

COST AND PERFORMANCE REPORT FOR LNAPL CHARACTERIZATION AND REMEDIATION

Partition Interwell Tracer Testing (PITT) and Rapid Optical Screening
Tool (ROST™) Characterization and Evaluation of the Feasibility of
Surfactant Enhanced Aquifer Remediation (SEAR)
at the Chevron Cincinnati Facility, Hooven, OH

February 2005



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ABBREVIATIONS AND ACRONYMS

AOC	Area of concern
BTEX bgs	Benzene, toluene, ethylbenzene, and xylene below ground surface
CMS	Corrective measures study
COPC	Contaminants of potential concern
CPT	Cone penetrometer
cm	centimeter
cm/s	centimeters per second
DEHP	Di(2-ethylhexyl) phthalate
EPA	U.S. Environmental Protection Agency
GWCMS g/cm ³	Groundwater corrective measures study grams per cubic centimeter
LNAPL	Light non-aqueous phase liquid
MCL	Maximum contaminant level
MNA	Monitored natural attenuation
MPPE	Macroporous polymer extraction
MW	Molecular weight
mg/L	milligrams per liter
mm	millimeter
mS /cm	millisiemens per centimeter
mV	millivolts
PITT	Partitioning inter-well tracer test
PRG	Preliminary remediation goal
P&T	Pump and treat
RCRA	Resource Conservation and Recovery Act
ROST™	Rapid optical screening tool
SEAR	Surfactant-enhanced aquifer remediation
SVE	Soil vapor extraction
SWMU	Solid waste management unit
UST	Underground storage tank
µg/L	micrograms per liter
wt %	percent by weight

EXECUTIVE SUMMARY [1,2,3,4,5,6]

Light non-aqueous phase liquid (LNAPL) represents a continuing source of groundwater contamination and may extend the required time for site remediation by years to decades. This case study summarizes the characterization studies and technology evaluation of surfactant enhanced aquifer remediation (SEAR) conducted for LNAPL at the Chevron Cincinnati Facility in Hooven, OH. This report summarizes the evaluation of the use of SEAR as a potential innovative and aggressive technology to treat LNAPL at this site.

Site characterization using a partitioning inter-well tracer test (PITT) and cone penetrometer with rapid optical screening tool (CPT/ROST™) was performed to further define the LNAPL contamination and to provide information about the potential applicability of SEAR at this site. The characterization studies identified typical residual LNAPL saturation within the smear zone ranging from 1 to 8% of the soil pore volume. The highest LNAPL saturations were observed in zones of mobile LNAPL during times of low water table levels. Based on the characterization and treatability testing described in this report, it was determined that SEAR could potentially reduce the LNAPL saturation to less than 1%. The specific goal for the SEAR system was to reduce the LNAPL to levels where SEAR can no longer mobilize the LNAPL, determined to be between 0.5% and 1%. If reduced to this level, the LNAPL was expected to remain immobile after the completion of the SEAR. The studies also found that a mixture including proprietary anionic and cationic surfactants would be the optimal formulation for this site.

The draft Corrective Measures Study (CMS) [1] identified the time to reach final cleanup goals, present value cost, and compatibility with site redevelopment for the SEAR system. The preliminary cleanup goal used as a basis to select the remedy was a benzene concentration in groundwater below the drinking water maximum contaminant level (MCL) of 5 µg/L. It was estimated that SEAR operations, in conjunction with soil vapor extraction (SVE), would take from 8 to 12 years. However, application of these technologies would not achieve final cleanup goals, and would need to be followed by hydraulic containment and monitored natural attenuation (MNA), which would need about 100 years to reach cleanup goals. Uncertainty in the volume of LNAPL at the site precluded more refined estimates. The CMS recommended hydraulic containment as a remedy because using any of the remedial options considered, including the SEAR technology, it was “not possible to return the aquifer to its maximum beneficial use in a reasonable time period.” Although the CMS did not define a reasonable time period, it did note that all of the remedial options considered required 100 years or more.

The evaluation of SEAR at this site resulted in observations and lessons learned that may be helpful when this technology is evaluated for other sites. It was assumed that the extracted LNAPL and groundwater emulsion could be treated using aboveground technologies to recover LNAPL and reduce contaminants prior to reinjection. However, the feasibility of the aboveground treatment has not been proven. Based on

the size of the LNAPL plume at this site, the SEAR system was estimated to be two orders of magnitude larger than the largest SEAR operation conducted through October, 2001, which was when the technology evaluation was completed. The CMS stated that substantial technology development would be required to bridge this experience gap.

1.0 INTRODUCTION

This case study summarizes the results of an evaluation of the applicability of surfactant-enhanced aquifer remediation (SEAR) to treat LNAPL contamination at the Chevron Cincinnati Facility in Hooven, OH. Remediation of LNAPL in contaminated media is a particularly challenging problem. LNAPLs usually consist of volatile organic compounds such as benzene, toluene, ethylbenzene, and xylene (BTEX). When released into the subsurface, they become intermixed with the soil matrix and groundwater, and are held in the soil by capillary forces. The LNAPL continues to release dissolved contaminants to surrounding media for an extended period of time. As the water table changes in depth over time, the LNAPL also rises and falls, creating a contaminant “smear zone” that is difficult to treat. No single technology has been identified as the best solution for all sites contaminated with LNAPLs. The most commonly used groundwater treatment technology, pump-and-treat (P&T), requires very long treatment times to reach cleanup goals and restore contaminated aquifers when LNAPLs are present.

In some cases, innovative technologies may effectively treat LNAPLs, restore contaminated aquifers to productive use more quickly than P&T, assist P&T in achieving cleanup, or reduce treatment costs. However, such technologies might not be used if site managers are not aware of their capabilities, or determine that their effectiveness has not been demonstrated. Additional information on the evaluation and application of innovative technologies to treat LNAPLs is needed to promote their acceptance and use as an alternative to P&T. This case study provides such additional information.

2.0 SITE INFORMATION

2.1 IDENTIFYING INFORMATION [1]

Site Name: Chevron Cincinnati Facility

Location: Hooven, Ohio

Regulatory Context: RCRA corrective action (Facility ID: OHD004254132)

Technology: Surfactant Enhanced Aquifer Remediation (SEAR)

Scale: Not applicable. Based on results of site characterization studies, SEAR was not tested at the site.

2.2 TECHNOLOGY APPLICATION [1,3]

Period of Operation: At the time of this report, SEAR had not been tested at the site; the characterization studies used to evaluate the feasibility of SEAR at this site were conducted in September 1999 (see Section 5.2).

Type/Quantity of Media Treated During Application: Not applicable

2.3 BACKGROUND [1,2]

The site is a former petroleum refinery owned by Chevron Products Company (Chevron) near Hooven in Whitewater Township, Ohio, approximately 20 miles west of Cincinnati, Ohio. It occupies 600 acres along the Great Miami River, which borders the site to the east, northeast, and southeast. The town of Hooven borders the site to the west. Refinery operations occurred on approximately 250 acres containing the plant process areas, storage tanks, and other facilities. The remainder of the site consists of tracts of upland and bottomland forests, open brushy areas, and isolated wetlands, which served as a buffer zone along the river. The general layout while the site was in operation is shown on Figure 1, which is based on areal photographs from about 1962.

The refinery was constructed in 1931 and operated until May 1986. Major products produced at the refinery were gasoline, jet fuel, diesel, heating fuel, liquefied petroleum gas, asphalt, and sulfur. Accidental spills, pipeline failures, and tank leaks during historical operations at the site released an estimated 7 million gallons of LNAPL to the aquifer. Decommissioning, dismantling, and environmental remediation have been underway since May 1986. As of 2001, nearly all of the above-ground buildings and structures had been razed.

