DOE/MC/31388--13-PL.9

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

**Semi-Annual Report
April 1 - September 30, 1997**

**By
Steven B. Hawthorne**

**RECEIVED
JUN 29 1998
OSTI**

Work Performed Under Contract No.: DE-FC21-94MC31388

For

U.S. Department of Energy
Office of Environmental Management
Office of Technology Development
1000 Independence Avenue
Washington, DC 20585

U.S. Department of Energy
Office of Fossil Energy
Federal Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

MASTER

By
University of North Dakota
Energy & Environmental Research Center
P. O. Box 9018
Grand Forks, North Dakota 58202-9018

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

LIST OF FIGURES	i
1.0 INTRODUCTION AND BACKGROUND	1
2.0 OBJECTIVES	2
3.0 ACCOMPLISHMENTS/WORK PERFORMED	3
4.0 FUTURE WORK	5

LIST OF FIGURES

1. Extraction behavior of individual PAHs with subcritical water at 275°C	4
---	---

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

1.0 INTRODUCTION AND BACKGROUND

This activity involves 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 are being 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 are also being performed.

Liquid water is normally considered to be too polar a solvent to be effective for removal of organic contaminants from contaminated soils and sludges. However, the Energy & Environmental Research Center (EERC) has demonstrated that the polarity of liquid water can be changed from that of 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° to 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), then 250°C (to remove PAHs [polycyclic aromatic hydrocarbons]). 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, ethyl benzene, and xylene], PAHs, PCBs [polychlorinated biphenyls, 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:

- Water is widely available and is environmentally and politically acceptable.
- The proposed technology uses pure water without the need for adding surfactants or organic cosolvents.

- Unlike steam stripping, this technique also applies to semi- and nonvolatile pollutants, using water in the liquid state, which reduces the erosion and corrosion associated with steam.
- Compared to supercritical water, the corrosivity, 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.
- 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.
- No pretreatment of wastes or contaminated soils is required.
- Even though some water will be contaminated by the extraction process, simply returning the water to ambient temperature should remove the vast majority (e.g., >99.999% of PAHs based on solubility changes) from the water by physical separation. 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.
- 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 (and also indicate that the method will be useful for many additional hazardous organics).
- The moderate temperature conditions employed should not cause any significant chemical changes in the soil (e.g., unlike incineration), which should simplify the return of a contaminated site to normal use.
- 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 nor 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 is being 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 was selected for the lab- and pilot-scale studies, and the following objectives are being pursued:

- The optimal remediation conditions using hot/liquid water will be determined at the lab (e.g., 10-g) 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 is being 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/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 as follows:

- *Sample selection.* With the cooperation of the Gas Research Institute (GRI), about 20 kg of a PAH-contaminated soil from a town gas site was obtained. This sample is of particular interest, since the EERC received the sample "fresh," i.e., at the beginning of a separate remediation project being performed on the site.
- *Initial lab-scale extractions.* A reliable lab-scale system to perform the optimization studies was previously built and thoroughly tested. Lab-scale extractions of the PAH-contaminated soil described above show that complete removal (down to detection limits) is achieved for all of the individual PAH components. The extraction behavior for this soil was consistent with the previous results for other soils, indicating that the optimal conditions for PAH extractions should be similar for different soils. As shown in Figure 1, the lower-molecular-weight PAHs (e.g., naphthalene) extract more rapidly than the higher-molecular-weight PAHs (e.g., chrysene). However, all of the PAHs extract fairly well at 275°C. Slightly slower extraction rates were observed at 250°C. Please note that these extractions were performed at the same water flow rate-to-soil weight ratio (i.e., 0.5 mL/min for 5-g samples) as is planned for the pilot-scale extraction (i.e., 0.5 L/min for 5 kg of soil).
- *Construction of the pilot-scale system.* An 8-liter system has been designed and has been approved by the EERC Engineering Safety Committee. The construction of the unit was completed in September, 1997. The unit has been tested successfully over the entire design range for water flow rate (up to 1 L/min), temperature (up to 280°C), and pressure (up to 2000 psi).

Extraction of PAHs by subcritical water at 275C, 0.5ml/min

Figure 1. Extraction behavior of individual PAHs with subcritical water at 275°C. Samples (5 grams) were extracted at 0.5mL/minute with pure water.

- *Shakedown extractions.* Shakedown extractions with two uncontaminated soils are being conducted. A successful run was performed with a New Mexico soil, which is a moderately sandy soil. A second high-clay soil (from the Red River Valley) was also used for the shakedown extractions. Initial attempts plugged the reactor, presumably because the clay swells under the high temperature and pressure conditions. Solutions to the plugging are now being evaluated.
- *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 expressed a very high level of interest in joint development of the EERC's subcritical water extractions and 3M's wastewater sorbents. A representative of 3M has visited EERC, and a tentative agreement has been reached to evaluate their sorbents. Initial discussions have also been conducted with West Environmental (a small business), and with CAMAS Corporation (Minneapolis) regarding remediation of contaminated soils.

4.0 FUTURE WORK

The final quarter of 1997 will focus on the pilot-scale extraction of the PAH-contaminated soil from the town gas site discussed above.