

Project # 64979

Title - Basic Engineering Research for D&D of R. Reactor Storage Pond Sludge: Electrokinetics, Carbon Dioxide Extraction, and Supercritical Water Oxidation

Year of Award: 1998 **Amount of Award:** \$979,808

Problem Area: Decontamination and Decommissioning

Science Category/Subcategory: Engineering Science / Design, Process, and Modeling

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Research Objective

Collaborating researchers at the University of South Carolina (USC), Clemson University (CU), and the Savannah River Site (SRS) are investigating the fundamentals of a combined extraction and destruction process for the decontamination and decommissioning (D&D) of PCB-contaminated materials as found at DOE sites. Currently, the volume of PCBs and PCB-contaminated wastes at DOE sites nationwide is approximately 19,000 m³. While there are a number of existing and proposed processes for the recovery and/or destruction of these persistent pollutants, none has emerged as the preferred choice. Therefore, this research focuses on combining novel processes to solve the problem. The research objectives are to investigate benign dense-fluid extraction with either carbon dioxide (USC) or hot water (CU), followed by destruction of the extracted PCBs via either electrochemical (USC) or hydrothermal (CU) oxidation. Based on the results of these investigations, a combined extraction and destruction process that incorporates the most successful elements of the various processes will be recommended for application to contaminated DOE sites.

Highlights for Annual Report:

Diffusion coefficients for model contaminants phenol, 1,2,4 trichlorobenzene, phenanthrene, and benzoic in near-critical CO₂ have been measured. Near the mixture lower critical end point (LCEP), diffusivities decrease dramatically due probably to the thermodynamic correction term. Two papers on this topic have been accepted for publication in 1999-2000.

We have conducted 16 runs on dense phase CO₂ extraction of 1,2,4 trichlorobenzene (a model contaminant) from "Toxi-Dry," a commonly used adsorbent that is used in decontamination of facilities. This adsorbent is made from plant material and is a major component of job control waste. The complex nature of the adsorbent impedes complete extraction of organics with CO₂ under mild (<4,000 psi, 40 °C) supercritical conditions; more extreme conditions lead to >90% single pass extraction efficiency.

We have constructed a high-pressure reactor for conducting electrochemical superoxide chemistry in the presence of high pressure CO₂. We have confirmed the generation of superoxide in aprotic solvents, and have also confirmed the diffusion coefficients of O₂ under these conditions. We are proceeding to experiments in which electrochemistry is conducted under high pressure.

We have constructed a continuous-flow supercritical water oxidation apparatus (shown in the figure below) in which to conduct hydrothermal oxidation of PCBs. Chemical analysis will be performed with a new GC/electron capture detector system. We have conducted SCWO screening tests with both *tert*-butanol and 1,2,4 trichlorobenzene as model contaminants, obtaining decompositions between 80 and about 90 %, using hydrogen peroxide as the oxygen source.

A high pressure, high temperature view cell with continuous recirculation has been constructed for measuring solubilities of chlorinated compounds in hot water or supercritical water. Analysis of the equilibrium phases will be done with a novel *in situ* fiber optic UV detector system. We have reviewed existing solubility and vapor pressure data for certain PCB congeners and will collect additional solubility data in the new apparatus.

Research Progress and Implications

This report summarizes work through eighteen months of the three-year project. This project involves personnel from two universities and the Savannah River Site; quarterly meetings at alternating sites have been held to share progress reports, make presentations, and plan future activities.

Task 1: Use of dense phase CO₂ solvent extraction to remove PCBs from waste

Task 1 Objectives:

1. Find optimal supercritical CO₂ extraction conditions for chlorinated aromatics, esp. polychlorinated biphenyl (PCBs) samples
2. Find cosolvents and CO₂-soluble surfactants to enhance PCB extraction rate and recovery.

3. Develop new processes for the extraction of PCBs for D&D of DOE matrix materials

Experimental approach:

The experimental extraction apparatus is a commercial unit from ISCO, and is shown in [Figure 1](#). Samples of 1,2,4-trichlorobenzene (TCB) adsorbed on Toxi-dry were extracted between 40°C and 80°C, and 2,000 to 6,000 psia with pure supercritical carbon dioxide. After 2 hours extraction, 1,2,4-trichlorobenzene extraction efficiencies are between 10% and approaching 100%. A total of 15 runs have been made to date. At 80 °C, we observed much higher removal efficiencies than at 40 °C. Complete results to date are shown in Table 1. For the next step, we will continue to change the experimental conditions to find out the influence of temperature, pressure and flowrate on extraction.

