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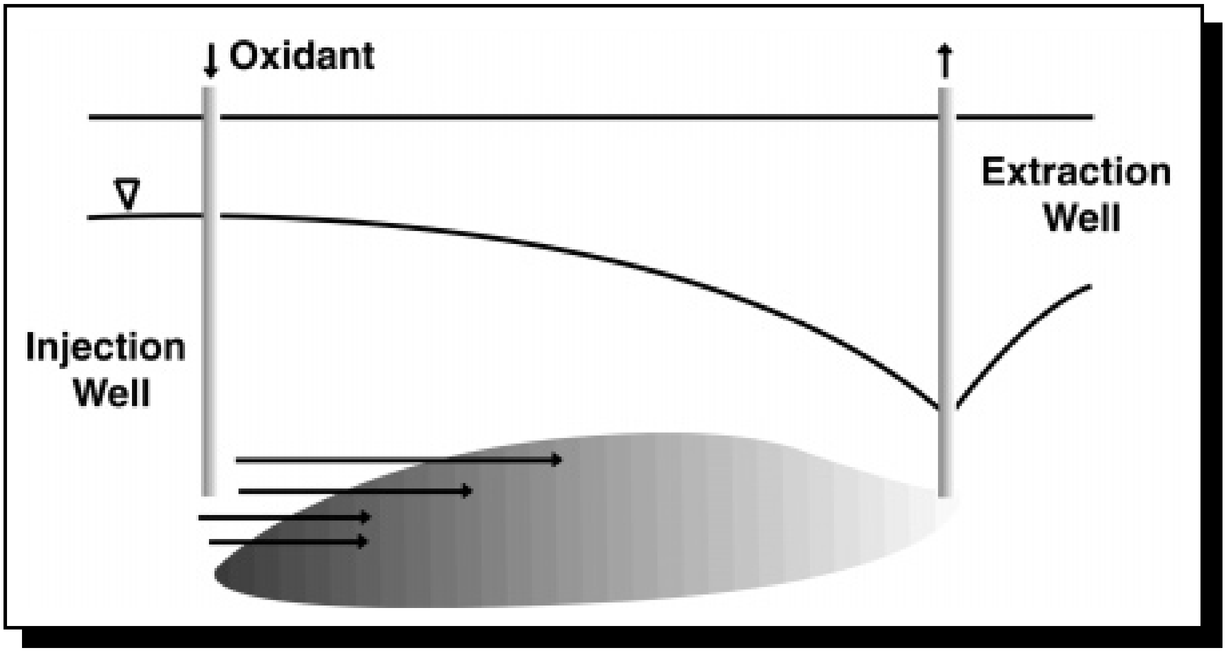
Field Applications of *In Situ* Remediation Technologies:

Chemical Oxidation



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U.S. Environmental Protection Agency
Office of Solid Waste and Emergency Response
Technology Innovation Office
Washington, DC 20460

Notice

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Foreword

Some 80 percent of the hazardous waste sites in the United States have contaminated ground water. Conventionally, the treatment of contaminated ground water has been done by extracting the contaminated water, treating it above ground, and reinjecting or discharging the clean water ("pump-and-treat"). The extracted contaminants must be disposed of separately. It is becoming increasingly apparent that pump-and-treat technologies require considerable investment (between $14-17 million) over a long time (30 years or longer), and may not actually clean up the source of the contamination. Current policies and law stress "permanent" remedies over containment. Consequently, there is considerable interest and effort being expended on alternative, innovative treatment technologies for contaminated ground water.

This report is one in a series that document recent pilot demonstrations and full-scale applications that either treat soil and ground water in place or increase the solubility and mobility of contaminants to improve their removal by other remediation technologies. It is hoped that this information will allow more regular consideration of new, less costly, and more effective technologies to address the problems associated with hazardous waste sites and petroleum contamination. This and the other reports listed below are available to the public from the Technology Innovation Office website: http://clu-in.org/pubitech.htm.

Surfactant Enhancements
Treatment Walls
Hydrofracturing/Pneumatic Fracturing
Cosolvents
Electrokinetics
Thermal Enhancements
In Situ Chemical Oxidation
Ground-Water Circulation Wells

Contents

Introduction

Purpose and Process

The purpose of this document is to describe completed and ongoing pilot demonstrations and full-scale applications of *in situ* chemical oxidation technologies for the remediation of soil and ground water at waste disposal and spill sites.

Information for this report came from commercial and government databases, such as the Dialog Information Services and the Environmental Protection Agency's (EPA) Vendor Information System for Innovative Treatment Technologies (VISITT). Additional materials were obtained from EPA Regional Offices, Department of Energy staff at the Oak Ridge National Laboratory and Westinghouse Savannah River, Department of Defense site staff, and Battelle Laboratories. Personal interviews and discussions with representatives of EPA and other federal agencies, state environmental quality offices, academic research centers, hazardous waste remediation consulting firms, and technology vendors provided supplementary information.

Technology Needs

In situ chemical oxidation is one of several innovative technologies that show promise in destroying or degrading an extensive variety of hazardous wastes in ground water, sediment, and soil. The oxidants used are readily available, and treatment time is usually measured in months rather than years, making the process economically feasible.

Enrichment with dissolved oxygen has been shown to stimulate *in situ* biological processes, but also is used at at least one site to oxidize arsenic. Potassium permanganate is a stable and easily handled oxidant in both solid and solution form. Hydrogen peroxide can be costly, and because of its volatility requires protective measures. Nevertheless, the shorter process may save on labor and operating costs.

In situ chemical oxidation can be applied in conjunction with other treatments such as pump-and-treat and soil vapor extraction to break down remaining compounds. It is less costly and disruptive then other traditional soil treatments such as excavation and incineration. *In situ* chemical oxidation may be used in applications where the effectiveness of bioremediation is limited by the range of contaminants and/or climate conditions.

Technology Description

In situ chemical oxidation is based on the delivery of chemical oxidants to contaminated media in order to either destroy the contaminants by converting them to innocuous compounds commonly found in nature. The oxidants applied in this process are typically hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), ozone, or, to a lesser extent, dissolved oxygen (DO).

The most common field applications thus far have been based on Fenton's Reagent whereby hydrogen peroxide is applied with an iron catalyst creating a hydroxyl free radical. This hydroxyl free radical is capable of oxidizing complex organic compounds. Residual hydrogen peroxide decomposes into water and oxygen in the subsurface and any remaining iron precipitates out. This process has a history of application in waste treatment fields.

The volume and chemical composition of individual treatments are based on the contaminant levels and volume, subsurface characteristics, and pre-application laboratory test results. The methods for delivery of the chemical may vary. The oxidant can be injected through a well or injector head directly into the subsurface, mixed with a catalyst and injected, or combined with an extract from the site and then injected and recirculated. In the case of hydrogen peroxide, stabilizers may be needed because of the compound's volatility.