Interim actions began in the mid-1980s when a hydrocarbon sheen was observed seeping into the Great Miami River. A groundwater P&T system was installed to hydraulically contain the hydrocarbon plume. The system extracts groundwater through a series of 14 wells and treats it using an aerobic, fluidized bed bio-reactor to remove organic contaminants. The effluent from the bioreactor is further treated in lagoons to remove suspended solids before it is discharged to the river. The system pumps and treats 4 to 5 million gallons of groundwater on a seasonal basis. During low water-table periods, wells are pumped to create cones of depression, which allow LNAPL to be pumped. The LNAPL is recovered by skimming it from recovery wells and pumping it to storage prior to off-site shipment. As of 2000, approximately 3.5 million gallons of LNAPL have been recovered. At that time, about 8 million gallons of DNAPL was believed to remain in situ, however, more recent estimates indicate that only 3.5 million gallons of DNAPL remain. Groundwater monitoring is ongoing to verify hydraulic containment.

In 1995, soil vapor extraction (SVE) began seasonal operations to address hydrocarbon contamination in the vadose zone at Islands No. 1 and 2 (see Figure 2). The SVE system uses a thermal oxidizer to treat off-gas. Through 2000, air stripping removed approximately 21,000 pounds of hydrocarbons and biodegradation removed another 7,500 pounds. Since 2000, this system has been switched to bioventing with limited SVE. A more detailed description of the SVE and bioventing systems was not available in the references used for this report. In addition, a second SVE system consisting of three horizontal wells is being used to address LNAPL that has migrated off-site under the eastern half of Hooven. Horizontal

wells are being used to minimize off-site construction. This system began operation in 1999 and operates intermittently depending on the height of the water table.

In 1993, Chevron entered into an Administrative Order with EPA Region 5 to perform a RCRA Facility Investigation (RFI) to identify the nature and extent of contamination at the site and a Corrective Measures Study (CMS) to evaluate long-term corrective actions. Phase 1 of the RFI investigated the perimeter of the site to evaluate the extent of possible off-site contamination, while Phase 2 addressed surficial areas and groundwater located within the site. Phase 2 also included a facility-wide risk assessment. The RFI was completed and approved by EPA in 2000.

The RFI identified soil and sediment contamination, as well as both LNAPL and dissolved contamination in groundwater. Several high priority solid waste management units (SWMUs) and areas of concern (AOCs) were identified based on risks to human health and the environment and compatibility with anticipated future land use. These SWMUs and AOCs were remediated. With EPA's concurrence, Chevron decided to address soil, sludge and groundwater under a separate CMS. In October 2002, Chevron submitted the soil and sludge CMS and, in June 2003, EPA published a Statement of Basis for Sludges and Contaminated Soil that specified excavation and off-site disposal in a RCRA hazardous waste landfill as the proposed remedial alternative.

As of June, 2004, the groundwater CMS was not yet final. The CMS evaluated the following alternatives considered for addressing LNAPL-contamination at this site:

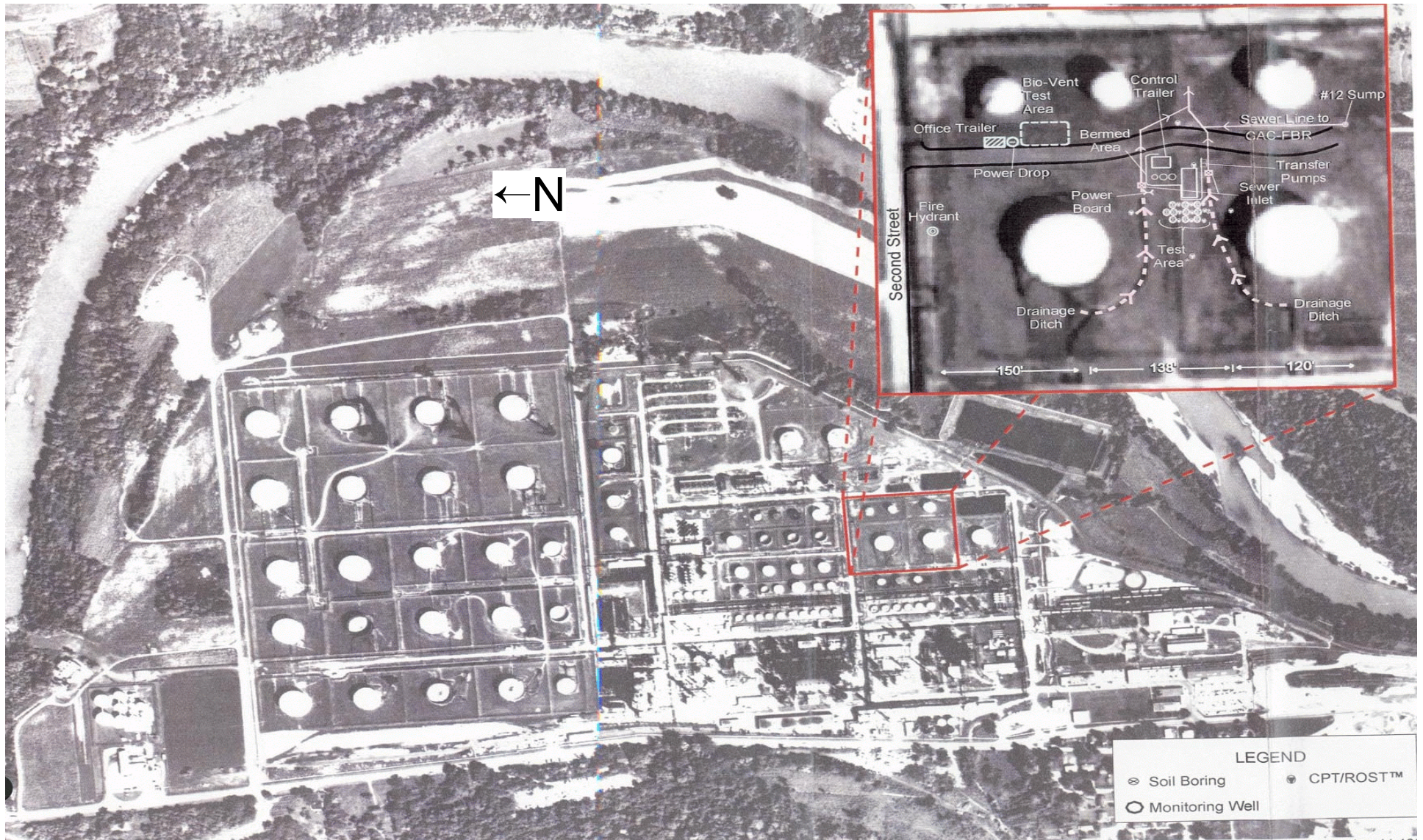
- Hydraulic containment
- Surfactant enhanced aquifer remediation (SEAR)
- In situ air sparging
- Soil vapor extraction (SVE)
- In situ chemical treatment
- Thermal enhancements of SVE, including six-phase heating, steam injection, and hot air injection
- Groundwater circulating wells
- Monitored natural attenuation
- Institutional controls

As of June, 2004, a final groundwater remedial alternative was not yet implemented. This report provides a description of the SEAR remediation system that was evaluated for this site. This report also includes the bench- and pilot-scale site characterization studies that were used as the basis for the SEAR evaluation. While no information was provided on the cost of the pilot-scale studies, a cost estimate for a full-scale SEAR system was developed (see section 5.4).

