WATER AS A REAGENT FOR SOIL REMEDIATION

Quarterly Report 2

Reporting Period: November 12, 1999, through February 12, 2000

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EXECUTIVE SUMMARY

SRI International is conducting experiments to develop and evaluate hydrothermal extraction technology for remediating petroleum-contaminated soils. Most current remediation practices generally fail (or are cost prohibitive) to remove the polycyclic aromatic hydrocarbons (PAHs) found in petroleum-contaminated sites or they require the use of organic solvents to achieve removal, at the expense of additional contamination and with the added cost of recycling solvents. Hydrothermal extraction offers the promise of efficiently extracting PAHs and other kinds of organics from contaminated soils at moderate temperatures and pressures, using only water and inorganic salts such as carbonate. Initial work is being conducted at SRI to measure the solubility and rate of solubilization of selected PAHs (anthracene, fluoranthene, pyrene, and chrysene) in water, using SRI’s hydrothermal optical cell with the addition of varying amounts of sodium carbonate to evaluate the efficiency of the technology for removing PAHs from the soil. Preliminary results with pyrene and fluoranthene in water clearly indicate a significant enhancement of solubility with increase in temperature.

During this quarter, we conducted experiments with pyrene in the temperature range 200° to 300°C and observed a great enhancement in solubility with an increase in temperature. We also started experiments with real-world soil samples purchased from the subcontractor.
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INTRODUCTION

Under DOE Contract No. DE-AC26-99BC15224, SRI International is conducting a research project to evaluate the efficiency of hot water extraction (or hydrothermal extraction) for remediating soil contaminated with petroleum-related pollutants. This two-year study is being conducted in two phases:

Phase 1 (Year 1): Evaluation of solubilities of neat polycyclic aromatic hydrocarbon (PAHs) in water. The emphasis is on determining the optimal pressure and temperature conditions for efficient removal of PAHs from real-world contaminated soils.

Phase 2 (Year 2): Technology demonstration using a bench-scale stirred reactor system, and assessment of important parameters for performance evaluation.

Phase 1 consists of three tasks: Task 1, measurements of solubilities of selected organic compounds (e.g., naphthalene, phenanthrene, fluoranthene, pyrene, and chrysene) in water with and without added compounds; Task 2, measurements of extraction efficiencies of selected soil samples under the conditions selected in Task 1; and Task 3, technical evaluation of contaminated petroleum sites.

This report is the second progress report, covering the period November 12, 1999, through February 12, 2000. During this period, we conducted experiments to determine the solubility of pyrene in the high temperature range 200° to 300°C. We also initiated the analysis of contaminated industrial soil samples.

PROGRESS THIS QUARTER

TASK 1: CONDUCT IN-SITU SPECTROPHOTOMETRIC STUDIES TO DETERMINE SOLUBILITY

The goal of Task 1 is to study the solubility of PAH under hydrothermal conditions, using an UV spectrophotometer to determine both the equilibrium solubility and the solubilization rates. We are conducting in-situ measurements to unambiguously determine and quantify organic solubility under hydrothermal conditions because the ability to process and separate
organic material from soil in a hydrothermal media depends on the equilibrium solubility of the organics. SRI’s UV spectrophotometer is equipped with several optical cells for using UV spectroscopy to perform in-situ concentration measurements on organic species. We have several high-temperature UV cells, stainless steel reactors for high-pressure applications, and quartz reactors for low pressure applications.

In the first report, covering the period August 12 to November 12, 1999, we described our initial experiments in the lower temperature range, RT-190°C, using quartz reactors. During this reporting period, we upgraded the UV software for the spectrophotometer from a DOS-based system to a Windows-based system. During the installation period, we encountered problems with the UV spectrophotometer, which is currently being repaired. While waiting for the UV spectrophotometer to be ready, we conducted experiments in the high temperature range (200°C to 300°C), using stainless steel reactors. We used pyrene as the PAH simulant for this study to confirm the preliminary solubility data provided in our last report.

**Experiments in Stainless-Steel Reactors**

Figure 1 shows a schematic of the stainless steel reactor system used for measuring solubilities of PAHs in the high temperature range (200°C to 300°C).
The experiments were conducted as follows. First, both reactors were weighted empty. Then, reactor 1 was prepared by weighing a known amount (e.g., 50 mg) of the selected PAH into the reactor and by adding 2 ml of Milli-Q water. Both reactors were then connected to the valve assembly as shown in Figure 1. The oven was set at a temperature selected between 200º and 300ºC. During the experiment, both reactors including the valve body stayed inside the heated section of the oven. The reactor was allowed to stay at the study temperature for at least 4 hours to attain equilibrium solubility. Once equilibration was achieved, the interconnecting valve was opened to pass a representative liquid sample to reactor 2. The valve was then closed to isolate the reactors, and the reactors were allowed to cool to room temperature.

