**CROWTM PROCESS APPLICATION FOR SITES
CONTAMINATED WITH LIGHT NON-AQUEOUS PHASE
LIQUIDS AND CHLORINATED HYDROCARBONS**

Final Report

**By
L. A. Johnson Jr.**

June 2003

**Work Performed Under Cooperative Agreement
DE-FC26-98FT40322 Task 1.1**

**For
U.S. Department of Energy
National Energy Technology Laboratory
Morgantown, West Virginia**

**By
Western Research Institute
Laramie, Wyoming**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agencies thereof, nor any of its employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe on privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

Western Research Institute (WRI) has successfully applied the CROWTM (Contained Recovery of Oily Wastes) process at two former manufactured gas plants (MGPs), and a large wood treatment site. The three CROW process applications have all occurred at sites contaminated with coal tars or fuel oil and pentachlorophenol (PCP) mixtures, which are generally denser than water and are classified as dense non-aqueous phase liquids (DNAPLs). While these types of sites are abundant, there are also many sites contaminated with gasoline, diesel fuel, or fuel oil, which are lighter than water and lie on top of an aquifer.

A third site type occurs where chlorinated hydrocarbons have contaminated the aquifer. Unlike the DNAPLs found at MGP and wood treatment sites, chlorinated hydrocarbons are approximately one and a half times more dense than water and have fairly low viscosities. These contaminants tend to accumulate very rapidly at the bottom of an aquifer. Trichloroethylene (TCE) and perchloroethylene, or tetrachloroethylene (PCE), are the major industrial chlorinated solvents that have been found contaminating soils and aquifers.

The objective of this program was to demonstrate the effectiveness of applying the CROW process to sites contaminated with light non-aqueous phase liquids (LNAPLs) and chlorinated hydrocarbons. Individual objectives were to determine a range of operating conditions necessary to optimize LNAPL and chlorinated hydrocarbon recovery, to conduct numerical simulations to match the laboratory experiments and determine field-scale recoveries, and determine if chemical addition will increase the process efficiency for LNAPLs.

The testing consisted of twelve TCE tests; eight tests with PCE, diesel, and wood treatment waste; and four tests with a fuel oil-diesel blend. Testing was conducted with both vertical and horizontal orientations and with ambient to 211 °F (99 °C) water or steam. Residual saturations for the horizontal tests ranged from 23.6% PV to 0.3% PV. Also conducted was screening of 13 chemicals to determine their relative effectiveness and the selection of three chemicals for further testing.

TABLE OF CONTENTS

	<u>Page</u>
LIST OF TABLES AND FIGURES	v
EXECUTIVE SUMMARY	vii
INTRODUCTION	1
OBJECTIVES	1
OPERATING PROCEDURES	2
Test Apparatus and Preparation	2
Experimental Description	3
RESULTS	6
Modeling	8
CONCLUSIONS	10
REFERENCES	11

LIST OF TABLES AND FIGURES

<u>Table</u>	<u>Page</u>
1. LNAPL and Chlorinated Solvent Physical Properties	12
2. Trichloroethylene Slim-Tube Reactor Test Summary	13
3. Chlorinated Hydrocarbon One-Dimension Flushing Tests	14
4. LNAPL One-Dimensional Flushing Tests	15
5. Tested Chemicals	16
6. One-Dimension Simulations of Chemical Enhanced Flushing	17

<u>Figure</u>	<u>Page</u>
1. Elevated-Temperature Reactor System	18
2. Ambient-Temperature Slim-Tube Reactor System	19
3. TCE Residual Saturation versus Temperature	20
4. Aqueous Phase Total Organic Carbon for CROW 179	20
5. Aqueous Phase Total Organic Carbon for CROW 196	21
6. PCE Residual Saturation versus Temperature	21
7. Aqueous Phase Total Organic Carbon for CROW 195	22
8. Diesel Residual Saturation versus Temperature	22
9. Bell Saturation Reduction versus Temperature	23
10. Bell Residual Saturation versus Temperature	23

LIST OF TABLES AND FIGURES (continued)

<u>Figure</u>	<u>Page</u>
11. Fuel Oil-Diesel Blend Residual Saturation versus Temperature	24
12. Chemical Addition Tests Saturation Reduction versus Temperature	24
13. Chemical Addition Tests Residual Saturation versus Temperature	25
14. Aqueous Phase Total Organic Carbon for CROW 220	25
15. TCE Modeling Comparison	26
16. Relative Permeability Curve	26

EXECUTIVE SUMMARY

Western Research Institute (WRI) has successfully applied the CROW™ (Contained Recovery of Oily Wastes) process at two former manufactured gas plants (MGPs), and a large wood treatment site. The three CROW process applications have all occurred at sites contaminated with coal tars or fuel oil and pentachlorophenol (PCP) mixtures, which are generally denser than water and are classified as dense non-aqueous phase liquids (DNAPLs). While these types of sites are abundant, there are also many sites contaminated with gasoline, diesel fuel, or fuel oil, which are lighter than water and lie on top of an aquifer.

A third site type occurs where chlorinated hydrocarbons have contaminated the aquifer. Unlike the DNAPLs found at MGP and wood treatment sites, chlorinated hydrocarbons are approximately one and a half times more dense than water and have fairly low viscosities. These contaminants tend to accumulate very rapidly at the bottom of an aquifer. Trichloroethylene (TCE) and perchloroethylene, or tetrachloroethylene (PCE), are the major industrial chlorinated solvents that have been found contaminating soils and aquifers. Chlorinated hydrocarbon sites include military facilities, railroad yards, and other locations where large numbers of trucks, airplanes, locomotives, and other vehicles have been routinely serviced.