2.4 TIME LINE OF SITE ACTIVITIES [3,4]

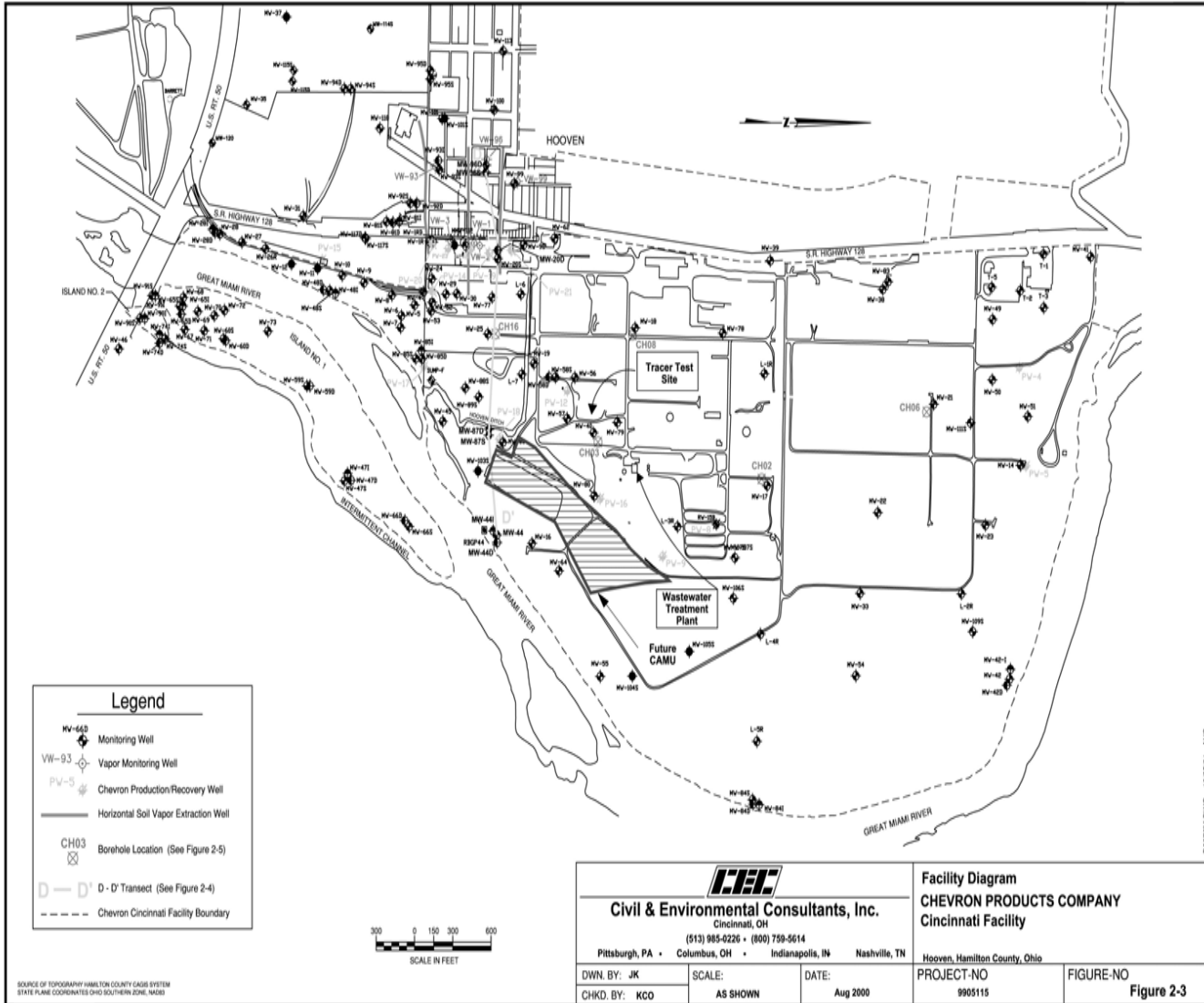
1931	Refinery constructed and operations begin
1986	Refinery operations shut down and site investigation and remediation activities begin
1988	Hydraulic containment with P&T begins
1995	SVE system to remediate on-site contamination begins
July - September 1998	CPT/ROST™ pilot-scale site characterization conducted
August 16 - 17, 1998	PITT pilot-scale site characterization conducted
1999	Second SVE system constructed to remediate off-site contamination
September 1999	Additional bench-scale feasibility studies conducted
2000	On-site SVE replaced with bioventing and limited SVE

Figure 1. Site Layout (with closeup of PITT Test Site Location), Chevron Cincinnati Facility, Hooven, OH



Source: Radian International and Duke Engineering Services, 1999

Figure 2. Facility Map, Chevron Cincinnati Facility, Hooven, OH



Source: GWCMS, 2001

U.S. Environmental Protection Agency
 Office of Solid Waste and Emergency Response
 Office of Superfund Remediation and Technology Innovation

3.0 MATRIX AND CONTAMINANT DESCRIPTION

3.1 SITE GEOLOGY/STRATIGRAPHY [1,3]

The site lies in a valley cut into the shale bedrock by the ancestral Great Miami River and then partially filled with glacial outwash. The shale bedrock has a low permeability, but contains fine cracks, joints, and thin layers of interbedded limestone. The glacial outwash is composed of unconsolidated sand and gravel, giving it a high permeability. Also, rapidly varying depositional conditions resulted in heterogeneous conditions, especially in the upper part of the aquifer, where lower permeability alluvial silt and sand cover the glacial outwash. Contractors at the site have categorized the site into the following three stratigraphic layers:

- Upper Zone (0 to 12 feet bgs) – Fine-grained alluvial deposits such as silts, clays, and some fine sand
- Transition Zone (12 to 22 feet bgs) – Gravely silts, fine sands, silty gravels, and small cobbles intermixed in a silt or sandy silt matrix
- Lower Zone (22 to 122 feet bgs) – Complex sequence of sands and sandy gravels

Under natural conditions, groundwater flow at the site is from north to south with discharge to the Great Miami River. Currently, the groundwater flow system is controlled by groundwater extraction, causing groundwater to flow from the facility boundary and the river to the extraction areas in the southern portion of the site. Groundwater elevation at the site varies seasonally (typically by 2 to 5 feet, but by as much as 18 feet) as the river stage rises and falls throughout the year. Within the PITT test site area, the depth to groundwater was measured between 17 and 32 feet bgs. The LNAPL extends from 12 to 30 feet bgs, and is present primarily in the transition zone.

3.2 NATURE AND EXTENT OF CONTAMINATION [1,3,4]

Type of Media Treated With Technology System: LNAPL, soil, and groundwater (LNAPL smear zone)

Primary Contaminants at the Site:

Petroleum hydrocarbons, LNAPL (mixture of leaded gasoline, diesel fuel, and crude oil)

LNAPL at the site is typically a mixture of approximately 80% leaded gasoline and 20% diesel fuel, but its composition across the site is a variable combination of gasoline, diesel, and crude oil. Generally, it can be identified as one of two types:

- Type 1 LNAPL – a low viscosity and low density LNAPL that underlies most of the facility and has migrated off the site under Hooven; Type 1 is the LNAPL primarily present in the PITT Test Site area. Based on the location where this type of LNAPL is found and its physical and chemical characteristics, it is likely to have originated from gasoline and diesel fuel leaks and spills.

- Type 2 LNAPL – a higher viscosity and higher density LNAPL containing heavier hydrocarbons (with approximately half of the LNAPL heavier than C14); Type 2 LNAPL is present primarily on the eastern edge of the facility. Based on the location where this type of LNAPL is found and its physical and chemical characteristics, it is likely to have originated from a mixture of crude oil and diesel fuel leaks and spills.

Table 1 summarizes selected properties of these two types of LNAPL.

