Subtask 1.17 - Subcritical Water Extraction of Mercury From Soils and Sediments

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SUBTASK 1.17 - SUBCRITICAL WATER EXTRACTION OF MERCURY FROM SOILS AND SEDIMENTS

1.0 INTRODUCTION

The U.S. Environmental Protection Agency (EPA) "National Sediment Quality Survey" lists the top pollutants responsible for toxicity in watersheds as 1) PCBs (polychlorinated biphenyls), 2) mercury, and 3) other organics such as PAHs (polycyclic aromatic hydrocarbons) and pesticides. In addition, these same pollutants are major contributors to chemical pollution on U.S. Department of Energy (DOE) and other contaminated sites (e.g., industrial sites and harbors). An ideal remediation method would allow cost-effective removal of both organic and mercury contamination using a single process.

The Energy & Environmental Research Center (EERC) has demonstrated that controlling the temperature (and to a lesser extent, the pressure) of water can dramatically change its ability to extract organics and inorganics from matrices ranging from soils and sediments to waste sludges and coal. The dielectric constant of water can be changed from ca. 80 (a very polar solvent) to < 5 (similar to a nonpolar organic solvent) by controlling the temperature (from ca. ambient to ca. 400°C) and pressure (from ca. 5 to 350 bar). The EERC has shown that hazardous organic pollutants such as pesticides, PAHs, and PCBs can be completely removed from soils, sludges, and sediments at temperatures (250°C) and pressures (< 50 atm) that are much milder than typically used for supercritical water processes (temperature $> 374^{\circ}\text{C}$, pressure > 221 atm). In addition, the process has been demonstrated to be particularly effective for samples containing very high levels of contaminants (e.g., parts per thousand).

The EERC has also demonstrated that mercury can be extracted using supercritical water at much harsher conditions (400°C and > 300 atm). However, the removal of mercury from contaminated solids at the lower temperature and pressure conditions (e.g., 250°C and 50 atm) has not been investigated. If successful, this project will provide the basis for using hot/liquid water to extract both organic contaminants and mercury from contaminated solids in a single-step process.

2.0 OBJECTIVE

- To determine the ability of hot/liquid water to extract mercury from contaminated soils and/or sediments using the same conditions of temperature and pressure that have previously been successful for removing organic pollutants including PAHs, PCBs, and pesticides.

3.0 SPECIFIC DELIVERABLES

- The ability (and conditions) of hot/liquid water to remove mercury from three or more highly contaminated soils and/or sediments will be reported.

4.0 ACCOMPLISHMENTS

4.1 Sample Selection

Three samples were selected for extraction. All samples are "real-world"; e.g., they were collected from contaminated environmental sites and used without significant preparation. One of the samples was obtained from the National Institute of Standards and Testing (NIST), so that certified values of the mercury concentrations were available. The three samples were contaminated (total mercury values) at 50, 213, and 3380 ppm.

4.2 Extraction

Extractions have been performed using a subcritical water extraction apparatus developed for this project. Flow rates were ca. 1 mL/minute. Sufficient pressure was maintained during the extractions to keep the water in the liquid state (ca. 50 bar and 100 bar for 250° and 300°C, respectively). Problems were encountered with plugging of the 1/16-in.-OD outlet lines for the most highly contaminated samples. Since the extraction cell outlet contained a 0.5- μ m frit, the plugging appeared to be deposition of extracted material as the extractant water was cooled. Successful extractions of the most highly contaminated sample were performed by using 2-g samples in a 3.4-mL extraction cell and placing an empty 0.8-mL cell after the sample cell before the water was cooled.

Since the goal of the extractions was to determine the removal efficiency of total mercury using subcritical water extractions, the concentration of mercury was determined in the original soils and in the soil residues after extraction. The results of the extractions are summarized in Table 1. As shown, the conditions typically used for the removal of organic pollutants from soils show substantial removal of mercury from the test soils in 15 to 30 minutes at conditions previously used to remove organic pollutants such as PAHs, PCBs, and pesticides (e.g., 250°C). Increasing the temperature to 300°C also increases the rate of extraction (Table 1). For the two samples with lower contamination levels, 30 minutes at 250°C was sufficient to remove ca. 95% of the mercury. However, extraction for 30 minutes at 250°C for the sample with 3380 ppm of mercury contamination was sufficient for only 45% removal. Additional extraction time (60 minutes) at 250°C resulted in 67% removal (Table 1), indicating that the removal of mercury was limited by its solubility in the subcritical water. However, when the extraction temperature was raised to 300°C, 30 minutes of extraction was sufficient to remove 84% of the mercury from this highly contaminated sample.

4.3 Conclusions

Subcritical water extraction can be used to remove mercury from highly contaminated soils. The conditions required (250° to 300°C) have previously been shown to yield quantitative removal of common organic pollutants such as PCBs and PAHs (e.g., coal tar), demonstrating that subcritical water extraction may be a useful approach for the remediation of materials cocontaminated with mercury and organic pollutants.

TABLE 1

Mercury Removal Efficiencies Using Subcritical Water

	Soil A	Soil B	Soil C (NIST)
Initial Concentration, ppm	213	3380	50 (43)*
Concentration after 250°C, 15 min, ppm	61	2190	6.2
Hg Removed after 250°C, 15 min, %	71	35	87
Concentration after 250°C, 30 min, ppm	10.5	1860	2.8
Hg Removal after 250°C, 30 min, %	95	45	94
Concentration after 250°C, 60 min, ppm	-	1110	-
Concentration after 250°C, 60 min, %	-	67	-
Concentration after 300°C, 30 min, ppm	1.1	551	3.4
Hg Removal after 300°C, 30 min, %	99	84	93

*The concentration certified by NIST was 50 ppm; 43 ppm was determined by the EERC.

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