In situ chemical oxidation is being used for ground water, sediment, and soil remediation. It can be applied to a variety of soil types and sizes (silt and clay). It is used to treat volatile organic chemicals (VOCs) including dichloroethene (DCE), trichloroethene (TCE), tetrachloroethene (PCE), and benzene, toluene, ethylbenzene, and xylene (BTEX) as well as semi-volatile organic chemicals (SVOCs) including pesticides, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs).

Hydrogen Peroxide (H_2O_2)

Anniston Army Depot, Anniston, AL

Installation Date:
1997

Media:
Soil

Contaminants:
TCE

Oxidant:
H_2O_2

Soil Type:
Clay backfill

Points of Contact:
Leslie Ware
Anniston Army Depot (SIOAN-RK)
Directorate of Risk Management
7 Frankford Avenue, Bldg 1
Anniston, AL 36201-4199
Tel: 256-235-7899
Fax: 256-235-7726
E-mail: warel@anad.army.mil

Richard S. Levin, P.G.
QST Environmental Inc.
P.O. Box 1703
Gainesville, FL 32603
Tel: 352-333-3633
Fax: 352-333-6627
E-mail: rslevin@qstmail.com

Full-scale soil remediation using *in situ* chemical oxidation for the removal of dense non-aqueous phase liquids (DNAPLs) such as chlorinated solvents, and hydrocarbons, was begun in 1997 at Anniston Army Depot, Anniston, Alabama.

Site Background

The site consists of three industrial waste lagoons backfilled with clay in 1978. It is approximately 2 acres with over 43,125 yd^3 of contaminated soil containing up to 31% trichloroethene (TCE), dichloroethene (DCE), methylene chloride, and benzene, toluene, ethylbenzene, and xylene (BTEX). TCE accounts for approximately 85% of the 72,000 lbs of volatile organic chemicals. The majority of contaminants were found at depths of 8 ft and greater. The highest concentrations of TCE occur at depths between 8 and 10 ft (maximum 20,100 mg/kg). The water table fluctuates from 25-30 ft below the surface.

Technology Application

Three differently sized injector wells were installed to target three distinct depth intervals. Single shallow injectors screened from 8-14 ft were installed in areas where contamination is shallower than 15 ft, single intermediate injectors were installed where contamination was found from 15-20 ft, and paired shallow and deep injectors screened from 20-26 ft were installed in areas where contamination was found at both deep and shallow depths. In addition, 25 deep ground-water injector wells were used for monitoring, and a vent flow balance system was installed to aid in maintaining an effective radial dispersion of catalyst and H_2O_2. The Geo-Cleanse® patented injection process was employed to deliver H_2O_2 and trace quantities of ferrous sulfate and acid (to control pH) into the contaminated soil. Chemical oxidation of the soil took place over a 120-day period during which 109,000 gallons of 50% H_2O_2 were injected through a total of 255 injectors. Post-treatment sampling began while the full-scale treatment was still in progress. In cases where contaminant concentrations remained above Soil Screening Levels (SSLs), the location was re-treated for polishing treatment.

The total cost to complete this project is estimated to be $5.7M. Project completion originally anticipated for the end of fiscal year 1998 is now contingent upon funding a final $500K and final sampling. Funding for this project was made available in increments. Therefore, the actual expenditures breakdown by cost categories are not available. Project managers estimate that approximately two-thirds of the funds have been allocated for capital costs including chemicals and the injection process and one-third for monitoring and support. Oversight by the Army Corps of Engineers is not included in this funding.

Results

This full-scale treatment was initiated in July 1997. For those areas where sampling and polishing has been completed, results indicate that this process was effective in reducing contaminant concentrations in clays to below SSLs. Soil concentrations of up to 1,760 mg/kg of TCE have been reduced to below detection. Additional polishing treatment may still be warranted depending upon the results of final sampling in the remaining blocks. As noted above, additional funding has been requested to complete this process. Operating data indicate no adverse migration of organics to surrounding soils or ground water.

Site-specific References

Levin, R. S; Wilson, J.; Ware, L.; Findley, J.; and Baehr, J. "Full-Scale Soil Remediation of Chlorinated Solvents in Clay Soils by *In Situ* Chemical Oxidation," Battelle, First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California May 1998

Bryant, J. Daniel and Wilson, J. "Rapid Delivery System Completes Oxidation Picture," *Soil & Groundwater Cleanup,* pp 6-11, August/September 1998

Former Sign Manufacturing Facility, Denver, CO

Installation Date:
1996

Media:
Ground water

Contaminants:
BTEX

A pilot followed by a full-scale treatment of *in situ* chemical oxidation (ISOTEC℠) for remediation of ground water contaminated with benzene, toluene, ethylbenzene, and xylene (BTEX) was conducted at a former sign manufacturing facility in Denver, Colorado, from 1996-1997.

Site Background

The approximate 100 x 100-ft site contained leaking gasoline and fuel oil underground storage tanks. A contaminant plume was found within a thin sandy gravel lens, with a clay layer above and bedrock below. The depth to ground water was 5 ft. Pre-treatment samples indicated BTEX in the ground water at a

Oxidant:
H_2O_2

Soil Type:
Sandy gravel

Point of Contact:
Andrew Schmeising
EWMA of Colorado
7600 Arapahoe Rd. Suite 114
Englewood, CO 80112
Tel: 303-843-9700
Fax: 303-843-9094
E-mail: ewmadenver@aol.com

maximum concentration of 24,595 µg/L.

Technology Application

The pilot program involved three treatment cycles, with 4 days per cycle. Each cycle involved injection of hydrogen peroxide and chelated iron through each of eight injection points. Full-scale remediation was ordered based on the results of this pilot application. The final application involved one six-day cycle using 14 injection points and 7 injection trenches.

The total cost of this demonstration, including pilot and full-scale programs, was approximately $200K. This included the cost of materials, injections, and sampling. The monitoring wells were pre-existing.

Results

The pilot program began in August 1996, and analyses of post-treatment samples from the full-scale operation were completed in March 1997. BTEX was not detected in the post-treatment samples from nine of the monitoring wells. The total BTEX concentration in the remaining four wells was 89 µg/L. As a result, the state issued an unrestricted “no further action letter” for the site. Based on this action, the property was sold.

Site-specific References

“Remediate Contaminated Property,” *Construction Design & Engineering Journal*, March 4-13, 1998, p 2B

Warehousing Facility, Union County, NJ

Installation Date:
1995

Media:
Ground water

Contaminants:
MTBE, BTEX

A pilot test and full-scale treatment of *in situ* chemical oxidation for remediation of ground water contaminated with methyl tert-butyl ether (MTBE) and benzene, toluene, ethylbenzene, and xylene (BTEX) were conducted at a warehouse in Union County, New Jersey, from 1995-1996.

Site Background

The approximately 100 x 80 ft site contained gasoline, waste oil, and fuel oil underground storage tanks that had leaked. The site soils were unsorted and unstratified pebbles, cobbles, and boulders in a matrix of sand, silt, and clay. The depth to ground water was approximately 18 ft. Pre-treatment samples from the well with highest concentrations of contaminants indicated total BTEX levels in excess of 25,000 µg/L and MTBE levels in excess of 6,000 µg/L.

