Subtask 1.7 - Hot-Water Extraction of Organics, Metals, and Chlorides from Coal and Mixed Wastes

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**By
Steven B. Hawthorne**

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

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

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HOT-WATER EXTRACTION OF ORGANICS, METALS, AND CHLORIDES FROM COAL AND MIXED WASTES

EXECUTIVE SUMMARY

Supercritical and subcritical water have been demonstrated at the Energy & Environmental Research Center (EERC) to give high removal efficiencies of sulfatic, pyritic, and organic sulfur from coal (IBC-101). Under similar conditions, 78% of the mercury was removed from the coal, indicating that water can be used as an extraction fluid to both reduce the sulfur and hazardous metal content. Water extractions of metal-contaminated soils also demonstrate very high removals of mercury and arsenic, although metals such as vanadium are not efficiently removed. An extraction cell that is reliable for multiple water extractions at conditions up to 450°C and 400 atm has been developed jointly with Keystone Scientific and is now being commercialized. Subcritical water was shown to be an extremely efficient extraction fluid for polychlorinated biphenyls (PCBs) from contaminated soils, and >99% removal of PCBs can be achieved in as little as 5 minutes. A method for determining the solubility behavior of organics in water up to 400°C and 400 atm has been developed and is currently being evaluated.

HOT-WATER EXTRACTION OF ORGANICS, METALS, AND CHLORIDES FROM COAL AND MIXED WASTES

1.0 INTRODUCTION

Controlling the temperature (and to a lesser extent, the pressure) of water can dramatically change its ability to extract organics and inorganics from 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 Energy & Environmental Research Center (EERC) has shown that ca. 70% of the total sulfur of Illinois coal can be extracted with water. The extraction of hazardous metals should also be possible since large solubility changes are known to occur for metals and their oxides and salts with changes in the pressure and temperature of water.

We propose to extend the sulfur studies to include hazardous metals (e.g., mercury, arsenic, selenium) and chlorine. This project will develop the basic extraction techniques (this will require home-built systems) and conditions to look at removal efficiencies. Emphasis will also be placed on developing collection methods for extracted metals to support mass balance and analytical speciation studies (e.g., are certain metals associated with inorganic or organic fractions of coal?). The first year should result in sufficient data to determine the ability of sub- and supercritical water to extract hazardous metals and chloride from bituminous coals and provide a basic understanding of the minimum temperatures and pressures required. The techniques developed will also be used to perform preliminary extractions of hazardous metals from soils. In addition, initial experiments will be performed in an effort to determine the effect of water temperature (and to a lesser extent, pressure) on the solubility of selected hazardous organics and metals.

2.0 OBJECTIVES

The objectives for Year 1 are:

- To develop and construct a reliable system for performing sub- and supercritical water extraction of solid samples.
- To determine the ability of sub- and supercritical water to remove hazardous metals and chloride from bituminous coal.
- To perform a preliminary evaluation of the use of sub- and supercritical water extraction of selected hazardous metals from soil.
- To determine the changes in solubility for selected hazardous organics and metals which occur with temperature (and to a lesser extent with pressure) in sub- and supercritical water.

3.0 ACCOMPLISHMENTS

3.1 Development of a Reliable Extraction Cell for Sub- and Supercritical Water

An extraction cell that is capable of operation with sub- and supercritical water at temperatures up to 450°C and pressures >400 atm was designed in conjunction with Keystone Scientific (Bellefonte, PA). The cell has proven to be very reliable (e.g., no leaks) through over 50 extractions using sub- and supercritical water. Keystone Scientific is now planning to offer commercial versions of this cell.

3.2 Extraction of Hazardous Metals and Sulfur from Coal

Supercritical water has been shown to be an efficient extraction media for the removal of sulfur from coal (joint investigations with the Illinois Clean Coal Institute). As shown in Table 1, supercritical water extraction removed substantial portions of each major form of sulfur from IBC-101. Mercury removal is also being evaluated for the same coal. As shown in Table 1, the removal of mercury from coal was 78% using subcritical water (350°C, 300 atm). Substantial reductions in arsenic and selenium were also observed. Further investigations will determine the effect of extraction conditions on mercury removal as well as on other hazardous metals and on chloride from coal.

3.3 Extraction of Hazardous Metals from Soil

The removal of mercury, arsenic, selenium, cadmium, and vanadium from two soils (NIST reference materials) was evaluated using supercritical water extraction. As shown in Table 2, the extraction of mercury was extremely efficient, and the removal of other hazardous metals such as arsenic was encouraging. However, the removal of metals such as vanadium was not significant.

TABLE 1

Reduction in Sulfur Forms, Total Sulfur, and Mercury from Raw IBC-101 with Sub- and Supercritical Water

	% Removed
Sulfatic Sulfur ^a	73
Pyritic Sulfur	73
Organic Sulfur	49
Total Sulfur	58
Total Mercury ^b	78

^a Extractions were performed for 60 minutes at 450°C and 400 atm (supercritical water).

^b Extractions were performed for 60 minutes at 350°C and 400 atm (subcritical water).

TABLE 2

Removal of Mercury, Arsenic, Cadmium, and Vanadium from Soils (SRM 2711 and SRM 2710)
Using Supercritical Water

Element	SRM 2711		SRM 2710	
	Cert. Conc., $\mu\text{g/g}$	% Removed	Cert. Conc., $\mu\text{g/g}$	% Removed
Hg	6.3	> 99	33	98
As	105	58	626	82
Cd	42	20	22	11
V	82	13	77	8

3.4 Extraction of PCBs from Contaminated Soil

Preliminary extractions of PCBs from contaminated soil using subcritical water were very successful. Therefore, further investigations were performed to optimize the extraction conditions. As described in the attached manuscript, subcritical water efficiently removed PCBs from contaminated soil using temperatures of either 250° or 300°C. At 250°C, liquid water (50 atm) was an efficient extraction solvent, and the removal of PCBs from soil was usually >90% after 15 minutes. However, extracting the soils at 300°C and 50 atm (steam) was even more efficient, and >99% removal of PCBs was achieved in 5 minutes. Please refer to the attached manuscript for detailed discussions of the extraction conditions and results.

3.5 Determination of Solubilities in Subcritical Water

A method for using a conventional gas chromatographic flame ionization detector (FID) to determine the solubility changes that occur for organic pollutants in water with temperature and pressure changes has been developed. (No suitable method for determining the solubility behavior in water over the temperature range required for this study has previously been reported by any investigators.) At present, the FID parameters have been optimized to allow solubility changes to be determined over water flow rates ranging from 5 to >50 $\mu\text{L}/\text{minute}$. The method is now being tested for solubility determinations for polycyclic aromatic hydrocarbons (PAHs) and is expected to be useful for temperature ranges up to at least 400°C and pressures up to 400 atm.

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