Influence of Subsurface Geochemistry on Surfactant Enhanced Aquifer Remediation (SEAR) Design

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Introduction

SURBEC originated in a university research program aimed at the application of surfactants to the difficult problem of removing NAPLs from aquifers and spun-off from the University of Oklahoma in 1997. Today, SURBEC delivers a technology portfolio that includes patented *surfactant* and *chemical oxidation* based processes and formulations for *in situ* environmental remediation. Nearly two decades of university and company research form the foundation of our technology, which is as unique in the remediation industry as our guarantee.

A long list of successful site applications supports the effectiveness of our technologies. We have cost-effectively remediated sites contaminated by gasoline, diesel, kerosene, styrene, ethyl benzene, heating oil, and mixtures of these contaminants. We have effectively applied our technology in aquifers of various geological settings and in complex geochemical and hydrological conditions. Successful site closures include applications under parking lots, asphalt and concrete pads, and busy highways; under operating grocery stores, truck stops, gas stations, a power plant, a petrochemical plant, and a post office; in active tank pits and at a public school.

Surfactant Enhanced Aquifer Remediation (SEAR) Technology for Gasoline and Diesel Source Zone Removal

- Basic Information of SEAR technology
- Case Studies
- Challenges and Innovative Solutions

SURBEC ENVIRONMENTAL L.L.C.

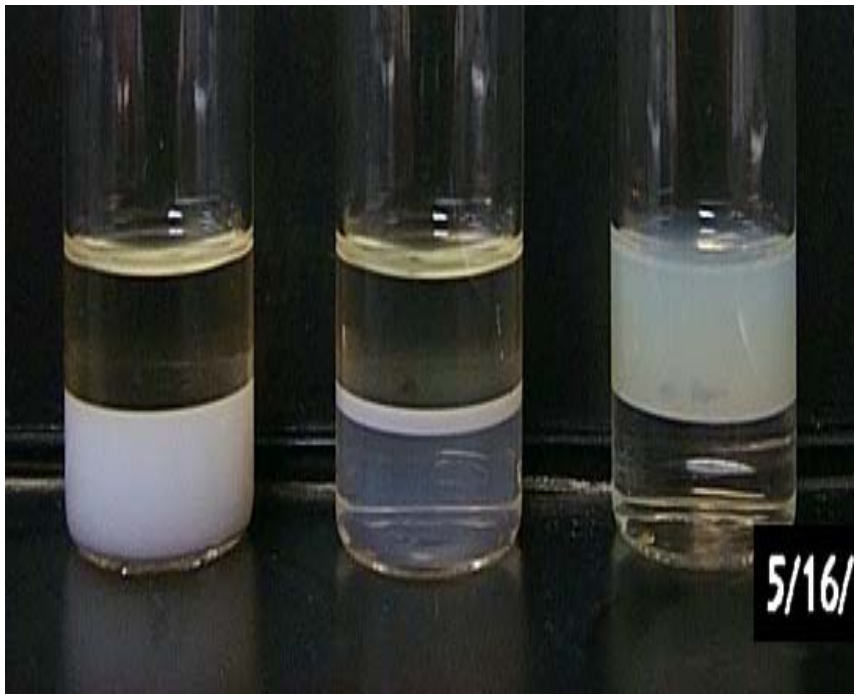
Basic Information of SEAR

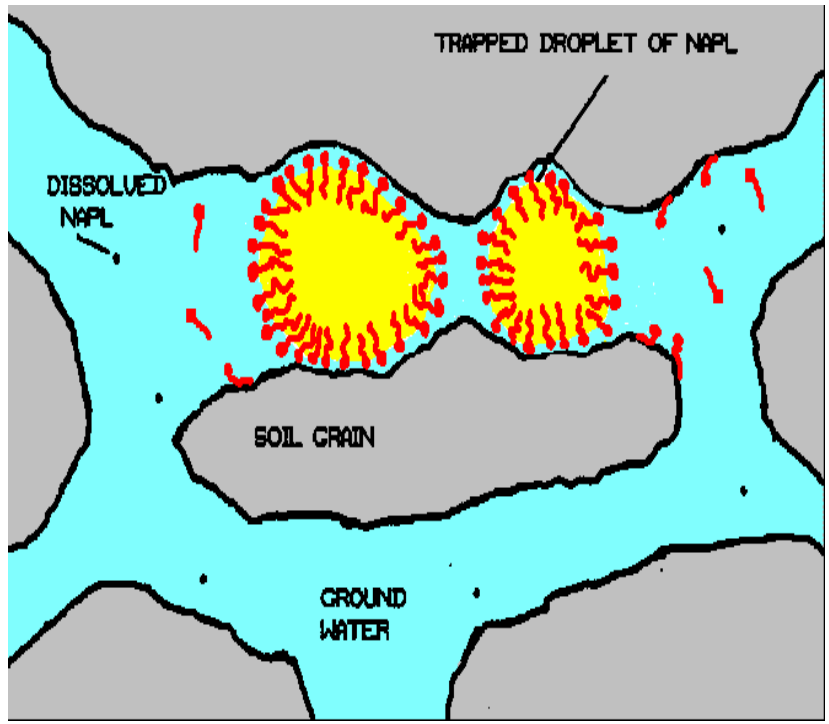
Problems: NAPL (e.g., gasoline, diesel) droplets are trapped in soil interstitial pores.