Oxidant:
H_2O_2

Soil Type:
Unsorted rocks in sand

Point of Contact:
Prof. Richard Watts
Washington State University
College of Engineering and Architecture
Pullman, WA 99164
Tel: 509-335-3761
Fax: 509-335-7632
E-mail: rjwatts@wsu.edu

Technology Application

A pilot application was performed using one injection point in the area of highest contamination and one injection point 18 ft away. A single treatment of reagent was completed over a 3-day period. Injections were performed in cycles with catalysts followed by the oxidizer. A site engineered injection apparatus was used to control the flow of hydrogen peroxide (H_2O_2) and the proprietary ISOTEC℠ catalyst (iron complex) into the capillary fringe of the vadose zone. Based on the results of this pilot, full-scale remediation was ordered. Six injection points were installed and three treatment cycles were performed over several days within a 3-month period.

The total cost of this demonstration, including pilot and full-scale programs, was approximately $220K. This included chemicals, injections, and sampling. Pre-existing monitoring wells were used for sampling, so installation costs are not included.

Results

The field pilot program began in December 1995, and analyses of post-treatment samples from the full-scale operation were completed in October 1996. Post-treatment samples taken 4 months after the final treatment application indicated that most of the contaminants, including MTBE, were below detection limits. Total BTEX concentrations were less than 25 µg/L in the same well that had registered in excess of 25,000 µg/L in pre-test samples. As a result, the case was closed in November 1996.

Site-specific References

Greenberg, R. S.; Andrews, T.; Kakarla, P.K.C.; and Watts, R.J. “In-Situ Fenton-Like Oxidation of Volatile Organics: Laboratory, Pilot, and Full-Scale Demonstrations,” *Remediation*, Spring 1998, pp 29-42

Former News Publisher Facility, Framingham, MA

Installation Date:
1996

Media:
Ground water

Contaminants:
TCA, DCE, VC

Oxidant:
H_2O_2

Soil Type:
Fine-grained silty sand

Point of Contact:
Carl Shapiro
TGG Environmental, Inc.
100 Crescent Road
Needham, MA 02494
Tel: 781-449-6450
Fax: 781-449-1283
E-mail: cshapiro@tgge.com

A pilot and full-scale application of *in situ* chemical oxidation (CleanOX®) for the remediation of 1,1-dichloroethene (DCE), 1,1,1-trichloroethane (TCA), and vinyl chloride (VC) in ground water was performed at a former news publisher facility in Framingham, Massachusetts, in 1996.

Site Background

A dry well discovered during a site assessment contained chlorinated solvents and petroleum hydrocarbons from disposal of ink and degreaser wastes. The site includes a plant, which is approximately 100 x 100 ft, and adjacent land of approximately the same dimensions. The area of cleanup consisted of crushed stone and soil surrounding the former dry well. Soil surrounding the dry well was a fine-grained silty sand. Depth to ground water averages approximately 2½ ft below ground surface. The contaminant plume is approximately 80 x 80 ft. Prior to CleanOX® treatment, remedial actions at the site included disposal of over 6,000 gallons of hazardous liquids and fifteen 55-gallon drums of hazardous sludge. Pre-treatment concentrations of TCA in the two monitoring wells were measured at 40,600 and 4,800 µg/L, and VC concentrations were 440 and 110 µg/L.

Technology Application

The pilot-scale application was conducted to evaluate site-specific geochemistry. Two CleanOX® application points were used over a 3-day period for treatment within the 30 ft diameter dry well area. The application involved a solution of H_2O_2, an iron catalyst, and an acid to control pH. Two 4-in diameter PVC wells and five surrounding monitoring wells were sampled prior to application and resampled 3 weeks after treatment.

The total cost of this application was $45K. This included the chemicals, the application, and the expertise required to apply and report on the treatment. It did not include the cost of monitoring wells.

Results

Samples collected 3 weeks after the treatment indicated that TCA at the two contaminated wells dropped from 40,600 to 440 µg/L and from 4,800 to 2,300 µg/L. Concentrations of VC dropped to levels ranging from below detection to 85 µg/L in nearby wells.

The reduction of chlorinated hydrocarbon contaminants achieved with the CleanOX® application, coupled with the quantity of source contaminants removed during the original remediation tasks, allowed the site owner to successfully close the site with state approval without additional treatment. No specific restrictions on the use of the site were necessary, and the site remains closed.

Site-specific References

Not available.

Active Industrial Facility, Clifton, NJ

Installation Date:
1995

Media:
Ground water

Contaminants:
VOCs, TCA

Oxidant:
H_2O_2

Soil Type:
Fill

Point of Contact:
Michael Tumulty
H2M
555 Preakness Ave.
Totowa, NJ 07512
Tel: 973-942-0700
Fax: 973-942-1333
E-mail: tumulty@h2m.com

A pilot and initial injection for full-scale application of *in situ* chemical oxidation (CleanOX®) for the remediation of trichloroethane (TCA) and other volatile organic compounds (VOCs) in ground water were performed at an active industrial facility in Clifton, New Jersey, from 1995-1996.

Site Background

Releases from an underground storage tank resulted in a ground-water plume. An existing ground-water pump-and-treat system was located outside the building and had operated for five years prior to this application with moderate reduction in contaminant concentrations. The high level of iron-metabolizing bacteria at the site caused frequent operations and maintenance problems for the pump-and-treat system. The aquifer is heterogeneous and highly stratified. Site soils are low in permeability (about 1 millidarcy) and conductivity (about 10^{-5} cm/sec), and the ground water has high organic carbon concentrations. Depth to ground water is approximately 16 ft. Pretreatment sampling indicated average total VOC concentrations at 44 mg/L. Maximum TCA concentration was measured at 101 mg/L in one monitoring well.

Technology Application

The pilot-scale application, using H_2O_2, an iron catalyst, and an acid for pH balance, was performed at an existing well. The chemicals were applied over a 3-week period. The full-scale application involved the installation of an additional eleven 4-in diameter PVC wells into the fractured bedrock underneath the facility building. The application wells were screened 10 - 30 ft below ground surface. Samples were taken following this application and repeated a couple of months later.

The cost of the pilot and full-scale applications was approximately $235K. This included drilling the wells, applying chemicals, sampling, testing, and engineering oversight.

Results

Average total VOC concentrations dropped from the original 44 mg/L to 15 mg/L. The post-treatment average level is assumed to be skewed since the project uncovered the fracture system containing most of the contaminant. Results of this application indicated a 98% reduction in TCA concentrations in the most contaminated well, from 101 mg/L to 2 mg/L. Another full-scale application probably would be required to achieve MCLs for drinking water. The water standard required for industrial application is 1 mg/L.

