UCRL-JC- 134080
PREPRINT

Thermal Cleanups Using Dynamic Underground Stripping and Hydrous Pyrolysis Oxidation

Robin L. Newmark, Roger D. Aines, Roald Leif, and Kevin Knauss
Lawrence Livermore National Laboratory

This paper was prepared for submittal to the
NATO/Committee on the Challenges of Modern Society Pilot Study Program Concerning the Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Ground Water - Phase III (NATO/CCMS)
Angers, France
May 12-16, 1999

May 1999

Project No. 14 Thermal Cleanups using Dynamic Underground Stripping and Hydrous Pyrolysis/Oxidation			
Location LLNL Gasoline Spill Site, Livermore, Ca. Visalia Pole Yard, Visalia, Ca.	Project Status Final Report	Contaminants PAHs, diesel and pentachlorophenol (Visalia) Gasoline (LLNL) (TCE, solvents and fuels at other sites)	Technology Type Dynamic Underground Stripping and Hydrous Pyrolysis/ Oxidation
Technical Contact Robin L. Newmark Lawrence Livermore National Laboratory L-208, P.O. Box 808 Livermore, Ca., 94550 United States Tel: (925)-423-3644 fax: (925)-422-3925 email: newmark@llnl.gov Paul M. Beam U.S. Department of Energy 19901 Germantown Road Germantown, MD 20874-1290 United States tel: 301-903-8133 fax: 301-903-3877 e-mail: paul.beam@em.doe.gov	Project Dates Accepted 1998	Media Groundwater and soil	
	Costs Documented? Yes	Project Size Full-scale: Livermore: 100,000yd^3 (76,000 m^3) Visalia: 4.3 acres, >130 ft deep (app. 600,000 m^3)	Results Available? Yes

1. INTRODUCTION

In the early 1990s, in collaboration with the School of Engineering at the University of California, Berkeley, Lawrence Livermore National Laboratory developed dynamic underground stripping (DUS), a method for treating subsurface contaminants with heat that is much faster and more effective than traditional treatment methods. More recently, Livermore scientists developed hydrous pyrolysis/oxidation (HPO), which introduces both heat and oxygen to the subsurface to convert contaminants in the ground to such benign products as carbon dioxide, chloride ion, and water. This process has effectively destroyed all contaminants it encountered in laboratory tests.

With dynamic underground stripping, the contaminants are vaporized and vacuumed out of the ground, leaving them still to be destroyed elsewhere. Hydrous pyrolysis/oxidation technology takes the cleanup process one step further by eliminating the treatment, handling, and disposal requirements and destroying the contamination in the ground. When used in combination, HPO is especially useful in the final "polishing" of a site containing significant free-product contaminant, once the majority of the contaminant has been removed.

2. BACKGROUND

Lawrence Livermore National Laboratory (LLNL) Gasoline Spill Site:

LLNL recently completed the cleanup and closure of a moderate-sized spill site in which thermal cleanup methods, and the associated control technologies, were used to remediate nearly 8,000 gallons (30,000 L) of gasoline trapped in soil both above and below the standing water table. The spill originated from a group of underground tanks, from which an estimated 17,000 gallons (64,000 L) of gasoline leaked sometime between 1952 and 1979. The gasoline penetrated the soil, eventually reaching the water table, where it spread out. Gasoline trapped up to 30 ft (9 m) below the water table was there due to a rise in the water table after the spill occurred, with the gasoline held below water by capillary forces in the soil. Groundwater contamination extended about 650 ft (200 m) beyond the central spill area. The soils at the site are alluvial, ranging from very fine silt/clay layers to extremely coarse gravels, with unit permeabilities ranging over several orders of magnitude. The site was prepared for long-term groundwater pump-and-treat with vapor extraction; recovery rates prior to thermal treatment were about 2.5 gal/day 9.5 L /day).