High oil/water interfacial tension - makes the NAPL immobile.

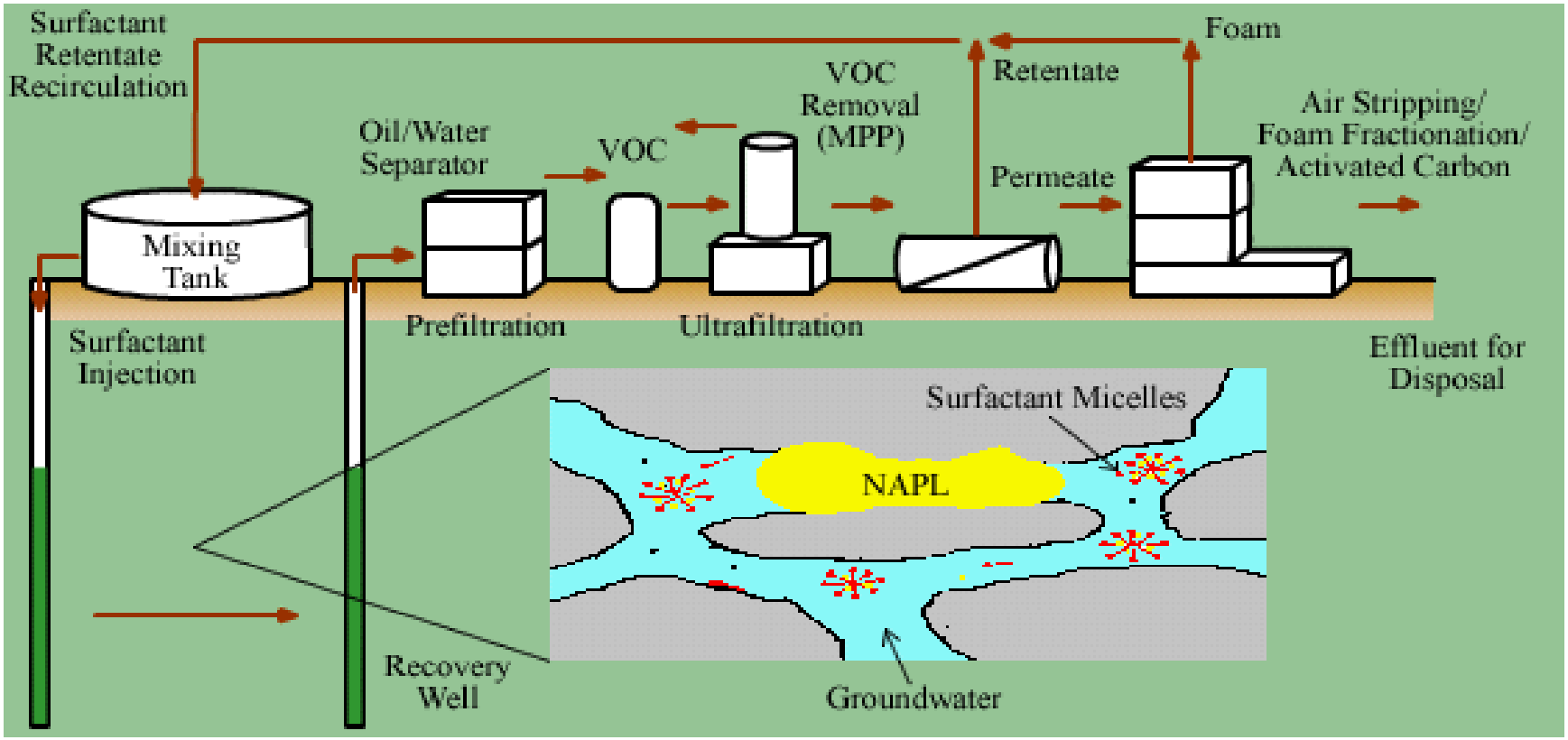
Low water solubility – needs 100s to 1000s of water flushings to dissolve the trapped NAPL droplets.

Mobilization – Injection of surfactant into ground water lowerd oil/water interfacial tension and removed NAPL from pores.





Solubilization – Adding surfactant into ground water formed aggregates(micelles) and increased NAPL removal rate.



Surbec's unique surfactant Techniques
(U.S Patent No. 7,021,863 and No.6,913,419)

- **Timely**: High level of NAPL removal in short time frame.
- **Economical**: Surbec's formulations reduced surfactant amount by a factor of 10. Costs are extremely competitive with conventional remediation techniques.
- **EPA approved**: All surfactants used are EPA approved. Combination of SEAR with chemical oxidation achieve MCLs and SSTLs.
- **Experience**: Successfully completed tens of NAPL contaminated sites with verification of results by State and Federal authorities.

