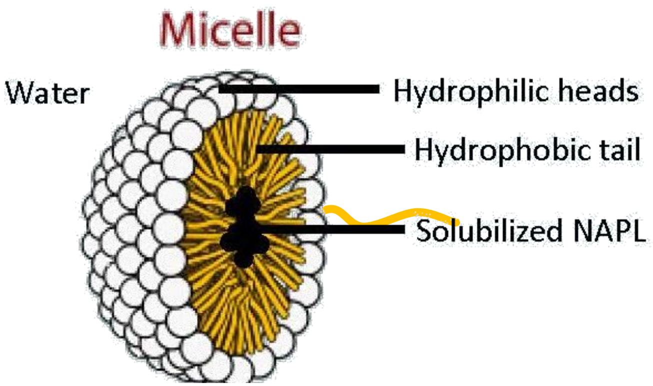
What Is NAPL?

Non-Aqueous Phase Liquid – liquid contaminant that does not readily dissolve or mix with groundwater

- **Can solubilize in surfactant micelles**
  - Hydrophobic tails pointing inward
  - Hydrophilic heads pointing outward
  - Contaminant encapsulated in center



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NAPL REMEDIATION TECHNOLOGIES

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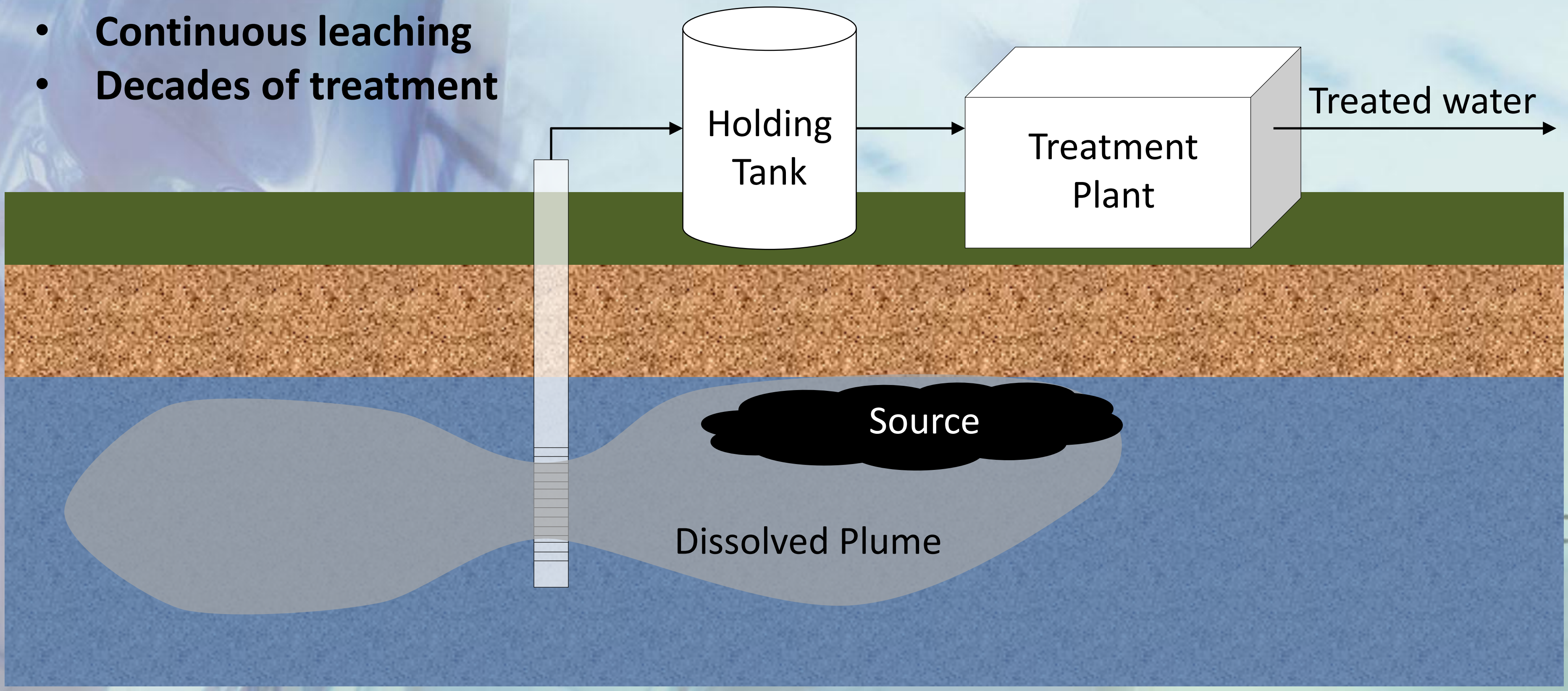
NAPL Remediation Technologies

- Pump & Treat
- Thermal
- ISCO
- Surfactant Flush
- SEPR/S-ISCO

NAPL Remediation Technologies

Pump & Treat

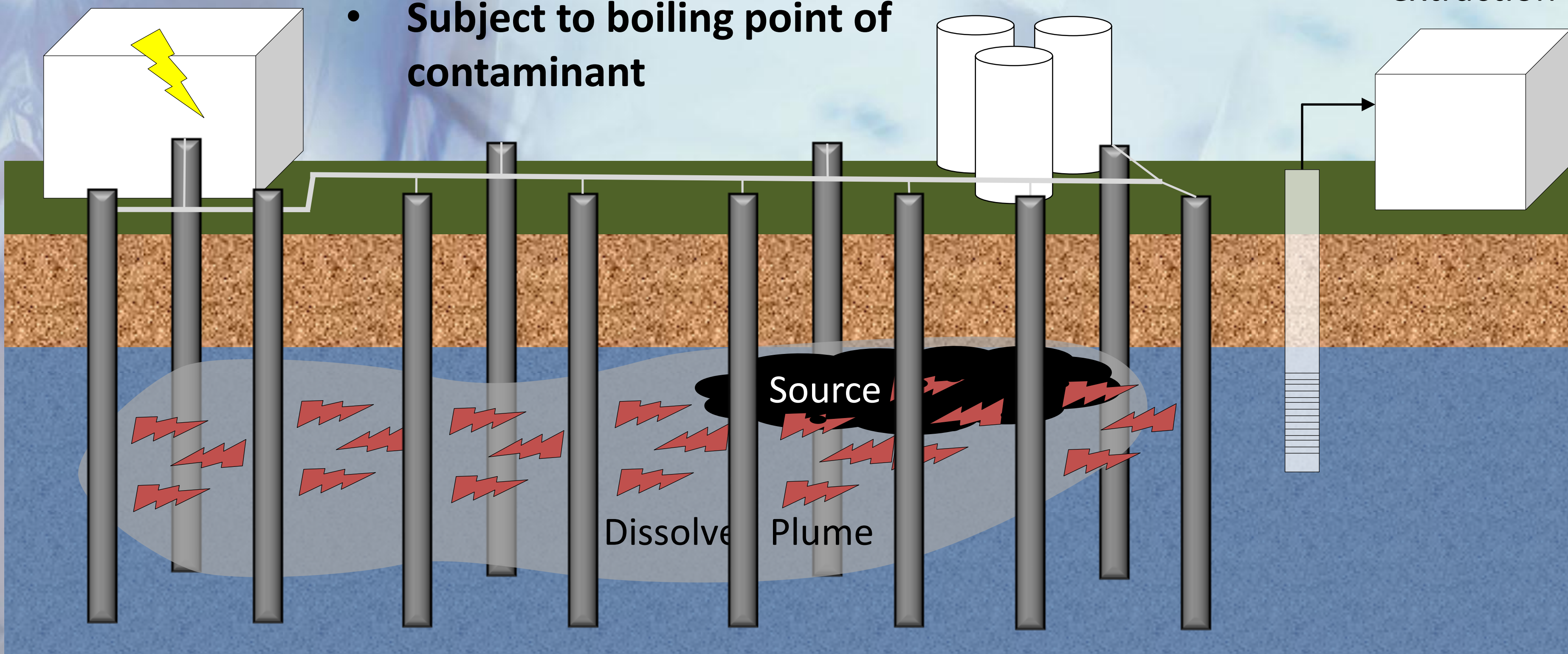
- **Groundwater only**
- **Continuous leaching**
- **Decades of treatment**