Visalia Pole Yard:

In 1997, DUS and HPO were applied for cleanup of a 4.3 acre (17,000 m^2) site in Visalia, California, owned by Southern California Edison Co. (Edison). The utility company had used the site since the 1920s to treat utility poles by dipping them into creosote, a pentachlorophenol compound, or both. By the 1970s, it was estimated that 40-80,000 gallons (150,000-300,000 L) of DNAPL product composed of pole-treating chemicals (primarily creosote and pentachlorophenol) and an oil-based carrier fluid had penetrated the subsurface to depths of approximately 100 ft (30 m), 40 ft (12 m) below the water table. Edison had been conducting pump and treat operations at the site for nearly 20 years. While this activity had successfully reduced the size of the offsite groundwater contaminant plume, it was not very effective at removing the NAPL source. Prior to thermal treatment, about 10 lb. (4.5 kg) of contaminant was being recovered per week. Bioremediation of the free-organic liquids is expected be prohibitively slow (enhanced bioremediation was predicted to take at least 120 years).

3. TECHNICAL CONCEPT

Dynamic Underground Stripping (DUS): *mobilization and recovery*

Dynamic Underground Stripping combines two methods to heat the soil, vaporizing trapped contaminants. Permeable layers (e.g., gravels) are amenable to heating by steam injection, and impermeable layers (e.g., clays) can be heated by electric current. These complementary heating techniques are extremely effective for heating heterogeneous soils; in more uniform conditions, only one or the other may be applied. Once vaporized, the contaminants are removed by vacuum extraction. These processes - from the heating of the soil to the removal of the contaminated vapor - are monitored and guided by underground imaging, which assures effective treatment through *in situ* process control.

Hydrous Pyrolysis/Oxidation (HPO): *in situ destruction*

At temperatures achieved by steam injection, organic compounds will readily oxidize over periods of days to weeks. By introducing both heat and oxygen, this process has effectively destroyed all petroleum and solvent contaminants that have been tested in the laboratory. All that is required is for water, heat, oxygen, and the contaminant to be together; hence the name. After the free organic liquids are gone, this oxidation will continue to remove low-level contamination. The oxidation of contaminants at steam temperatures is extremely rapid (less than one week for TCE and two weeks for naphthalene) if sufficient oxygen is present. In HPO, the dense, nonaqueous-phase liquids and dissolved contaminants are destroyed in place without surface treatment, thereby improving the rate and efficiency of remediation by rendering the hazardous materials benign by a completely *in situ* process. Because the subsurface is heated during the process, HPO takes advantage of the large increase in mass transfer rates, such as increased diffusion out of silty sediments, making contaminants more available for destruction.

Underground Imaging: *process control*

Most subsurface environmental restoration processes cannot be observed while operating. Electrical Resistance Tomography (ERT) has proven to be an excellent technique for obtaining near-real-time images of the heated zones. ERT gives the operator detailed subsurface views of the hot and cold zones at their site on a daily basis. Heating soil produces such a large change in its electrical properties that it is possible to obtain images between wells (inverted from low voltage electrical impulses passed between) of the actual heated volumes by methods similar to CAT scans. Combined with temperature measurements, ERT provides process control to ensure that all the soil is treated.

LLNL Gasoline Spill Site: DUS

The DUS application at the LLNL Gasoline Spill Site was designed to remove free-product NAPL. The targeted volume was a cylinder about 120 ft (36 m) in diameter and 80 ft (24 m) high, extending from a depth of 60 ft (18 m) to a depth of 140 ft (43 m). The water table is located at 100 ft (30 m). Due to the presence of relatively thick clay-rich zones, both electrical heating and steam injection were required to heat the target volume.

Visalia Pole Yard: DUS + HPO

Thermal treatment (DUS steam injection and vacuum extraction) was chosen for removal of the free product contaminant. The overall objectives of thermal remediation of the Visalia Pole Yard are to remove a substantial portion of the DNAPL contaminant at the site, thereby enhancing the bioremediation of remaining contaminant. This is expected to significantly shorten the time to site closure as well as improve the accuracy of the prediction of time to closure. As part of the final removal process, Edison is also implementing hydrous pyrolysis (HPO), an *in situ* method of destroying organic contaminants using small amounts of supplemental air or oxygen. The primary use of HPO at this site is for destruction of residual pentachlorophenol, which will not readily steam strip due to high solubility and low vapor pressure. The combination of rapid recovery and thermal destruction is expected to permit Edison to achieve their cleanup goals, which included termination of groundwater treatment.

