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Hydrocarbons
Bioremediation
Flare Pit Waste

CANADIAN BIO-REACTOR FLARE PIT WASTES - TEST RESULTS

Canada, which has an abundance of flare pit waste sites, selected flare pit wastes as the third waste to be tested in its Bio-Reactor. The Canadian Bio-Reactor Project tests the premise that hydrocarbon contaminated soils and soil-like wastes with high levels of salts can be treated effectively and efficiently by combining leaching with soil biological process by exerting strict controls on all inputs, the physical-chemical environment and the fate of the transformed waste products. TECH TRENDS has previously reported on the results of the first two wastes treated in the Bio-Reactor. A major Bio-Reactor Project axiom has been that good structure is essential for bioremediation of solid wastes. However, with the third waste to be treated, results suggest that super sophisticated controls and procedures may not be necessary to eliminate hydrocarbons from wastes as long as the basic needs of the microorganisms are satisfied in the combined leaching and bioremediation.

Flare pit wastes are common at sites in oil and gas producing regions; and most, if not all will require remediation. Flare pits are located at well sites and some pipeline pump stations where waste gases are burned off; and, periodically liquid waste hydrocarbons may be diverted to pits. Pits may also contain brine, condensates, lube oils, tank bottom sludges, pigging waxes and other wastes that comprise a cornucopia for microbes. For the Bio-Reactor, flare pit material in a solid form contained 8.5% hydrocarbons, a high level of brine salts (EC > 30 $dS\ m^{-1}$) and had a 7.5 pH. The waste had very heavy clay clods and balls of tar-like material and posed handling and wettability problems. Factors tested in the Bio-Reactor included the potential value of aggregation (i.e., does particle size have an effect); cultivation; inoculation practices; and waste depth under uniform conditions of nutrients, water and forced aeration (i.e., how deep can be wastes be layered before aeration becomes a problem --20 cm versus 40 cm).

Treatment in the Bio-Reactor resulted in a 30% decrease in hydrocarbons during the seven-month period for the "best" (i.e., amended) treatment. Unexpectedly, there were also substantial losses in the "worst" (i.e., no amendment) treatment which was characterized as having very poor structure and porosity. It did not matter whether or not the waste was aggregated, cultivated, or inoculated or to which depth it was piled. Differences in hydrocarbon loss rates among waste aggregated, cultivated, inoculated or piled to 20 or 40 cm depth appeared to be small. All of this suggests that the ability of microorganisms to function well under what appear to be very adverse conditions was underestimated.

The Bio-Reactor can effectively treat flare pit wastes by first removing the salts through leaching and then reducing the hydrocarbon contents through bioremediation. Although the treated material has relatively high residual hydrocarbon levels, these hydrocarbons have a low bioavailability so that the material is nontoxic in a battery of tests and will pass leachate requirements.

As a side note, see the companion article in this issue of TECH TRENDS, p. 3, which discusses the serious analytical problems encountered and the remedy.

For more information, call the Bio-Reactor Project's Project Manager, Lin Callow, of Gulf Canada Resources, Ltd. at 403-233-3924.

For progress reports and more detailed reports, contact Lisa Crichton at the Canadian Association of Petroleum Producers (CAPP) by phone at 403-267-1100 or by FAX at 403-261-4622. There is a charge for the reports. Information in this article is from the August 1995 issue of the "BIO-REACTOR PROJECT Newsletter," published by CAPP.

The Bio-Reactor Project is cofunded by the CAPP; by Environment Canada through its contributions to the Development and Demonstration of Site Remediation Technology Program (DESRT), GASReP and Federal Program on Energy Research and Development; and by the Alberta Environmental Research Trust. The research is conducted by the Alberta Environmental Centre in Vegreville and the University of Calgary. The Bio-Reactor is located at the Morrison Petroleums, Ltd. Nevis Sour Gas Plant.

For your information, the results of Bio-Reactor treatment of Waste 1, agricultural topsoil, and Waste 2, saline diesel invert mud drill cuttings, were reported in the May 1994 issue of TECH TRENDS (Document No. EPA 542-N-94-004) and can be ordered by sending a request to NCEPI by fax (513-489-8695) or by mail (P.O. Box 42419, Cincinnati, OH 45242-20419).