Surbec has served many clients, including:

- U.S. Air Force: Hill AFB, Tinker AFB, MsClellan AFB, Dover AFB
- U.S. Navy: Alameda NAS, Office of Naval Research
- DoE: 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: U.S. EPA(Spartan Chemical)
- International: Taiwan, Japan

Surbec Active SEAR Projects

Site Location	Task	Point of Activity for Project
Kodiak Island, Alaska	Treatability Study/Injection Test	Proposal Approved
Enid, OK	Installation	Proposal Approved
Woodward, OK	Installation	In Progress
Sherman, Texas	Treatability Study/Injection Test	Proposal Approved
Athens, Texas	Treatability Study/Injection Test	Proposal Approved
Bradford, Vermont	Surfactant Flush	Proposal Approved
Pauls Valley, OK	Treatability Study/Injection Test	Proposal Approved
Wynnewood, OK	Treatability Study/Injection Test	In Progress
North Little Rock, Arkansas	Tank Pit Flush	In Progress
North Oklahoma City, OK	Treatability Study/Injection Test	Proposal Approved
Weatherford, OK	Surfactant Flush	In Progress
Oklahoma City, OK (Kelly St.)	Treatability Study/Injection Test	In Progress
Fredricksburg, IA	Surfactant Flush (Heating Oil)	In Progress
Elk City, OK	Treatability Study/Injection Test	In Progress
Conaway, Arkansas	Tank Pit Flush	In Progress
Lake County, FL	Treatability Study/Injection Test	In Progress
Ogden, UT	Treatability Study/Injection Test	In Progress
Bemidji, Minnesota	Treatability Study/Injection Test	In Progress
Lawton, OK	Treatability Study/Injection Test	Proposal Approved
Iowa City, Iowa	Treatability Study/Injection Test	In Progress
Lewis, Iowa	Treatability Study/Injection Test	In Progress

SEAR Case Studies (1)

Site location: Love's Country Store, Oklahoma City, OK

Contaminants: UST gasoline-diesel leaks

Depth from ground: 3 - 15 feet

Aquifer geology: Poorly sorted fine sand

Treatment technique: low concentration surfactant flushing (Different surfactant system for gasoline and diesel pits)

Clean-up Level: Free product removal only

Treatment area: 1339 yd^3

Remediation cost: $22,800 (within $20K- 40K)

Project period: One month

Recycle/reuse of recovered ground water

Compact design without interrupting the routine activity

Surfactant Flushing of UST Pits

(Love's Country Store Gas Station in OKC)

Remobilization of free-phase of NAPLs through Surfactant Flushing Techniques at Love's Country Store Gas Station in Oklahoma City

Baseline ground water(1st bottle) show no free-phase (FP) of gasoline or diesel. The ground water was collected before the surfactant flushing.

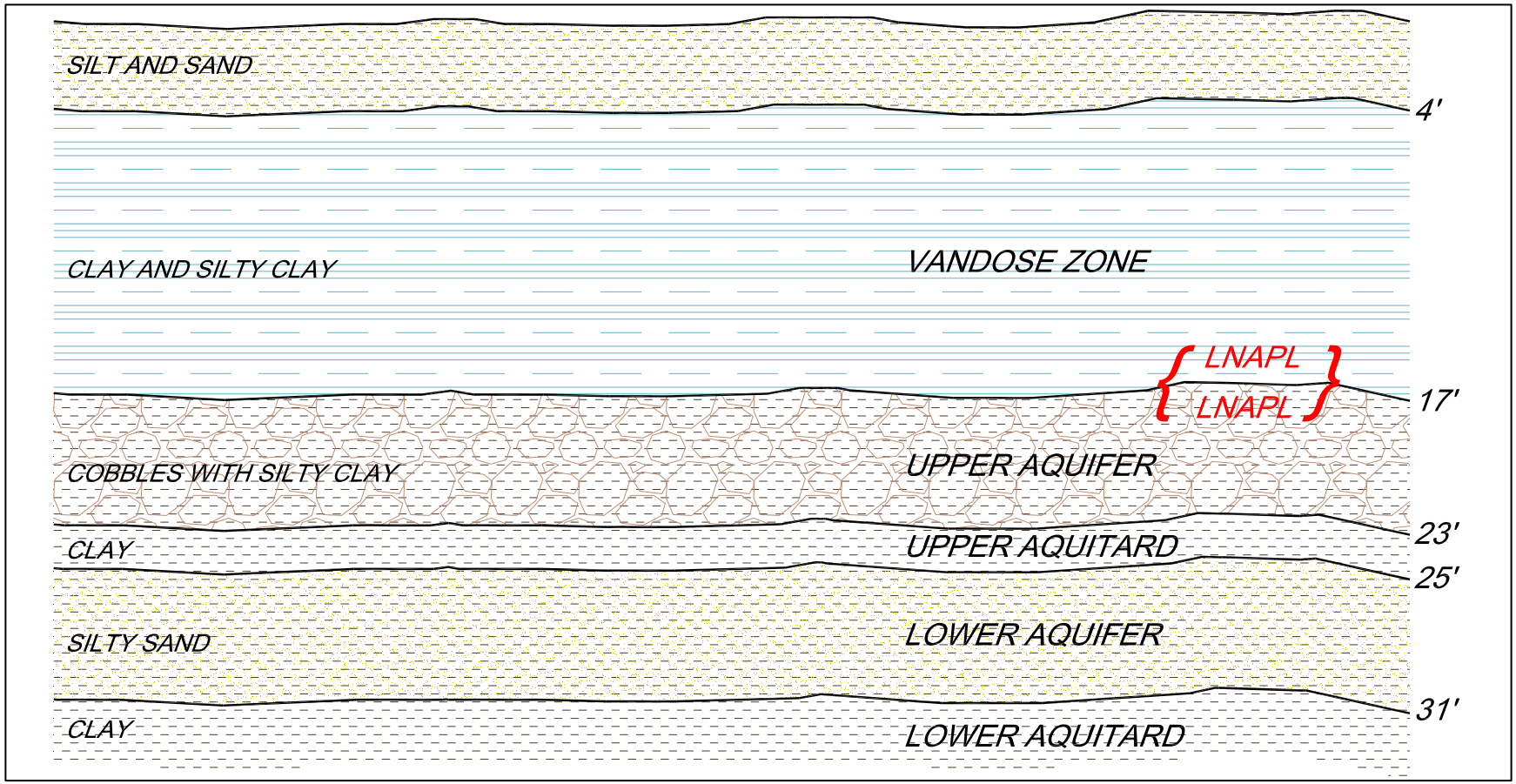
Remobilization of free-phase gasoline and diesel during surfactant flushing (from the 2nd bottle to 8th bottle.) The FP amounts increased to a maximum (4th bottle), then decreased to a minimum (8th bottle).