NAPL Remediation Technologies

Thermal Remediation

- **Invasive infrastructure**
- **Remove existing PVC wells**
- **Subject to boiling point of contaminant**



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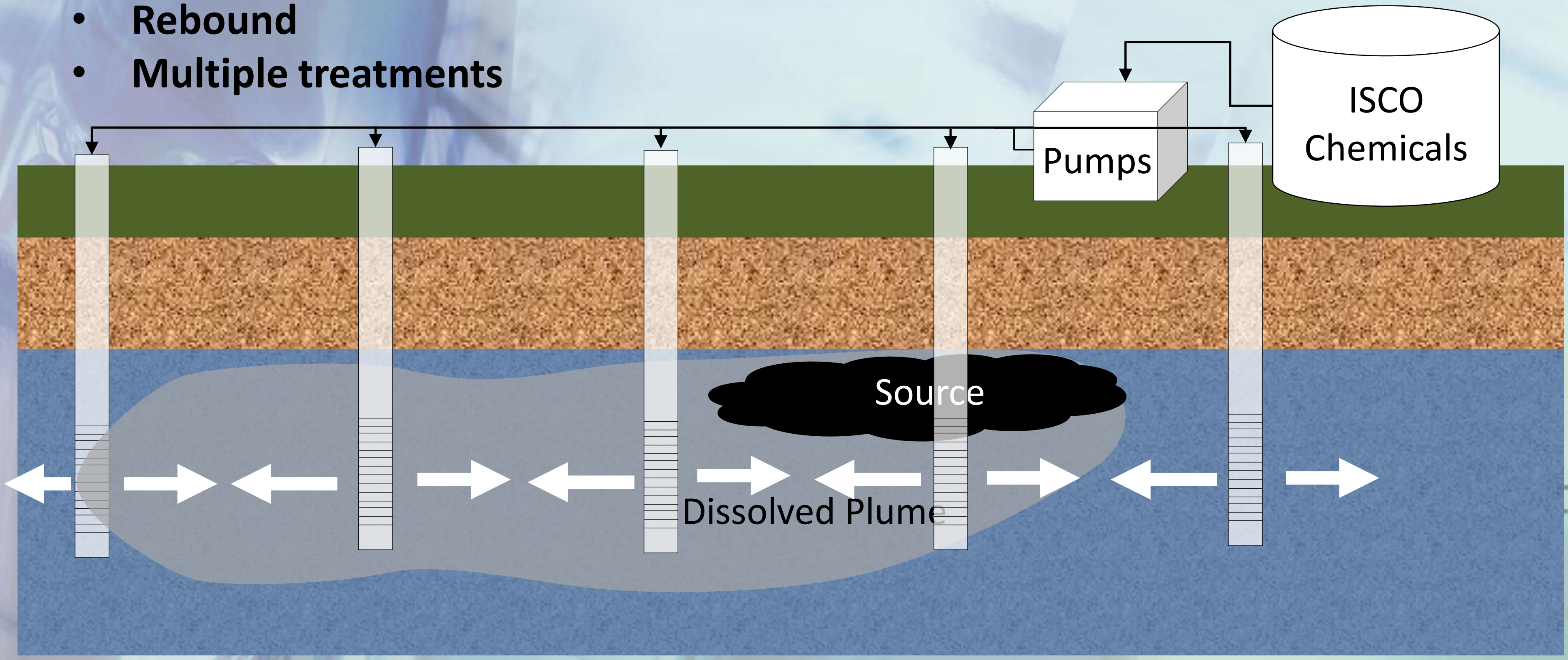
NAPL Remediation Technologies

ISCO

- **Groundwater treatment**
- **Contact with NAPL only at interface**
- **Rebound**
- **Multiple treatments**



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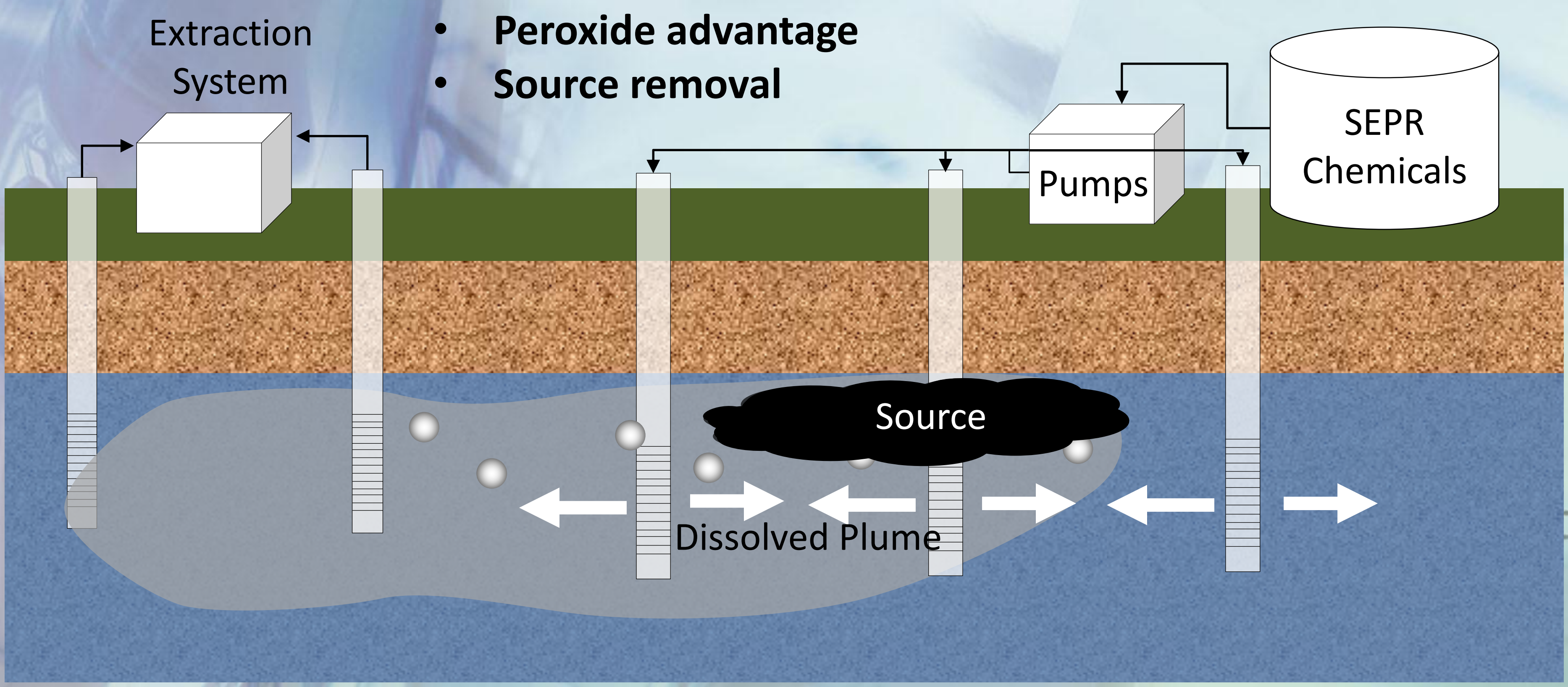
NAPL Remediation Technologies

Surfactant Enhanced Product Recovery (SEPR)