The objective of this program was to demonstrate the effectiveness of applying the CROW process to sites contaminated with light non-aqueous phase liquids (LNAPLs) and chlorinated hydrocarbons. Individual objectives were to determine a range of operating conditions necessary to optimize LNAPL and chlorinated hydrocarbon recovery, to conduct numerical simulations to match the laboratory experiments and determine field-scale recoveries, and determine if chemical addition will increase the process efficiency for LNAPLs.

The testing consisted of twelve TCE tests; eight tests with PCE, diesel, and wood treatment waste; and four tests with a fuel oil-diesel blend. Testing was conducted with both vertical and horizontal orientations and with ambient to 211 °F (99 °C) water or steam. Residual saturations for the horizontal tests ranged from 23.6% PV to 0.3% PV. Also conducted was screening of 13 chemicals to determine their relative effectiveness and the selection of three chemicals for further testing.

Temperature was the most important factor in remediating LNAPL or chlorinated hydrocarbon contamination. Gravity and specific gravity differences between water and the LNAPL or chlorinated hydrocarbon were important in determining the orientation that produced the best flushing results, horizontal for chlorinated hydrocarbons and vertical for LNAPL. Removal of TCE and PCE was greater than 99% for tests near or above steam temperature with significantly poorer recovery at lower temperatures. The tests with diesel, wood treatment waste, and fuel oil-diesel blend all showed significant reduction in organic saturation with increasing flushing temperature. At steam temperature, diesel removal exceeded 90%. The fuel oil-diesel blend was a viscous

LNAPL that required higher temperatures to have any significant removal and chemical addition enhanced the removal by three to four times at lower flushing temperatures compared to nonchemical addition tests.

INTRODUCTION

Western Research Institute (WRI) has successfully applied the CROW™ (Contained Recovery of Oily Wastes) process at two former manufactured gas plants (MGPs), and a large wood treatment site. The three CROW process applications have occurred at sites contaminated with coal tars or fuel oil and pentachlorophenol (PCP) mixtures, which are denser than water. These organics are classified as dense non-aqueous phase liquids (DNAPLs). While these types of sites are abundant, there are also many sites contaminated with gasoline, diesel fuel, or fuel oil, which are lighter than water and lie on top of an aquifer. These are classified as light non-aqueous phase liquids (LNAPLs).

A third site type occurs where chlorinated hydrocarbons have contaminated the aquifer. Unlike the DNAPLs found at MGP and wood treatment sites, chlorinated hydrocarbons are approximately one and a half times denser than water and have fairly low viscosities. These contaminants tend to accumulate very rapidly at the bottom of an aquifer. Trichloroethylene (TCE) is a common chlorinated hydrocarbon found contaminating aquifers. Perchloroethylene, or tetrachloroethylene (PCE), is another chlorinated solvent that has been used extensively in the dry-cleaning industry and has also been found contaminating soils and aquifers.

Chlorinated hydrocarbons have been used extensively as a cleaning solvent at military facilities, railroad yards, and other locations where large numbers of trucks, airplanes, locomotives, and other vehicles have been routinely serviced. Used chlorinated hydrocarbons and waste motor oils were often disposed of in pits. There are approximately 300 military bases in the United States and most may have underground contamination. In addition, numerous railroad yards and dry-cleaning sites have similar types of groundwater contamination.

Laboratory investigation of dissolution of TCE suggests it is a slow process and may take approximately 200 pore volumes of water flushing for complete TCE removal (Guarnaccia et al., 1992). Adding heat may decrease the number of pore volumes necessary for displacing or dissolution of the TCE. Similar requirements are expected for PCE, which has a higher viscosity, specific gravity, and boiling point and lower solubility compared to TCE.

OBJECTIVES

The objective of this program was to demonstrate the effectiveness of applying the CROW process to sites contaminated with LNAPLs and chlorinated hydrocarbons. Individual objectives were to determine a range of operating conditions necessary to optimize LNAPL and chlorinated hydrocarbon recovery, to conduct numerical simulations to match the laboratory experiments and determine field-scale recoveries, and determine if chemical addition will increase the process efficiency for LNAPLs.

OPERATING PROCEDURES

Test Apparatus and Preparation

WRI has two reactor systems to conduct laboratory simulations. The high-temperature tube reactor system has historically been used to conduct CROW flushing tests to determine optimal operating conditions and temperatures for field application. More recently, WRI has used a slim-tube flow test apparatus to study the effects of gas trapping on oil recovery. This system was also used to study the flow characteristics of chlorinated hydrocarbon liquids.

A tube reactor system used for the one-dimensional displacement tests is a stainless steel reactor tube, 3.8 in i.d. x 33 in (9.7 cm x 83.8 cm) long, packed with sand (Figure 1). Water, steam, or organic fluids are injected at one end of the tube, and fluids are produced from the other end. The tube is oriented vertically or horizontally within a series of insulated shield heaters. Auxiliary equipment includes inlet water injection and metering devices, a steam system, and production collection equipment. The entire system is instrumented and interfaced to a data acquisition computer that records temperatures and pressures every five minutes. Flow rates are preset on a calibrated metering pump and pressure is controlled by outlet valving.

Six internal reactor thermocouples are spaced approximately every 6 in (15 cm) within the center of the soil pack to monitor reactor/process temperatures. These thermocouples are also electronically paired with six wall-mounted thermocouples. Each pair is connected to an individual temperature controller and shield heater. This arrangement allows the reactor tube to operate isothermally or adiabatically. Steam, water, or organics are injected into the reactor by a positive-displacement metering pump. Water is injected through a heater to generate steam or hot water. Produced fluids are collected from the outlet of the reactor tube. The collection system pressure is maintained near atmospheric pressure by venting the product collection vessel to the atmosphere through a gas collection system.