SEAR Case Studies (2)

Client: Oklahoma Corporation Commission (OCC)
Contaminants: UST gasoline fuel leaks
Depth from ground: 5 - 25 feet
Aquifer geological settings: Sand, gravel, silt and clay
Treatment technique: *in situ* surfactant flushing combined with chemical oxidation treatment
Clean-up Level:

- Free product removal
- SSTL (benzene 9.0 mg/L)
- MCL (benzene 0.005 mg/L

Treatment area: 44,000 yd^3
Remediation cost: $860,800
Surfactant flushing period: 60 days (Post-monitoring One year)

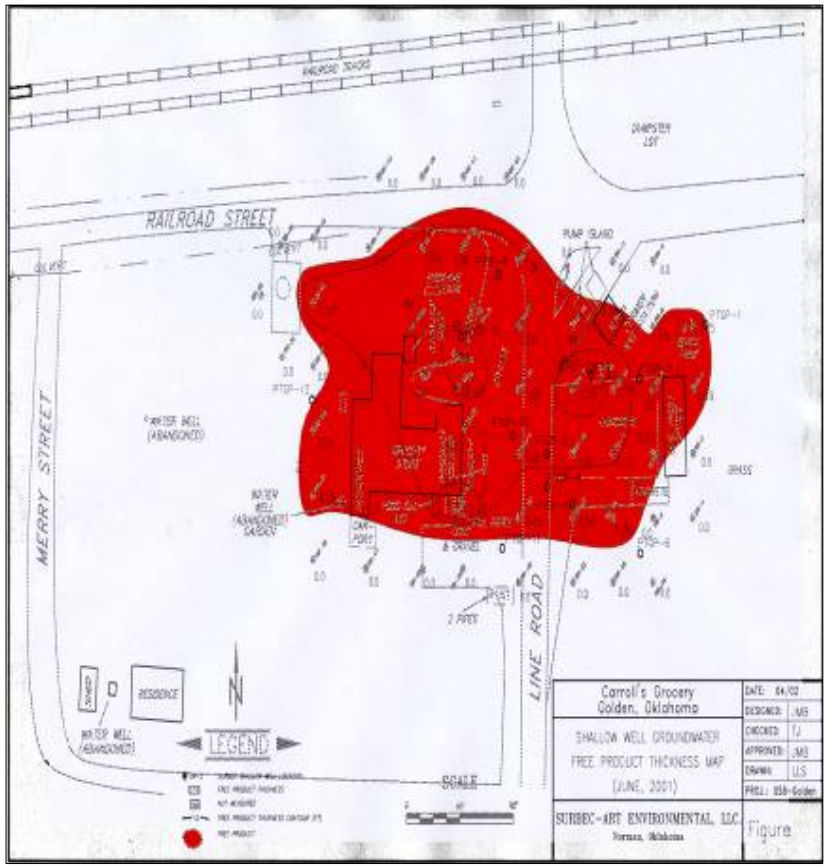


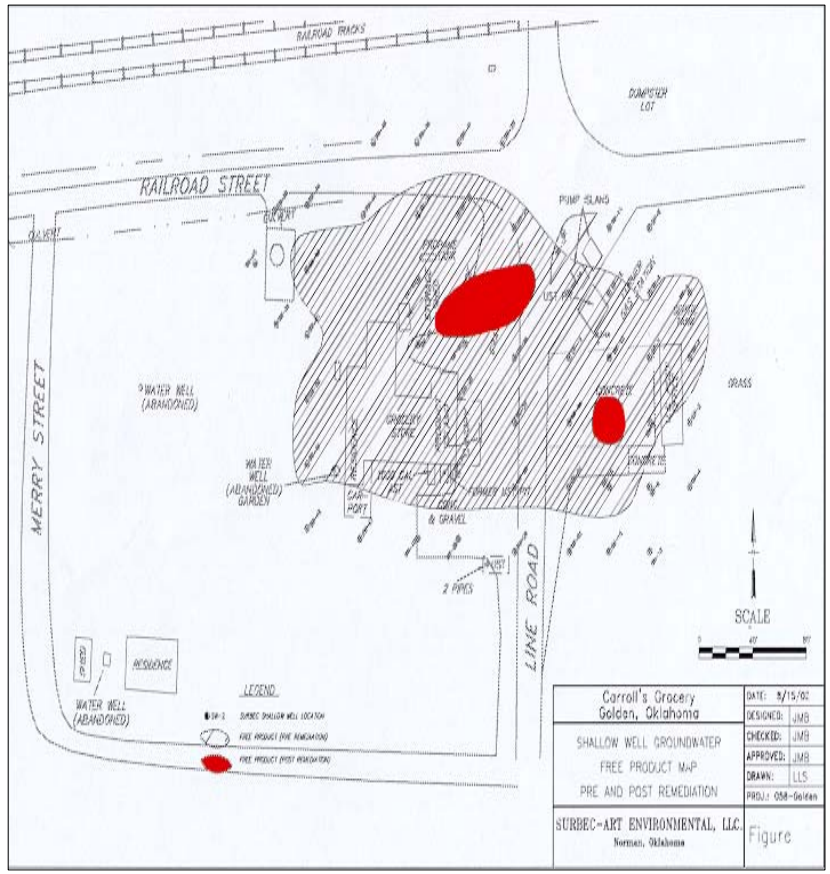
This figure showed the occurance of pre-flush NAPL plume at Golden UST site. The gasoline free-phase thickness was from 2.7-3.3 feet. The vadose zone consisted of a clay and silt layers. A cobble layer directly underlie the vadose zone. The free phase and residual LNAPLs occurred primarily at the interface between the vadose zone and the cobble layer, running from approximately 11 ft (3.4 m) to about 17 ft (5.2 m) below ground level. Below the cobble layer there was mainly silty fine sand intercalated with clay layers.