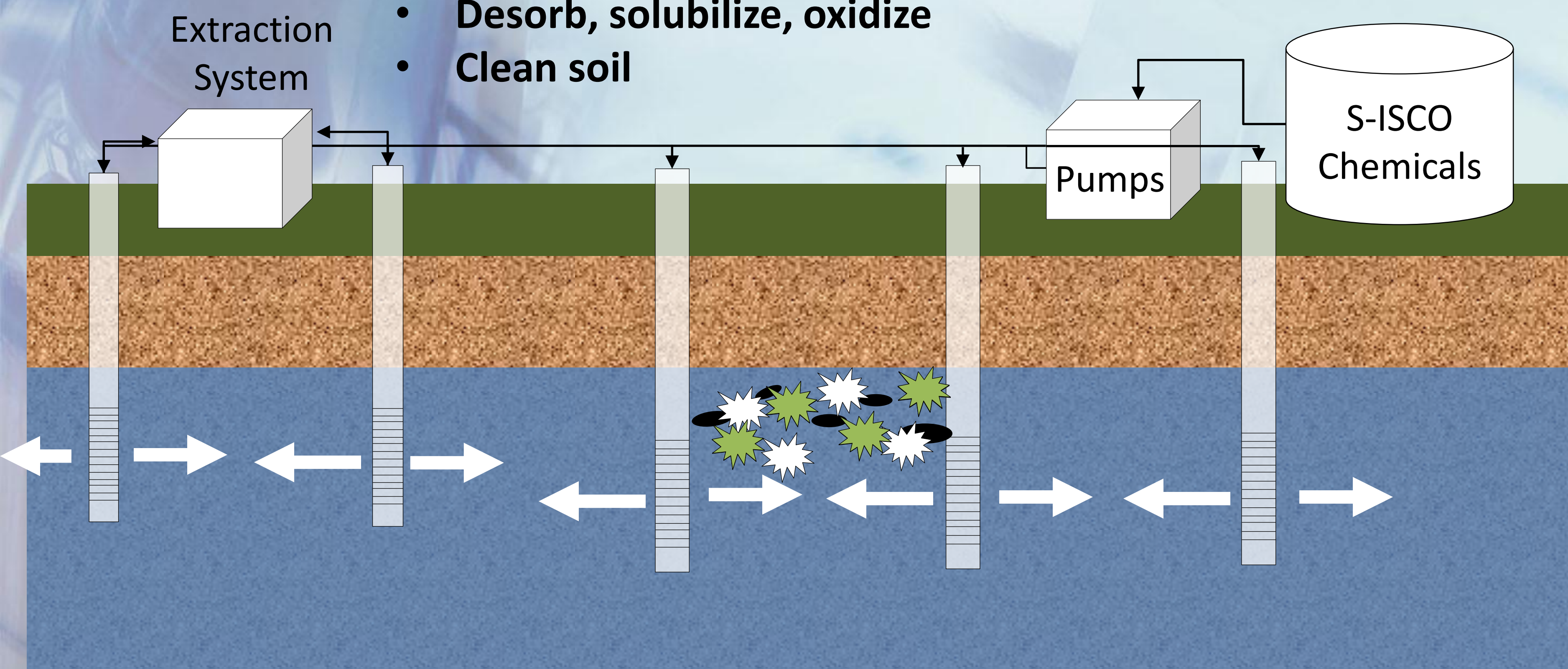
- **Peroxide advantage**
- **Source removal**



NAPL Remediation Technologies

Sequenced SEPR & S-ISCO

- **Simultaneous surfactant & oxidant**
- **Desorb, solubilize, oxidize**
- **Clean soil**



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NAPL Remediation Technologies

Pump & Treat	Thermal	ISCO	Surfactant Flushing	SEPR/S-ISCO
Continuous treatment of groundwater Treats the groundwater, not the source	Invasive infrastructure Replace existing PVC wells with SS Capital intensive set up and operations Generates waste	Oxidation takes place in groundwater – limited contact with NAPL Incomplete NAPL treatment – rebound Not cost effective to oxidize NAPL mass	Removes most of source Will elevate groundwater concentrations Generates waste	SEPR - Physical agitation of NAPL, improves removal efficiency Only generates waste during SEPR Removes source, oxidizes residual – cost effective S-ISCO treatment addresses residual contamination following extraction

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Optimal SEPR/S-ISCO Sites

- Short time frame
- Heavily contaminated – NAPL
- Full range of hydrocarbons
- Permanently clean soil

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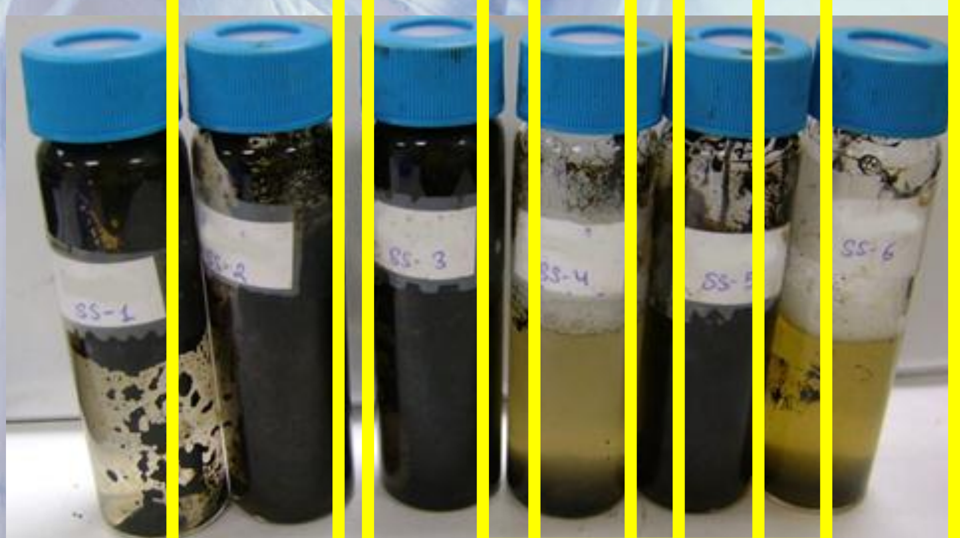
SEPR Implementation for Creosote Remediation

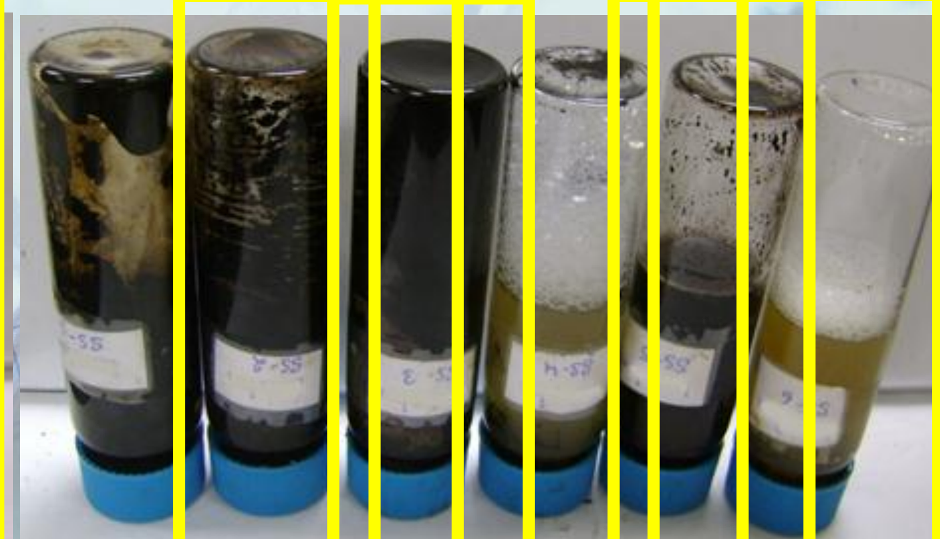
SURFACTANT SELECTION

Importance of Surfactant Selection

Surfactants can deliver different results.