After this treatment, the reactors were disconnected from the valve and were weighed to determine the amount of water in each reactor. PAH was extracted from water in each reactor by liquid-liquid extraction with dichloromethane. The extract was transferred to toluene and the amount of PAH was determined by gas chromatography-mass spectrometry (GC-MS). The repeat experiments were conducted with pyrene at 200º, 250º, 275º, and 300ºC.

**Chromatographic Conditions**

- Chromatograph: HP 5890
- Column: DB-5MS (20 m x 0.18 mm i.d., 0.18 µm film thickness)
- Carrier gas: Helium 5.0 (5 psi)
- Injection: Manual; splitless (1 min)
- Injector temperature: 250ºC
- Splitter flow: 50 ml/min
- Septum purge flow: 5 m/min
- Interface temperature: 300ºC
- Temperature program:
  
  | Rate A: 30ºC/min | Initial Temperature: 75ºC | Initial time: 1.2 min |
  | Rate B: 10ºC/min | Final Temperature: 90ºC   | Final time: 1 min     |
  |                 | Final Temperature: 300ºC  | Final time: 5 min     |

- Detector: HP 5970 mass selective detector
- Ionization: Electronic impact (70 eV)
- Acquisition: Single ion monitoring
Table 1 gives the GC/MS information for selected PAHs, and Figure 1 gives a chromatogram of a standard.

Table 1
GC/MS INFORMATION FOR SELECTED PAHs

<table>
<thead>
<tr>
<th>Time</th>
<th>Monitored Masses (Swell 50)</th>
<th>Compounds*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-13</td>
<td>128, 152, 154, 166</td>
<td>naphthalene, acenaphthylene, acenaphthene, fluorene</td>
</tr>
<tr>
<td>13-21.5</td>
<td>178, 202, 216</td>
<td>phenanthrene, anthracene, \textit{fluoranthene}, pyrene, 4-methylpyrene</td>
</tr>
<tr>
<td>21.5-27</td>
<td>228, 252</td>
<td>benzo(a)anthracene, \textit{chrysene}, benzo(b)fluoranthene, benzo(k)fluoranthene, \textit{benzo(a)pyrene}</td>
</tr>
<tr>
<td>27-28.5</td>
<td>276, 278</td>
<td>indeno(1,2,3-c,d)pyrene, dibenzo (a, h)anthracene, benzo(g,h,i)perylene</td>
</tr>
</tbody>
</table>

* All these compounds can be analyzed under these conditions; however, only those marked in bold are included in the standards.

Figure 2. Chromatogram of standard (10 µg/ml in each PAH).
TASK 2: EXTRACT NEAT ORGANIC COMPOUNDS FROM SOIL

The goal of this task is to determine the efficiency of the hot water process for several soil types and sediments. Data from Task 1 will provide information on equilibrium solubility, which will determine the maximum removable organic quantity and the rate of solubilization, which determines the rate of organic removal.

We selected two types of samples for this study: (1) neat soil samples spiked with known PAHs and (2) real-world contaminated soil samples. During this period, we developed analytical techniques for preparing and analyzing the spiked samples.

We purchased real-world contaminated soil samples from two sites: (1) the Organic Wood Preserve site and (2) the Tallman Oil Company site. The Appendix gives more information on these two sites, provided by the subcontractor, Matrix Remediation. We also began analyzing the soil sample from the Organic Wood Preserve site. Preliminary studies were conducted to determine the extraction efficiency in hot water.

Spiked Sand Experiments

Four spiked sand samples were prepared by mixing a known volume (e.g., 5 ml) of solutions of pyrene and fluoranthene in acetone with 10 g of commercially washed and dried sand [CAS 14808-60-7] in a 200-ml flask. Spiked samples were prepared to obtain two concentration levels of PAH in sand: 25 µg/ml and 250 µg/ml. Blank soil samples were also prepared by spiking with acetone alone to establish a baseline measurement. After being spiked, the samples were shaken vigorously to favor the interaction of the PAH with the sand matrix. Prepared samples were allowed to equilibrate for several hours. The flasks containing spiked soil samples were left in a fume hood for 7 days to completely remove the solvent.

The extraction studies for the spiked samples are being conducted between 200ºC and 300ºC, using the stainless-steel reactors, as explained in Task 1. For each experiment, 1 g of spiked sand was extracted with 2 ml of water at temperatures between 200ºC and 300ºC. In addition, 1 g of spiked sand was extracted with acetone/dichloromethane 1/1 by shaking to compare the efficiency of hot water with solvent extraction. Although we have some results now, we will report the whole set in the next quarterly report.