Ambient-temperature experiments were conducted in the slim-tube flow test apparatus (Figure 2). The tubes were made from 1.9 in i.d. (4.8 cm), schedule-80 pipe, 48 or 120 in (121.9 or 304.8 cm) long. Oil and water injection and metering were done by two calibrated Ruska pumps. Static pressure transducers and gauges were used to measure the tube inlet pressure, the system back pressure, and the Ruska pump pressure. The injection fluid temperature was also measured at the top of the tube. All pressures and the injection fluid ambient temperature were monitored with the data acquisition system, and the data were stored at five-minute intervals. The oil and water injection rates were recorded manually from the Vernier scales on the Ruska pumps.

To prepare for packing, the elevated-temperature tube bulk volumes were determined by water displacement. For each test, unsieved 40–140 mesh silica sand was packed in each tube. Small amounts of water-soaked sand were added to fill the tube approximately 1 in (3 cm) at a time.

The placement of the internal thermocouples within the sandpack minimized vibration. A composite sample of the wet sand was extracted to determine the water content of the initial sandpack. From the weight of the sand and the sand density, the sandpack pore volume and porosity could be determined.

In the slim tubes, known quantities of dry sand and water were added and tamped to achieve the desired permeability. It was found that the achievable tube permeability varied with each sack of sand, and as sand was removed from a sack, the sand size distribution changed. Consequently, the amount of tamping had to be increased or decreased to obtain the desired permeability range. After the tube was packed to the top with sand, water was added until a thin film of water was maintained above the sandpack. The volume of water added during packing was the tube pore volume. From the tube pore volume and bulk volume, the sandpack porosity could be determined.

Experimental Description

Three slim-tube tests and twelve ambient- and elevated-temperature one-dimensional tube tests were conducted, and the effects of temperature, porosity, permeability, gravity, and injection fluid velocity on TCE contamination remediation were evaluated. One-dimensional tests were also conducted on soil contaminated with diesel, PCE, wood treatment waste from Bell Lumber and Pole, New Brighton, Minnesota (referred to as Bell), and a fuel oil-diesel blend (referred to as Blend). These materials were used to concentrate primarily on determining the effects of temperature. The physical properties of the organics are summarized in Table 1.

The first slim-tube apparatus test was conducted with a 120 in (304.8 cm) long tube. For this test, the tube was first flooded with water vertically from top to bottom. After steady-state flow was achieved and the tube pore volume was 100% saturated with water, TCE was injected vertically from top to bottom. When all the mobile water was displaced, water injection was reinitiated at ambient temperature and continued until organic production ended and residual TCE saturations were achieved.

The second and third TCE slim-tube apparatus tests were also conducted with a shorter, 48 in (121.9 cm) long tube. As in the first test, water was injected vertically downward. TCE was then injected until residual water saturation conditions were achieved. With TCE injection occurring, the tube was then laid down such that horizontal flow was initiated. After steady-state conditions occurred, horizontal water injection was reinitiated and continued until TCE recovery ended and residual TCE saturations were achieved. Ambient slim-tube TCE tests were conducted with permeabilities of 3.5, 11.2, and 17.8 Darcies (3.5, 11.1, and 17.5 μm^2) (Table 2).

All TCE, PCE, diesel, and the first two of the Blend elevated-temperature reactor tubes were prepared as follows. Water-soaked 40–140 mesh quartz sand was packed in a one-dimensional tube and waterflooded. Water injection was stopped and organic material was injected until residual

water saturation conditions were reached. Weights of the tube and material were recorded manually for each phase of packing and saturating. Volumes of water and organic material injected and produced were also measured. At that point, each tube was ready for the CROW process simulation phase. In the vertical orientated tests, the tubes were placed in the vertical position and water was injected at the bottom, flushing the contaminant to the top where it was collected. For horizontal tests, the reactor tube was placed on its side with water injected into one end and production out the other.

The tubes for the Bell and the other two Blend tests were prepared by mixing the organic with the water-wet frac sand prior to packing in the tube. This saturation method was switched because of problems using the saturation method on the first two Blend tubes. This was done because the consistency of the organics at room temperature caused problems with getting any type of uniform organic saturation in the tube. The tests were then conducted similar to those for the other organics.

For the majority of the TCE tests conducted in the elevated-temperature reactor system, water was injected at nominal temperatures of ambient and 140 °F to 172 °F (60 °C to 79 °C) until no more organic material was produced, signaling that residual conditions were achieved. Several of the tests used an ambient-temperature flush followed by an elevated-temperature flush. The elevated temperatures were chosen over a range of temperatures that might typically be applied in the field. The remaining TCE tests were conducted near or above the boiling temperature of TCE, 190 °F (88 °C). TCE test properties are given in Table 3.

Elevated-temperature TCE tests were conducted with the tube in both the vertical and horizontal position. With the tube in a vertical position, water or steam was injected into the bottom, with production occurring from the top of the tube. These tests were to evaluate the effects of gravity and the specific gravity differences between water and chlorinated hydrocarbons. The horizontal tests simulated the field injection-extraction profile.

For the PCE tests, water or low-quality steam was injected at nominal temperatures of ambient and 167 °F to 206 °F (74 °C to 96 °C). As with the TCE tests, several of the tests used an ambient-temperature flush followed by an elevated-temperature flush. Because of PCE's high boiling point, 250 °F (121 °C), higher temperatures were primarily targeted. As with the TCE, tests were conducted with the tube in both vertical and horizontal positions to evaluate the effects of gravity and specific gravity (Table 3).