Table 1. Properties of LNAPL at the Chevron Cincinnati Facility, Hooven, OH

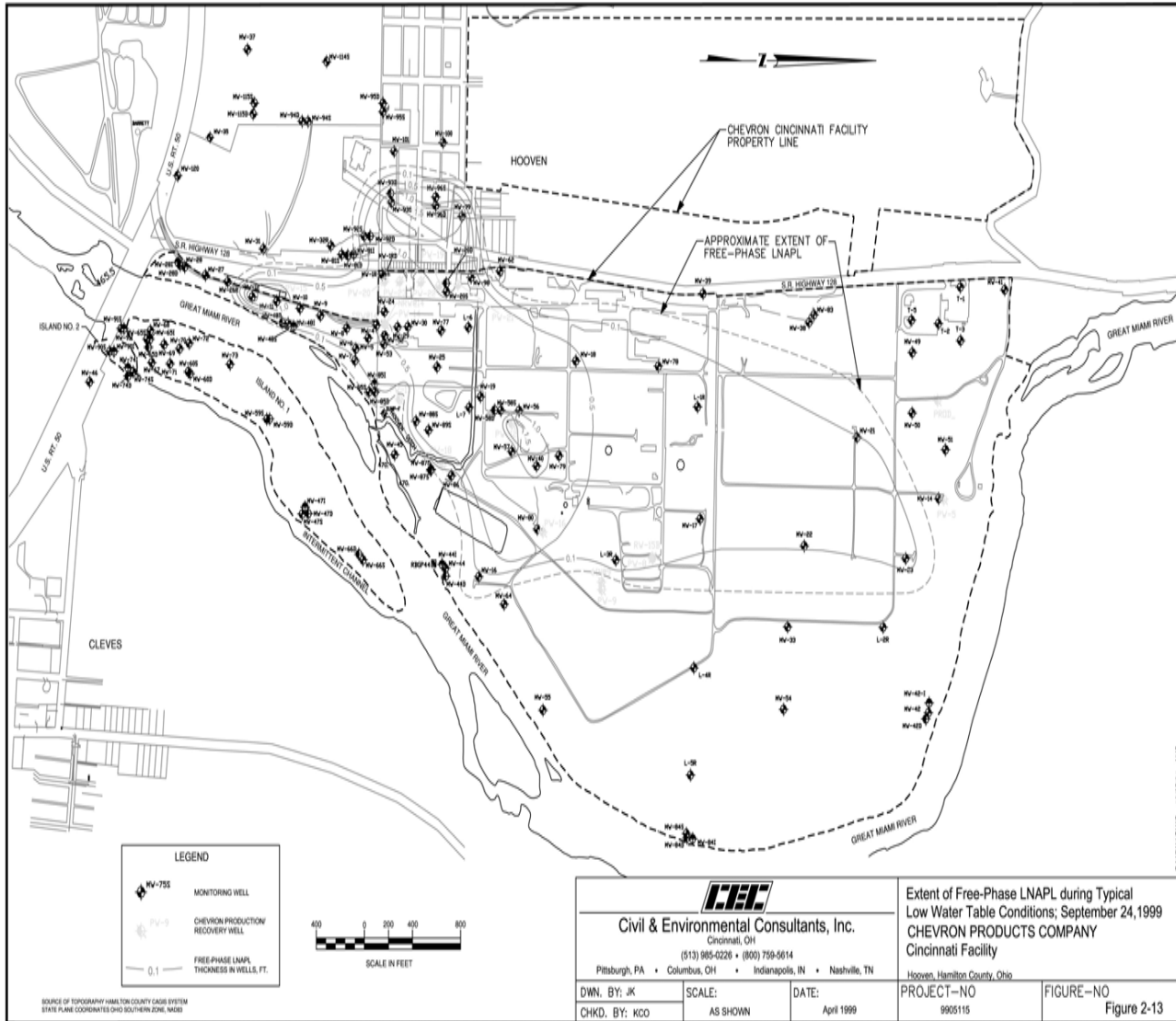
Property	Type 1 LNAPL	Type 2 LNAPL
Density	<0.85 g/cm ³	>0.85 g/cm ³
Viscosity	<2 centipoise	>5 centipoise
Interfacial Tension	~24 dynes/cm	~12 dynes/cm
Benzene	0.1 – 0.45 wt%	0 – 0.03 wt%
Xylene	~5 wt %	<0.8 wt %
Compounds > C ₁₄	~7 wt%	~53 wt%

Source: Radian International and Duke Engineering & Services, 2000

Table 2 lists the contaminants of potential concern (COPC), the maximum concentration of each COPC detected at the site, and the preliminary cleanup goals. The LNAPL is present in a smear zone extending from approximately 12 to 30 feet bgs, which is primarily in the transition zone described in Section 3.1. The area of LNAPL contamination is approximately 200 acres. At times of year when the groundwater table is low (typically in winter), most of the smear zone is present above the water table. Figure 3 shows the site at typical low water table conditions and includes the approximate extent of the free-phase LNAPL, as well as LNAPL thickness. Free-phase LNAPL thickness ranges from 0.1 ft to 1.5 feet at some wells. Approximately half of the plume has a free-phase LNAPL thickness less than 0.5 feet, while the other half

has a thickness greater than 0.5 feet. Additional figures showing LNAPL at typical high water table and extreme low water table conditions are included in the GWCMS [1]. When the groundwater table is high

Figure 3. LNAPL at Typical Low Water Table Conditions, Chevron Cincinnati Facility, Hooven, OH



(typically in the spring), most of the LNAPL smear zone is submerged and, in some cases, no free-phase layer is present.

Table 2. Contaminants of Potential Concern (COPC) in Groundwater at the Chevron Cincinnati Facility, Hooven, OH

Contaminant of Potential Concern	Maximum Concentration Detected (ug/L)	Cleanup Goal (ug/L) (Basis)
Benzene	5,000	5 (MCL)
Ethylbenzene	2,000	700 (MCL)
1,4-Dichlorobenzene	440	75 (MCL)
Acetophenone	21	0.042 (PRG)
Di(2-ethylhexyl) phthalate (DEHP)	46	6 (MCL)
Naphthalene	450	6.2 (PRG)
Pyrene	630	180 (PRG)
Dissolved Lead	39	15 (MCL)
Total Arsenic	81	10 (MCL)

Cleanup Level Basis:

MCL – Federal Safe Drinking Water Act Maximum Contaminant Level

PRG – U.S. EPA Region 9 Preliminary Remediation Goal

Source: GWCMS, 2001

Most of the documents used as references for this report describe the distribution of the LNAPL in the subsurface as following the “pancake” model , which is based primarily on the difference in density between LNAPL and water, and the adsorption of LNAPL onto soil. In this model, LNAPL is believed to float on top of the groundwater table. As the groundwater table fluctuates, the LNAPL layer rises and falls with the groundwater, creating a “smear zone” of contamination where the LNAPL adsorbs to soil. The LNAPL characterization and remedial design described in this report was based in part on this model of LNAPL behavior.

Since the publication of those references, new research into the behavior of LNAPL indicates that it may follow a model that is based on the capillary forces that soil exerts on water and LNAPL in addition to density differences. In this model, LNAPL, water, and air exist in the subsurface in different zones. In the deepest zone the soil pore space contains primarily water. Above this zone, capillary forces and density differences create a mixture of water and LNAPL, rather than a zone of pure LNAPL, as in the “pancake” model. Above this is a capillary fringe that includes a mixture of LNAPL, water, and air, above which is the vadose zone. One of the practical implications of this model is that the LNAPL zone is believed to contain significant amounts of water, rather than primarily LNAPL. Therefore, the total volume of LNAPL estimated for an observed LNAPL thickness can be significantly less than the “pancake” model.

The characterization and design activities described in this report were conducted before the current model was widely accepted, and were based, in part, on the “pancake” model. The effects of applying the current model to the test results and design assumptions described here have not been assessed.

3.3 MATRIX DESCRIPTION AND CHARACTERISTICS [3,4]

Table 3 lists the matrix characteristics of the Chevron Cincinnati Facility within the PITT test site area, which was conducted primarily in the transitional zone (see Section 3.1 for a description of the geologic zones at the site).

Table 3. Matrix Characteristics Expected to Affect Technology Cost or Performance at the Chevron Cincinnati Facility, Hooven, OH

Parameter	Value
Soil classification	Alluvial silt and sand and unconsolidated sand and gravel glacial outwash over shale bedrock with interbedded limestone layers
Clay content and/or particle size distribution	5 – 15% less than 0.25 mm diameter (fine sand, silt, clay) 40 – 80% greater than 2 mm diameter (gravel)
Hydraulic conductivity (horizontal)	10 ⁻⁴ – 10 ⁻² cm/s (based on permeameter testing) 0.1 cm/sec (based on pumping tests)
Groundwater velocity	2 - 4 feet per day
Permeability	0.13 – 12 darcies
pH	6.7 – 7.0
Depth of water table below ground surface	17 – 32 feet bgs
Presence of NAPLs	LNAPL present (estimated 3.5% LNAPL saturation from 22 – 32 feet bgs within the PITT test site area)
Electrochemical potential (E _H)	130 – 160 mV
Electrical conductivity	520 – 1,070 mS-cm
Dissolved oxygen	0.02 – 0.09 mg/L
Nitrate	<0.5 mg/L
Iron	4 – > 10 mg/L

Source: Radian International and Duke Engineering & Services, 1999

4.0 PERFORMANCE OBJECTIVES [1]

The CMS proposed an overall site strategy using a tiered approach of identifying Corrective Action Objectives in the form of short-term protectiveness goals, intermediate performance goals, and final cleanup goals. EPA's final cleanup goals for the site are "to return 'usable' groundwater to its maximum beneficial use, wherever practicable, within a time frame that is reasonable given the particular circumstances of the facility." Based on the conceptual design in the CMS, the specific goal for SEAR at the site was to reduce LNAPL saturation to between 0.5% and 1%, at which level, studies suggest that SEAR would no longer be capable of mobilizing the LNAPL. If reduced to this level, the LNAPL was expected to remain immobile after completion of the SEAR application. Table 2 in Section 3.2 lists the cleanup goal for each of the COPCs identified in Section 3.

