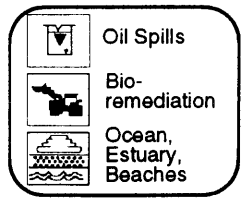
United States Environmental Protection Agency | Solid Waste Emergency Response (5102W) | EPA 542-N-95-005 August 1995 Issue No. 21

EPA

TECH TRENDS

The Applied Technologies Journal for Superfund Removals & Remedial Actions & RCRA Corrective Actions

DELAWARE OIL SPILL BIOREMEDIATION FIELD STUDY



By Albert D. Venosa, EPA National Risk Management Research Laboratory

Last summer, an important field study was undertaken on the shoreline at Fowler Beach in the Delaware Bay. As part of a carefully designed study, 540 gallons of light crude oil were intentionally released onto fifteen replicate plots to evaluate bioremediation. The research design overcame the flaws of previous studies reported in the literature that based conclusions on comparisons between one large nutrient-treated plot and one large control plot. The problem with those experiments is that no replicate plots were established to provide a basis for estimating experimental error.

The objectives of the Delaware study were to obtain highly credible statistical evidence (1) to determine if bioremediation with inorganic mineral nutrients and/or microbial inoculation enhanced the removal of crude oil contaminating mixed sand and gravel beaches; and (2) to compute the rate at which such enhancement takes place. Biodegradative loss of oil from the plots was tracked by GC/MS analysis of oil analytes normalized to hopane, a non-biodegrable compound present in all crude oils. A randomized complete block design was used to assess treatment effects. Three treatments were evaluated: a no nutrient control; water soluble nutrients (biostimulation); and water soluble nutrients supplemented with a natural microbial inoculum from the site (bioaugmentation). An unoiled and untreated plot served as a background control for microbiological characterization and baseline bioassays. Five replicates (blocks) of each of four plots (20 plots in all) were set up in random fashion so that whatever inferences could be ascertained from the data would be applicable to the entire beach, not just the test plots.

The experimental design provided the best chance to detect if significant treatment effects existed. Statistically significant differences between treated and untreated plots were observed at weeks 2, 4, 8 and 14 for the alkanes and weeks 8 and 14 for the polycyclic aromatic hydrocarbons (PAHs). First order rate constants for treated plots were significantly different from those of the untreated plots. At no time were any significant differences observed between plots treated with nutrients alone and plots treated with nutrients and the indigenous inoculum. Notable from the data is the fact that the hydrocarbon biodegradation occurred to a significant extent in the untreated plots. This was attributed to the high levels of background nitrogen measured on the beach from Delaware Bay (upwards of 1 milligram (mg) nitrate-nitrogen per liter interstitial pore water continuously over the course of the 14-week study). Had the background nutrient levels been closer to those typical of Prince William Sound beaches (i.e., a thousand-fold less), the slopes of the control plots would likely have been much flatter, thus giving rise to highly significant differences between treated and control plots for both alkanes and PAHs, perhaps as early as two weeks after the release. The latter conclusion is speculative, since such low background nutrient levels were not encountered in Delaware. However, the goals of the project were met: bioremediation via nutrient enrichment was demonstrated unequivocally with statistically credible data; computed biodegradation rates were high, with an alkane half-life of approximately two weeks and a PAH half-life of approximately four weeks; and bioaugmentation even with indigenous organisms does not stimulate further declines in hydrocarbons beyond simple nutrient addition.

Based on the fact that nutrient levels in the area were high enough to support significant biostimulative hydrocarbon decay, the recommendation would be not to encourage active bioremediation activities if an oil spill were to occur along the Delaware Bay shoreline. However, for coastlines having low natural input levels of nutrients, bioremediation should definitely be considered a major cleanup option.

The study was conducted under a Clean Water Act, section 311, permit. Section 311 allows the Administrator to approve the intentional discharge of less than 1,000 gallons of oil for research programs. In October 1994, the Administrator received an application from the State of Delaware to intentionally discharge 540 gallons of crude oil onto a private beach for a bioremediation study. The proposal was strongly supported by EPA's Office of Research and Development and Region 3, the U.S. Coast Guard, the U.S. National Oceanographic and Atmospheric Agency, the U.S. Department of Interior and several Delaware environmental groups. After an intra- and interagency review, EPA granted the permit in June 1994.

For more information on the study, call Albert D. Venosa at EPA's National Risk Management Research Laboratory at 513-569-7668. A report will be available in the Fall; to get on the mailing, send a FAX request to Albert Venosa at 513-569-7105.

REMEDIATION MARKETPLACE

See the special insert in this issue of TECH TRENDS for information on the Mid-Atlantic Remediation Marketplace, sponsored by the EPA's Technology Innovation Office and Region 3 and the Pennsylvania Department of Environmental Resources.