Site-specific References

Not available

Westinghouse Savannah River Site, Aiken, SC

Installation Date:
1997

Media:
Ground water, soil

Contaminants:
TCE, PCE

Oxidant:
H_2O_2

Soil Type:
Sand, clay

Point of Contact:
Karen M. Jerome
Westinghouse Savannah River Company
Tel: 803-725-5223
Fax: 803-725-7673
E-mail: karen.jerome@srs.gov

A field demonstration of *in situ* chemical oxidation to treat dense non-aqueous phase liquids (DNAPLs)—primarily tetrachloroethylene (PCE) and trichloroethene (TCE)—was conducted in 1997 at the Savannah River Site in Aiken, South Carolina.

Site Background

The site selected for this demonstration was a 50 x 50 ft area adjacent to a seepage basin. The treatment zone consisted of 64,000 ft^3 of soil containing approximately 600 lbs of DNAPL. The soils consist of sand and clayey sands. DNAPL is present at approximately 140 ft below ground surface and about 20 ft below the top of the water table. The average ground-water contaminant concentrations in the treatment area were approximately 119 mg/L PCE and 21 mg/L TCE. The soil contained PCE concentrations of 10-150 µg/kg. The highest concentrations were found at approximately 140 ft below ground surface. This area of the Savannah River site was once a fuel and target fabrication facility where uranium, lithium, aluminum, and other materials were processed into fuel elements and targets for use in the nuclear production reactors.

Technology Application

Four injector wells, three monitoring wells, and three vadose zone lysimeters were installed. Holes were drilled to depths of approximately 155 ft, and samples were collected at various levels to determine the soil concentration of TCE and PCE in soil. The treatment zone was approximately 30 ft deep. The Geo-Cleanse® patented injection process was then employed to inject H_2O_2 and a catalyst (ferrous sulfate) over a 6-day period in a circular area with a radius of 27 ft. Injection was conducted in batch mode with one batch injected per day. The volume of the injection varied from 500-1000 gallons per batch. Three days after the last injection, post-test drilling was initiated to verify destruction of DNAPL. In addition, post-test sampling of monitoring wells was conducted weekly for a 3-month period.

The total cost of the demonstration was approximately $511K. This included approximately $60K for site preparation, $151K for pre-test drilling and characterization, $184K for a technology test, $49K for post-test drilling and characterization, $7K for demobilization, and $60K for documentation and project management.

Results

The demonstration, from pre-test characterization of the site through post-test activities, took place between January and July 1997. A comparison of pre- and post-test soil borings indicated a 94% destruction of DNAPL in the treatment zone. The estimated pre-test DNAPL mass was 593 lbs, and the estimated post-test mass was 36 lbs. Total destruction was not achieved and can be attributed to the process not contacting all DNAPL globules in the fine-grained sediments. Average contaminant concentrations in the ground water were reduced to 0.65 mg/L PCE and 0.07 mg/L TCE at the completion of treatment.

Follow-up work was conducted in the summer of 1998 to determine the effects of the chemical reactions on the geochemistry and microbiology of the test zone and surrounding areas.

Site-specific References

Jerome, K.M.; Riha, B.; Looney, B.B. *Final Report for Demonstration of In Situ Oxidation of DNAPL Using the Geo-Cleanse® Technology*, U.S. Department of Energy, Westinghouse Savannah River Company, Aiken, South Carolina, September 1997

Jerome, K.; Looney, B.B.; and Wilson, J. “Field Demonstration of *In Situ* Fenton’s Destruction of DNAPLs,” Battelle, First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 1998

"Field Demonstration of *In Situ* Fenton's Destruction of DNAPLs," in Wickramanayake, G.B. and Hinchee, R.E. (eds.), *Physical, Chemical, and Thermal Technologies, Remediation of Chlorinated and Recalcitrant Compounds*, Battelle Press, Columbus, Ohio, 1998

Bryant, J. Daniel and Wilson, J. "Rapid Delivery System Completes Oxidation Picture," *Soil & Groundwater Cleanup,* pp 6-11, August/September 1998

Potassium Permanganate ($KMnO_4$)

U.S. Army Cold Regions Research & Engineering Laboratory, Hanover, NH

Installation Date:
1997

Media:
Soil

Contaminants:
TCE

Oxidant:
$KMnO_4$

Soil Type:
Sand, silt

Point of Contact:
Daniel McKay
U.S. Army CRREL
72 Lyme Road
Hanover, NH 03755
Tel: 603-646-4738
Fax: 603-646-4640
E-mail:
dcmkay@crrel.usace.army.mil

Pilot-scale testing is being performed at the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, New Hampshire, to evaluate the feasibility of using a 1.5% concentrated solution of potassium permanganate ($KMnO_4$) to promote *in situ* chemical oxidation of trichloroethene (TCE) in low-permeability lenses of silt with clay in the vadose zone. Testing was done at two sites.

Site Background

The presence of TCE is assumed to have resulted from either a leak or an explosion at the facility, which had been used extensively for refrigeration and ice coring. Residual TCE contamination has been identified in unsaturated soils 15-35 ft below the surface. Site soil consists largely of fine sands with some silts, interbedded with veneer-thin stringers of sand and thicker layers of nearly saturated silts and clays. The depth to ground water is approximately 130 ft. Two locations at the site were selected for the pilot tests, representing moderate (approximately 170 mg/kg) and high (maximum 60,000 mg/kg) levels of TCE contamination.

Technology Application

Following pre-test sampling and analysis, a 1.5% $KMnO_4$ solution (15 g/L) was injected to the subsurface via two direct-push wells, one a ¾-in diameter piezometer and the other a 2-in stainless steel screened well, to enable injection at discrete depths from 19.7 to 21 ft. Three samplers were placed near the injection well to collect pore water samples during the treatment process. Approximately 200 gallons of $KMnO_4$ solution was injected in several batches at Site 1 over a 53-day period, while 358 gallons were delivered to Site 2 over a 21-day period.

The cost of this particular pilot has not been itemized. It is part of an overall remediation demonstration program at the site, which is budgeted at $790K for fiscal year 1998.

Results

Pre-treatment sampling began in November 1997, with actual oxidant injection beginning in early 1998. Pre and post-injection monitoring of pore water showed increases of chloride concentrations from 20 to 6,420 mg/L, indicating that

TCE was being oxidized. Analyses of post-injection soil samples also indicated cleanup may have been occurring, but confirmation required additional treatment and sample collection since the samples collected were too small to have been statistically significant. It was determined that significantly larger volumes of $KMnO_4$ solution or higher concentrations of the oxidant would be required to achieve complete cleanup. A second pilot took place in the spring 1998 with a larger volume of the oxidant (1,200 gal/week), and post-treatment samples were collected in June. Preliminary results of these samples indicate the need to inject the oxidant under pressure using smaller boreholes to better contain the oxidant. Actual data are not yet available. CRREL anticipates having two additional larger-scale demonstrations up and running in the fall of 1998. These sites will involve the use of boreholes with packers to inject the $KMnO_4$ under pressure.