5.0 TECHNOLOGY DESCRIPTION AND EVALUATION

SEAR is an innovative and aggressive technology that has the potential to remediate LNAPL and may allow for site redevelopment more quickly than other technologies. The following describes the SEAR remediation system, as well as the PITT and CPT/ROST™ pilot characterization studies and additional bench-scale studies used as a basis for evaluating SEAR as a remedial option for treating LNAPL at the Chevron Cincinnati Facility.

5.1 PILOT-SCALE SITE CHARACTERIZATION STUDIES [1,3,4,5,6,7,8]

PITT and CPT/ROST™ pilot tests were conducted as part of a site characterization and method selection field study to provide data used in the conceptual design and evaluation of a SEAR remedial approach for the site. This study also served to determine if a less costly and time consuming (compared to conventional soil-core and LNAPL testing) characterization method, such as CPT/ROST™, could be used to effectively investigate the nature and extent of LNAPL contamination throughout the site.

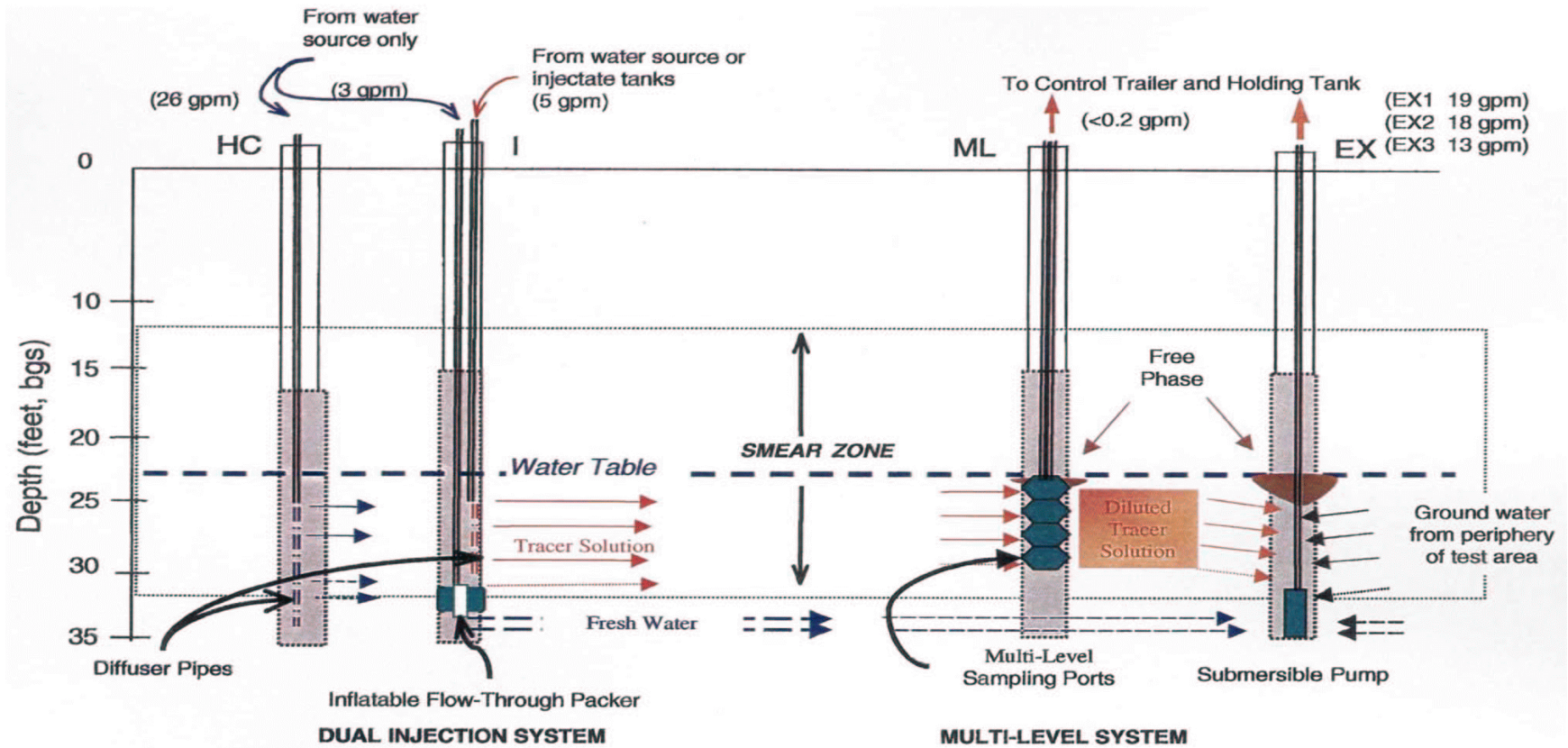
5.1.1 PITT Pilot Test

The in situ migration characteristics of LNAPL and heterogenous subsurface characteristics can cause the pattern of LNAPL distribution to be complex. Using conventional methods (such as soil-core sampling) that only examine a small fraction of the in situ volume can lead to significant inaccuracies in the estimates of the LNAPL saturation and volume, and may not provide information about the LNAPL distribution patterns. Application of PITTs can provide better information about the in situ LNAPL conditions at some sites. Unlike discrete soil sampling, a PITT allows a spatially integrated examination of the in situ volume.

PITT is an intensive characterization approach that employs the injection of multiple tracer chemicals, such as aliphatic alcohols, into the subsurface under controlled conditions in which the groundwater flow rate and direction are known. Typically, one of the tracers does not react or partition to the LNAPL, while the others partition into the LNAPL at varying rates. During testing, the appearance of these tracers at downgradient extraction wells at different rates is measured dynamically. Because each tracer has specific partitioning characteristics with the aquifer material and LNAPL within the smear zone, these data can be used to develop an accurate (estimated to be +/-25%) estimate of LNAPL saturation in the subsurface. The data developed from a PITT can then be used to optimize the remedial design and SEAR operations. Figure 4 is a schematic of a PITT.

During the PITT conducted at the Chevron, Cincinnati site, controlled conditions were created through the automation of injection and extraction wells along with the injection of fresh water into peripheral wells to

Figure 4. Schematic of a Partitioning Interwell Tracer Test



Source: Radian International and Duke Engineering Services, 1999

create a constant hydraulic head. The partitioning characteristics within the smear zone were established through rigorous bench testing. The tracers used for PITT testing at this site included various aliphatic alcohols. PITT testing identified typical LNAPL saturation in the range of 1 to 5% within the smear zone. Figure 1 in Section 2 of this case study shows an areal photograph of the PITT test area.

5.1.2 CPT/ROST™ Pilot Test

Petroleum-based fuels, such as gasoline, diesel, and kerosene, and other polyaromatic hydrocarbons, such as coal tar and creosote, contain compounds that fluoresce when excited by ultraviolet light. A soil sample contaminated with petroleum substances will exhibit fluorescence intensity that is proportional to the contaminant concentration. The concentration of the hydrocarbon fraction in an unknown sample can be determined by comparing its fluorescence intensity to that of calibration standards.

The ROST™ detects the presence and quantitates the amount of aromatic petroleum hydrocarbons by the laser-induced fluorescence in the sample. It is a tunable dye laser-induced fluorescence system designed as a field screening tool for detecting petroleum hydrocarbons in the subsurface. The ROST™ system uses a pulsed laser coupled with an optical detector to make fluorescence measurements via optical fibers. The measurement is made through a sapphire window on a probe that is pushed into the ground with a truck-mounted cone penetrometer (CPT). As the instrument is advanced through the soil, hydrocarbons are detected in situ. The ROST™ technology is intended to determine both the quantity, by measuring total fluorescence, and type, by measuring the intensities of several different wavelengths of fluorescent light, of LNAPL. The direct measurements of fluorescence are typically calibrated against known standards generated via bench scale testing of soil-core and site-specific LNAPL samples.