A series of noble gas tracer tests were conducted to verify the extent of HPO under field conditions. Evidence of hydrous pyrolysis/oxidation came from the disappearance of dissolved oxygen, the appearance of oxidized intermediate products, the production of CO_2, and the distinct isotopic signature of the carbon in the CO_2 produced, indicating contaminant origin. These results constrain the destruction rates throughout the site, and enable site management to make accurate estimates of total *in situ* destruction based on the recovered carbon using the system-wide contaminant tracking system being used on the site.

4. ANALYTICAL APPROACH

Standard laboratory analyses were performed on all samples unless noted specifically in the references.

5. RESULTS

LLNL Gasoline Spill Site:

During 21 weeks of thermal treatment operations conducted over about a year, DUS treatment removed more than 7600 gallons (29,000 L) of an estimated 6200 gallons (23,000 L) of gasoline trapped in soil both above and below the water table. Prior to thermal treatment, separate phase contamination extended to >120 ft (37 m) deep. Approximately 100,000 yd^3 (76,000 m^3) were cleaned. The maximum removal rate was 250 gallons (950 L) of gasoline a day. The process was limited only by the ability to treat the contaminated fluids and vapors on the surface.

Dynamic underground stripping removed contaminants 50 times faster than with the conventional pump-and-treat process. The cleanup, estimated to take 30 to 60 years with pump-and-treat, was completed in about one year. As of 1996, following removal of more than 99% of the contaminant, and achievement of Maximum Contaminant Limit (MCL) levels in groundwater for five of the six contaminants, the site is being passively monitored under an agreement with the California Regional Water Quality Control Board (RWQCB), California EPA's Department of Toxic Substances Control (DTSC), and the Federal EPA Region 9. These regulatory agencies declared that no further remedial action is required.

The initial objective of the LLNL DUS demonstration was to remove the separate phase gasoline from the treatment area. Not only was the separate phase gasoline removed, but the groundwater contamination was reduced to or near the regulatory limits. Thermal treatment under these conditions did not sterilize the site, and instead led to the establishment of flourishing indigenous microbial ecosystems at soil temperatures up to 90 °C. The very positive response of regulators, who provided quick closure authorization for the site, indicates that these methods will be accepted for use.

Visalia Pole Yard:

During the first six weeks of thermal remediation operations, between June and August 1997, approximately 300,000 pounds (135 metric tons) of contaminant was either removed or destroyed in place, a rate of about 46,000 pounds (22 metric tons) per week. That figure contrasts sharply with the 10 pounds (0.003 metric ton) per week that Edison had been removing with conventional pump and treat cleanup methods. In fact, the amount of hydrocarbons removed or destroyed in place in those six weeks was equivalent to 600 years of pump-and-treat, about 5,000 times the previous removal rate.

Edison achieved their initial goal of heating over 500,000 yd^3 (380,000 m^3) to at least a temperature of 100 °C by the beginning of August 1997. Uniform heating of both aquifer and aquitard materials was achieved. At this point, about 20,000 gallons (76,000 L) of free-product liquid had been removed. Vapor and water streams continued to be saturated with product. Continued destruction by HPO was indicated by high levels of carbon dioxide (0.08 - 0.12% by volume) removed through vapor extraction. Initial destruction accounted for about 300 lb/day 136 kg/day) of contaminant being destroyed via HPO. Operations were changed to a huff and puff mode, where steam is injected for about a week, and then injection ceases for about a week while extraction continues. Maximum contaminant removal is obtained during this steam-off period as the formation fluids flash to steam under an applied vacuum.