Site-specific References

McKay, D.; Hewitt, A.; Reitsma, S.; LaChance, J.; and Baker, R. "*In Situ* Oxidation of Trichloroethylene Using Potassium Permanganate: Part 1. Theory and Design," Battelle, First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, May 1998

McKay, D.; Hewitt, A.; Reitsma, S.; LaChance, J.; and Baker, R. "*In Situ* Oxidation of Trichloroethylene Using Potassium Permanganate: Part 2. Pilot Study," Battelle, First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, May 1998

Canadian Forces Base Borden, Ontario, Canada

Installation Date:
1996

Media:
Ground water

Contaminants:
TCE, PCE

Oxidant:
$KMnO_4$

A field demonstration of *in situ* chemical oxidation using potassium permanganate ($KMnO_4$) to treat dense non-aqueous phase liquid (DNAPL)—primarily trichloroethene (TCE) and tetrachloroethene (PCE)—was conducted at the Canadian Forces Base Borden in Ontario, Canada, from 1996-1997. It follows two similar but smaller field demonstrations on the base in the early 1990s.

Site Background

The approximately 50 x 50 meter (164 x 164 ft) site is in a 4-meter (13-ft) thick sand aquifer. The sand is highly homogeneous and has hydraulic conductivity of approximately 86 cm/day. The source zone is located 1 m (3.3 ft) below the water table. Typical ground-water velocities at the site are on the order of 9 cm/day. At the initiation of an oxidant flush in 1996, it was estimated that the source zone contained an average of 1,200 mg/kg TCE and 6,700 mg/kg PCE.

Soil Type:
sand

Point of Contact:

Dr. Neil Thomson, PhD, PEng
Dept. of Civil Engineering
University of Waterloo
200 University Ave. W.
Waterloo, Ontario N2L3G1
Tel: 519-885-1211 (ext 2111)
Fax: 519-888-6197
E-mail: nthomson@uwaterloo.ca

Technology Application

This demonstration used a series of six injection and five oxidant recovery wells. While previous experiments were conducted in sheetpile containment wells, the only form of hydraulic control on the injected oxidant in this demonstration were the wells. The reaction was monitored using a fence of seven bundled mini-piezometers (98 sample points total) perpendicular to ground-water flow and 1 m (3.3 ft) downgradient of the source zone. The DNAPL source zone was flushed with a solution of approximately 8 g/L $KMnO_4$ for almost 500 days.

The total cost of the demonstration is approximately $45K.

Results

The oxidant flush was conducted between May 1996 and September 1997. Preliminary analyses indicate a 99% reduction in peak concentrations for both PCE and TCE; final sampling results are expected in late 1998. The mass flux (mg/day) dissolved contaminants seems to have reduced by four or five orders of magnitude. Further work to confirm these preliminary results, including an estimate of solvent mass currently in the source zone, is continuing.

Site-specific References

Schnarr M.; Truax, C.; Farquhar, G.; Hood, E.; Gonullu, T.; and Stickney, B. "Laboratory and Controlled Field Experiments using Potassium Permanganate to Remediate Trichloroethylene and Perchloroethylene DNAPLs in Porous Media," *Journal of Contaminant Hydrology*, 29(3), p 205-224, 1998.

Hood, E. D.; Thomson, N. R.; and Farquhar, G. J. "*In Situ* Oxidation: An Innovative Treatment Strategy to Remediate Trichloroethylene and Perchloroethylene DNAPLs in Porous Media," Sixth Symposium and Exhibition on Groundwater and Soil Remediation, Montreal, Canada, March 18-21, 1997

Hood, E. D.; Thomson, N. R.; and Farquhar, G. J. "*In Situ* Oxidation: Remediation of a PCE/TCE Residual DNAPL Source," Battelle, First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 1998

Kansas City Plant, Kansas City, MO

Installation Date:
1996

Media:
Ground water, soil

Contaminants:
TCE, DCE

Oxidant:
$KMnO_4$

Soil Type:
Clay

Points of Contact:
Steve Cline
Oak Ridge National Laboratory
Box 2008
Oak Ridge, TN 37831
Tel: 423-241-3957
Fax: 423-576-8646
E-mail: qc2@ornl.gov

Joe Baker
Allied Signal
2000 E. 95 Street
Kansas City, MO 64131
Tel: 816-997-7332
Fax: 816-997-5903
E-mail: jbaker@kcp.com

An *in situ* chemical oxidation field demonstration using potassium permanganate ($KMnO_4$) for the remediation of chlorinated solvents was conducted in 1996 at the U.S. Department of Energy (DOE) Kansas City Plant in Kansas City, Missouri. It was part of a larger study in which three technologies—bioaugmentation, chemical oxidation, and mixed-region vapor stripping with calcium oxide—were combined with deep soil mixing.

Site Background

The test site occupied approximately 60 x 140 ft in stiff clay soils just north of a former lagoon. Depth to ground water is approximately 8-10 ft below ground surface. Ground-water samples indicated high concentrations of trichloroethene (TCE), 1,2-dichloroethene (DCE) (over 15,000 µg/L) and chloroethene (over 1,500 µg/L). Previous soil investigations indicated elevated levels of total petroleum hydrocarbons (TPH) ranging up to 6,961 mg/kg, polychlorinated biphenyls (PCBs) as high as 9.8 mg/kg, and concentrations of TCE and 1,2-DCE in soil below the water table as high as 81 mg/kg and 15 mg/kg, respectively.

Technology Application

The field demonstration, testing, and evaluation activities involved a crane-mounted vertical rotating blade system designed to mix the soil using 8-10 ft diameter blades. During the *in situ* mixing process, treatment agents were injected through a vertical, hollow shaft into the soil. Fifteen soil columns, 8 ft in diameter, grouped three to a treatment cell, were treated to depths of approximately 25 to 47 ft. A shallow (25 ft) and a deep (47 ft) cell were used for *in situ* mixing with a 4-5% $KmnO_4$ solution. The cells were treated separately over two 2-day periods in three overlapping test columns. Although soil mixing redistributed the media making it impossible for post-treatment sampling to replicate pre-treatment sampling, post-treatment samples were collected in similar fashions and locations as pre-treatment samples.

The total cost of the demonstration was approximately $1M. This included all pre- and post-testing, permitting, equipment, and labor. Actual cost breakdowns are not available. On a pro-rated basis, the costs by technology are estimated to be $128/yd^3 for $KMnO_4$ compared to $77/yd^3 for bio-augmentation and $62/yd^3 for vapor stripping.

Results

This demonstration was conducted in July 1996. The goal of the project was to achieve a 70% removal rate of contaminants. Comparing pre- and post-treatment TCE mass values at the two cells treated with $KMnO_4$, one cell indicated an overall removal of 83% of TCE from the unsaturated soil and the other a reduction of 69% from the saturated soil. This compares to a 65% reduction in the unsaturated soil treated by vapor stripping, and a 38% reduction for that treated with bioaugmentation. The results also show that the physical and biological properties of the soil treated with $KMnO_4$ remain essentially intact. Additional sampling was performed in Spring 1998 and analysis is underway.