- Desorption
- Emulsification – stable/unstable
- Change viscosity/mobility





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Importance of Surfactant Selection

SEPR Implementation for Creosote Remediation

CASE STUDY EXAMPLE

Creosote Remediation with SEPR Technology

U.S. Gulf State

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Superfund Creosote Site in U.S. Gulf State

Site

- 34 acre Former Wood Treating Facility,

Contaminants of Concern

- Creosote DNAPL

Objectives

- Creosote NAPL removal
- Enhance performance of existing recovery wells
- Reduce soil concentrations of TPH in vadose zone

Superfund Creosote Site in U.S. Gulf State

Frac Tank Containing Extracted Fluid

Samples of Extracted Fluid

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Superfund Creosote Site in U.S. Gulf State

Results:

- Achieved 84% TPH mass reduction in the vadose zone
- Successfully removed free phase creosote NAPL from the vadose and the saturated zone
- Enhanced recovery rates between 100% and 1,200% in saturated zone extraction wells

FREQUENTLY ASKED QUESTIONS

FAQs: Mobilization

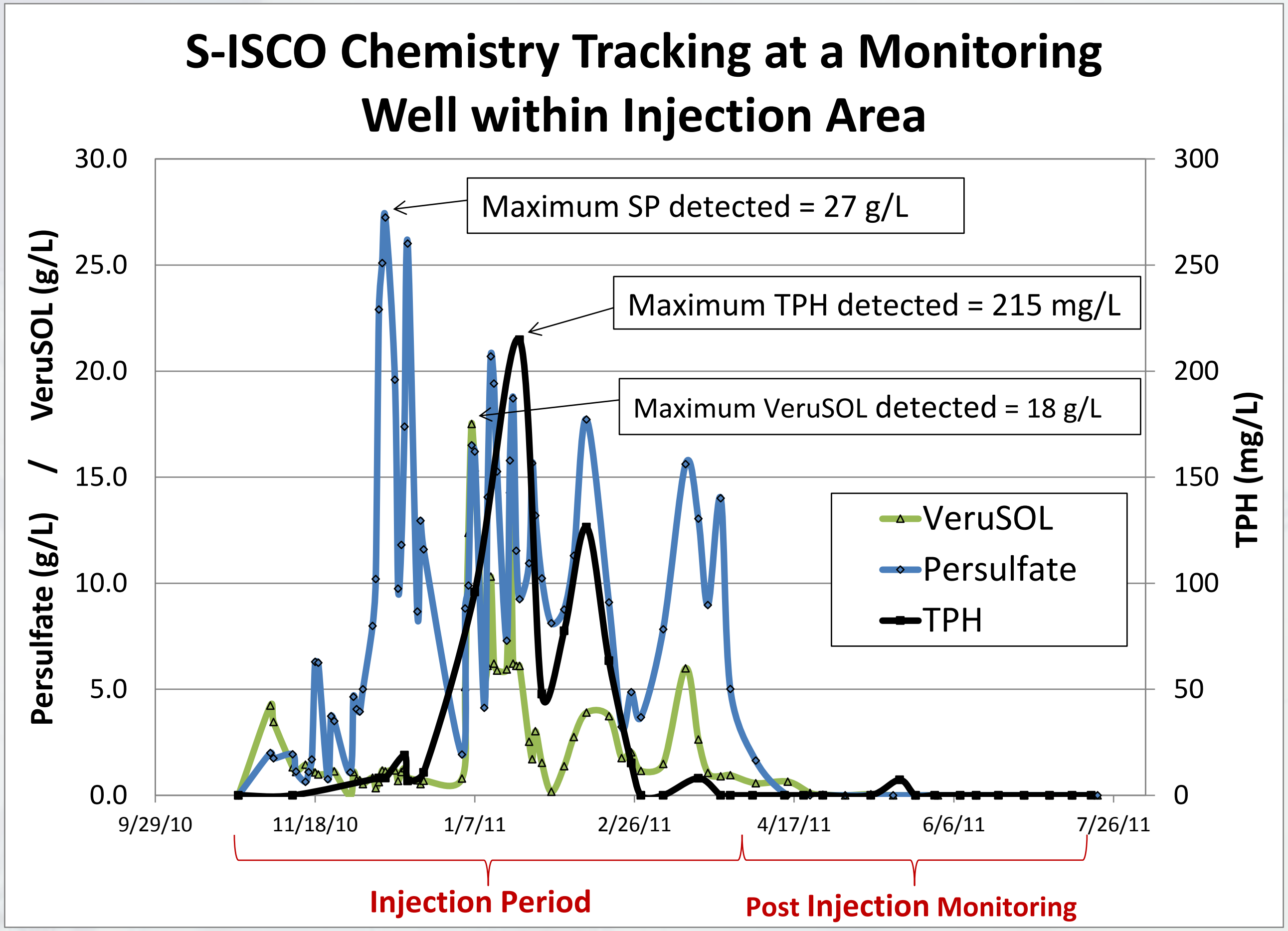
Question: Will surfactants mobilize contaminants?

- During SEPR treatment extraction wells are positioned to optimize capture of NAPL
  - Monitoring plans & contingency measures provide added protection for sensitive receptors

- During S-ISCO, surfactant and oxidant are injected together as a homogeneous solution
  - Injected chemistry travels together through subsurface
  - Emulsification and oxidation take place simultaneously
  - Average groundwater speeds do not carry emulsion offsite prior to destruction

FAQs: Mobilization

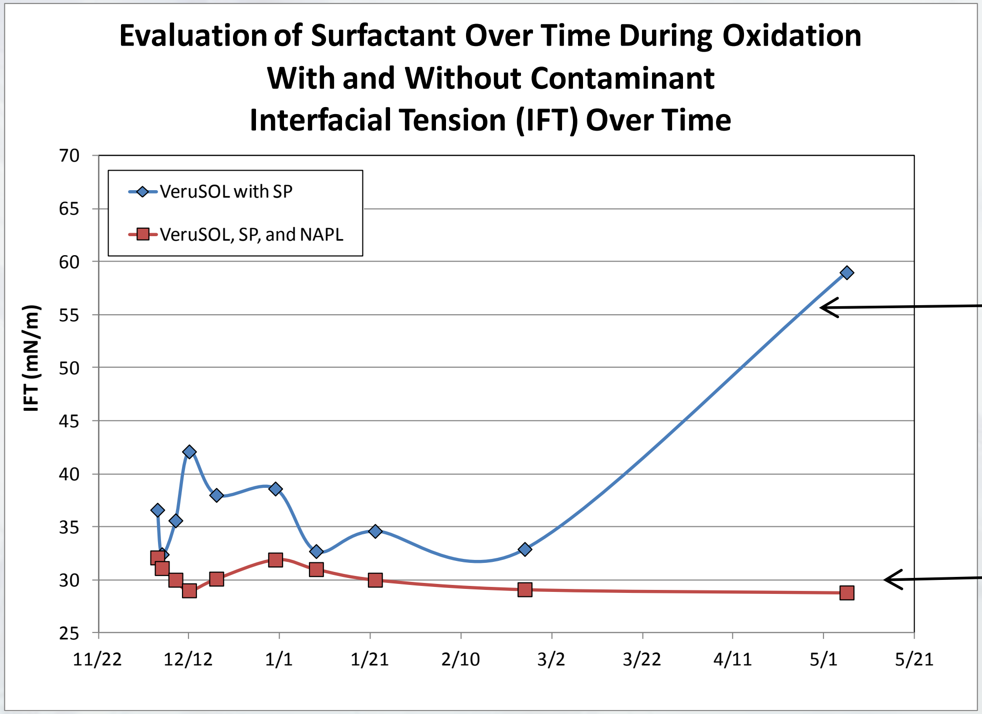
- S-ISCO chemistry travels together
- Data from an on site monitoring well during and after injections



FAQs: Surfactant Consumption by Oxidant

Question: Do the surfactants compete with contaminants for the oxidant?