The pilot test of CPT/ROST™ at the Chevron Cincinnati Facility consisted of 15 pushes in locations where PITT injection, extraction, and monitoring wells were being installed. The pushes were advanced to depths ranging from 36 to 40 feet bgs (through the smear zone) during which geophysical measurements (based on CPT tip resistance and sleeve friction) were made concurrently with fluorescence measurements. Fluorescence measurements were converted to percent saturation measurements based on calibration data from soil-core samples collected concurrently in some locations. Based on the data from the pilot test, the vendor concluded that CPT/ROST™ was capable of semi-quantitatively delineating the vertical extent of LNAPL within the smear zone. It was capable of determining minimum, maximum, and average LNAPL saturation at a very fine frequency (less than 0.5 foot). However, the study concluded that CPT/ROST™ can only provide accurate measurements of percent saturation if reference samples are taken over a wide range of concentrations and if various soil types and LNAPL types are used to calibrate the ROST™ for the specific site. The vendor noted that, in some cases, two or more

adjacent ROST™ pushes may be required in locations where quantitative measurements of LNAPL saturation are required.

Based on the results of the PITT and the CPT/ROST™ pilot tests, the vendor concluded that the extent of site-wide LNAPL could be investigated at the site using CPT/ROST™ as the primary characterization tool, supported by a program of soil-core testing and LNAPL sampling to calibrate the CPT/ROST™. In addition, this testing also resulted in a better understanding of the conditions within the smear zone at the PITT test site, such as the following:

- The vertical boundaries of the smear zone appeared to be distinct (a sharp increase in LNAPL saturation within 1 -2 feet)
- Average LNAPL saturation within the saturated zone is about 3.5% with some strata containing an average of as much as 6 – 8%
- Based on ROST™ data (the PITT test used at this site was not capable of measuring LNAPL saturation in the unsaturated zone), average LNAPL saturation within the unsaturated zone appeared to be similar to that in the saturated zone (average of about 3.5%); however, higher saturations (as high as 13%) were identified in certain strata, most significantly directly above the water table
- Aquifer materials were heterogeneous in both vertical and horizontal dimensions
- LNAPL saturation within the smear zone was less than expected (1 – 5%)

5.2 ADDITIONAL BENCH-SCALE STUDIES

Additional bench-scale studies, including a LNAPL characterization bench study, a film drainage and wettability characterization bench study, and a phase behavior testing of surfactants bench study, were conducted to provide further information to evaluate the feasibility of using SEAR at the site.

5.2.1 LNAPL Characterization Bench Study

A characterization of LNAPL samples collected from the Chevron Cincinnati Facility was conducted to provide data that could be used to develop the conceptual design for SEAR and the other remedial alternatives for the site. Some of the results of these analyses were presented previously in this report, in

Table 1. This information was used as a basis to select surfactants that would potentially be capable of achieving ultra-low interfacial tensions and ultra-high contaminant solubilization of the LNAPL at the site.

5.2.2 Film Drainage and Wettability Characterization Bench Study

Centrifuge experiments were conducted to better quantify the effect of naturally occurring film drainage and to determine the wettability of the aquifer material in the presence of the LNAPL at the site. The results of this testing concluded that when the groundwater level at the site is low, the LNAPL present in the smear zone above the water table likely will drain to the water table to form a free-phase LNAPL layer, which is consistent with the “pancake” model of LNAPL distribution. As noted in Section 3.2, new research into the behavior of LNAPL indicates that it may follow an different model that is based on the capillary forces that soil exerts on water and LNAPL in addition to density differences.

Wettability testing was used to provide data about how LNAPL reacts with and flows within the aquifer material at the site. The results of this testing suggest that LNAPL could be located in inaccessible pores in types of soil with narrow pore spaces within the aquifer, potentially constraining the effectiveness of conventional pump and treat as well as SVE. This fact suggested that the use of anionic surfactants, which can be used to change the aquifer wetting characteristics, could be used to increase contaminant recovery efficiencies at the site.

5.2.3 Phase Behavior Testing of Surfactants Bench Study

Phase behavior experiments were conducted to design and select a surfactant formulation with the most desirable behavior (most rapid mixture equilibrium; low viscosity of the surfactant and contaminant-rich microemulsion; and the absence of liquid crystals, gels, and emulsions) in the presence of the site LNAPL. Table 5 lists the commercial and chemical names of the surfactants that were tested in these experiments along with their manufacturer and type.

These seven different surfactants were used to prepare 25 different surfactant formulations, which were tested on the site LNAPL by mixing each formulation with site LNAPL and groundwater, agitating for set periods of time, and measuring the characteristics of the resulting mixture. In addition, secondary butanol (2-butanol) was incorporated as a cosolvent into some of the surfactant configurations. Calcium chloride, an electrolyte, was also incorporated into some of the surfactant configurations to control contaminant solubilization and interfacial tension reduction. Each configuration was tested with pure-phase site LNAPL. The following two surfactant formulations were identified as having the most desirable characteristics (all percentages shown are percent weight):

- Mixture of 4% Alfoterra 123-4-PO sulfate, 8% 2-butanol, and 0.5% Emcol-CC-9, and calcium chloride

- Mixture of 4% Alfoterra 123-4-PO sulfate, 8% 2-butanol, and calcium chloride

Table 4. Surfactants Tested in Phase Behavior Experiments

Commercial Name	Chemical Name or Description	Manufacturer	Type
Alfoterra 123-4-PO sulfate	beta-Branched, alcohol polypropoxy sulfate	Condea Vista	Anionic
Alfoterra 123-8-PO sulfate	beta -Branched, alcohol polypropoxy sulfate	Condea Vista	Anionic
Alfoterra 145-4-PO sulfate	beta -Branched, alcohol polypropoxy sulfate	Condea Vista	Anionic
Emcol CC-9	Polypropoxy tertiary amine (MW 600)	Witco	Cationic
Emcol CC-42	Polypropoxy tertiary amine (MW 2500)	Witco	Cationic
Ethoquad O/12	Bis-(2hydroxyethyl)oleyl amine (MW 403)	Akzo Nobel	Cationic
LB-65 (Non-ionic)	Butanol polypropoxylate (MW 340)	Union Carbide	Non-ionic