Diesel tests were conducted similarly to the TCE tests. Earlier, WRI conducted four two-dimensional tests with diesel (Johnson et al., 1995). In these tests, water injection was conducted at ambient, 120 °F, and 160 °F (49 °C and 71 °C) with recoveries ranging from 14.6% to 55%. These early tests suggested that higher temperatures (approaching steam conditions) would be needed. For the diesel tests, after the saturation phase was completed, the final steamflooding and

diesel displacement phase was conducted with either horizontal or vertical orientation at ambient temperature or elevated temperatures of 196 °F to 218 °F (91 °C to 103 °C). As with prior series, some of the tests used an ambient-temperature flush followed by an elevated-temperature flush. This high-temperature range is expected to be near the maximum achievable in a shallow contaminated aquifer.

The tests conducted with the Blend used conditions similar to previous tests with injected water temperatures of ambient and 149 °F to 201 °F (65 °C to 94 °C) (Table 4). All Blend tests used an ambient-temperature flush followed by an elevated-temperature flush. A fuel oil-diesel blend was selected because of the high viscosity of the fuel oil. To create a pumpable material at ambient temperatures, addition of diesel was required. These tests evaluated ambient and steam conditions with vertical and horizontal organic displacement. Blend tests were conducted to provide a baseline for later chemical addition tests.

Testing with the Bell material consisted of water injected at nominal temperatures of ambient and 138 °F to 206 °F (59 °C to 96 °C) (Table 4). Most Bell tests used an ambient-temperature flush followed by an elevated-temperature flush. The contaminant in the Bell soil is a combination of fuel oil, creosote, and PCP and has a density very close to water (Table 1). Prior CROW studies have used the Bell material and a field-scale demonstration was conducted at the Bell facility (Mones et al., 1996; Johnson and Fahy, 2002).

After the completion of each test, the material was removed from the tube, and the water and organic contents were measured. Representative samples of the water and organic-contaminated sand were collected. These samples were analyzed using WRI standard operating procedures. The organic and water saturations of the samples were determined by Soxhlet extraction combined with azeotropic distillation. From the extraction results, the residual saturation conditions were determined for each test. When an ambient test was conducted prior to injecting hot water or steam, the residual organic content of the sandpack could not be measured directly between test phases. For these tests, residual organic content prior to elevated-temperature flooding was calculated by determining how much organic material was produced during the ambient- and elevated-temperature flooding and from the final residual organic saturation measured after completion of the tests.

Testing to evaluate the effectiveness of adding chemicals to the flushing system involved two setups. To screen a number of chemicals for use in the flushing, a jar-test procedure was used. The procedure involved placement of 20 g of solids and 400 g of liquid into a glass jar, placement of the jar onto a rocker arm shaker, and shaking the mixture for a minimum of 18 hours. The sample was then removed, allowed to settle, and a total organic carbon (TOC) sample was removed for analysis. The mixture, both solids and liquid, was then transferred to a boil flask with a magnetic stirrer. The mixture was then heated for a minimum of 18 hours at either a nominal 170 °F or 200 °F (77 °C or 93 °C) while stirred. The mixture was then allowed to cool and another liquid TOC sample was removed. The liquid was then decanted and the organic saturation of the sand was determined by

Soxhlet extraction. For these screening tests, clean 40–140 mesh frac sand and Bell organic was used. Clean sand was used to evaluate chemical uptake by solid material while the Bell-contaminated sand was used to evaluate organic removal. Thirteen chemicals, all surfactants, were evaluated by this method (Table 5).

To complete the testing, one-dimensional simulations were conducted using the elevated-temperature reactor system used in previous tests. Preparation and conduct of these tests were the same as previous tests with the exception of the addition of 1% chemical to the flushing stream for one PV of flush. All post-test sampling and analyses were the same as in previous tests. For these tests, Blend-contaminated sand was used with one of three surfactants (Table 6). Flushing temperatures used for these tests were ambient and 149 °F to 191 °F (65 °C to 88 °C) with the reactor tube in the vertical orientation.

RESULTS

Procedures were developed to conduct one-dimensional tube tests and evaluate the results. Tube bulk volume measurements, sand volumes, and injected and produced fluid rates and volumes were routinely measured in all tests. From these measurements, the porosity and initial organic saturations were calculated. Injection fluid pore volumes were also determined. Residual organic saturations were determined by Soxhlet extraction. From the initial and residual organic saturations, an organic reduction percentage was determined for each test. A material balance was done for each test to validate calculations and measurements.

The TCE reduction in the four vertical tests ranged from 48.2% at ambient temperature to 99.0% at 198 °F (92 °C), with respective residual saturations of 39.7% PV to 0.8% PV (Table 3). In comparison, the eight horizontal tests had organic reduction of 58.7% to 99.6% over the temperature range of ambient to 211 °F (99 °C). Residual saturations for the horizontal tests ranged from 23.6% PV to 0.3% PV. For both the vertical and horizontal tests near complete TCE removal was achieved near the boiling point of the TCE (Figure 3). At lower temperatures, lower residual saturations were produced in the horizontal tests. In addition to evaluating the temperature effects on TCE remediation, other conditions were also evaluated. The TCE tests suggest that porosity, permeability, and water injection velocity are not as important as temperature. However, the specific gravity difference between water and the chlorinated hydrocarbon did play an important role in the vertical movement of the TCE at lower temperatures. At higher temperatures, it appears that the TCE was in the vapor phase and therefore the vertical movement was not hindered by the specific gravity difference.