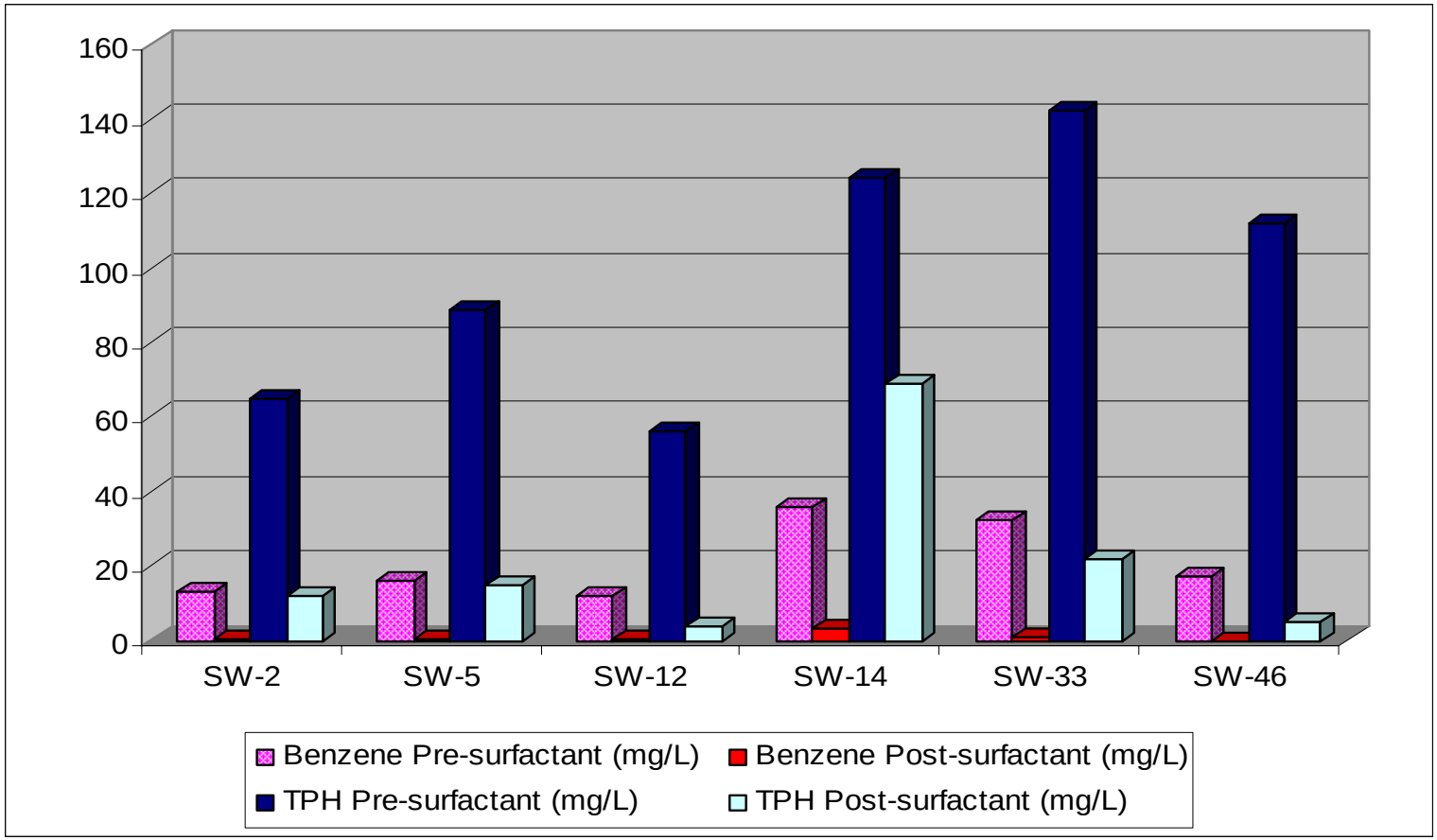
Clean-up level at Golden UST site

- After repair of the leaking fuel system in 1991, full scale remediation of the site began in 1994. In the period from 1994 to 2001 several advanced remediation technologies were tried at the site, including air sparge/SVE, bladder pumps, an eductor system, and an eductor system with venting, under three different consultants and at a total cost of approximately $1 M.
- Despite these aggressive efforts at remediation, substantial contamination remained at the site. The Oklahoma Corporation Commission (OCC) was considering declaring the site irremediable.
- The remediation plan for the site was based on the observation that surrounding homes drew their drinking water from the lower aquifer, and that natural attenuation was adequately removing dissolved benzene from the lower aquifer before it could reach any potential receivers. It was concluded that if free-phase NAPL could be removed from the upper aquifer, and if ground water benzene concentrations in the upper aquifer dropped below 9,000 µg/L, then the lower aquifer should remain safe.
- The primary remedial goal for the site using SEAR technique was, therefore, free-phase gasoline removal from the upper aquifer, with reduction in ground water concentrations of benzene being a secondary goal. No remedial goals were set for the lower aquifer, though some free product found in the lower aquifer was removed by surfactant flushing.