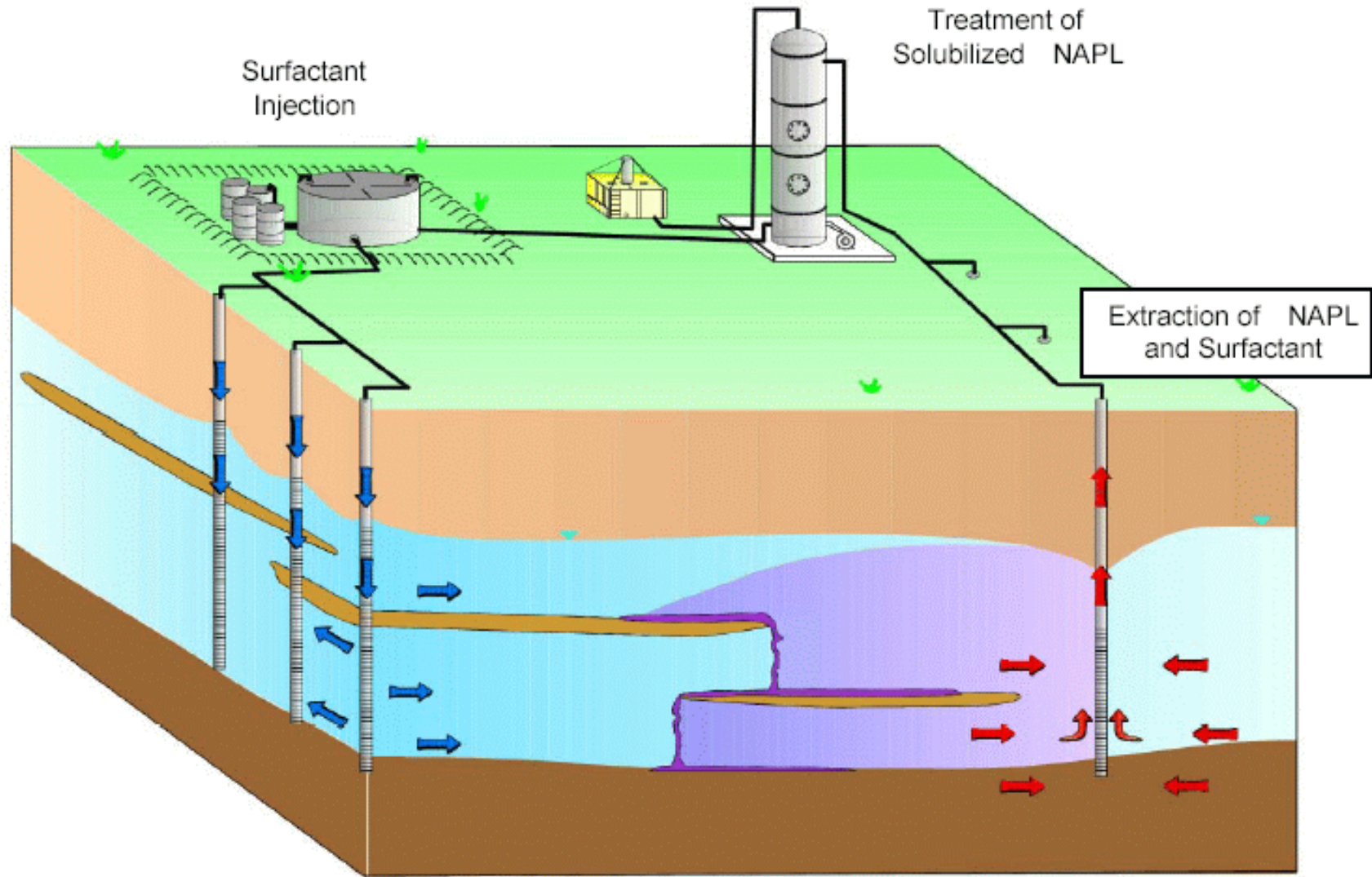
Source: Radian International and Duke Engineering & Services, 2000

Both of these formulations had equilibrium times on the order of 10 to 60 minutes, high contaminant solubilization, and low microemulsion viscosity. These surfactant configurations were recommended for soil column experiments to validate their performance under site subsurface conditions. Information about whether soil column experiments were conducted was not provided.

5.3 DESCRIPTION OF SEAR TECHNOLOGY [1,3,4]

Surfactants are surface active agents that have two different chemically active parts, a hydrophilic head and a hydrophobic tail. Thus, they exhibit solubility in both water and oil. It is this unique property that allows these agents to greatly increase the solubility of nonaqueous-phase liquids (NAPLs) in water for NAPL removal by enhanced solubilization, and also to greatly reduce the interfacial tension between the NAPL and water phases for NAPL removal by enhanced mobilization. SEAR involves the injection of a surfactant solution consisting of surfactant, electrolyte, cosolvent (i.e., alcohol), and water. Surfactant flooding is followed by water flooding to remove injected chemicals and solubilized or mobilized contaminants remaining in the aquifer. The extracted fluids are treated aboveground to separate the NAPL-phase and dissolved-phase contaminants for disposal. The surfactants can be recovered for reinjection if desired. A conceptual illustration of the SEAR process is shown in Figure 5.

Figure 5. Conceptual Model of Surfactant Enhanced Aquifer Remediation



Source: Naval Facilities Engineering Service Center, 2001.

Based on the results of the studies described in Sections 5.1 and 5.2, other characterization work conducted at the site, and the assumption that 8 million gallons of LNAPL remained at the site, a conceptual design for a SEAR system was developed. The conceptual design assumed that surfactant injection would take place only when the site water table was low and much of the LNAPL trapped in the smear zone had drained and collected on top of the water table. It assumed that such an approach would minimize the total volume of the treatment area, thereby reducing the volume of surfactant required.

Since surfactant was estimated to be the largest cost element in SEAR, this approach was expected to minimize the overall remediation costs. However, this assumption is based on the “pancake” model of LNAPL distribution, which recent research has shown may not accurately describe its behavior. The characterization and design activities described in this report were conducted before the current model was widely accepted, and were based, in part, on the “pancake” model. The effects of applying the current model to the test results and design assumptions described here have not been assessed. The LNAPL models are described in more detail in Section 3.2.

The SEAR conceptual design was geared toward maximizing LNAPL recovery and reducing residual LNAPL saturation to between 0.5 and 1%. The design involved conducting SEAR in 500-foot-long, 100-foot-wide panels; each panel having between 30 and 50 central injection wells (spaced 10 to 15 feet on center) and a similar number of extraction wells. One of the two surfactant formulations identified during Phase Behavior Testing would be injected to mobilize the LNAPL.

The injection/extraction system was designed as a dual-line system, in which a row of central injection points for surfactant is placed between two rows of extraction points situated parallel to the injection points, 50 feet away on either side. The design used peripheral wells to inject clean water to provide hydraulic control by raising the hydraulic head outside of the treatment area, inducing groundwater flow inward toward the extraction wells. The design also considered (but did not incorporate) that injected polymers, foams, or water injected below the surfactant flood could be used to minimize the volume of surfactant wasted due to downward channeling beneath the smear zone.

The groundwater extracted from the SEAR operations would contain surfactant, mobilized LNAPL, and dissolved contaminants. The options considered for managing the groundwater extracted during SEAR implementation included treatment and discharge to surface water, and treatment and reuse as injection water in the SEAR application. Treating the extracted fluid containing LNAPL, surfactant, and contaminated groundwater generated during SEAR to a point where it could be discharged to the river was deemed to be uneconomical (estimated to require reducing contaminant concentrations by three to six orders of magnitude). The system was assumed to be required to meet the same discharge

requirements as the existing site P&T system. Therefore, the conceptual design assumed that extracted groundwater would be treated to remove more than 95% of hydrocarbons and then reinjected. Detailed design of a treatment train for the extracted groundwater was not conducted, but the CMS indicated that such a treatment train could include phase separation followed by macroporous polymer extraction (MPPE). Additional information supporting these assumptions, specific cost estimates, and design details were not available in the references used for this report.

As a remedial alternative in the groundwater CMS, SEAR was incorporated with ongoing groundwater containment through pump and treat for hydraulic control, institutional controls, and SVE. This alternative represented the most aggressive approach evaluated for the site in the CMS. Hydraulic containment and institutional controls (which were not specifically described in the CMS) would be used to continue to minimize off-site migration of contaminants and to minimize impact on future site tenants. SEAR and SVE would be used in conjunction during periods when the groundwater table was seasonally low. SEAR would be used to flush most of the LNAPL from the saturated zone and remove the free-phase LNAPL, while SVE would be used to remediate the residual soil contamination in the vadose zone. SEAR would be implemented in panels; each treated for a few weeks, after which time the operation would move to the next downgradient panel. This process would extend over several low groundwater seasons, progressing downgradient until the entire site was treated. SVE would be installed and operated immediately after SEAR was completed in a particular panel until it became ineffective (estimated in the CMS to be approximately eight years).

5.4 CMS EVALUATION OF SEAR TECHNOLOGY [1,5,6]

The following discussion summarizes the evaluation of the SEAR technology discussed in the CMS. The time to reach final cleanup goals and present value costs included in the CMS are estimates. The groundwater CMS evaluated the remedial alternative incorporating SEAR based on the following criteria:

Time to Reach Final Cleanup Goals – The remediation approach incorporating SEAR was the most aggressive source removal approach evaluated and the only one that was expected to remove residual LNAPL saturation in the smear zone. The conceptual design included a combination SEAR/SVE system that would be expected to reduce residual LNAPL contamination by 99% or better, after which hydraulic control and monitored natural attenuation would be used to reduce groundwater contaminants to below final cleanup goals (MCLs). The CMS estimated that this system would take eight years to implement across the entire site. Using this assumption, dissolution modeling conducted as part of the CMS suggested that it would take an additional 93 years for benzene (which is the groundwater contaminant currently present at the highest multiple of its cleanup goal) in groundwater to dissipate (solely through

dissolution) to concentrations less than cleanup goals. The CMS includes an estimate of 458 years to achieve cleanup goals using only hydraulic control. This value of 458 years does not include natural losses in the vapor phase, which were later found to be significant.