It was hoped that TOC measurements made on the water produced during the flushing would show the dissolution effects, particularly after the major portion of the TCE was displaced. Several pore volumes of water were flushed through TCE-contaminated sand in a manner similar to what might be expected to occur with time in a contaminated aquifer. Most of the tests showed the

anticipated TOC trend of starting at a high value then rapidly decreasing to a constant low value with a secondary trend when the flushing temperature was increased (Figures 4 and 5). This trend was used to determine when to terminate the tests.

Five horizontal and three vertical tests were conducted with PCE. Reductions in PCE concentrations over the ambient to near steam temperature varied between 50.8% and 99.0% for the vertical tests and 60.8% to 99.7% for the horizontal tests (Table 3). As with TCE, PCE residual saturations were similar for the horizontal and vertical tests conducted near steam temperature (Figure 6). Also, at lower flushing temperatures, the horizontal tests performed better than the vertical tests. The TOC trend for the PCE tests was similar but with values generally a factor of ten less than for TCE (compare Figure 7 with Figures 4 and 5). These lower TOC values were not unexpected since the solubility of PCE in water is one-fifth that of TCE.

Eight tests, two vertical and six horizontal, were conducted with diesel as the contaminant. These tests simulated remediation of aquifers contaminated with a LNAPL. The vertical tests had diesel reductions of 77.1% and 97.7% for ambient and 204 °F (95 °C) flushing temperatures (Table 4). The residual for these tests was 17.7% PV and 1.6% PV, respectively (Table 4 and Figure 8). The corresponding horizontal tests had average reductions of 65% and 87% with average residual saturations of 31% PV and 10% PV. The lighter than water specific gravity of the diesel benefitted the vertical configured tests. The TOC trend for the produced water resembled those for the PCE and TCE tests.

Testing with the Bell material consisted of one vertical and seven horizontal tests. Horizontal testing was concentrated on because the 0.99 specific gravity of the material is essentially the same as water. The saturation reduction for this series had a general trend of increasing reduction with increasing temperature, but there was a wide range of values for each given temperature set (Figure 9). The residual saturations also had a general trend but variation within each temperature region (Figure 10). The produced flushing water TOC content had the same trend as previous tests.

Four tests were conducted with the fuel oil-diesel blend. Each test was conducted with ambient-temperature flush followed by hot-water/steam flush. Three tests were conducted with vertical injection and one was conducted with horizontal injection. The horizontal and one vertical test used tubes prepared by the injection of the blend into a water-saturated sandpack. This method resulted in displacement of all the water, producing a 100% PV Blend saturation (Table 4). The total organic saturation resulted in higher than normal water injection pressures, intermittent plugging of the tube, and creation of an oil/water emulsion. The other two vertical tests used material prepared by mixing a predetermined amount of blend with water-wet sand prior to placement in the tubes. This method produced 50% PV or less organic saturations and resulted in better test operations. The vertical tests were conducted at ambient and nominal temperatures of 150 °F and 180 °F (66 °C and 82 °C), while the horizontal test was at ambient and 201 °F (94 °C). The variation in saturation

methods and operational problems produced inconsistent saturation reductions. The residual saturations for the tests did have the general trend of decreasing saturation with increasing temperature (Figure 11).

The preliminary chemical testing was jar tests to screen 13 chemicals to determine their relative effectiveness (Table 5). The chemicals were tested on two materials, a clean 40–140 mesh frac sand and the same sand contaminated with Bell organics. To start testing two control tests were conducted with only water and the two materials. To evaluate each chemical, tests were conducted with both materials and at nominal temperatures of 180 °F and 200 °F (83 °C and 93 °C). The screening tests consisted of 31 tests with sand and 44 tests with Bell-contaminated sand. Based on the contaminate removal, the chemical uptake on the clean sand, and the physical appearance of the chemical solution (was it a jelly or a flowable solution), three chemicals were selected for further testing (Table 6).

The contaminated material for the one-dimensional, chemical-augmented, flushing tests was frac sand mixed with the fuel oil-diesel blend prior to packing. For the tests, the three chemicals were injected as a one-percent-by-weight solution for one PV of flush (Table 6). Before the chemical was injected, three to five PV of ambient-temperature flush was conducted to establish flow. Tests were conducted at ambient temperature and nominal 150 °F and 180 °F (66 °C and 82 °C). All three chemicals significantly increased the removal of the Blend compared to the baseline test (Figure 12) with a lowering of the residual saturation for each temperature range (Figure 13). The baseline trendline in Figure 12 is believed to be erroneous since the initial saturation appears to be lower than the residual saturation for the test conditions. As expected, the TOC of the produced water followed the same trend as previous tests but was significantly higher because of the solubility of the chemicals in the aqueous phase (Figure 14).

Modeling

In conjunction with the laboratory testing, a numerical simulation study has also been initiated to match the laboratory experiments using WRI's thermal simulator (Mones et al., 1996). To date, the modeling has been confined to matching the results from horizontal TCE tests that were first waterflooded at ambient temperature until no more organic material was recovered and then hot water was injected until no more additional oil was recovered.