- Contaminants oxidized first
- Surfactant oxidation is minimal while contaminant is present

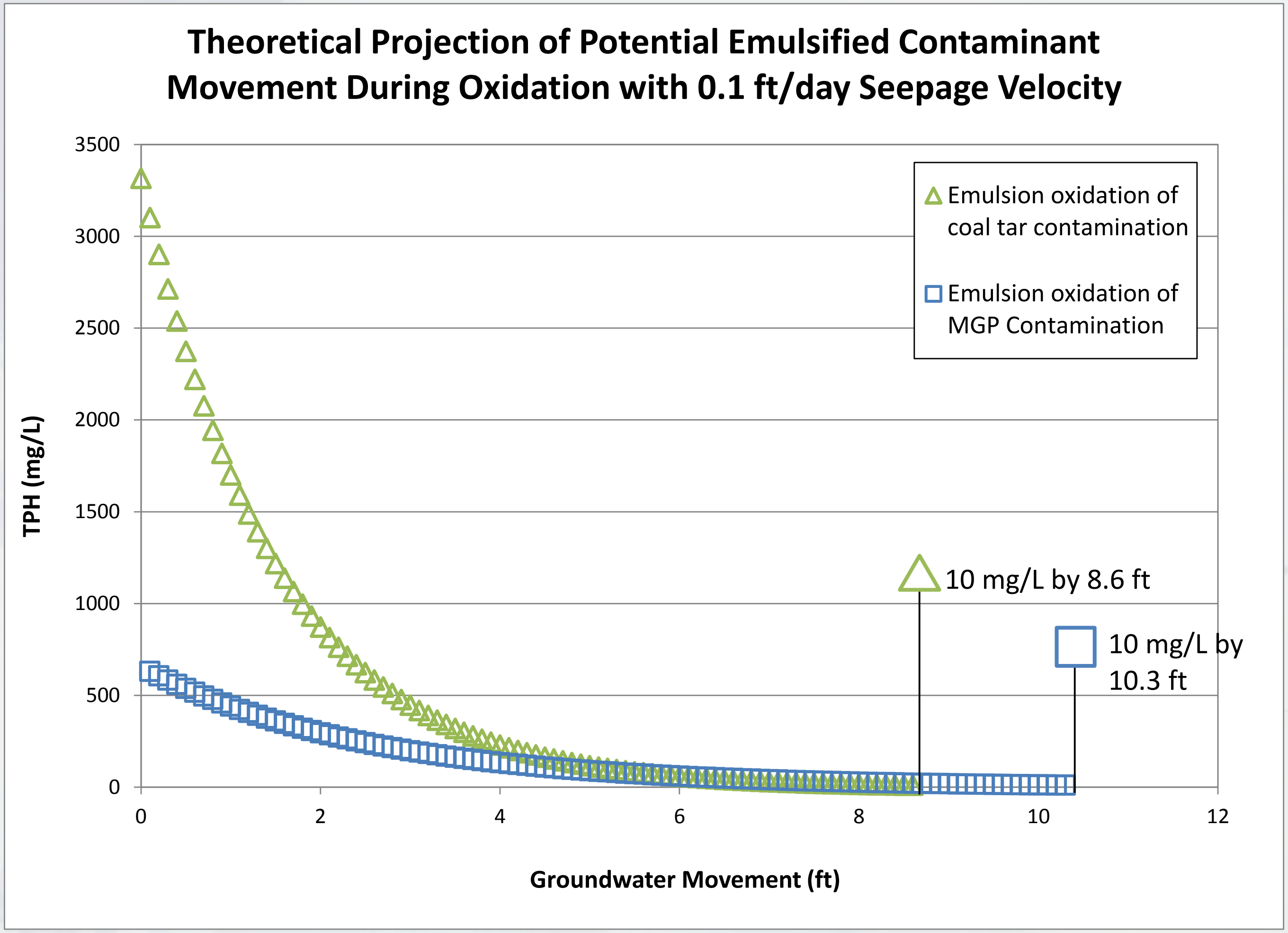


Increase in IFT indicates destruction of surfactant

Stable, low IFT indicates stable presence of surfactant

FAQs: Mobilization

Lab projection of two emulsions, traveling vs. destruction



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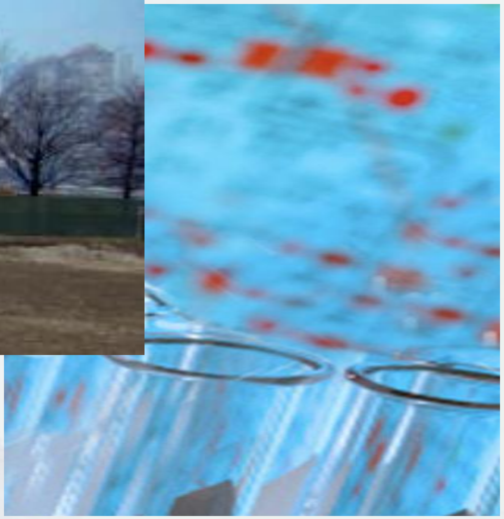

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Seaboard Lumber Site Remediation

Utilizing Surfactant Enhanced Product Recovery and In Situ Chemical Oxidation

Site Background

Site
Former Wood Treatment Facility, Bridgeville, DE

Contaminants of Concern
Creosote NAPL

Objectives
Full-scale soil remediation

Remedial Implementation
SEPR & S-ISCO

SEPR & S-ISCO Treatment of Creosote

Site Background

- Wood Treating Facility (1963 – 1986)
- Entered DNREC-Hazardous Substances Cleanup Act (HSCA) Program after initial EPA PA.
- Creosote waste oil & condensate water was gravity-fed into unlined waste lagoon.
- Lagoon was excavated in 1986 but the vertical extent of NAPL was greater than originally reported.

Site Background – *cont.*

Site Investigation History

- SI, RI and FS conducted from 1997-1999 under DNREC lead. Initial findings indicated presence of NAPL and PAH-impacted soils but with minimal gw impact.
- TS / FS recommended thermal desorption with enhanced bioremediation as the RA.
- However, only gw monitoring from 1999-2008.
- 2009 Supplemental RI was conducted to evaluate deeper soils. NAPL found at depth in 9 of 11 borings.
- Updated FS looked at in-situ and ex situ options to deal with NAPL. Based upon the results of bench test study SEPR/S-ISCO identified as the preferred RA.

Two-Phase Implementation Plan

- **Phase 1 - SEPR**
  - Surfactant enhanced product recovery
- **Phase 2 – S-ISCO**
  - In situ chem-ox using persulfate, VeruSOL, and hydrogen peroxide

SEPR & S-ISCO Treatment of Creosote

Remedial Design

Observations of free product/NAPL in soil borings were used to define the area of the NAPL plume in each 1-ft interval from 6 to 15 ft below ground surface (bgs).

Initial Parameters

- **Target Area:**
  - 4,000+ gal of creosote DNAPL
  - 510 yd^3 of soil, ranging from 6 –15 ft. bgs

- **Treatment Sequence*:***
  - SEPR to remove NAPL
  - S-ISCO to remove residual contamination

Project Implementation Plan

Approach

- Based upon characterization data the vast majority of NAPL was detected in the 7-10 ftbgs zone.
- Plan was to implement initial test grid to address "heart of the plume" where NAPL is present.
- If initial pilot is successful expand grid to target addt'l recovery of NAPL.
- Installed initial grid of 9 injection wells screened from 6-11 ft. bgs.

