Task 15 - Remediation of Organically Contaminated Soil Using Hot/Liquid (Subcritical) Water

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TASK 15 – REMEDIATION OF ORGANICALLY CONTAMINATED SOIL USING HOT/LIQUID (SUBCRITICAL) WATER

1.0 INTRODUCTION AND BACKGROUND

This activity will perform a pilot-scale demonstration of the use of hot/liquid water for the removal of organic contaminants from soil at the pilot (20 to 40 kg) scale. Lab-scale studies will be performed to determine the optimum temperature, contact time, and flow rates for removal of the organic contaminants. Initial investigations into using carbon sorbents to clean the extractant water for recycle use and to concentrate the extracted contaminants in a small volume for disposal will also be performed.

Liquid water is normally considered to be too polar a solvent to be effective for the removal of organic contaminants from contaminated soils and sludges. However, the Energy & Environmental Research Center (EERC) has demonstrated that the polarity of liquid water changes from a very polar solvent at ambient conditions to that of an organic solvent (e.g., ethanol or acetonitrile) by simply raising the temperature. The EERC has exploited this unique property of liquid water to obtain highly selective extractions of polar (at lower temperatures) to nonpolar (at 200°–250°C) organics from contaminated soils and sludges. For example, class-selective extractions of hazardous organics from a petroleum waste sludge were achieved by simple sequential water extraction of the sludge at 100°C (to remove phenols) and 250°C (to remove PAHs). Only moderate pressures (a maximum of about 45 atm at 250°C, and lower pressures at lower temperatures) are required. With this procedure, all detectable hazardous organics were removed from the sludge, thus making the remaining material (about 99% of the original mass) a nonhazardous material.

Hot/liquid water extraction has also been demonstrated by the EERC at the lab scale to selectively and quantitatively remove hazardous organics (e.g., BTEX [benzene, toluene, ethylbenzene, and xylene], polycyclic aromatic hydrocarbons [PAHs], polychlorinated biphenyls [PCBs], chlorophenols, pesticides, and heteroatom aromatics) from a variety of contaminated solids, including waste catalysts, soils, sludges, and sediments. For many hazardous organics, the extraction system can be very inexpensive to construct and operate. For example, an extraction system was recently constructed from about \$3 worth of plastic plumbing pipe and was effectively used to extract the pesticide atrazine from contaminated soil.

Compared to presently available technologies, remediation with subcritical water should have several practical and political advantages:

1. Water is widely available and is environmentally (and politically) acceptable.
2. The proposed technology uses pure water without the need for adding surfactants or organic cosolvents.
3. Unlike steam stripping, this technique also applies to semi- and nonvolatile pollutants (and utilizes water in the liquid state which reduces the erosion and corrosion associated with steam).

4. Compared to supercritical water, the corrosivity and engineering requirements (and cost) are much reduced. The requirements for low pressure and only low to moderate temperatures should also allow the process to be used at a relatively large scale for ex situ remediation on-site.
5. The polarity of water in the liquid state can be controlled over a much broader range than for either steam or supercritical water; therefore, the selectivity of subcritical (liquid) water extractions are much better than either steam or supercritical water.
6. No pretreatment of wastes or contaminated soils is required.
7. Even though some water will be contaminated by the extraction process, simply returning the water to ambient temperature should remove the vast majority of PAHs (e.g., >99.999% based on solubility changes) from the water by physical separation based on solubility changes. This should allow a single volume of water to be recycled for decontamination processes. For contaminants with high solubilities in ambient water, conventional wastewater treatments will apply.
8. Our lab-scale studies clearly demonstrate that subcritical water extraction can clean the sample below regulatory limits for BTEX, PAHs, PCBs, and a variety of pesticides. Lab-scale studies also indicate that the method will be useful for many additional hazardous organics.
9. The moderate temperature conditions employed should not cause any significant chemical changes in the soil (unlike incineration) which should simplify the return of a contaminated site to normal use.
10. The process should apply to a broad range of solid matrices. Since water is the extraction fluid, it will not matter whether the sample is wet or dry. Residual solvent (water) left on the solid matrix causes no environmental harm as does accidental release of the extraction water (unless highly contaminated).

