Task 1.15 - Enhanced Bioremediation of Coal Tar- Contaminated Soil

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TASK 1.15 – ENHANCED BIOREMEDIATION OF COAL TAR-CONTAMINATED SOIL

1.0 BACKGROUND

The remediation of sites where soils have been contaminated with hydrophobic organic compounds is a major problem. This is especially true for manufactured gas plants (MGP) and similar industries. Gasification of fossil fuels has resulted in the production of tars that contain polyaromatic hydrocarbons (PAHs). PAHs are of concern because they are persistent in the environment and because many of them are carcinogenic. When soils contain very high concentrations of PAHs and other tar components, it is generally most feasible to use a chemical-physical remediation technique such as incineration. However, when the contaminant concentrations are medium to low, the most inexpensive technology is generally biological treatment. Biological treatment is an environmentally acceptable method of remediation that is relatively low-cost for many organic contaminants. PAHs and similar hydrophobic compounds, however, present major challenges to the microbial methods. These problems can be broken down into two related areas: mass transfer and bioavailability.

The water solubility of most PAHs is very small, and they have very low vapor pressures. As a result, the diffusion of the sorbed PAHs to a location where a biodegrading microorganism can encounter it is often limiting. Complicating this is that especially in aged samples, the PAHs are bound so strongly to soil components, they are not available for the microorganisms. These two phenomena can be better understood by examination of a typical biodegradation curve, such as might be observed for mixed PAHs. In Figure 1, there are three phases of the biodegradation process plotted with respect to time. In the first phase, concentrations are changing only slowly as the microbes adapt to the conditions, grow to a larger population, and begin to biodegrade the PAHs. The second phase is the phase of rapid, often logarithmic, biodegradation. The third and last phase is that period when available concentrations of PAHs are dropping so that the microorganisms cannot degrade them. The rate observed during the second phase is dependent on the size of the microbial population that can degrade the contaminants, the availability of the contaminants, and suitable nutrients (e.g., phosphorus) and electron acceptors (e.g., oxygen). When readily biodegradable contaminants are present, this phase is often very rapid. However, when any one of the above factors is limiting, a reduced rate is observed.

Studies where conditions have been optimized for mass transfer of hydrophobic compounds, such as by rapid mixing or by the addition of surfactant, have shown that these rates are generally much lower than would be possible with higher mass transfer rates (mass transfer limited). Techniques to improve mass transfer would allow this phase to end more quickly, resulting in reduced costs. In the third phase, the availability of contaminants has dropped to near zero, and even with prolonged incubation, concentrations will not drop significantly. If the lower limit achievable in a particular soil is above the regulatory limit, the biological technology will not be suitable, and a more expensive and disruptive technique (e.g., incineration) must be considered.

Figure 1. Total PAHs vs. time for three phases of the biodegradation process.

Studies have shown that the concentration of contaminants in that third phase is on the soil and is removable by strong solvents. In fact, these contaminants can be removed by a strong solvent, and when these contaminants are added back to a soil containing a suitable biodegrading microbial population, they will be rapidly and nearly completely degraded. This indicates that although the strong solvent can solubilize the contaminants, the microbes are not able to encounter them. Other investigators have suggested that the contaminants are present in a physical or kinetic trap within the soil matrix. Gas Research Institute has been active in a program to investigate these bioavailability phenomena because of the great impact they have on these and related industries.

Techniques are needed to mobilize contaminants to improve their availability for biodegradation to lower the achievable remediation end point (Phase 3) and to improve mass transfer so that remediation goals can be achieved more quickly (Phase 2). One technique that has potential for both of these problems is through the use of acoustic energy. The addition of energy is apparently necessary to overcome the binding energy of the contaminants and mobilize them. Acoustic energy has a history of use in the laboratory and in industry to make emulsions and solutions and to remove scale and fouling, among others. Weiss Associates of Emeryville, California, has conducted tests using lower-frequency acoustics to mobilize nonaqueous-phase liquids with good success. The use of lower frequency is important because although ultrasound is more energetic, it is also dampened quickly in soils, greatly reducing the radius of influence and applicability. Lower-frequency acoustics have the potential to supply the required energy in a more cost-effective manner. In addition, research by Weiss Associates has shown that it is possible to steer the beam of sonic energy to the zones that contain the most contamination.

2.0 OBJECTIVES

The objective is to determine the ability of acoustic energy to improve bioavailability or improve mass transfer of PAHs from soil to water phases where microorganisms can access them.

3.0 STATEMENT OF WORK

A sample of soil will be collected that is contaminated with PAHs and has been exposed to the PAHs for a relatively long period of time (aged). The soil will be homogenized and distributed into borosilicate serum vials. The aliquots of soil will be slurried with an aqueous nutrient solution, oxygen will be added to the headspace, and the vial will be sealed with a Teflon-faced silicone stopper. Replicate vials will be exposed to acoustic energy using a bench-scale laboratory unit supplied by Weiss Associates. At time intervals, replicate vials will be extracted with solvent and analyzed by gas chromatography to determine the quantity of PAHs remaining. Some replicates will be treated to kill the microorganisms in the soil by autoclaving or chemical sterilization. These killed vials will be controls for abiotic loss of PAHs. The effect of acoustics on PAH biodegradation kinetics can be determined from a comparison of the loss of PAHs between untreated and acoustically treated samples.

4.0 ACCOMPLISHMENTS

Progress on this project has been delayed somewhat because of difficulties in obtaining and operating the acoustic unit. This unit was received at the Energy & Environmental Research Center (EERC) earlier; however, the datalogging software and associated hardware was not functional. The data-logging system has just recently been put on-line, and work on this project will be completed in the coming quarter.

In order to properly demonstrate the ability of acoustic energy to increase bioavailability, an aged, PAH-contaminated soil from a MGP site is desired. This soil was obtained from a Des Moines, Iowa, site. Samples of this soil will be the subject of another project that will analyze the soil to determine the difficulty of extraction, which is taken as a measure of how tightly the contaminants are bound. These data are expected to complement this project.

An analysis supplied with the soil shows that it has an aliphatic content of about 1500 $\mu\text{g/g}$ and an aromatic content of about 9000 $\mu\text{g/g}$. A breakdown of the key components is shown in Table 1.

TABLE 1

Analysis of PAHs in MGP Soil from Des Moines, Iowa

Compound	ng/g
Naphthalene	310,000
C1-4 Naphthalenes	798,000
Acenaphthylene	120,000
Biphenyl	39,000
Fluorene	100,000
C1-3 Fluorenes	87,000
Anthracene	78,000
Phenanthrene	280,000
C1-4 Phenanthrenes/Anthrenes	447,000
Dibenzothiophene	44,000
C1-3 Dibenzothiophenes	110,000
Fluoranthene	85,000
Pyrene	140,000
C1-3 Fluoranthenes/Pyrenes	249,000
Benzo[a]anthracene	51,000
Chrysene	45,000
C1-4 Chrysenes	97,300
Benzo[b-k]fluoranthene	53,000
Benzo[a-e]pyrene	75,000
Perlyene	8,000