In September, 1997, following the initial contaminant removal by steam injection and vacuum extraction, air was injected along with the steam to enhance hydrous pyrolysis of the remaining contaminant. *In situ* destruction rates increased to about 800 lb/day (360 kg/day). Recovery/destruction rates matched expectations. By the summer of 1998, decreasing contaminant concentrations indicated that the bulk of the contaminant had been removed from the main treatment volume. Groundwater concentrations indicated that the site was being cleaned from the periphery inward, with all but two wells showing contaminant concentrations similar to the pre-steam values by September, 1998. Active thermal remediation of this zone was nearing completion. At this point, Edison chose to begin injecting steam into a deeper aquifer to heat and remove the remaining contamination that had leaked into the overlying silty aquitard which represented the "floor" of the initial treatment zone. Contaminant is being recovered from this aquitard today.

In the ensuing months, recovery rates have remained high. As of March 1999, over 960,000 lb (440,000 kg) or 116,000 gallons of contaminant had been removed or destroyed. About 18% of the total has been destroyed in situ via HPO. Contaminant concentrations in the recovery wells are decreasing.

Edison plans to continue steam injection through the end of June, 1999. This will be followed by groundwater pumping, vacuum extraction and air injection to enhance HPO and bioremediation. Monitoring of groundwater concentrations is expected to continue for a period of 2 to 5 years.

6. HEALTH AND SAFETY

This high-energy system needs to be handled in accordance with standard safety procedures. Monitoring of air emissions has revealed low emissions with no worker safety or public health impacts.

7. ENVIRONMENTAL IMPACTS

Permits were required for water discharge (treated effluent) and NO_x emissions from the boilers. The site is being remediated under a state-lead Remedial Action Plan (RAP). Vapor is destroyed in the boilers under air permit from the regional air board. Standard regional groundwater monitoring is conducted to ensure public health protection.

8. COSTS

DUS at the LLNL Gasoline Spill Site:

The first application of dynamic underground stripping at the Livermore gasoline spill site in 1993 cost about $110 per cubic yard ($140 per cubic meter); removing the additional research and development costs suggested the project could have been repeated for about $65 per cubic yard ($85 per cubic meter). The alternatives would have been significantly higher. Because contamination at the gasoline spill at the Livermore site had migrated downward over 130 ft (40 meters), digging up the contaminated soil and disposing of it would have cost almost $300 per cubic yard ($400 per cubic meter). Soil removal and disposal costs are more typically in the range of $100 to $200 per cubic yard ($130 to $260 per cubic meter); pump-and-treat method costs are as high as or higher than soil removal costs.

DUS and HPO at the Visalia Pole Yard:

Use of DUS and HPO in combination can permit huge cost savings because HPO eliminates the need for long-term use of expensive pump and treat treatment facilities by converting some contaminants to benign products in situ and mobilizing other contaminants. Site operators can adjust process time to enhance removal DUS or in situ destruction through HPO. Because the treatment is simple, it can be readily applied to large volumes of earth.

Edison has projected the life-cycle cost of steam remediation at the Visalia pole yard to be under $20 million, which includes all construction, operation and monitoring activities. The total treatment zone includes about 800,000 yd^3 (600,000 m^3) of which about 400,000 yd^3 (300,000 m^3) contained DNAPL contamination. Approximately $4.2 million was spent on capital engineering, design, construction, and startup. In addition, about $12 million had been spent on operations, maintenance, energy (gas and electric), monitoring, management, engineering support, and regulatory interface by the end of 1998. Since Edison (the site owner) has acted as primary site operator for the cleanup, the aforementioned project costs do not reflect a profit in the overhead costs. Post-steaming operations will consist of the operation of the water treatment system for an expected duration of two to five years to demonstrate compliance with the California State EPA Remediation Standards. The annual operations and maintenance costs for the water treatment plant is $1.2 million. The previously-approved cleanup plan of pump and treat with enhanced bioremediation was expected to cost $45 million (in 1997 US dollars) for the first 30 years; it was expected to take over 120 years to complete the cleanup.

The Visalia pole yard cleanup is the only commercial application of this method to date, but indications are that large-scale cleanups with hydrous pyrolysis/oxidation may cost less than $25 per cubic yard ($33/m^3), an enormous savings over current methods. Perhaps the most attractive aspect of these technologies is that the end product of a DUS/HPO cleanup with bioremediation as a final step is expected to be a truly clean site.