Present Value Cost – The CMS contains an estimate of the total present value cost (incorporating an assumed 1.94 percent effective annual discount rate) to reach cleanup goals at the site using a remedial approach incorporating SEAR compared to the total costs for other alternatives. The total present value cost estimate for using the SEAR/SVE remedial approach in the CMS to reach groundwater cleanup goals for the site is \$150 million, compared to a total present value costs of \$51 million to reach groundwater cleanup goals using no source treatment with only ongoing hydraulic control and MNA. The total cost for the SVE/SEAR approach includes the capital and O&M costs associated with the SVE/SEAR system, as well as the on-going containment portion of the alternative. The capital cost of the SVE/SEAR system, estimated at \$90 million, was not discounted and assumed to be incurred in the first year of remedy implementation. The present worth of O&M for this system is \$16 million over 8 years; however, this O&M value only includes the SVE system. The O&M of the SEAR portion was assumed to be incurred in the first year of its implementation to simplify the calculation of this cost, and was included in the capital cost for this alternative. For the containment portion of the alternative, free product recovery was estimated to continue for 16 years with approximately 30,000 gallons being removed each year. The cost for free-product disposal is currently \$0.67/gallon. It was also assumed that the fluidized bed reactors would need to be replaced every 25 years at an estimated cost of \$2.3 million with the first replacement taking place in 10 years. This cost estimate is for a full-scale SEAR system. Actual cost data for the SEAR testing conducted at this site are not available. Table 5 summarizes these costs. Additional details on the costs for SEAR application were not provided in the references used for this report.

Table 5

Present Worth of All Costs for Two Remedial Approaches at the Chevron, Cincinnati Facility

Remedial Approach	Present Worth (\$ Millions)				
	Initial Source Removal		Ongoing Site Operations	Additional Fixed Costs ¹	Total
	Capital	Operation and Maintenance			
Hydraulic Containment and MNA	0	0	49	1	50
SVE, SEAR, Hydraulic Containment, and MNA	90	16	42	1	150

- Additional fixed costs are described in the GWCMS, Appendix B.

Source: GWCMS, 2001

Cost Sensitivity to Effects of Biodegradation Rate And Groundwater Velocity – Effects of biodegradation of groundwater contaminants was not factored into the CMS analysis. The CMS concluded that, although biodegradation may occur at the site, it would have little impact on the present worth costs because biodegradation generally only affects duration far in the future when the changes in discounted value are minimal. It further stated that biodegradation in areas with LNAPLs was expected to be minimal, because of a lack of electron acceptors necessary for bioremediation. Additional details on this assumption were not provided in the references used for this report.

The CMS based its analysis on the effects of groundwater velocity on an assumed groundwater flow velocity of 4 feet per day, but acknowledged that the groundwater velocity in some areas of the site may be slower. The value of 4 feet per day reflects nearby groundwater pumping. However, the CMS concluded that, although a slower groundwater velocity than what was assumed in the dissolution model (4 feet/day) would increase the time needed to reach cleanup goals via dissolution, adding additional costs so far out in the future would have minimal effects on the present worth cost.

Compatibility with Site Redevelopment – Currently, there are plans to redevelop the site for mixed commercial, industrial, and recreational uses. The plans assume that groundwater hydraulic control will be ongoing during and after site redevelopment (that is, groundwater will not be required to meet final cleanup goals prior to beginning site redevelopment). The CMS concluded that if the SEAR/SVE approach were implemented, site redevelopment could not occur until the remedy was completed. The eight-year schedule for SEAR/SVE was based on the time needed to complete infrastructure upgrades, application of SEAR/SVE, and site plans for redevelopment. The estimated time to implement SEAR alone at the site was 5 years.

6.0 OBSERVATIONS AND LESSONS LEARNED

General

The CMS did not recommend SEAR for remediation of the Chevron Cincinnati Facility because this remedy could not be completed in a reasonable time frame (the remedial approach including SEAR would require 100 years), it was more expensive than an alternative remedy (\$150 million present worth for a remedial approach including SEAR vs. \$50 million for hydraulic containment and MNA), and the SEAR technology had not been demonstrated on the scale needed at this site. Based on the above evaluations, the CMS recommended that remediation of groundwater at the site be conducted through ongoing hydraulic containment using pump and treat, rather than implementing source removal, such as the SEAR/SVE alternative.

The data presented for cost and time for treatment are from the CMS. Different assumptions or methodologies may have resulted in different conclusions. Although the CMS did not recommend SEAR at the Chevron Cincinnati Facility, the evaluation of SEAR at this site resulted in a number of observations and lessons learned about this technology that may be helpful when SEAR is evaluated at other sites. For example:

PITT and CPT/ROST™ [3]

- PITT testing was conducted to provide a basis for comparing the performance of CPT/ROST™ in accurately measuring the vertical and horizontal extent of LNAPL saturation at the site. PITT proved capable of estimating the percent LNAPL saturation within the saturated portion of the smear zone. Although PITT is capable of characterizing the unsaturated zone using gas tracers, this type of characterization was not used.
- Data from the CPT/ROST™ pilot test suggested that this technology, as it was applied during the testing, was only capable of semi-quantitatively delineating the vertical extent of LNAPL within the smear zone. In order to achieve more accurate measures of LNAPL saturation using this technology, a more comprehensive calibration approach or duplicate samples would be needed.

SEAR [1,4,5,6]

- The conceptual model for the LNAPL source removal using SEAR assumed an LNAPL volume of 8 million gallons and an average benzene mole fraction of 0.4%. The estimate of the LNAPL

volume was based on an area of 200 acres, a smear zone thickness of 10 feet, an average LNAPL saturation of 4%, and a soil porosity of 0.3. The estimate of 8 million gallons of LNAPL was based on the “pancake” model of LNAPL behavior in the subsurface. Subsequent estimates based on a different model indicated that the volume of LNAPL was significantly less. As of June, 2004, the estimate for residual LNAPL at the site was 3.5 million gallons.

- Bench-scale studies concluded that SEAR potentially could be used to reduce LNAPL saturation at the site to less than 1% residual saturation through mobilization and solubilization of LNAPL using a surfactant formulation.
- Bench-scale studies that evaluated surfactant formulations and their interactions with LNAPL from the site identified a surfactant formulation, containing proprietary anionic and cationic surfactants, a cosolvent (2-butanone), and an electrolyte (calcium chloride), that was optimized for SEAR treatment at this site. However, the bench-scale study concluded that soil column testing would be necessary to determine whether the surfactant formulation would behave adequately during in situ SEAR.
- The conceptual model for LNAPL source removal using SEAR assumed that SEAR would be conducted during periods when groundwater at the site was relatively low, minimizing the volume of subsurface groundwater that would need to be treated. Since the surfactant cost was expected to be the largest cost component of SEAR, such an approach was expected to minimize cost. However, SVE would need to be used in conjunction with SEAR because SEAR would not treat the contaminated vadose zone during low groundwater periods.
- The conceptual model for LNAPL source removal using SEAR was based on the assumption that the resulting extracted LNAPL/groundwater emulsion could be treated using aboveground technologies to adequately recover surfactant and to reduce contaminant levels to the extent that the treated water could be reinjected. The CMS noted that the feasibility of this assumption needed to be proven.
- The CMS noted that the implementation of SEAR in the piecemeal manner (working its way downgradient) described in the conceptual design could delay redevelopment of the site because of the dense network of wells required. SEAR would have to be completed in any given area before site redevelopment could begin. In the case of this site, the most downgradient contaminated area, which would have to be treated last under the conceptual design in the CMS, would benefit from the earliest development.

- Site contacts stated that, when SEAR is used to remove LNAPL from large sites, such as refineries and tank farms, it is generally applied only to the “hot zone”. Planned applications at other sites are designed to use SEAR to remove LNAPL “hot zones” and create an “attenuation zone” where benzene concentrations will be reduced.

7.0 SITE CONTACTS

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