Reduction of NAPL area after surfactant flushing





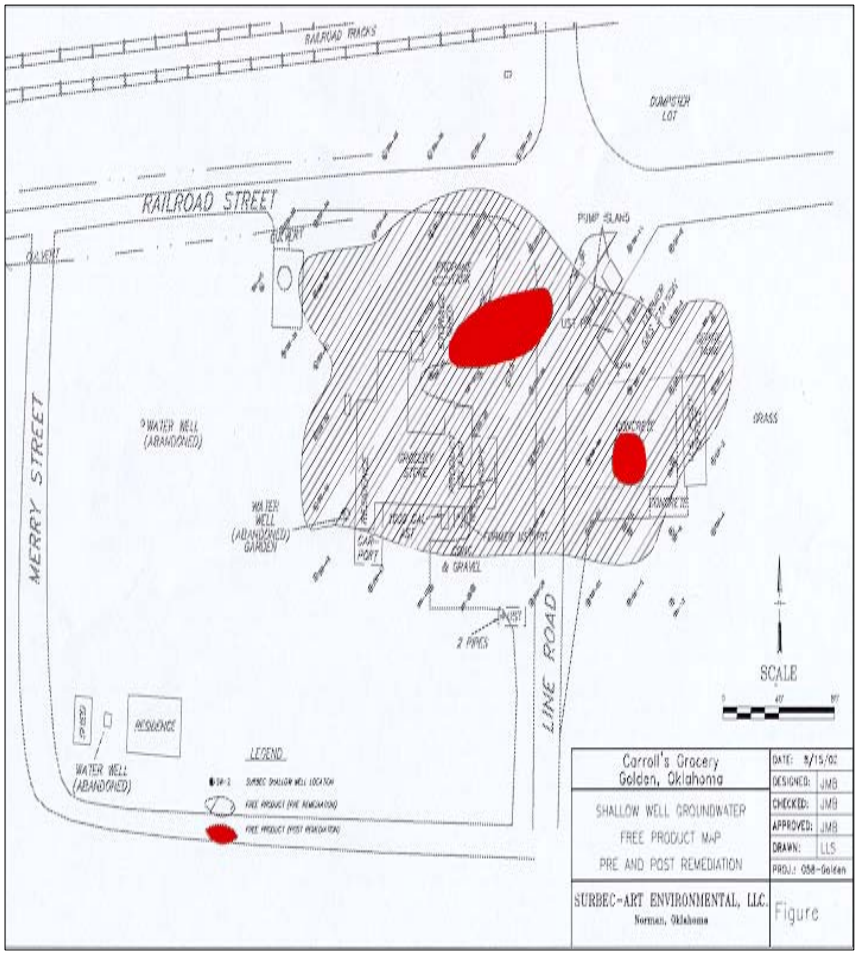


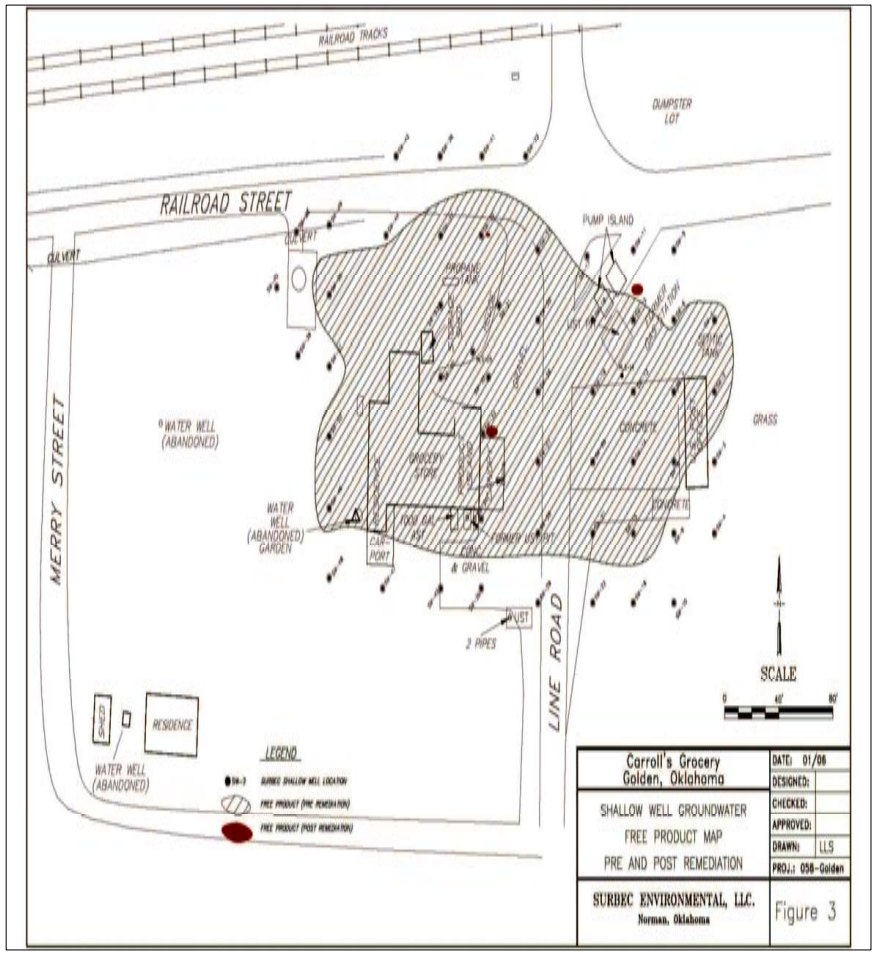
A 60-day surfactant flushing (injected 190,000 gallons of co-sufactant mixture) achieved all project goals for free-phase gasoline removal and benzene concentration reduction in ground water.

Surfactant Flushing/Chemical Oxidation Treatment at Golden UST Site

- It was desired by the OCC to determine if benzene concentrations of the ground water in the lower aquifer could be reduced to MCLs, and whether benzene concentration of the ground water would rebound to above MCLs.
- To achieve MCL goal, combination of surfactant flushing and chemical oxidation treatment (<1wt% of Fenton's Reagent) was applied at Golden site. Following completion of the treatment, all monitoring wells in the lower aquifer had benzene concentrations near or below MCLs. No subsequent treatment was considered at this time, and the well field was shut down, though no wells were plugged.

The Results of Surfactant-flushing (Left) vs Combination of Surfactant/Chemical Oxidation (Right) at Golden UST Site





Post-flushing monitoring at Golden Site, Oklahoma

- From summer to late winter 2005, Golden, Oklahoma experienced a drought and the water table dropped 6 ft (1.8 m). Subsequently the OCC and SURBEC re-sampled the monitoring wells at the site in January 2006. Of the 25 monitoring wells in the original free product zone, all remained free of NAPL except for monitoring well SW-33, about 15 ft (4.6 m) from the product island, which contained a thin sheen. One monitoring well near the original leak but outside the initial free product zone also contained NAPL sheen; this area had not been flushed with surfactant during the site cleaning. Additionally, all monitoring wells remained below the site specific benzene ground water concentrations set for closure.