Industrial Soil Experiments

We initiated this study with the soil sample received from the Organic Wood Preserve Site. The soil was polluted with PAH and pentachlorophenol (PCP) according to chemical analysis provided by the subcontractor (Table 2).
Table 2
CHEMICAL ANALYSIS OF THE STUDIED POLLUTED SOIL PROVIDED BY MATRIX

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (µg/g d.w.)</th>
<th>Compound</th>
<th>Concentration (µg/g d.w.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentachlorophenol</td>
<td>60.0</td>
<td>Pyrene</td>
<td>39.2</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>4.7</td>
<td>Benzo(a)anthracene</td>
<td>5.8</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>bdl</td>
<td>Chrysene</td>
<td>11.4</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>bdl</td>
<td>Benzo(b)fluoranthene+</td>
<td>14.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Benzo(k)fluoranthene</td>
<td></td>
</tr>
<tr>
<td>Fluorene</td>
<td>bdl</td>
<td>Benzo(a)pyrene</td>
<td>14.5</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>5.2</td>
<td>Indeno(1,2,3-c,d)pyrene+</td>
<td>bdl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>dibenzo(a,h)anthracene</td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>4.2</td>
<td>Benzo(g,h,i)perylene</td>
<td>bdl</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>13.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*bdl = below detection limit.

After reviewing the bibliography about the extraction of PAH from soils (Berset et al., 1999; Guerin, 1999), we decided to compare several solvent extraction procedures with each other and with hot water extraction. We initiated experiments with shaking extraction and will perform Soxhlet extraction and sonication. We selected a mixture of dichloromethane/acetone (50/50) as the extraction solvent. This mixture is known for its superior performance for extracting PAHs from soil matrices; dichloromethane solubilizes PAH, while acetone interacts with the polar sites of the soil matrix.

The shaking extraction was conducted as follows: 1 g of soil was weighed in a 20-ml glass vial, then 1 g of anhydrous sodium sulfate and 10 ml of dichloromethane/acetone 1/1 were added. The vial was shaken for 30 minutes (medium speed) in a Burrell Shake-Wrist Action. The extract was transferred to another vial, and the solvent was evaporated under an argon stream until near dryness. Then, 1 ml of toluene was added and the sample was analyzed using GC/MS to determine the recovery of PAH.

Hot water extraction was performed at 275°C in stainless-steel reactors as described before. In this experiment, 1 g of soil was extracted with 2 ml of water under hydrothermal conditions. Then, the pollutant solubilized in hot water was extracted into dichloromethane. After solvent evaporation, 1 ml of toluene was added and the sample was analyzed using GC/MS to determine the recovery of PAH.
TASK 3: EVALUATE SITE REPORTS

During this reporting period, we started a literature search on site reports related to the remediation of sites containing PAHs. Thus far, three sites have been identified for evaluation:

1. Thermal desorption at the Mckin Company Superfund site, Gray, Maine
2. Soil vapor extraction at the Sacramento Army Deport Superfund site

We are now evaluating these reports to select the additional pollutants to include in Task 2 of this study.

RESULTS AND DISCUSSION

EXPERIMENTS IN STAINLESS-STEEL REACTORS

The solubility of pyrene in water was studied at 200º, 250º, 275º, and 300ºC. The results in this temperature range are shown in Table 3 and Figure 3. In each experiment, we measured not only the amount of pyrene in reactor 2, but also that in reactor 1 to check the total recovery of PAH. In all the experiments reported, recovery of pyrene was higher than 90%, and the recovery of water was always higher than 90%. As expected, the solubility of pyrene in water increases with temperature, ranging between 0.21 and 1.45 mg/ml. Compared with the bibliographic solubility of pyrene in water at room temperature (0.14 ppm; Mackay and Shiu, 1977), these values are 1500-10000 fold higher. The solubility experiments for chrysene have been started, and the results will be reported in the next quarterly report.

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>Solubility (mg PAH/ml water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.21</td>
</tr>
<tr>
<td>250</td>
<td>0.77</td>
</tr>
<tr>
<td>275</td>
<td>1.00</td>
</tr>
<tr>
<td>300</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Table 3
SOLUBILITY OF PYRENE IN WATER AT HIGH TEMPERATURE
INDUSTRIAL SOIL EXPERIMENT

The data presented below are for the soil sample from the Organic Wood Preserve site.

SRI developed the analytical protocol for extraction and analysis of heavy PAHs from the soil matrix. Figure 4 shows the GC/MS (scan mode) chromatogram corresponding to the organics present in the soil sample before the hydrothermal treatment. The extract obtained by shaking the soil in dichloromethane/acetone 1/1 was injected in GC/MS in both SCAN and SIM mode.
Figure 4. GC/MS (scan) chromatogram from solvent extraction of soil.