Applying heat to a contaminated aquifer through the CROW process can aid organic removal through viscosity reduction, reduction in the residual organic saturation, thermal expansion effects, improvement in the mobility ratio, and possible steam distillation effects (Farouq Ali, 1974). Numerous studies have also reported temperature effects on two-phase relative permeability in porous media, which is another important effect for improved remediation with the CROW process. Early thermal modeling suggested that temperature dependence of relative permeability must be incorporated into the model to reproduce experimental results (Coats et al., 1974). Review of the

early literature on the effects of temperature on relative permeability suggests the following (Nakornthap and Evans, 1986):

- Relative permeability can be expressed in terms of water saturation and irreducible water saturation.
- Relative permeability can be related to temperature if the irreducible water saturation has been found to increase with temperature.
- Relative permeability to oil increases and relative permeability to water decreases as temperature increases.
- Ignoring temperature-dependent relative permeability may lead to pessimistic organic recovery predictions.
- Residual organic saturation decreases with a temperature increase.

One-dimensional tests in which an ambient-temperature waterflood was conducted first, followed by an elevated-temperature water or steam injection period are believed to give the most realistic recovery expectations and also provide important confirmation of the improvement in organic removal with elevated temperature. In all of these experiments, significant additional removal was achieved after the organic-contaminated sandpack had been waterflooded to residual conditions.

To match the TCE test results, a one-dimensional simulation case was developed. Injection rates, temperatures, and initial organic saturations were closely matched. A relative permeability relationship that had been developed in earlier one-dimensional tube testing and that used unconsolidated sand was initially used to match the laboratory test results (Fahy et al., 1998). To match the ambient waterflood portion of the test, the residual organic saturation of the starting relative permeability relationship was adjusted by renormalizing the water saturation while maintaining the same organic and water relative permeability curve. An ambient residual oil saturation of 15% provided the match given in Figure 15. Model-predicted residual organic saturations at the end of the ambient waterflooding phase ranged from 18.4% to 23.9% on a pore volume basis throughout the simulated sandpack.

Without adjusting the relative permeability curves, the model predicted less additional organic removal at elevated temperature than was achieved in the one-dimensional tube test. On the basis of the findings summarized from Nakornthap and Evans (1986), to match the elevated temperature portion of the test, the residual organic saturation was allowed to decrease from 15% to 1%, and the elevated temperature irreducible water saturation was increased to 60% (Figure 16).

Model-predicted residual organic saturations at the end of the hot-water injection phase ranged from 2.7% to 5.9% on a pore volume basis throughout the simulated sandpack.

Matching efforts for the PCE and diesel tests are ongoing, initially using the relative permeability relationships developed here for matching the TCE ambient- and elevated-temperature tests.

CONCLUSIONS

Operating procedures were developed and tests conducted to simulate remediation of chlorinated hydrocarbon contamination and LNAPL remediation with and without chemical addition. Following are the conclusions based on the testing.

Temperature was the most important factor in remediating LNAPL and chlorinated hydrocarbon contamination. Other parameters such as porosity, permeability, and water injection velocity did not appear to be as important.

The TCE and PCE tests suggest that poor recoveries will be achieved unless flushing temperatures are near or above steam temperature. Removal of TCE and PCE was greater than 99% for tests with steam injection.

Tests with three LNAPLs, diesel, wood treatment waste, and fuel oil-diesel blend all showed significant reduction in organic saturation with increasing flushing temperature. At steam temperature, diesel removal exceeded 90%. The fuel oil-diesel blend, a viscous LNAPL, required higher temperatures to have any significant removal.

Gravity and specific gravity differences between water and the LNAPL or chlorinated hydrocarbon play an important role in their remediation. As expected, the heavier chlorinated hydrocarbons responded better to lateral flushing whereas the light LNAPL had better vertical response. As the specific gravity of the LNAPL approached the specific gravity of water, the difference between vertical and lateral response decreased.

Model simulations have resulted in an acceptable match of the test data.

Chemical addition enhanced the removal of viscous LNAPLs. Removal rates were three to four times greater for lower flushing temperatures for the three surfactants tested.

REFERENCES

Coats, K.H., W.D. George, Chieh Chu, and B.E. Marcum, 1974, Three-Dimensional Simulation of Steam Flooding. *SPEJ*, Dec. 1974, 573–592, Transaction AIME, 257.

- Fahy, L.J., C.G. Mones, L.A. Johnson Jr., and F.M. Carlson, 1998, Miscible/Immiscible Gas Injection Processes. Laramie, WY, WRI Report to DOE. WRI-98-R004, Morgantown, WV.
- Farouq Ali, S.M., 1974, Steam Injection in Secondary and Tertiary Oil Recovery Processes. Interstate Oil Compact Commission, p. 127.
- Guarnaccia, J.F., P.T. Imhoff, B.C. Missildine, M. Dostrom, M.A. Celia, J.H. Dane, P.R. Jaffe, and G.F. Pinder, 1992, Multiphase Chemical Transport in Porous Media. *EPA Environmental Research Brief*, EPA-600/5-92/002.
- Johnson, L.A. Jr., and L.J. Fahy, 2002, CROWTM Field Demonstration with Bell Lumber and Pole. Laramie, WY, WRI Report to DOE. WRI-02-R005, Morgantown, WV.
- Johnson, L.A. Jr., C.G. Mones, and K.P. Thomas, 1995, CROWTM Process Modeling. Laramie, WY, WRI Report to DOE. WRI-95-R012, Morgantown, WV.
- Mones, C.G., F.M. Carlson, L.J. Fahy, L.A. Johnson Jr., and R. Satchwell, 1996, CROWTM Process Modeling. Laramie, WY, WRI Report to DOE. WRI-95-R039, Cooperative Agreement DE-FC21-93MC30126 Subtask 1.1, Morgantown, WV.
- Nakornthap, K., and R.D. Evans, 1986, Temperature-Dependent Relative Permeability and Its Effect on Oil Displacement by Thermal Methods. *SPE Reservoir Engineering*, May 1986, pp. 230–242.