SEPR & S-ISCO Treatment of Creosote

Implementation Plan

- **SEPR – 8 weeks**
  - Hydrogen Peroxide (up to 4%)
  - Surfactant (5 – 30 g/L)
  - Extraction of NAPL and fluid

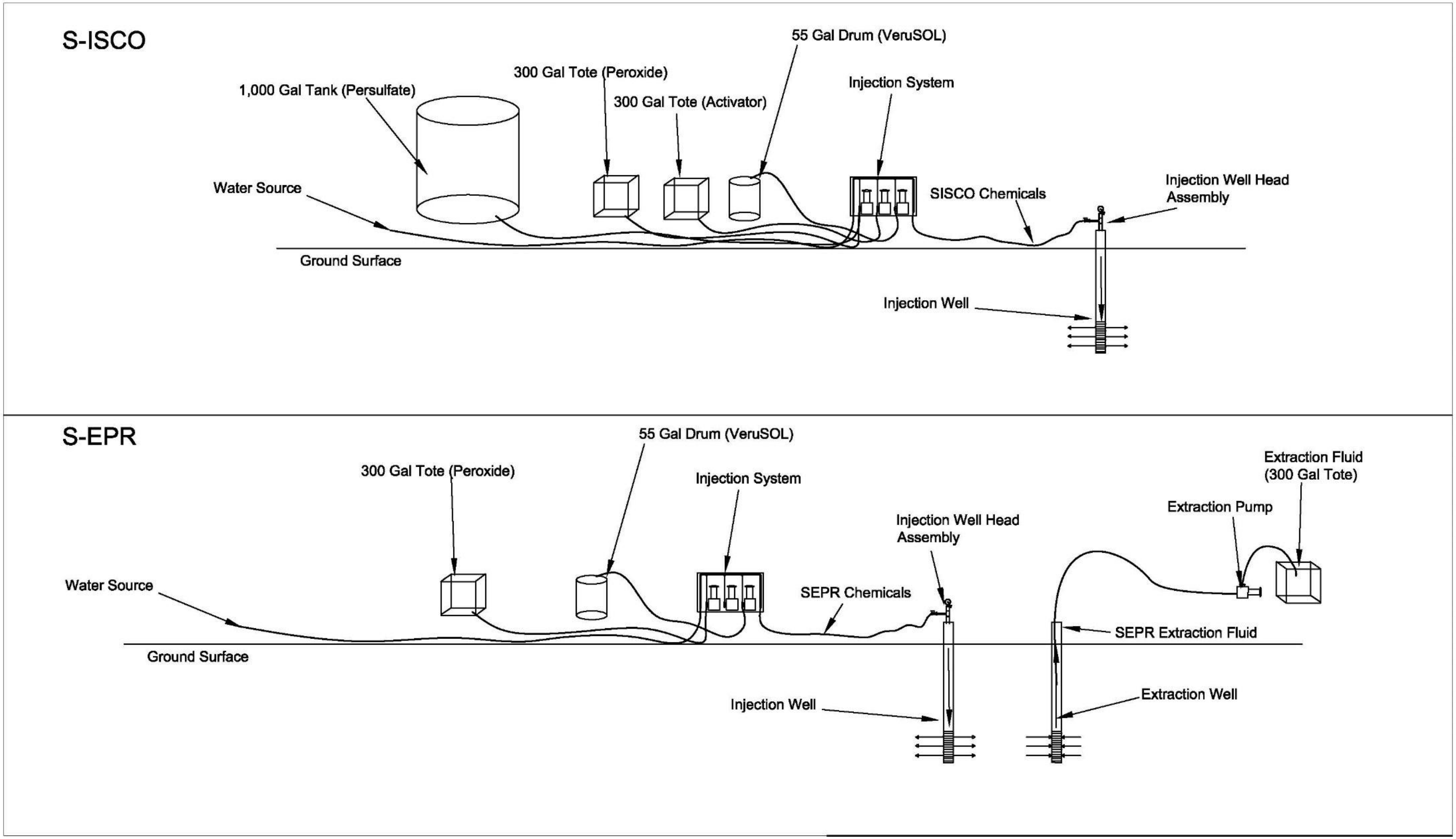
- **S-ISCO – 8 weeks**
  - VeruSOL (5 – 10 g/L)
  - Hydrogen Peroxide (4 – 8%)
  - Sodium Persulfate (50 – 100 g/L)

Phase I – SEPR Injection

Overview – Initial Injection Grid

- Nine 2-inch diameter injection/extraction wells were installed.
- The well spacing between the wells is approximately 15 feet.
- The radius of influence (ROI) during the SEPR injections was estimated to be 7.5 ft. (based upon slug test and grain-size analysis).
- K-Values range from 10-35 ft./day
- The SEPR® chemistry was injected into these dedicated wells and followed by extraction events.
- SEPR Chemistry injectate (per well) consists of
  - VeruSOL-3®;
  - VeruSOL® XFA
  - 4% hydrogen peroxide;
- Approximately 0.25-pore volume of SEPR™ solution in each of the nine injection wells (based upon K-value and bench test).

Injection Schematic



Injection Grid Layout

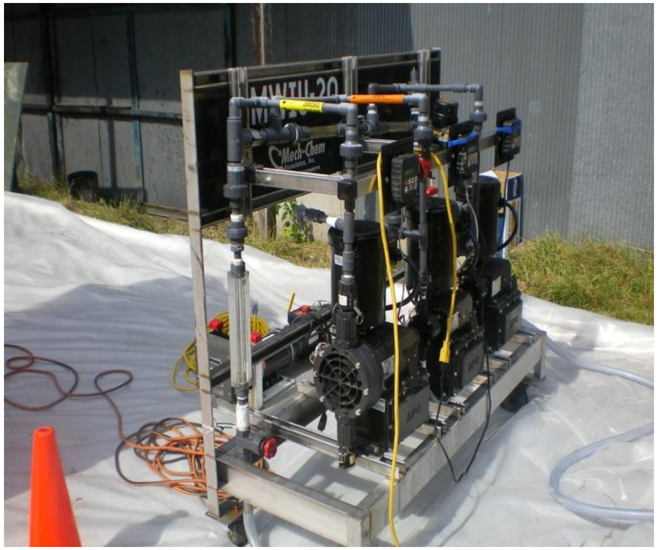
Tetra Tech
Phone: (302) 738-7551
www.tetratech-de.com
www.tetratech.com

0 15 30 60 Feet
1 inch = 30 feet
(approximate scale)

Legend
- Confirmatory Soil Boring
- Injection Well
- Pipe on structure
- March 2012 Confirmatory Soil Boring