9. CONCLUSIONS

Breakthrough cleanups of seemingly intractable contaminants are now possible using a combined set of thermal remediation and monitoring technologies. This "toolbox" of methods provides a rapid means to clean up free organic liquids in the deep subsurface. Previously regarded as uncleanable, contamination of this type can now be removed in a period of 1-2 years for a cost less than the many-decade site monitoring and pumping methods it replaces. The groundwater polishing by HPO provides the means to completely clean serious NAPL-contaminated sites.

The gasoline spill demonstration clearly showed that thermal methods can quickly and effectively clean a contaminated site. With respect to the Visalia Pole Yard cleanup, tremendous removal rates have been achieved. More than 970,000 lb. of contaminants was removed or destroyed in about 20 months of operations; previous recovery amounted to 10 lb/week. Contaminant concentrations are dropping in the extraction wells; the site is cleaning from the periphery inward. Site management plans to terminate active thermal treatment soon, returning to pumping and monitoring the site. The expectations are that groundwater treatment will no longer be necessary after a few years.

The Visalia field tests confirmed *in situ* HPO destruction in soil and ground water at rates similar to those observed in the laboratory, under realistic field remediation conditions. HPO appears to work as fast as oxygen can be supplied, at rates similar to those measured in the laboratory. The predictive models used to design HPO steam injection systems have been validated by using conservative tracers to confirm mixing rates, oxygen consumption, CO_2 release, and effects of real-world heterogeneity. Accurate field measurements of the critical fluid parameters (destruction chemistry, oxygen content, steam front location) were demonstrated, using existing monitoring wells and portable data systems with minimal capital cost.

Several sites are designing DUS/HPO applications similar to Visalia. These include both solvent and pole-treating chemical contaminated sites, ranging in depth from relatively shallow (<40 ft (10 m)) to relatively deep (>185 ft (56 m)). In January 1999, steam injection began at a relatively shallow (>35 ft (11 m)) site in Ohio in which DNAPL TCE is being removed.

10. REFERENCES AND BIBLIOGRAPHY

Aines, R.D.; Leif, F.; Knauss, K.; Newmark, R.L.; Chiarappa, M.; Davison, M.L.; Hudson, G.B., Weidner, R.; and Eaker, C.; Tracking inorganic carbon compounds to quantify in situ oxidation of polycyclic aromatic hydrocarbons during the Visalia Pole Yard hydrous pyrolysis/oxidation field test, 1998 (in prep).

Cummings, Mark A.; Visalia Steam Remediation Project: Case Study of an Integrated Approach to DNAPL Remediation. *Los Alamos National Laboratory Report, LA-UR-9704999; 1997; 9 pp.*

Knauss, Kevin G.; Aines, Roger D.; Dibley, Michael J.; Leif, Roald N.; Mew, Daniel *A.;* Hydrous Pyrolysis/Oxidation: In-Ground Thermal Destruction of Organic Contaminants. *Lawrence Livermore National Laboratory, Report, UCRL-JC 126636, 1997; 18 pp.*

Knauss, Kevin G.; Dibley, Michael J.; Leif, Roald N.; Mew, Daniel A.; Aines, Roger D. "Aqueous Oxidation of Trichloroethene (TCE): A Kinetic and Thermodynamic Analysis". In *Physical, Chemical and Thermal Technologies, Remediation of Chlorinated and Recalcitrant Compunds, Proceeding of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds;* Wickramanayake, G.B., Hinchee, R.E., Eds.; Battelle Press, Columbus, OH, 1998a; pp359-364. Also available *as Lawrence Livermore National Laboratory, Report, UCRL-JC-129932*, 1998; 8 pp.

Knauss, Kevin G.; Dibley, Michael J.; Leif, Roald N.; Mew, Daniel A.; Aines, Roger D. "Aqueous Oxidation of Trichloroethene (TCE): A Kinetic analysis." Accepted for Publication, *Applied Geochemistry*; 1998b.