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ALTERNATIVE TREATMENT FOR PAH AND PCP

By Teri Richardson, EPA National Risk Management Research Laboratory

PAHs, TCPs
Bioremediation
Soil

The DARAMEND™ bioremediation technology is an effective alternative to soil washing, incineration or landfilling soils containing high levels of polynuclear aromatic hydrocarbons (PAHs) and chlorinated phenols, including pentachlorophenol (PCP). These contaminants are typically considered too toxic for bioremedia - tion and are found at approximately 400 industrial wood treatment facilities in the United States and an additional 200 sites in Canada. The patented DARAMEND™ technology, applicable to both in-situ and ex-situ remediation of soils, was developed by GRACE Dearborn Inc.'s Environmental Consulting Group in Mississauga, Ontario, Canada. A full-scale demonstration of the ex-situ application was conducted at the Domtar Wood Preserving Facility in Trenton, Ontario, by the EPA's Superfund Innovative Technology Evaluation (SITE) Program. The SITE evaluation built upon previous evaluations of bench and pilot scale testing by the Developer under Canada's Development and Demonstration of Site Remediation Technology (DSERT) Program. The technology provides short- and long-term protection because it provides irreversible treatment of PAHs and total chlorinated phenols (TCPs) by eliminating these contaminants from the soil, thus preventing further ground water contamination and pollutant migration.

An important operating parameter of the technology is an understanding the specific physical and chemical properties of the contaminated soil that could limit the effectiveness of bioremediation. Once an evaluation of various soil properties is completed, the developer selects an organic amendment formulation with the specific particle size distribution and nutrient profile to create ideal soil microbiological conditions. The organic amendments enable the soil matrix to supply biologically available water and nutrients to contaminant-degrading microorganisms, transiently binding pollutants to reduce the acute toxicity of the soil's aqueous phase. This allows the microorganisms to survive in soils containing very high concentrations of toxicants.

The technology is a relatively simple soil remediation system, both in design and implementation. It consists of three integrated treatment components: (1) addition of the appropriate specially formulated solid-phase organic soil amendments to the target matrix; (2) distribution of the soil amendments through the target matrix and the homogenization and aeration of the target matrix using specialized tilling equipment; and (3) soil moisture control using a specialized system to maintain moisture content within a specified range, to facilitate rapid growth of an active microbial population and prevent the generation of leachate. The process involves a certain amount of materials handling -- the ex-situ application more so than the in-situ application.

For in-situ applications, soil is initially broken up with excavation equipment to a depth of 0.6 meters, which is the limit for the specialized tilling equipment,. For ex-situ applications, contaminated soil is excavated and screened to 10 cm to remove debris that might interfere with the incorporation of organic amendments. Screened soil is spread uniformly in the constructed treatment plots to a depth of 0.5 meters. The plots are lined with a high-density polyethylene liner (impermeable to the target compounds), underlain with 10 cm of screened sand to prevent structural damage. Another 15-cm thick sand layer and a 4mm-thick fiber-pad are spread on top of the liner to minimize the potential for direct contact between the liner material and tillage quipment. The SITE treatment

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SONIC PULSE BURNER SYSTEM

By Marta Richards, National Risk Management Research Laboratory

VOCs
Combustion
Soils, Sludges, Liquids

Sonotech, Inc. of Atlanta, Georgia has developed the Cello™ pulse combustion burner that incorporates a combustor that can be tuned to induce large amplitude sonic pulsations inside combustion process units such as boilers or incinerators. The pulsations are claimed to increase heat release, mixing and mass transfer rates in the combustion process, resulting in faster, more complete combustion. Sonotech has targeted waste incineration as a potential application for the system. The Superfund Innovative Technology Evaluation (SITE) Program evaluated the Cello™ system on the pilot-scale rotary kiln incineration system at the EPA Incineration Research Facility in Jefferson, Arkansas. In the demonstration, the Cello™ system was retrofit to the primary combustion chamber.

A pulse combustor typically consists of an air inlet, a combustor section and a tailpipe. In the Cello™ pulse combustor, fuel oxidation and heat release rates vary periodically with time, producing periodic variations or pulsations in pressure, temperature and gas velocity. Sonotech claims that large amplitude resonant pulsations excited by its frequency-tunable pulse combustor can significantly improve an incinerator's performance, thereby reducing capital investment and operating costs for a wide variety of incineration systems. The Cello™ combustor can be incorporated into the construction of most new combustion devices or can be retrofit to many existing systems. It is designed to be used to treat any material typically treated in a conventional incinerator; and, Sonotech believes the technology is ready to be used for the full-scale incineration of contaminated solids, liquids, sludges and medical wastes. Contaminated soil, sludge and tar samples collected from two manufactured gas plant Superfund sites were blended for use in this SITE demonstration.

The primary objective of the demonstration was to develop test data to evaluate the treatment efficiency of the Cello™ combustor system compared to conventional combustion. The Cello™ system increased the incinerator waste feed rate capacity by 13 to 21% compared to conventional combustion. The capacity increase was equivalent to reducing the auxiliary fuel needed to treat a unit mass of waste from 27.3 thousand British thermal units per pound of waste (kBtu/lb) for conventional combustion to 21.5 kBtu/lb for the Cello™ system; however, the demonstration waste had significant heat content. Visual observations indicated improved mixing in the incinerator cavity with the Cello™ system operating.