The most abundant peaks in the chromatogram were identified as pentachlorophenol and pyrene by their respective mass spectra. In addition, pyrene was confirmed by coincidence of retention time with that of standard. Figure 5 shows the mass spectra of pentachlorophenol and pyrene.

Figure 5. Mass spectra of peaks at retention times of 15.2 and 19.4.

In addition, the baseline spectra of the central part of the chromatogram (12 min to 25 min) revealed a high amount of hydrocarbons (probably branch hydrocarbons of high molecular weight) in the extract. These compounds can be removed from the extract by clean-up in silica or alumina open chromatographic columns, avoiding their injection in the GC/MS equipment. A clean-up procedure will be developed during the next period.

The GC/MS analysis of the same sample in SIM mode, monitoring the masses described previously, results in the total ion chromatogram shown in Figure 6, where several of the 16 PAH
regulated by EPA were detected. Therefore, we believe that this industrial soil sample is a good candidate for evaluating the efficiency of hydrothermal extraction for removing PAHs.

The extraction efficiency under hydrothermal condition was studied at 275°C. The extraction of this soil with hot water in the stainless-steel reactors system yielded a chromatogram in which most of the PAHs were detected. Currently, we are completing the quantitation of the PAHs present in the hydrothermal extract to determine the extraction efficiencies for each individual PAH. Initial evaluation of the relative abundancies of selected PAHs indicates that the extraction efficiency decreases with molecular weight as expected.

CONCLUSIONS

In our first report, based on preliminary estimates, we suggested that, if the solubility of pyrene keeps increasing with temperature, the estimated solubility at 300°C would be more than 4 orders of magnitude higher than the solubility at 20°C. The measured solubility numbers given in Table 3 for pyrene confirm this prediction. We are continuing the work with other PAHs (e.g., anthracene, fluoranthene, pyrene, or chrysene), and we expect to see increases in solubility with temperature. We will study two systems: organic-water and organic-sodium salt water. The results from experiments without salt will serve as the baseline for comparison with results from the salt-added experiments.

The preliminary experiments conducted with both spiked soil samples and the real-world samples were successful. During this period, we spent a reasonable length of time developing
the analytical protocol for separating and identifying PAHs in the soil samples, and we will continue to evaluate the extraction efficiency of selected PAHs under hydrothermal conditions.

REFERENCES


APPENDIX

CONTAMINATED, REAL-WORLD SOIL SAMPLES PROVIDED BY MATRIX REMEDIAL TECHNOLOGIES, INC.

SOIL SAMPLE NUMBER 1 (Organic Wood Preserve Site)

Soil Sample Source. The samples were obtained from a heterogeneous pile of contaminated soil that was generated during the past operations of an organic wood preserver company in the northwest United States. The pile's volume is in excess of 10,000 cubic yards. The soil samples reportedly contain two basic types of contamination: pentachlorophenol (PCP) and creosote, and those are the typical contaminants of concern for sites affected by organic wood preservatives. Organic wood preserver sites are among the most common sites on the National Priorities List (NPL) maintained by the U.S. Environmental Protection Agency (EPA).

Soil Remedial Goals. The PCP concentration in the soil samples is estimated to be about 200 mg/kg, and the PCP remedial goal established by the EPA for the site is 37 mg/kg. Creosote is a mixture of hazardous organic compounds, and the EPA has established a remedial goal of 58 mg/kg of benzo(a)pyrene (BaP) equivalents for this particular site's soils. BaP is one of a series of polynuclear aromatic hydrocarbon (PAH) compounds present in creosote formulations and of particular concern to the EPA. "BaP equivalents" is a number that equals the sum of the BaP concentration and the toxicity equivalents of the concentrations of the other PAH compounds of EPA concern present in the soil sample.

SOIL SAMPLE NUMBER 2 (Tallman Oil Company Site)

Soil Sample Source. The sample was obtained from a large stockpile of contaminated soil generated during the excavation of a contaminated site at 2401 North Elizabeth Street in Pueblo, Colorado, formerly occupied by the Tallman Oil Company. The subsurface soils were reportedly affected by uncontrolled releases of petroleum products from leaking underground storage tanks (LUSTs). The soil sample reportedly contains petroleum hydrocarbon compounds including benzene, ethylbenzene, toluene, and three xylene isomers (collectively referred to as BETX). A key aspect of this particular site is that the soil has an elevated clay content.
Soil Remedial Goals. According to the State of Colorado's cleanup standards for hydrocarbon contaminated soil, the following cleanup standards are applicable for the soil at the Pueblo site:

- Total petroleum hydrocarbons: 500 mg/kg
- Benzene: 0.26 mg/kg
- Toluene: 170 mg/kg
- Ethylbenzene: 200 mg/kg
- Xylenes: 1900 mg/kg.