2.0 OBJECTIVES

Our present understanding of hot/liquid water extraction for the removal of hazardous organics from contaminated soils and sludges will be used to develop the engineering parameters needed to perform a pilot-scale demonstration of the remediation technology. First, a "real-world" soil that has been contaminated with semivolatile organic pollutants (e.g., pesticides, PAHs, or PCBs) will be selected for the lab- and pilot-scale studies. After the selection of the sample, the following objectives will be met:

- The optimal remediation conditions using hot/liquid water will be determined at the lab (e.g., 10 gram) scale. Major parameters to be optimized include water temperature, water flow rate, and contact time. Since we have already demonstrated that pressure has no effect on the removal efficiencies (other than that the pressure must be sufficient to maintain the liquid state of water at temperatures above 100°C), optimal conditions will

include the lowest effective temperature which, in turn, will determine the pressure required for a pilot-scale system. Note that previous work at the EERC has demonstrated that the highest pressure required will be about 40 atm and that the removal of many organics can be performed at even lower pressures (e.g., < 10 atm).

- A pilot-scale system will be constructed, and a demonstration will be performed using the optimized parameters from the lab-scale optimization studies. Large quantities of the contaminated soil (20 to 40 kg) will be extracted. The efficiency of the remediation process will be determined by analyzing representative subsets of the soil before and after the remediation process. This task will provide the essential engineering data to allow a commercial partner to be identified.

3.0 ACCOMPLISHMENTS AND WORK PERFORMED

Because of a delay in funding, the project was started in late December 1996. The progress on the study to date has been:

1. Sample selection: With the cooperation of the Gas Research Institute (GRI), ca. 50 kg of a PAH-contaminated soil from a town gas site will be provided in April 1997. This sample is of particular interest, since the EERC will receive the sample "fresh," i.e., at the beginning of a separate remediation project being performed on the site.
2. Initial lab-scale extractions: A reliable lab-scale system to perform the optimization studies has been built and thoroughly tested. The system uses 10-gram samples and incorporates a heated solvent collection device which allows the quantitative collection of PAHs and other pollutants that are extracted by the subcritical water process. This laboratory system will allow complete mass balances to be determined since both the extracted and unextracted PAHs can be quantitatively measured. Although the exact sample to be used will not arrive at EERC until April, the systems performance has been verified with several other similar contaminated soils.
3. Construction of the pilot-scale system: An 8-liter (20 kg soil) system has been designed and has been approved by the EERC Engineering Safety Committee. A schematic of the system is shown in Figure 1. All components have been procured, and assembly of the system has begun. The initial design included the use of electric heaters designed to heat 0.5 liter/minute of water from ambient to 250°C. However, since the estimated cost of these heaters was ca. \$10K and since the heaters required quantities of electricity (ca. 20,000 watts) that are not convenient in field applications, an alternate system was designed based on a simple and inexpensive (\$130) propane heater. This heater has been modified with a simple heat exchanger constructed of ¼-inch stainless steel tubing. The second design of this system was capable of heating ca. 0.45 liter per minute of water to 240°C. Based on this initial success, we expect that small improvements should make this inexpensive and portable system sufficient for the requirements of the 8-liter pilot-scale unit.

4. Commercial Partnerships: A confidentiality agreement has been signed with 3M Corporation to allow us to discuss the use of their new wastewater sorbent technology as an in-line method to clean the extracted pollutants from our extractant water. In preliminary discussions, 3M has stated a very high interest in joint development of EERC's subcritical water extractions and 3M's wastewater sorbents. A representative of 3M is scheduled to visit EERC in April to discuss the project in more detail.

4.0 FUTURE WORK

The next quarter will have two major focuses. First, the lab-scale optimization of the extraction conditions of the town gas soil sample supplied by GRI (discussed above) will be performed. Second, the assembly of the pilot-scale system will continue.

Pilot Scale Remediation System

Figure 1. Schematic of the pilot-scale system.

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