Benzene Destruction and Removal Efficiencies (DREs) for all 12 test runs

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Hydrocarbons
Bioremediation
Flare Pit Waste

"TOTAL HYDROCARBON" MEASUREMENTS CAUSE CONFUSION

Canada's Bio-Reactor Project turned up an unexpected "by-product" when it set out to assess the rate of remediation of flare pitwastes. The finding should provide some sound guidance for methodology to quantify bioremediation success.

During bioremediation of the flare pit waste, a serious analytical problem was identified. The first results on hydrocarbon contents in the various treatments after four and seven months surprisingly indicated that the losses of oil were much higher than predicted by either chemical composition or the lab treatability study. As a result a critical evaluation was made of the standard methodology for extraction and quantification of hydrocarbons in soil-like wastes. This study, involving two independent methods for measuring TEH, indicates that the first losses were overestimated and that actual losses were much less than estimated by the original method. Therefore, selection of analytical method is crucial; and, remediation operators may be seriously misled by results obtained by inappropriate methods. The analytical method should be picked based on the knowledge of the specific hydrocarbon material to be tested. Carbon number scans can be used to measure hydrocarbon fraction that is present.

Currently, all regulatory agencies and developers of remediation technologies rely on analytical results generated by laboratories specialized in chemical analysis. Precise and accurate methods are required to meet key criteria for hydrocarbon residuals set by regulators or to assess the success of a remediation strategy. Analysts use numerous methods; and, the results of comparisons of these methods may be made under the assumption that all of them measure the same pool of hydrocarbons. The determination of TEH requires two separate steps: (1) extraction from the solid waste and (2) quantification of the material extracted. Each of these steps is subject to errors or shortcomings and extraction efficiency cannot be assessed without a "good" detection/quantification method -- hence the importance of the Canadian study of TEH procedures.

To quantify TEH, the study chose two methods routinely used by analytical service labs, but which are distinctly different: the gravimetric method (extractable material dried and weighed) and the Gas Chromatographic (GC) method (extractables separated based on mean boiling point).

The gravimetric quantification measures heavy hydrocarbons, with light hydrocarbons lost as volatiles. The GC method measures light hydrocarbons and cannot detect very heavy hydrocarbons. Both methods would give similar results only when there is no heavy hydrocarbon fraction and when no volatiles are present in the light hydrocarbon fraction. Since gasoline, jet fuel, diesel fuel, crude oil and oily sludges never satisfy these conditions, results using the two detection methods are guaranteed to be different. Most importantly, assessing the biotreatability of a waste using one method or the other will lead to different conclusions, as the light fraction will be lost and the heavy fraction conserved.

Since the choice of organic solvent used to generate the extract may influence the TEH estimate, the flare pit waste was extracted with standard solvents and quantified by both methods. The solvent extractions yielded a complete mixture of heavy and light hydrocarbons. Thus, the method of extracting the flare pit waste had little effect in this TEH estimate.

However, the quantification method had a dramatic effect on the TEH estimate. Using dichloromethane (DCM) extraction solvent, extractable hydrocarbons were 5.9% with gravimetric detection method and 4.0% with GC. .Using the toluene solvent, extractable hydrocarbons were 5.9% with gravimetric and 2.9% with GC. With the super-critical fluid (CO2) solvent, extractable hydrocarbons were 5.8% with gravimetric and 3.0% with GC. In certain cases, different extractions will remove different fractions.

The conclusion of the Bio-Reactor methods study is that exactly the same method should be used throughout a remediation sequence. Further, for reporting routine analyses, the term TPH should be reserved exclusively for methods that truly estimate total hydrocarbons. For methods which estimate some unknown fraction, terms such as "DCM extractable or GC detectable TEH" should be adopted to reflect more accurately what is being measured.

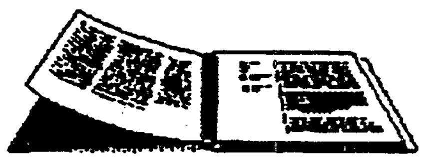
For more information, call Lin Callow of Gulf Canada Resources, Ltd., who is the Bio-Reactor Project's Project Manager, at 403-233-3924.

Material for this article is based on information in the "BIO-REACTOR PROJECT Newsletter," Issue 3, August 1995, published by the Canadian Association of Petroleum Producers.