Conclusions

The Golden site illustrates that surfactant flushing can be used to quickly and effectively remove residual and free product from a site with a complex geology and low permeability that has resisted remediation from aggressive application of advanced technologies including air sparging, soil vapor extraction, bladder pumps, and eductors. Prior to the surfactant flush, monitoring wells at the site contained up to 11 ft of NAPL free product, despite 7 years of remedial efforts at a cost approaching $1 M.

The smear zone was completely flushed of residual and free product by only 60 days of surfactant flush. After the surfactant flush, 22 of 25 monitoring wells showed no free product after being shut in for 3 months, and the remaining 3 wells showed only free product sheen. The zones containing these wells were re-flushed and subsequently showed no free product sheen. Ground water benzene concentrations in all zones dropped from 75% to 99% following the surfactant flush alone. Surfactant/chemical oxidation treatment dropped ground water benzene concentrations at all monitoring wells to MCLs in the lower aquifer.

Unfortunately, cross contamination between the upper and lower aquifers through monitoring wells screened between the two aquifers led to a rise in benzene levels in the lower aquifer to levels about MCL.

Challenges and Solutions

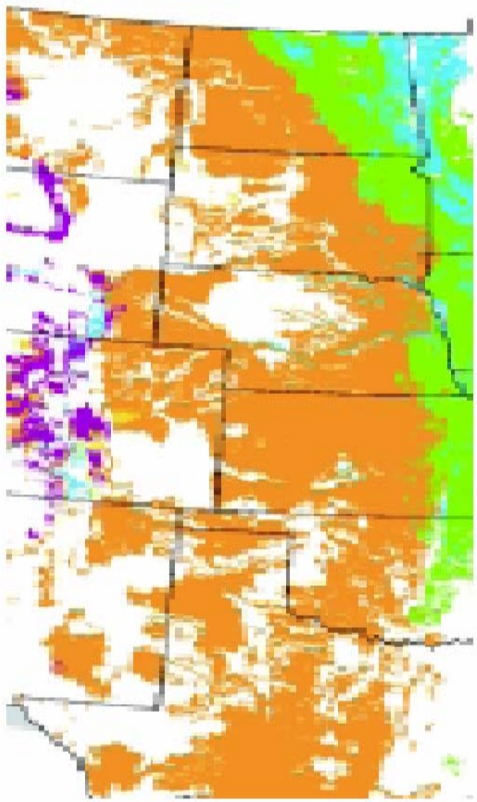
1. Ca^{++} increased due to ion exchange of clay minerals