Site-specific References

U.S. DOE, *Implementation of Deep Soil Mixing at the Kansas City Plant*, Oak Ridge National Laboratory, Grand Junction, CO, February 1997

Cline, S.R.; West, O.R.; Siegrist, R.L.; and Holden, W.L., *Performance of In Situ Chemical Oxidation Field Demonstrations at DOE Sites*, presented at the *In Situ* Remediation of the Geoenvironment Conference, Minneapolis, Minnesota, October 5-8, 1997

Portsmouth Gaseous Diffusion Plant, Piketon, OH

Installation Date:
1997

Media:
Ground water, soil

Contaminants:
TCE

Oxidant:
$KMnO_4$

Soil Type:
Sand, gravel

A full-scale demonstration of *in situ* chemical oxidation through recirculation (ISCOR) to remediate soil and ground water for chlorinated solvents, primarily trichloroethene (TCE), was conducted at the X-701B site of the Portsmouth Gaseous Diffusion Plant in Piketon, Ohio, in 1997.

Site Background

The site was 200 x 90 ft, with four distinct underlying strata: silt and clay (25-30 ft thick), a sand and gravel (2-10 ft thick), shale (10-15 ft thick), and sandstone (47 ft deep). The field test was targeted at treating contamination in the relatively permeable sand and gravel layer, since it has the highest risk for off-site migration. This layer is 5-6 ft thick and approximately 30 ft below ground surface. The layer is contaminated primarily with TCE. Ground water is 12-14 ft below the surface. Pre-treatment testing of soil samples detected an average TCE concentration of 54 mg/kg with a maximum concentration of 302 mg/kg. Ground-water samples revealed concentrations up to 800 mg/L.

Technology Application

This demonstration used a pair of previously installed parallel horizontal wells, 90 ft apart with 200-ft screened sections consisting of 5-inch diameter, high-density polyethylene porous filters. Water for the oxidant injection solution was extracted from the upgradient horizontal well, mixed with crystalline potassium permanganate ($KMnO_4$) in concentrations of 1.5-2.5%, and re-injected into the downgradient horizontal well. Twenty-two boreholes were drilled between the wells and samples were taken at 1-ft intervals from 20-30 ft below ground surface. Three-quarter-inch-diameter PVC wells with 5-ft screens were installed in 14 of the boreholes.

The total cost of the demonstration was $562K. Approximately $56K was allocated for project planning and management, $163K for pre-treatment sampling and mobilization, $163K for operations and maintenance, $101K for post-treatment sampling, $68K for resistivity monitoring, and $11K for support.

Results

This field test was conducted from July-August 1997, and post-treatment characterization was completed in August 1997. Post-treatment characterization showed that ISCOR was effective at reducing TCE in both soil and ground water to non-detectable levels in those areas where the oxidant was able to migrate. Lateral and vertical heterogeneities within the treatment zone impacted the uniform delivery of the oxidant.

Monitoring of the ground water in the area was conducted between October 1997 and June 1998 and analysis continues to date. New field testing at a different location on this facility using sodium permanganate and vertical injection and extraction wells is expected to begin in the summer of 1998. Sodium permanganate was selected because of its considerably higher solubility in aqueous solutions than $KMnO_4$. Its higher solubility allows for the use of alternate modes of delivery such as liquid chemical feed.

Points of Contact:

Dr. Robert L. Siegrist
Colorado School of Mines
112 Coolbaugh Hall
Golden, CO 80401
Tel: 303-273-3490
Fax: 303-273-3629
E-mail:
rsiegris@slate.mines.edu

Dr. Olivia R. West
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831
Tel: 423-576-0505
Fax: 423-576-8543
E-mail: qm5@ornl.gov

Site-specific References

West, O.R.; Cline, S.R.; Holden, W.L.; Gardner, F.G.; Schlosser, B.M.; Thate, J.E.; Pickering, D.A.; and Houk, T.C. *A Full-Scale Demonstration of In Situ Chemical Oxidation Through Recirculation at the X-701B Site,* Oak Ridge National Laboratory, Oak Ridge, Tennessee, December 1997

Cline, S.R.; West, O.R.; Siegrist, R.L.; and Holden, W.L., "Performance of *In Situ* Chemical Oxidation Field Demonstrations at DOE Sites," *In Situ* Remediation of the Geoenvironment Conference, Minneapolis, Minnesota, October 5-8, 1997

West, O.R.; Cline, S.R.; Siegrist, R.L.; Houk, T.C.; Holden, W.L.; Gardner, F.G.; and Schlosser, B.M. "A Field Scale Test of *In Situ* Chemical Oxidation Through Recirculation," International Conference of Decommissioning and Decontamination and on Nuclear and Hazardous Waste Management, American Nuclear Society, Denver, Colorado, September 13-18, 1998

Ozone (O_3)

Former Service Station, Commerce City, CO

Installation Date:
1997

Media:
Ground water, soil

Contaminants:
TPH, BTEX

Oxidant:
Ozone

Soil Type:
Sand-gravel mix

Point of Contact:
Gordon Davitt
Moiety Associates
1080 Fifth Street
Penrose, CO 81204
Tel: 719-372-6970
Fax: by appointment
E-mail: moietyrands@juno.com

A full-scale application using a combination of an air/ozone (C-Sparge™) system and a vacuum extraction system to remediate soil and ground water contaminated with petroleum hydrocarbons and benzene, toluene, ethylbenzene, and xylene (BTEX) was administered at a former service station site in Commerce City, Colorado, in 1997.

Site Background

The site, which once served as a bulk storage and service station facility, is part of a metal recycling facility. Subsurface material consists of sand and gravel mixtures to approximately 43 ft below ground surface, grading to a blue clay. Ground water is approximately 28 ft below ground surface. A soil and ground-water investigation indicated that total petroleum hydrocarbons (TPH) in the soil ranged from 90-2,380 mg/kg. Total BTEX in soil ranged from 7,800-36,550 µg/kg. TPH in the ground water ranged from free product to 490 mg/L and BTEX ranged from 22-2,260 µg/L. Concentrations of benzene, the contaminant by which the cleanup standard was measured, ranged from below detection limits to 16 µg/L.

Technology Application

The C-Sparge™ process consists of a combination of *in situ* air stripping with encapsulated ozone to oxidize contaminants. Two master panels, each controlling three wells, were installed. Each well consists of an in-ground sparge point that injects pulsating ozone and air into the ground water, an in-well sparge point that injects pulsating water in the well casing under pressure, a water-circulation pump, and a packer. The pressurized system allows the fine bubbles that transport the encapsulated ozone to infuse the formation without fracturing it. Each well was drilled 50 ft deep, and sealed from 10 ft below grade to the ground surface. Sparge-point pressures ranged from 14-20 psi, depending on the distance from the well to the surface equipment. The system was augmented with a large blower pulling 160 ft^3/min at 48-inch-vacuum water column. The entire system ran through 12 complete cycles per day. Each cycle involved all six wells going through the approximately 25 minute/well process of blowing ozone and air into the ground water, blowing water into the casing, and pumping. The blower operated continuously.