Table 1. LNAPL and Chlorinated Solvent Physical Properties

	TCE	PCE	Diesel	Blend	Bell
Molecular Weight	131.4	165.9	180	--	–
Boiling Point, °C	88	121	160-290	>150	>200
Specific Gravity					
15 °C	--	--	--	0.92	0.99
21 °C	1.47	--	0.85	–	–
25 °C	--	1.62	--	–	–
49 °C	1.42	--	0.82	–	0.98
60 °C	1.41	--	0.82	–	–
77 °C	--	--	--	0.88	0.95
94 °C	--	--	--	0.87	–
Viscosity, kPa-s					
15 °C	--	--	--	--	–
21 °C	0.56	0.88	2.47	–	11.6
49 °C	0.44	0.67	1.47	–	–
60 °C	--	0.54	--	99.1	3.1
94 °C	--	0.47	--	22.0	–

Table 2. Trichloroethylene Slim-Tube Reactor Test Summary

Test #	1	2	3
Tube Length, in (cm)	120 (304.8)	48 (121.9)	48 (121.9)
Tube Diameter, in (cm)	1.9 (4.8)	1.9 (4.8)	1.9 (4.8)
TCE Injection	Vertical	Vertical	Vertical
	Downward	Downward	Downward
Water Injection	Vertical	Horizontal	Horizontal
	Downward		
Permeability, D/ μm^2	11.2/11.1	17.8/17.5	3.5/3.5
Injection Temperature	Ambient	Ambient	Ambient
Porosity ^a , %	34.4	32.1	34.6
TCE Injection at Breakthrough, Pore Volume	0.58	0.75	0.55
Initial TCE Saturation ^b , wt %	14.3	16.6	16.9
Residual TCE Saturation ^b , wt %	10.7	7.4	6.1
TCE Reduction, %	25.2	55.3	64.0
Water Injection at Breakthrough, Pore Volume	0.38	0.24	0.20
Total Water Injection at End of TCE Recovery, Pore Volume	4.6	2.2	1.4
Organic Balance, %	100.0 ^c	99.8	96.7

^a Initial porosity. Compaction during testing ignored.

^b Saturations are given on a water-free basis.

^c Organic Balance forced to 100%. Mobile TCE and water remaining in tube at end of test were not measured.

Table 3. Chlorinated Hydrocarbon One-Dimensional Flushing Tests

WRI Test No.	Organic	Flushing Properties			Porosity	Saturation			Saturation Reduction	
		Flow Direction	Temp.	Volume		Initial	Ambien t Residua l	Final Residua l		
			°F	PV		% PV	% PV	% PV	Ambien t	Total
152	TCE	Vertical	68	2.19	35.1	68.5	35.4	35.4	48.2	48.2
153	TCE	Vertical	140	23.91	39.5	81.0		29.7		51.0
154	TCE	Vertical	168	34.22	34.1	82.9		3.2		96.1
155	TCE	Vertical	198	26.89	30.0	82.5		0.8		99.0
176	TCE	Horizontal	143	2.49	38.9	78.9		13.2		83.3
177	TCE	Horizontal	157	8.00	38.6	83.4		16.7		79.9
178	TCE	Horizontal	169	16.60	42.3	77.4		4.1		94.7
179	TCE	Horizontal	66/169	14.80	39.8	77.7	32.1	4.5	58.7	94.3
161	TCE	Horizontal	170	8.18	36.2	87.4		8.1		90.8
168	TCE	Horizontal	63/172	10.17	41.2	76.5	23.6	1.1	69.1	98.6
196	TCE	Horizontal	71/207	17.59	39.9	84.9	30.9	2.3	63.6	97.3
175	TCE	Horizontal	211	3.56	38.5	83.2		0.3		99.6
180	PCE	Vertical	67	14.02	35.4	91.3	44.7	44.7	51.0	51.0
182	PCE	Vertical	66/197	12.62	39.0	88.6	43.5	0.9	50.8	99.0
181	PCE	Vertical	199	5.94	38.0	87.4		0.9		99.0
173	PCE	Horizontal	64	10.69	39.2	86.9	32.7	32.7	62.4	62.4
174	PCE	Horizontal	167	12.90	36.9	81.0		21.4		73.6
171	PCE	Horizontal	65/204	9.67	38.4	78.8	30.9	3.0	60.8	96.2

172	PCE	Horizontal	205	8.58	40.4	81.6		2.5		96.9
195	PCE	Horizontal	69/206	10.35	42.1	82.1	27.6	0.3	66.3	99.7

Table 4. LNAPL One-Dimensional Flushing Tests

WRI Test No.	Organic	Flushing Properties			Porosity	Saturation			Saturation Reduction	
		Flow Direction	Temp	Volume		Initial	Ambien t Residua l	Final Residua l	Ambien t	Total
			°F	PV		% PV	% PV	% PV		
166	Diesel	Vertical	65	12.98	40.4	77.0	17.7	17.7	77.1	77.1
165	Diesel	Vertical	204	9.17	38.7	71.9		1.6		97.7
162	Diesel	Horizontal	66	16.20	34.9	88.5	30.7	30.7	65.3	65.3
164	Diesel	Horizontal	196	7.43	39.1	80.4		19.8		75.4
194	Diesel	Horizontal	70/208	24.35	41.7	77.3	23.4	12.0	69.8	84.4
193	Diesel	Horizontal	69/210	25.49	40.5	77.7	21.8	11.4	72.0	85.3
167	Diesel	Horizontal	65/211	16.62	39.8	77.8	25.8	5.0	66.8	93.6
163	Diesel	Horizontal	218	17.56	35.8	87.1		13.6		84.4
188	Bell	Vertical	144	12.02	39.6	88.5		23.9		73.0
185	Bell	Horizontal	138	17.12	37.7	88.0		28.7		67.4
187	Bell	Horizontal	69/138	12.46	39.1	85.5	33.7	26.0	60.6	69.6
186	Bell	Horizontal	141	14.70	36.8	89.7		28.7		68.0
189	Bell	Horizontal	68/146	18.39	41.2	83.1	36.1	27.4	56.6	67.0
183	Bell	Horizontal	65/166	26.35	39.8	87.4	50.1	39.4	42.7	54.9
184	Bell	Horizontal	68/206	21.98	40.7	55.0	12.3	6.8	77.6	87.6
192	Bell	Horizontal	65/206	19.22	39.9	83.8	35.4	24.7	57.8	70.5
234	Blend	Vertical	66/149	74.45	41.0	49.3	33.7	22.2	31.4	54.7