Some aquifer settings containe a large portion of clay layers. When the surfactants reacte with the clay minerals, sodium (Na^{+}) associated with surfactants can exchange with calcium (Ca^{++}) and magnesium (Mg^{++}) adsorbed by clay minerals. As a result, ground water can enrich in Ca^{++} and Mg^{++}, which can result in surfactant precipitation, and consequently, negatively affect the surfactant phase behavior. The aquifer settings of Aurora site in Colorado and Woodward site in Oklahoma showed a large increase of Ca^{++} and Mg^{++} in water due to ion exchange of clay minerals.

Results of ion exchange of A-site, mg/L

Well # and Depth	Matrix	Soil description	Na	K	Mg	Ca
CW1, 25-27'	DI water	Silty fine sand intercalated with clay layers	28.6	ND	3.2	19.9
	1.5% NaCl		1260	18.8	210	855
CW6, 28-30'	DI water	Silty clay intercalated with fine sand layers	55.8	ND	1.6	4.0
	1.5% NaCl		1321	16.8	237	601
CW8, 32-35'	DI water	Fine to medium sand intercalated with clay layers	31.0	ND	0.6	3.0
	1.5% NaCl		1369	17.7	102	428

Challenges and Solutions



Ustolls (yellow color on left map) widely occur in Oklahoma. Most Ustolls have a horizon with identifiable secondary carbonates or have a calcic horizon.

2. Soil containing high carbonates

The vadose zone of a few contaminated sites contained high carbonate soils (Ustolls). During surfactant injection, carbonates leached into ground water and precipitated as scales on well screen walls, injection tubes and pipes. Consequently, the scales plugged the injection system and greatly reduced surfactant flow rate. The problem caused additional expense and increase of site remediation time.

Solutions to Geochemical Problems

Solution 1: Addition of chelating agents into the surfactant system. The selected chelating chemicals must be safe for both humans and environment. Currently we use STPP (CAS:7758-29-4) as a chelating agent at sites with high carbonate content in vadose zone. STPP has been used in food and oil-recovery industries.

Solution 2: Use of new surfactant formulations that have good phase behavior with ground-water consisting of high Ca^{++} and Mg^{++} .

Geochemistry affects NAPL occurrence in subsurface environment

When petroleumhydrocarbon compounds are released into the environment, changes in composition take place. Collectively, these changes are referred to as weathering. The main weathering processes are dissolution in water, volatilization and biodegradation. Each of the weathering processes affects hydrocarbon compounds differently. In general, the more water soluble and volatile compounds are lost most rapidly from contaminated soil. These volatile compounds have the lowest molecular weight. The weathering leads to an increase of higher molecular weight compounds in residual materials.

Fingerprinting analysis and SEAR

Fingerprinting analysis of NAPL types can help to determine the contaminant compounds, understand contaminant transformation and site contamination history. The results can help us to understand the geochemistry of the subsurface environment and are important to the site engineering design.

Surbec has developed an analytical method using a static headspace GCMS system (HS-GC-MS method). The following table present two types of free phase gasoline from Woodward and Nathan's sites.

The results of fingerprinting analysis using HS-GC-MS method showed the Woodward gasoline was freshly released (see Table on next slide).

The Woodward gasoline samples were analyzed by PTS Laboratories in California and the PTS concluded that the gasoline was minimally weathered (maybe one or two percent). The inter-laboratory analytical results validated the HS-GC-MS method.

Fingerprinting Analysis of Gasoline

Site	Nathan's, OK		Woodward, OK			Com. gasoline		Ratio Range*
Well #	MW 21	MW18	EW15	EW24	MW17	89#	91#	
	%							
Benzene	0.7	0.3	1.6	1.9	1.9	1.8	2.0	1.6-2.3
Toluene	2.8	1.7	7.7	7.6	7.3	7.8	7.6	6.4-10
Ethylbenzene	2.2	1.2	1.6	1.5	1.5	1.7	1.8	1.4-2.0
Xylenes	0.8	0.6	8.7	8.2	7.9	7.9	7.9	7.6-10.8
1,3,5,-Trimethylbenzene	7.2	3.7	0.9	0.9	0.8	0.8	0.7	0.84-1.1
2-Methylpentane	1.9	1.9	3.9	4.5	4.4	7.4	5.5	3.2-4.5
2,2,4-Trimethylpentane	10.5	9.7	3.4	3.2	3.1	4.0	5.0	0.87-4.2
Cyclopentane	1.2	1.4	1.2	1.4	1.3	1.8	1.8	0.34-0.61
Cyclohexane	2.6	2.3	3.2	3.2	3.0	3.1	2.7	0.23-0.6
Hexane	2.7	1.1	3.5	4.0	3.6	4.8	4.2	1.8-3.2
Methylcyclohexane	0.9	0.7	0.5	0.5	0.5	0.5	0.6	0.39 -0.75
1,2,4-Trimethylbenzene	4.3	5.0	3.6	3.0	2.8	2.6	2.8	0.66 -3.3
Decane	0.6	0.6	0.1	0.2	0.2	0.2	0.2	0.04-0.5