The anticipated cost of the demonstration from site investigation through final monitoring is approximately $160K. Of this, $20K was allocated for site investigation, $55K for equipment, $35K for installation, and $15K for sparge wells.

Results

The system started in August 1997. The ground-water wells at the site are monitored quarterly. The March 1998 results showed dissolved TPH at 37 mg/L in the well that contained free product during previous monitoring. No TPH or BTEX was detected in any other monitoring wells, so the remediation system was turned off. Monitoring results in June 1998 indicated levels remaining below the state maximum contaminant levels for drinking water. The state did not require confirmatory soil sampling. Samples will need to be taken for four consecutive quarters following the shutdown of the system in March 1998.

Site-specific References

Not available

Dry Cleaning Facilities, Hutchinson, KS

Installation Date:
1997

Media:
Ground water

Contaminants:
PCE

Oxidant:
Ozone

Soil Type:
Sand, silt, clay

A pilot test using ozone and air injection for remediation of tetrachloroethene (PCE) in ground water was conducted in Hutchinson, Kansas, in 1997. This pilot was part of a test designed to compare and evaluate the cost-effectiveness of three remediation technologies. It involved three similar locations within the city. The technologies included a combination of air sparging with soil vapor extraction (AAS/SVE); in-well stripping (NoVOCs™); and a combination of air and ozone injection with vertical circulation of ground water (C-Sparge™).

Site Background

All three test sites were located near former and existing dry-cleaning facilities within the city limits. Sediments underlying the sites consist of unconsolidated stream and terrace deposits (sand, silt, and clay). The water table is from 14 to 16 ft below ground. Dissolved-phase PCE appeared limited to the top 15 ft of the aquifer with maximum concentrations ranging from 30-600 µg/L.

Technology Application

Each of the 3 test configurations consisted of above-ground remediation hardware in a temporary enclosure or trailer, a

Points of Contact:
Leo G. Henning
Kansas Dept. of Health &
Environment
Bldg 740 at Forbes Field
Topeka, KS 66620
Tel: 785-296-1914
Fax: 785-296-4823
E-mail:
lhenning@kdhe.state.ks.us

Douglas Dreiling
Burns & McDonnell
3839 Dora
Wichita, KS 67213
Tel: 316-941-3921
Fax: 316-941-4730
E-mail: ddrel@burnsmcd.com
http://www.burnsmcd.com

single or combination remediation well configuration, above- and below-grade piping, and ground-water monitoring wells. The placement of monitoring wells varied for each site to accommodate the technology-specific data collection requirements.

The ozone injection test involved a C-Sparge™ process which combines air stripping with oxidation. The system included a 4-in diameter PVC remediation well installed to 35 ft below grade with a micro-porous sparge point placed 33-35 ft below grade. The wells were screened in the vadose and saturated zones. A self-contained down-hole unit, containing a second sparge point and fluid pump, was then installed in the well. Ground-water information was collected from a cluster of five monitoring wells. The average rate of injection was 3 standard cubic ft per minute. To better understand the effects of ozone, a second identical configuration was installed to inject air only through the sparge points. A cluster of three monitoring wells was used to collect information from this test.

The cost of this field demonstration for all three sites was approximately $195K, of which $52K was for the C-Sparge™ test, $95K was for the NoVOCs™ test, and about $48K for the AAS/SVE test. A cost comparison indicated that the AAS/SVE system was the least expensive to install and the C-Sparge™ the most economical to operate.

Results

Pilot test activities for all sites were conducted over a 5-month period and included monitoring well and system installation, pre-test ground-water sampling, a 6-day system start-up period, on-going data collection and operation and maintenance, and post-test ground-water sampling.

Monitoring wells 10 ft from the remediation well using ozone indicate a 91% reduction in concentration of PCE, from 34 to 3 µg/L. Air-only injections resulted in a 71% reduction, in-well stripping an 87% reduction, and AAS/SVE a 66% reduction.

Site-specific References

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Former Industrial Facility, Sonoma, CA

Installation Date:
1998

Media:
Ground water, soil

Contaminants:
PCP, PAHs

Oxidant:
Ozone

Soil Type:
Sand, clay

Point of Contact:
Christopher Nelson
Fluor Daniel GTI, Inc.
1527 Cole Blvd.
Golden, CO 80401
Tel: 303-231-8912
Fax: 303-231-8901
E-mail: cnelson@gtionline.com

A field demonstration of *in situ* chemical oxidation using ozone is underway at a former industrial site in Sonoma, California to remediate the vadose zone and ground water for pentachlorophenol (PCP) and polycyclic aromatic hydrocarbons (PAHs).

Site Background

This site (approximately 300 x 300 ft) was once the location for a wood treating facility, a cooling tower, and a water tank manufacturer. These operations involved the use of PCP and creosote. Contamination extends from shallow soils down to the water table. The geology consists of semi-continuous layers ranging from fine sands to clays, resulting in highly stratified contamination. The application was designed to address contamination in all layers. Initial sampling of 10 locations on the site indicated an average concentration of 1,800 mg/kg of total PAHs and 3,300 mg/kg of PCP.

Technology Application

This demonstration involves at least four multi-level ozone injections (for all the stratigraphic layers) utilizing a variety of instrumentation including soil gas probes, piezometers, lysimeters, monitoring wells, thermocouples, and reflectometry instruments to measure soil moisture content. Soil vapor extraction wells were placed outside the treatment areas to ensure that fugitive ozone emissions were minimized. Ozone was injected through wells in the vadose zone at varying rates up to 10 ft^3/min.

The inclusive cost of this field demonstration, once completed, is anticipated to be approximately $300K (half the cost was for capital equipment and half for operations and maintenance).

Results

This field study was begun in the spring of 1998 and is anticipated to continue for an additional six months. After one month of continuous ozone injection, sampling from the 10 locations averaged 530 mg/kg PAHs and 570 mg/kg PCP. Concentrations of PAHs were reduced 67 - 99.5% and concentrations of PCP were reduced 39 - 98%. Subsurface gaseous ozone concentrations appear to be relatively uniform, decreasing with increasing distance from injection points. Soil gas data suggests that ozone utilization of greater than 90% is achieved. The study calls for additional data to be acquired, soil borings to be advanced after three and six months of treatment, respirometry to be performed to determine the effects of ozonation on microbial activity, and various engineering issues to be investigated.

Site-specific References

Marvin, B.K.; Nelson, C.H.; Clayton, W.; Sullivan, K.M.; and Skladany, G. "*In Situ* Chemical Oxidation of Pentachlorophenol and Polycyclic Aromatic Hydrocarbons: From Laboratory Tests to Field Demonstration," Battelle, First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, May 1998

Park Between Commercial and Residential Area, Utrecht, The Netherlands

Installation Date:
1997

Media:
Ground water

Contaminants:
TCE, BTEX

Oxidant:
Ozone

Soil Type:
Fine sand

Point of Contact:
Mr. Anne Fijma
Mateboer Milieutechniek B.V.
Ambachtsstraat 27
Postbus 99
8260 AB Kampen, The Netherlands
Tel: 011-31-38-3315020
Fax: 011-31-38-3320211
E-mail:
mateboer.kampen@wxs.nl

A pilot test of micro-encapsulated ozone oxidation for remediation of a deep plume of dissolved chlorinated solvents in ground water was conducted in Utrecht, The Netherlands, in 1997. Micro-encapsulated ozone is emplaced in fine bubbles to allow it to penetrate the subsurface.