235a	Blend	Vertical	69/150	33.52	46.9	30.9	30.9	30.9	0	0
235b	Blend	Vertical	180	14.9	46.9	30.9		24.4		21.0
169	Blend	Vertical	75/182	20.88	41.0	100.0	47.6	26.2	52.4	73.7
170	Blend	Horizontal	66/201	45.99	39.7	100.0	41.0	24.7	59.1	75.4

Table 5. Tested Chemicals

Chemical	Manufacturer	Chemical Type	Form	Specific Gravity	Boiling Point, °F
Iconol NP-4	BASF Corporation	Alkyl phenol exhoxylate	liquid	1.02	>300
Iconol NP-6	BASF Corporation	Alkyl phenol exhoxylate	liquid	1.14	>350
Iconol NP-9	BASF Corporation	Alkyl phenol exhoxylate	liquid	1.06	>350
Iconol NP-10	BASF Corporation	Alkyl phenol exhoxylate	liquid	1.06	>350
Iconol TDA-10	BASF Corporation	Tridecyl alcohol exhoxylate	paste	1.03	>480
Neodol 23-5	Shell Oil Company	Linear primary alcohol ethoxylate	liquid	0.96	>500
Neodol 45-13	Shell Oil Company	Linear primary alcohol ethoxylate	paste	1.01	>500
Neodol 91-6	Shell Oil Company	Linear primary alcohol ethoxylate	liquid	0.99	>450
PES-51	Practical Environmental Solutions	Turpene-based surfactant	liquid	0.84	325
Plurfac A-38	BASF Corporation	Alkoxylated fatty alcohol	solid	1.01	NA
Plurfac C-17	BASF Corporation	Alkoxylated fatty alcohol	liquid	1.03	NA
SWR One	SWR Corporation	Nonyl ethoxylate with phosphate esters	liquid	1.03	212
Triton X100	Aldrich Chemical	Octyl phenol ethoxylate	liquid	1.07	400

Table 6. One-Dimensional Simulations of Chemical Enhanced Flushing

WRI Test No.	Surfactant	Flushing Properties		Porosity	Saturation			Saturation Reduction
		Temp.	Volume		Initial		Final	
		°F	PV		% PV	wt %	wt %	
235a	No chemical	69	13.32	46.9	30.9	7.00	7.00	0
235b	No chemical	150	20.20	46.9	30.9	7.00	7.00	0
235c	No chemical	180	14.90	46.9	30.9	7.00	5.53	21.0
214	Iconol NP-10	68	33.44	45.9	29.9	6.60	6.05	8.3
213	Iconol NP-10	68	39.64	45.2	36.5	7.80	6.81	12.7
215	Iconol NP-10	149	31.96	44.0	41.2	8.67	5.23	39.7
218	Iconol NP-10	151	30.37	47.4	28.4	6.56	4.03	38.6
217	Iconol NP-10	157	27.66	49.1	26.1	6.26	4.57	27.0
216	Iconol NP-10	182	29.54	44.9	26.6	5.87	4.73	19.4
219	Neodol 91-6	72	38.44	45.0	29.0	6.45	5.94	7.9
220	Neodol 91-6	153	29.16	44.9	31.3	6.98	5.19	25.6
221	Neodol 91-6	179	27.78	44.7	27.9	6.12	4.13	32.5
222	SWROne	69	36.42	46.6	29.0	6.75	5.44	19.4
223	SWROne	151	32.17	45.1	30.4	6.83	4.97	27.2
225	SWROne	183	30.99	48.0	25.6	5.56	2.88	48.2
224	SWROne	191	29.65	44.1	21.3	5.58	4.41	21.0

Figure 1. Elevated-Temperature Reactor System

Figure 2. Ambient-Temperature Slim-Tube Reactor System

Figure 3. TCE Residual Saturation versus Temperature

Figure 4. Aqueous Phase Total Organic Carbon for CROW 179

Figure 5. Aqueous Phase Total Organic Carbon for CROW 196

Figure 6.

PCE Residual Saturation versus Temperature

Figure 7. Aqueous Phase Total Organic Carbon for CROW 195

Figure

Diesel Residual Saturation versus Temperature

Figure 9. Bell Saturation Reduction versus Temperature

Figure 10. Bell Residual Saturation versus Temperature

Figure 11. Fuel Oil-Diesel Blend Residual Saturation versus Temperature

Figure 12.

Chemical Addition Tests Saturation Reduction versus Temperature

Che

Figure 13. Chemical Addition Tests Residual Saturation versus Temperature

Figure 14.
Total

for CROW 220

**Aqueous Phase
Organic Carbon**

Figure 15. TCE Modeling Comparison

Figure 6.

relative Permeability Curve