Knauss, Kevin G.; Dibley, Michael J.; Leif, Roald N.; Mew, Daniel A.; Aines, Roger D. "Aqueous Oxidation of Trichloroethene (TCE) and Tetrachloroethene (PCE) as a Function of Temperature and Calculated Thermodynanmic Quantities, Submitted to *Applied Geochemistry*; 1998c.

Leif, Roald N.; Chiarrappa, Marina; Aines, Roger D.; Newmark Robin L.; and Knauss, Kevin G. "In Situ Hydrothermal Oxidative Destruction of DNAPLS in a Creosote Contaminated Site." In *Physical, Chemical and Thermal Technologies, Remediation of Chlorinated and Recalcitrant Compunds, Proceeding of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds;* Wickramanayake, G.B., Hinchee, R.E., Eds.; Battelle Press, Columbus, OH, 1998; pp 133-138. Also available as Lawrence Livermore National Laboratory, Report, *UCRL-JC-129933*, 1998a; 8 pp.

Leif, Roald N.; Knauss, Kevin G.; and Aines, Roger D.; Hydrothermal Oxidative Destruction of Creosote and Naphthalene, *Lawrence Livermore National Laboratory, Report, UCRL-JC*, 1998b 21 pp (in prep).

Leif, Roald N.; Aines, Roger D.; Knauss, Kevin G. Hydrous Pyrolysis of Pole Treating Chemicals: A) Initial Measurment of Hydrous Pyrolysis Rates for Napthalene and Pentachlorophenol; B) Solubility of Flourene at Temperatures Up To 150°C; *Lawrence Livermore National Laboratory, Report, UCRL-CR-129938*, 1997a; 32pp.

Leif, Roald N.; Knauss, Kevin G.; Mew, Daniel A.; Aines, Roger D. Destruction of 2,2',3-Trichlorobiphenyl in Aqueous Solution by Hydrous Pyrolysis / Oxidation (HPO). *Lawrence Livermore National Laboratory, Report, UCRL-ID 129837*, 1997b; 21 pp.

MSE Technology Applications, Inc., "Dynamic Underground Stripping and Hydrous Pyrolysis/Oxidation Cost Analysis", *report prepared for the U.S. Department of Energy, HMP-44,* June, 1998.

Newmark, R.L., ed., Dynamic Underground Stripping Project: LLNL Gasoline Spill Demonstration Report ; *Lawrence Livermore National Laboratory, Report UCRL - ID - 116964*, July, 1994 (1600 pages).

Newmark, Robin L.; Aines, Roger D.; Dumping Pump and Treat: Rapid Cleanups Using Thermal Technology. *Lawrence Livermore National Laboratory, Report, UCRL-JC 126637*, 1997; 23 pp.

Newmark, R.L., R. D. Aines, G. B. Hudson, R. Leif, M. Chiarappa, C. Carrigan, J. Nitao, A. Elsholz, C. Eaker, R. Weidner and S. Sciarotta, *In Situ* destruction of contaminants via hydrous pyrolysis/oxidation: Visalia field test, *Lawrence Livermore National Laboratory, Report UCRL-ID-132671*, 1998; 45 pp.

Newmark, R.L., R. D. Aines, G. B. Hudson, R. Leif, M. Chiarappa, C. Carrigan, J. Nitao, A. Elsholz, and C. Eaker, 1999. An integrated aproach to monitoring a field test of in situ contaminant destruction, *Symposium on the Application of Geophysics to Engineering and Environmental Problems* (SAGEEP) '99, Oakland, Ca., March 15-18, 1999, 527-540.

Ramirez, A.L., W. D. Daily and R. L. Newmark, Electrical resistance tomography for steam injection monitoring and process control, *Journal of Environmental and Engineering Geophysics,* (July, 1995), v. 0, no.1, 39-52.

Udell, K and McCarter, R (1996) Treatability Tests of Steam Enhanced Extraction for the Removal of Wood Treatment Chemicals from Visalia Pole Yard Soils, University of California, Report to Southern California Edison. (<http://abacus.me.berkelley.edu/BERC/Projects/Visalia/index.html>)

This work was performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.