Site Background

The field test took place in a small park midway on a long plume of chlorinated solvents, primarily trichloroethene (TCE), originating from a commercial building and extending over 800 ft across a predominantly commercial and residential area. The plume lies in a thick fine-sand deposit containing gravel lenses. About one-half of the area of ground water overlying the TCE plume was contaminated with benzene, toluene, ethylbenzene, and xylene (BTEX) from a nearby fuel spill. Borings showed a surface loam to 6 ft deep, ground water at 9 ft deep, fine sand beginning at 19 ft deep, and clay from 124-130 ft deep. Initial sampling at four wells indicated concentrations of halogenated volatile organic compounds (HVOCs) from 1,450-14,500 µg/L and BTEX from 62-95 µg/L. The mean concentrations were 3,000 µg/L HVOCs and 60 µg/L BTEX.

Technology Application

The test involved a C-Sparge™ well consisting of an in-ground sparge point, an in-well sparge point, a packer and a fluid pump, four monitoring wells, of previously installed mini-wells, and a fire well. Mini-wells, commonly used in Europe, are small points installed using cone penetrometer rigs to help determine the position of the plume and function as part of the monitoring system. The C-Sparge™ system consists of a combination of *in situ* air stripping, where the dissolved

Mr. Ted Vendrig
Mateboer Milieutechniek B.V.
Steurstraat 7
Postbus 10174
1301 AD Almere, The Netherlands
Tel: 011-31-36-5302410
Fax: 011-31-36-5301128
E-mail:
mateboer.almere@wxs.nl

chlorinated solvents are extracted from aqueous solution into small bubbles, and the introduction of encapsulated ozone to oxidize the contaminants. Water and fine bubbles were injected from the lowest screen in the system (75 ft below grade), and return water entered the middle screen (42 ft below grade). The uppermost screen (8 ft below grade) collected the gases from just above the water table to assure vapor control.

The cost of this field demonstration was approximately $35K. This included placing the C-Sparge unit on site, a trailer to house the work area and monitoring equipment, a generator system for the blower unit, drilling, enclosing part of the site, laboratory sampling, and report preparation. It did not include the cost of installing the pre-existing wells.

Results

This field test ran for a 10-day period in April 1997. Its purpose was to determine the rates of contaminant removal. A kinetic analysis of the reaction rates was performed. HVOC concentration for the well with 14,500 µg/L fell to below 1,000 µg/L during the test period. Mean BTEX levels were reduced from 54 to 17 µg/L in the central monitoring wells. Full-scale treatment is expected to bring these concentrations to a level between acceptable commercial and drinking water levels. Negotiations are currently underway to treat the entire plume.

Site-specific References

Kerfoot, W. B.; Schouten, C.J.J.M; and Van Engen-Beukeboom, V.C.M., “Kinetic Analysis of Pilot Test Results of the C-Sparge™ Process,” Battelle, First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 1998

Dissolved Oxygen (DO)

Peterson/Puritan, Inc. Superfund Site, Cumberland, RI

Installation Date:
1996

Media:
Ground water

Contaminants:
Arsenic

Oxidant:
DO

Soil Type:
Sand, gravel

Points of Contact:
David J. Newton, RPM
Office of Site Remediation and Restoration
U.S. EPA, Region 1
J.F.K. Federal Bldg (HSV-CAN5)
Boston, MA 02203-2211
Tel: 617-573-9612
Fax: 617-573-9662
E-mail: newton.dave@epamail.epa.gov

Laurie Sclama, PM
RI DEM
235 Promenade Street
Providence, RI 02908
Tel: 401-222-3872 x 7143
Fax: 401-222-3812
E-mail: lsclama@dem.state.ri.us

An Oxidant Delivery System was installed in 1996 at the Peterson/Puritan, Inc. Superfund Site in Cumberland, Rhode Island, to reduce arsenic concentrations in ground water to less than 50 µg/L.

Site Background

The site continues to support general and specialty chemical manufacturing industries. Historically, high organic-content wastewater at the source area were disposed through subsurface leachfields. The 1993 Record of Decision (ROD) specified that part of the remediation include the construction and installation of an *in situ* chemical oxidation system comprised of an infiltration gallery for delivering oxygenated water to the former leachfield locations and an above-ground oxidant delivery system. Some wells in the remediation area indicated concentrations of arsenic on the order of 1,000 µg/L. These elevated levels of arsenic are, to a degree, the result of reductive dissolution of the metal from native soil. The history of the site indicates that arsenic has also been reported in the wastewater stream going to the leachfield. This oxidant delivery system was constructed and became operational following excavation and removal of leachfield soils from the site.

Technology Application

A 35 x 65 ft infiltration gallery, a membrane-lined excavation, which holds the oxygenated water allowing it to percolate into the subsurface, was installed within the former leachfield at a depth of 14 ft. Monitoring wells were installed within the gallery, and the leachfield excavation was backfilled. Eleven additional micro-wells were installed around the site. A prefabricated treatment building was constructed on site, and the Oxidant Delivery System, composed of a degassing skid, an oxygen dissolution skid, a degassing tank, and an oxygen dissolution tank was assembled in the building. The system was designed to degas, superoxygenate, and inject municipal water (at 8-9 gpm) into the aquifer. The goal of this application is to increase ground-water dissolved oxygen (DO) concentrations to a level greater than 0.5 mg/L causing the arsenic to precipitate and rendering it immobile. It is intended to reduce the concentrations of dissolved arsenic and prevent its

Michael Resch or
Linda McCarthy
ENSR
35 Nagog Park
Acton, MA 01720
Tel: 978-635-9500
Fax: 978-635-9180
E-mail: mresch@ensr.com
or: lmccarthy@ensr.com

migration in the ground water. The long-term objective is to return the geochemical balance of the site to its pre-leachfield state, which includes some level of arsenic because it occurs naturally in the native soil.

The total capital cost of the remediation is estimated at $1.4M. This includes $620K for design, $460K for gallery installation and system construction, and $320K for pilot startup. Annual operations and maintenance costs, including sampling, utilities and reporting are estimated to be $175K. Indirect costs, such as project management and oversight, are included in these figures.

Results

The system was installed in 1996, a pilot test was performed in early 1997, and full-scale operations began in April 1997. EPA is assessing the success of this technology on an ongoing basis. Data are being compiled for submission as part of the five-year review, which is due in the 4th quarter of the Year 2000. No data are currently available.

Site-specific References

U.S. EPA, *Remedial Action Report, Peterson/Puritan Superfund Site*, prepared by ENSR Consulting and Engineering, revised edition, March 1998

General References

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