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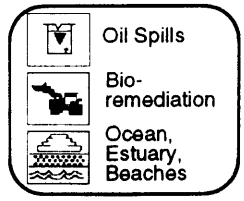

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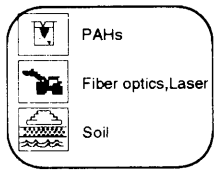
SITE Subjects

CONE PENETROMETER MOUNTED SENSORS

By Lary Jack, EPA National Exposure Research Laboratory, Las Vegas



In August 1994, the EPA Superfund Innovative Technology Evaluation (SITE) Program completed a field demonstration of cone penetrometer-mounted chemical sensors. Two of the technologies evaluated were: (1) the Rapid Optical Screening Tool (ROST®) marketed by Loral Corporation; and (2) the Site Characterization and Analysis Penetrometer System (SCAPS) Laser Induced Fluorescence (LIF) developed by the Army, Navy and Air Force. These technologies were designed to detect fluorescing compounds such as petroleum wastes and coal tars with rapid sampling and real-time, relatively low cost analysis of the physical and chemical characteristics of subsurface soil. The inherent advantages of such cone penetrometer sensor systems are the high rate of penetration (speed) and the low level of waste generation. Of particular note, is that much of the data is acquired without stoppage and plotted on continuous logs as the data is obtained.

The SITE demonstration took place at three sites within EPA Region 7, which were selected because of their varying concentrations of wastes (coal tar and petroleum fuels) and their ranges in soil textures. Both technologies are attachments designed to fit a standard cone penetrometer (CP) rig which simultaneously provides a continuous log of subsurface materials. Two fiber optic cables run from the sensor up through the center of the penetrometer rods along with the wires coming from the load cells in the CP. One fiber optic transmits laser induced, monochromatic light from the truck down to the sensor where it passes through a sapphire window on the side of the tool. Since the cone is pushing its way into the earth, the window is in direct contact with the soil; and, the light passes through the window into the soil. The light energy excites hydrocarbon compounds and causes them to fluoresce, with the resultant energy passing up to the second fiber optic cable to an analyzer in the truck. This produces a log of the contamination while the signal from the standard CP head produces (after translation by software) a similar continuous soil classification log.

The SITE demonstration evaluated the effectiveness of these sensor systems in sampling and analyzing the physical and chemical characteristics of each waste site's subsurface soils, by comparing each technology's results to the results obtained using conventional reference methods. The demonstration found that the SCAPS and ROST® technologies produced screening level data for the contamination while the standard CP produced screening level soil classifications. Specifically the qualitative assessment showed that the stratigraphic and the chemical cross sections of the SCAPS and ROST®, and associated CP sensors, were comparable to the reference methods in their ability to map subsurface contaminant plumes at petroleum fuel and coal tar contamination sites. In most cases, a consistent relationship between the fluorescence data and the reference method data was identified. Increases in contaminant concentrations were generally followed by increases in measured fluorescence. Data from both technologies identified similar zones of subsurface petroleum and coal tar contamination at each of the three demonstration sites relative to the reference methods. Both technologies produced continuous profiles, while the reference methods took only a few selective samples targeting boundaries and zones of contamination. For the SITE demonstration, both technologies could produce relatively continuous data on petroleum or coal tar contaminant distribution over a 30-foot depth in approximately 1.5 hours. (The use of these sensors is restricted to the maximum push depth of the cone penetrometer truck. This depth can be as much as 300 feet, or in the case of the demonstration, 30 to 70 feet.)

Based on the SITE demonstration, these technologies produce screening level data. A powerful aspect of both technologies is that they can be advanced with a standard cone penetrometer to provide continuous descriptions of the subsurface soil concurrently with the chemical data. The combination of chemical and physical sensors allows investigation and remediation decisions to be made more efficiently onsite and will reduce the number of samples that need to be submitted for costly confirmatory analyses. The added benefit of these sensors functioning without requiring physical sampling allows them to produce data in subsurface environments that restrict conventional sampling.

The ROST® technology is currently available as a service from the developer. The technology is designed to be operated by trained technicians. The SCAPS technology is designed to be operated by trained technicians from the Army Environmental Center, Army Corps of Engineers, Navy, Air Force and the Waterways Experiment Section. The SCAPS technology is not currently available for use by private citizens or corporations, although it is available to State and Federal agencies. The target contaminants are primarily polycyclic aromatic hydrocarbons; and, most often, this technology is applied at petroleum fuel release sites.

For more information, call Lary Jack at EPA's National Exposure Research Laboratory at 702-798-2373. Innovative Technology Evaluation Reports on ROST® and SCAPS, as well as the other cone penetrometer systems evaluated in the SITE demonstration should be available by November 1995.