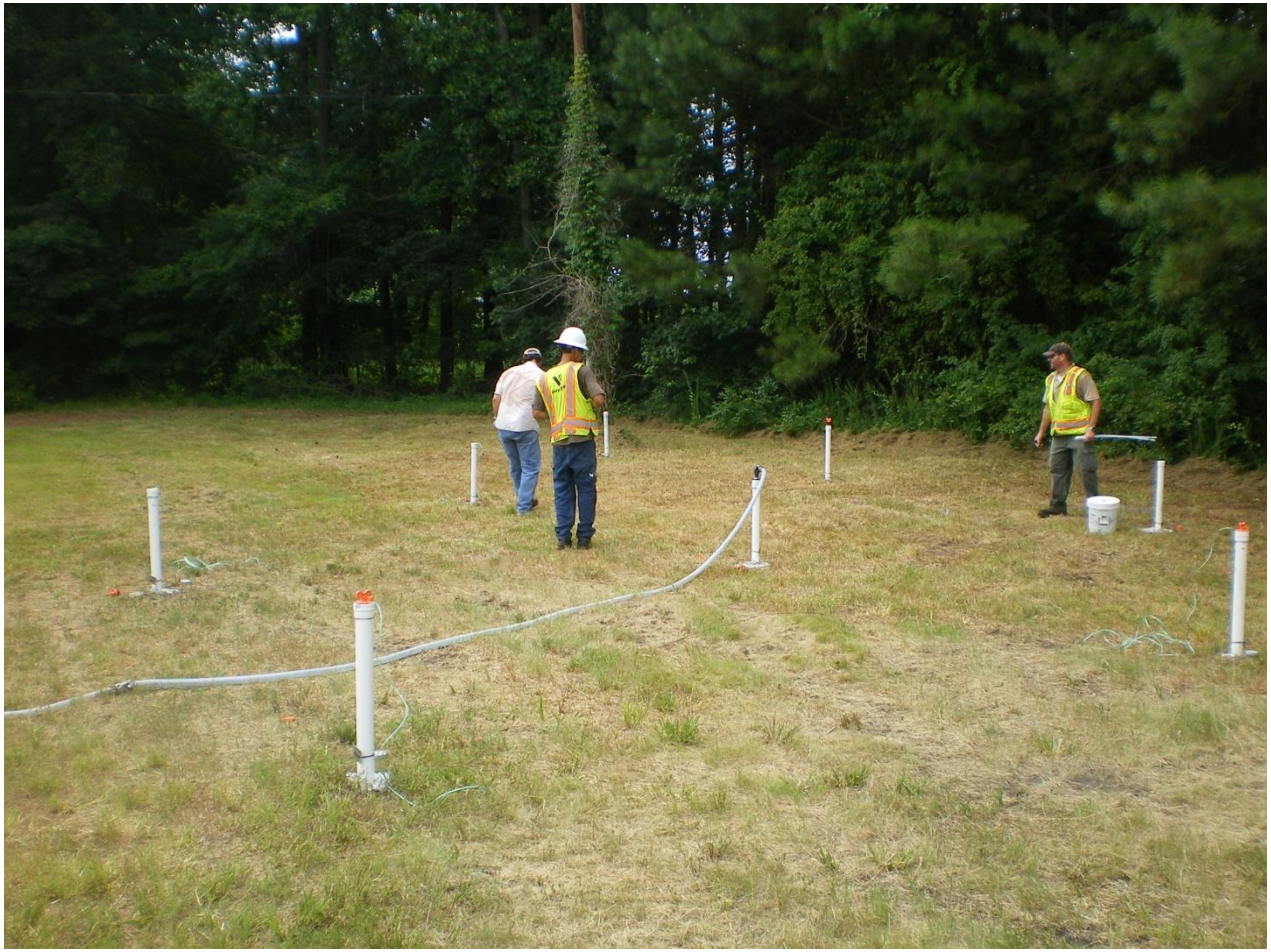
FIGURE 2
Injection Points Layout
Seaboard Lumber Site
Bridgeville, Sussex Co., Delaware

SEPR/S-ISCO Set-up Photos



Initial Injection Grid

IW-1 through IW-9



Phase I – SEPR Injection *(Cont.)*

- SEPR injected at about 2 gpm two wells at a time and allowed a minimum of 24 hours residence time to allow chemistry to react, desorb and mobilize NAPL for extraction.
- Extracted liquids were recovered into totes/tanks and measurement of the amount of free-phase product recovered from each well recorded.
- Process was performed at all injection wells across the grid until no further NAPL was recovered.
- Approximately 4,400 gallons of NAPL/emulsion recovered from first 9 IW's.
- Recovered fluids were disposed of as K001 at DuPont Chambersworks @ $0.97/gallon.
- Since the recovered fluids were in a non-oily emulsion phase and could be safely handled by their equipment. (if was in an oily phase then would need incinerated).

Phase II – Surfactant Enhanced In Situ Chemical Oxidation (S-ISCO)

- Upon completion of the SEPR™ events and demonstration of diminished product recovery, approx. 2,700 gallons/well of S-ISCO® solution into each of the injection points.
- S-ISCO® *In-Situ chemical oxidation injectate (per well) comprised of*
    - VeruSOL-3®
    - VeruSOL® 400
    - 4-8% hydrogen peroxide
    - sodium persulfate (FMC)
    - ROI during the S-ISCO® injections estimated at 7.5-feet.
- Approximately 0.5-pore volumes were injected during the S-ISCO® process.
- S-ISCO® typically effective for 30 to 90 days.

Typical Samples of Extracted Fluids

Samples collected on a daily basis (typically beginning and/or end of day) to monitor the process at each injection well.

SEPR & S-ISCO Treatment of Creosote

Pre-SEPR
No Product Recovery; Clear Samples

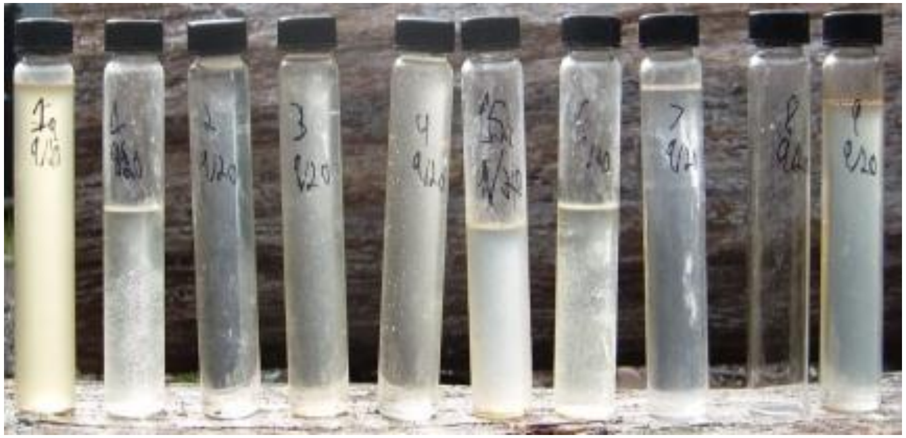
Day 1
Product + Emulsion Recovered

Day 2
Increased Product Recovery

Day 3
Product Flow

SEPR & S-ISCO Treatment of Creosote

Late Stage of SEPR Treatment / Pre-S-ISCO Treatment



End of S-ISCO Treatment

Pilot Test Findings -*Cont.*

- As part of the analysis, borings with creosote were measured for each 1 foot depth interval from 6 feet below grade surface (bgs) to 11 feet bgs.

- A creosote volume was then determined for each 1 foot depth interval before and after the injection test occurred.

- This method of evaluation produces a numeric estimate of creosote contaminated soil, before and after the initial injection test.

- The relative percent reduction of total creosote was used as the measure of success of the injection/extractions.

Pilot Test Findings

After an initial analysis of the product recovery data and post-injection soil evaluation we concluded the following:

- The injection/extraction program appears to have successfully removed the top 3-4 feet of residual creosote tar and oil in soils.
- The majority of confirmatory soil samples, collected from the mid-points between each injection well, continued to exhibit the presence of VeruSOL and S-ISCO in them indicating that the VeruTEK chemistry was doing its job at breaking down the viscous and sticky oil into now a more recoverable state as well as addressing the dissolved phase.
- Confirmatory soil samples indicate the continued presence of oil at several borings at depth intervals of 10 to 12 ftbgs and 12 to 14 ftbgs.
- These zones are deeper than the original target injection zone of 5-10 ftbgs indicating that additional injection points needed in areas where the creosote was observed at greater depth.

Pilot Test Findings - *Cont.*

- Achieved 100% removal of creosote in the 6-9 ft. bgs interval and some removal from 9-11 ft. interval.

- All but one of the injection wells were free of creosote oil and have remained so since the SEPR injection/extraction activities completed.

- Estimate that of the original ~ 9,000 cubic feet of soil impacted with creosote product, only 1,050 cubic feet (12%) remains to be treated within the initial injection grid area.

- In addition, confirmatory samples outside and beneath the pilot test area (CSB-1, CSB-13, CSB-14, and CSB-16) indicated another 1,770 cubic feet of soil impacted with creosote product exists adjacent to the pilot test areas.