NEW FOR THE BOOKSHELF

EPA has published INNOVATIVE SITE REMEDIATION TECHNOLOGY; BIOREMEDIATION, Volume 1. This monograph on bioremediation is one of a series of eight on innovative site and waste remediation technologies that are the culmination of a multi-organizational effort involving more than 100 experts. It provides the experienced, practicing professional guidance on the application of innovative processes considered ready for full-scale application. Other monographs in this series will address chemical treatment, soil washing/soil flushing, stabilization solidification, solvent/chemical extraction, thermal desorption, thermal destruction and vacuum vapor extraction.

Volume 1 can be ordered from the American Academy of Environmental Engineers by phone (410-266-3311), by FAX (410-266-7653) or by mail (130 Holliday Court, Suite 100, Annapolis, MD21401). Please refer to the Document No. EPA 542-B-94-006 when ordering. The cost for Volume 1 is $59.95. The cost for the series is $395.00.



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area covered an area of 2,300 sq. meters and allowed treatment of approximately 1,500 tons of soil.

The treatment plots may also be contained within a temporary waterproof structure to produce a warmer environment in northern latitudes, and to aid in the retention of soil moisture. The waterproof structure consists of an aluminum frame covered by a shell of polyethylene sheeting and is left open at each end to allow for equipment access.

The SITE evaluation consisted of two plots, a Treatment Plot and a No-Treatment Plot, both containing excavated contaminated soil from the same source on-site. The plots were constructed identically, with the exception that the No-Treatment Plot was only 2 meters x 6 meters, while the Treatment Plot was a 6 meter x 36 meter area. The No-Treatment Plot was left idle over the course of the demonstration and was isolated

After 254 days of treatment, the DARAMEND™ bioremediation treatment process achieved an overall approximate 94% removal of PAHs and an overall 88% reduction of chlorinated phenols in the Treatment Plot. Total PAHs were reduced from an average of 1,710 milligrams per kilogram (mg/kg) to 98 mg/kg and TCPs were reduced from an average of 352 mg/kg to 43 mg/kg. At the end of the treatment process, the treatment plot soil sample was considered non-toxic. The earthworms exhibited a 0% mean mortality rate compared to a 100% mean mortality rate prior to treatment. Lettuce and radish seeds exhibited a 100% to 52% mean inhibition of germination rate before treatment and a 33% and 0% rate respectively post treatment. No significant reduction occurred in the No-Treatment Plot during the demonstration. A full-scale cleanup of this site using this technology would cost between $640.00 for an in-situ plot with an attendant unit cost of $133/cubic m ($100/cubic yard), and $480,000 for an ex-situ plot with an attendant unit cost of $420/ cubic m. ($320/sq. yard).

For more information, call Teri Richardson of EPA's National Risk Management Research Laboratory, Cincinnati, Ohio at 513-569-7949. To get on the mailing list for a SITE Capsule Report and Innovative Technology Evaluation Report, send a FAX (513-569-7105) to Teri Richardson

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were greater than 99.994%, with a slight improvement in the third decimal place for the Cello™ test results. With the Cello™ system operating, the average benzene emission rate was reduced from 7.7 to 5.7 milligrams per hour (mg/hr) at the afterburner exit. This represents a 25% reduction, although changes of this magnitude are within the precision of this type of measurement. Naphthalene DREs were greater than or equal to 99.998% for all test runs. With the Cello™ system operating, the average naphthalene emission rate was reduced from 1.2 to 1.1 mg/hr at the afterburner exit. This represents a reduction, although again this magnitude of change is also within the precision of the type of measurement. The average afterburner carbon monoxide emissions, corrected to 7% oxygen, decreased from 20 parts per million (ppm) with conventional combustion to 14 ppm with the Cello™ system. This represents a 6% reduction. Average afterburner nitrogen oxide emissions, corrected to 7% oxygen, decreased from 82 ppm with conventional combustion to 77 ppm with the Cello™ system. This represents a 6% reduction. Average afterburner soot emissions, corrected to 7% oxygen, were reduced from 1.9 milligrams per dry standard cubic meter (mg/dscm) for conventional combustion to less than 1.0 mg/dscm with the Cello™ system. This represents a 53% or greater decrease in soot. However, all soot measurements were within a factor of 3 of the method detection limit; so, the significance of this reduction is uncertain. Total system combustion air requirements, determined from stoichiometric calculations, were 5% lower with the Cello™ system in operation.

For more information, call Marta Richards at EPA's National Risk Management Research Laboratory at 513-569-7692. A Technology Capsule (Document No. EPA/540/R-95/502a) is available from CERI by calling 513-569-7562 and referring to the document number. To get on the mailing list for an Innovative Technology Evaluation Report, send a FAX (513-569-7620) to Marta Richards.

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