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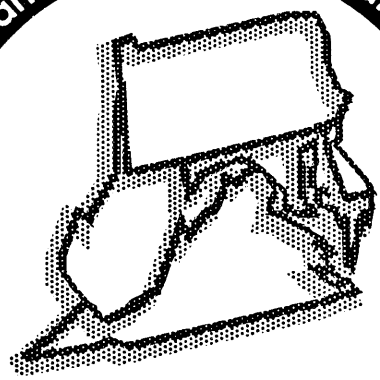
Mid-Atlantic Remediation Marketplace



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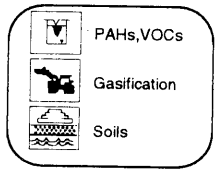
SITE Subjects

GASIFICATION TREATMENT FOR SOILS

By Marta K. Richards, EPA National Risk Management Research Laboratory



Texaco, Inc. has developed waste gasification as an innovative extension of their conventional fuels gasification technology. The Texaco Gasification Process (TGP) was evaluated by EPA's SITE (Superfund Innovative Technology Evaluation) Program to determine the applicability of the TGP to treatment of a hazardous waste-contaminated soil. Since the TGP is operating at temperatures above the melting point of the inorganic materials in the feed stream, the solid residuals form a glassy slag, while the TGP converts carbonaceous organic materials into a gas mixture, called syngas, consisting primarily of hydrogen and carbon monoxide. This is accomplished by reaction with a limited amount of oxygen (partial oxidation) in a refractory-lined gasifier at temperatures in excess of 2,200 F and at pressures greater than 250 psig. According to Texaco, these temperatures and pressures are sufficient to destroy hydrocarbons and organics in the feed and prevent the formation of undesirable organic by-products associated with other coal/fossil fuel conversion processes. The TGP produces syngas as a chemical intermediate product which can be used in the production of hydrocarbons, ammonia, methanol and other chemicals. Alternatively, the syngas can be combusted directly in a gas turbine to produce electricity.

The process works as follows. Waste feed, along with coal, oil and/or coke is ground and mixed with water in a high-solids' concentration slurry (generally 55 to 70% by weight). The water serves as a reactant, a temperature moderator and a transport medium. Liquid and gas fuels, which can be fed directly to the gasifier, need no pretreatment but may require water or steam moderators. For the SITE demonstration at the Texaco Montebello Research Laboratory in South El Monte, California, the slurry feed consisted of coal, water, waste soil from the Purity Oil Sales Superfund Site in Fresno, California, and clean soil. The composite slurry was spiked with heavy metals (lead and barium) to ensure that the feed contained sufficient levels of contamination to fail the Toxicity Characteristic Leaching Procedure (TCLP) test. The addition of approximately 6.42 lbs. per hour of chlorobenzene, a volatile organic, was fed into the gasifier with the slurry to facilitate the calculation of the Destruction and Removal Efficiency (DRE).

In the SITE demonstration, slurry was fed into the gasifier, along with oxygen, through an injector nozzle. The chlorinated species in the feed formed hydrogen chloride in the raw syngas; the hydrogen chloride dissolved into the scrubber water before being purged from the process. The sulfur in the feed formed hydrogen sulfide or carbonyl sulfide in the product gas. Commercial acid gas and sulfur removal processes scrubbed these sulfides from the product gas. The residual ash was recovered as a glassy slag.

The DRE for chlorobenzene was greater than 99.99%. The average composition of the combustible dry syngas from the TGP was 37% hydrogen, 36% carbon monoxide and 21% carbon dioxide. No organic compound, other than methane (55 parts per million) was above 0.1 ppm. On the average, the primary TGP solid product, coarse slag, complied withthe TCLP regulatory requirement for lead [5 milligrams per liter (mg/L)] and the TCLP and California Waste Extraction Test (WET) regulatory requirements for barium (100 mg/L). The coarse slag did not meet the WET standard for lead (5 mg/L). Volatile heavy metals, such as lead, tend to partition and concentrate in

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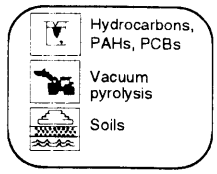
NORTH OF THE BORDER

VACUUM PYROLYSIS FOR ORGANICS IN SOILS

From Environment Canada



Environment Canada's Development and Demonstration of Site Remediation (DESRT) Program supported the evaluation of the Pyrovac vacuum pyrolysis process developed by Pyrovac International, Inc. The evaluation was carried out by the Laval University in collaboration with Pyrovac, with support from DESRT and the Ministère de l'Environnement et de la Faune du Québec at the Le Vidangeur de Montréal Inc. site in Mascouche, Québec. The site, previously a sand-quarry, was used from 1969 to 1974 for the dumping of solid residues, as well as for the incineration of petroleum sludges. Fissured basins containing liquids and hydrocarbon sludges were abandoned. Today, hydrocarbon tar slabs can be found in several places on the site whose soil and water have been highly contaminated with hydrocarbons, polycyclic aromatic hydrocarbons and polychlorinated biphenyls (PCBs).

The samples collected at the Mascouche site were chosen so as to represent a variety of types of soils (sand, clay, tar slabs) and a variety of contamination concentrations. The objectives of the treatment were to reduce the level of organic contamination so as to respect the Québec criteria for soil contamination.

Prior to pilot-scale demonstration, laboratory scale batch runs were carried out in a vacuum pyrolysis reactor and confirmed the potential of the vacuum pyrolysis concept. The evaluation continued with the pilot unit. Petroleum hydrocarbon reductions in milligrams per kilogram were: Clay A, from 290 to 5.0; Clay B, from 150

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