Expanded Footprint

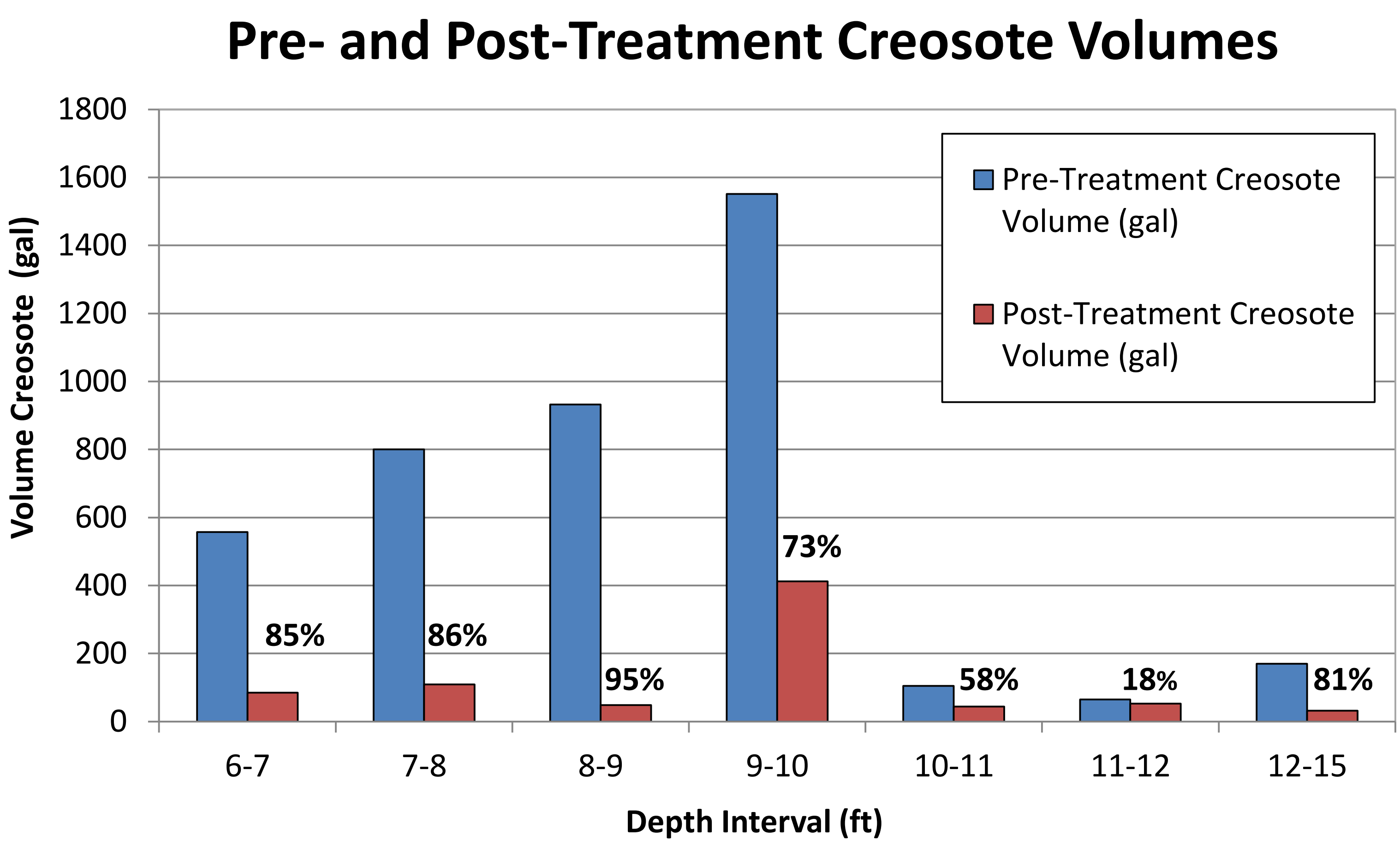
- Based upon the successful recovery of NAPL from the initial 9 points, the grid expanded to additional 9 pts on 7/29/11.
- The additional points installed with 5-ft screen (6 to 11 ftbgs) with a projected ROI of 7.5 ft.
- Injection/extraction activities on new wells started on 8/3/11.
- SEPR injection/extraction lasted through end of August, at this point very little NAPL detected in any of the 19 IW's.
- S-ISCO injections initiated and ran through 9/28.
- Confirmatory samples and lab analysis showed effectiveness of injection program at the additional points.

Expanded Footprint

Still More NAPL!

- Based upon confirmatory soil borings more NAPL identified in areas previously thought to be clean.
- NAPL detected in isolated areas as deep as 9-19 ft.
- Additional 9 IW installed in these areas.
- Impacted areas screened for targeted injection.
- SEPR/ISCO process repeated.
- Approx. 3,200-gallons of product/emulsion recovered during the addt'l rounds of injections.
- Confirmatory SB showed the process to be effective with no addt'l NAPL observed/detected.

SEPR & S-ISCO Treatment of Creosote



SEPR & S-ISCO Treatment of Creosote

RESULTS SUMMARY

- 81% of NAPL removed from targeted treatment areas.
- Cost of remediation <\$100/cubic yard
  - ➢ Emulsified material less expensive to dispose of than NAPL-containing liquids.
  - ➢ Less than 1/3 the cost of previously identified alternative in 1999 - thermal desorption followed by bioremediation.

Project Timeline Overview

Date	Activity
July 2011	Install initial nine injection points; mobilize SEPR™ - and S-ISCO-related equipment and materials, and system startup
August 2011	Expand test injection grid from 9 to18 points, perform SEPR/ISCO injection/extraction
September 2011	System shutdown and conduct Phase I post-injection confirmatory soil sampling
October 2011	Data Evaluation
December 2011	Install 9 additional injection/extraction points to expand the horizontal footprint and address deeper contamination detected in post-injection confirmatory soil samples
January 2012	Restart System for Additional injections
March 2012	System shutdown and demobilize SEPR™ and S-ISCO® equipment
April 2012	Post injection confirmatory soil sampling

Current Site Status

WHERE ARE WE NOW?

- Injection work completed Spring 2012

- Fall 2015-Spring 2016
  - Asbestos abatement of old wood treatment building
  - Decon and removal of tanks, vessels, sumps and piping
  - Demolition of building and associated structures
  - Post demolition subsurface investigation (under bldg. slab)
    - Soil was free of NAPL

- Site is ready to move forward to the closure process!

Lessons Learned

REGULATORY / CLIENT ACCEPTANCE

Endorsement

- Gaining endorsement from the planning stage with both regulators and clients is essential.
  - Sometimes necessary to educate to gain endorsement.
  - Focusing on life cycle reduction costs, risk mitigation and expedited closure can often overcome initial reservations.
  - Emphasize that the VeruSOL products are FDA GRAS, plant-based derivatives resulting in a “green” remediation with no toxic by-products; as a result was well-received given the nearby properties uses were mixed residential/agricultural on private wells.
  - Regulators and many clients like the idea of a green solution (especially when it saves them money and is good PR!)

Lessons Learned

TECHNICAL

Accurate Characterization and up to date CSM are Essential!!

- The injection/extraction design was based, in part, on characterization data obtained over a period of more than 10 years. Much of the older data turned out to be inadequate to fully characterize the vertical and horizontal extent of NAPL.

- Consider use of innovative characterization technologies such MiHPT, TARGOST®, or a GeoTrax™ survey to provide an effective model of the subsurface for remedial design purposes.
  - Although more expensive initially, these type of technologies enable a focused, cost-effective approach to remediation and lessen the probabilities of surprises.

Lessons Learned

PROCESS RELATED

- During colder weather, heating the injected fluids increased the rate of creosote extraction by decreasing the product viscosity. Winterizing equipment and supplies proved beneficial.
- Because NAPL and soil characteristics are likely to vary from site to site, bench-scale testing to select the most cost-effective surfactant and dosage is crucial.
- It is important to begin the injection process at a low flow rate, to minimize the potential for daylighting of injected liquids-reagent mixture.
- Because of limitations of gravity, vacuum extraction will not work as well in wells deeper than 20 to 25 ft bgs. Below these depths, high velocity liquid entrainment extraction may be necessary, potentially reducing the liquid recovery rate and increasing extraction cost. Alternatively, submersible pumps could be used for extraction from deeper wells.