A miniature fiber-optic spectrometer is being developed for on-line, real-time absorbance measurements. This tool will allow us to monitor the progress of the extraction process under supercritical CO₂ conditions. The design is a simple one, composed of an Upchurch Scientific, Inc. PEEK cross and ferruled fittings, opposing fiber optics, and an ultraviolet light source (see [Figure 2](#)). Ultraviolet light is sent through a fiber optic where it shines through the mid-section of the cross. A syringe is used to suspend a solution of known or unknown concentration in this area, which serves as a sample chamber. A second fiber optic picks up the transmitted light and sends the signal to computing software. The software and hardware are from Ocean Optics, Inc. Standard calibration solutions of 1,2,4-trichlorobenzene in hexane and hexachlorobenzene in acetone have been prepared with concentrations ranging from 20 ppm to 1000 ppm. These solutions were first analyzed using a Shimadzu 2101 PC spectrophotometer to obtain reference spectrums. The results from the Shimadzu are compared to those obtained by the miniature spectrometer. Early results show that the instrument is very sensitive at low concentrations. Solutions around 1000 ppm saturate the instrument, so it seems that the fiber optics instrument is reliable for solutions less than 500 ppm down to 5 ppm. These results are very promising since most extracts fall in the range well below 500 ppm. A sample comparison of absorbance spectra is shown below for a 1,2,4-trichlorobenzene in hexane solution at a concentration of 500 ppm ([Figures 3 and 4](#)). In both cases, a triplet occurs between 265 nm and 290 nm. The large peak at the left of the Shimadzu spectrum is also depicted in the fiber-optic spectrum. However, the instrument appears to be saturated around 235 nm, which would explain why the data acquisition stops at that wavelength. Currently, tests are being run on solutions of lower concentration to eliminate this problem.

Plans:

1. The Ocean Optics fiber optic UV spectrometer will be installed on-line with the extractor when it is calibrated.
2. A cosolvent metering pump will be installed so that samples can be extracted with CO₂ and cosolvents.
3. We have ordered a portable fume hood to house the supercritical extraction apparatus.

Task 2: Electrochemical superoxide chemistry for destruction of PCBs

Task 2 Objectives:

1. Demonstrate basic superoxide electrochemistry in a high-pressure, CO₂-rich environment.
2. Quantify destruction of PCBs and chlorinated aromatics in the presence of CO₂.
3. Design an electrochemical cell for bulk destruction of PCBs.

Experimental approach:

We have developed a low-cost reactor and electrode system for rapid screening of electrochemical reactions under high pressure. A schematic of the electrochemical cell is shown in Figure 5. The reactor has been validated for operation and is electrochemically functional for both gas, liquid, and supercritical phases. Initial high-pressure electrochemical conductivity tests for the supercritical carbon dioxide (scCO₂) and synthesized novel CO₂-soluble supporting electrolyte tetrakis(decyl)ammonium tetraphenylborate (TDATPhB) system at 70°C and 3000psi were inconclusive. A simpler, standard system of aprotic solvent acetonitrile and supporting electrolyte tetraethylammonium perchlorate (TEAP, 0.1M) was tested successfully outside the cell at atmospheric conditions. Superoxide ion (O₂⁻), the destruction agent, was generated successfully with cyclic voltammetry, and a diffusion coefficient of 5x10⁻⁵cm²/s for oxygen in the superoxide reduction was determined. A gas chromatograph has been prepared for analysis of chlorinated compounds and will be used to evaluate both extraction and electrochemical destruction results.

Plans:

1. Finish electrochemical tests in cell observing effects of CO₂ overpressure
2. Initiate destruction experiments in cell.
3. Switch to scCO₂/TDATPhB system for electrochemical destruction
4. Design a continuous-flow electrochemical destruction system

Task 3: Hydrothermal oxidation of PCBs**Task 3 Objectives:**

1. Design and construct an apparatus for hydrothermal oxidation of PCBs and surrogate materials.
2. Determine destruction efficiencies and kinetics of destruction of PCB congeners.

Experimental approach:

At Clemson University, a supercritical water oxidation (SCWO) reactor design has been completed. The design includes a specialized mixing tee, which will be custom designed and fabricated at Clemson. The heat source for the reactor, a Techne sand bath oven, has been installed and is being optimized for the desired experimental conditions. Heat transfer analyses have revealed the depth to which the reactor coil should be immersed into the sand bath and customized holding brackets have been designed and implemented. The SCWO reactor, shown in Figure IV, is equipped with a computer controlled data acquisition system capable of recording temperatures and pressures throughout the apparatus. A Hewlett-Packard mass spectral analyzer has been installed and used for analysis of SCWO reaction products. Initial testing of the reactor used the decomposition of methanol as probe reaction since this data could be easily compared to existing literature data on methanol decomposition.

Plans:

1. Continue literature search for SCWO data
2. Continue SCWO experiments with PCB simulants and PCBs
3. Compare the performance of different oxidizing agents (O_2 vs. H_2O_2)
4. Examine reaction kinetics
5. Determine the effects of organic cosolvents (e.g. methanol) on PCB degradation

Task 4: Solubility of PCBs in hot water:**Task 4 Objectives:**

1. Build high pressure view cell with recirculating phases to determine PCB solubility in hot water and near critical water.
2. Obtain solubility data on several PCB congeners and correlate with an equation of state.

Experimental Approach:

A high-pressure view cell (Figure 7) equipped with a UV-Vis fiber optic flow cell has been designed, built, and installed in an existing temperature controlled forced convection oven. This vessel will be used for in-situ measurements of PCB solubility at elevated pressures in hot and supercritical water. The design also features an inline magnetically actuated pump that can operate at elevated temperatures. A highly sensitive UV-Vis spectrometer equipped with a CCD array detector has been purchased from Spectral Instruments and will be connected to the fiber optic flow cell following initial testing with UV-Vis standards.

Plans:

1. Determine detection limits of fiber optic UV-Vis detection system
2. Complete testing of solubility apparatus using benzene
3. Begin measuring solubility of PCB pure components (e.g., 3-chlorobiphenyl)

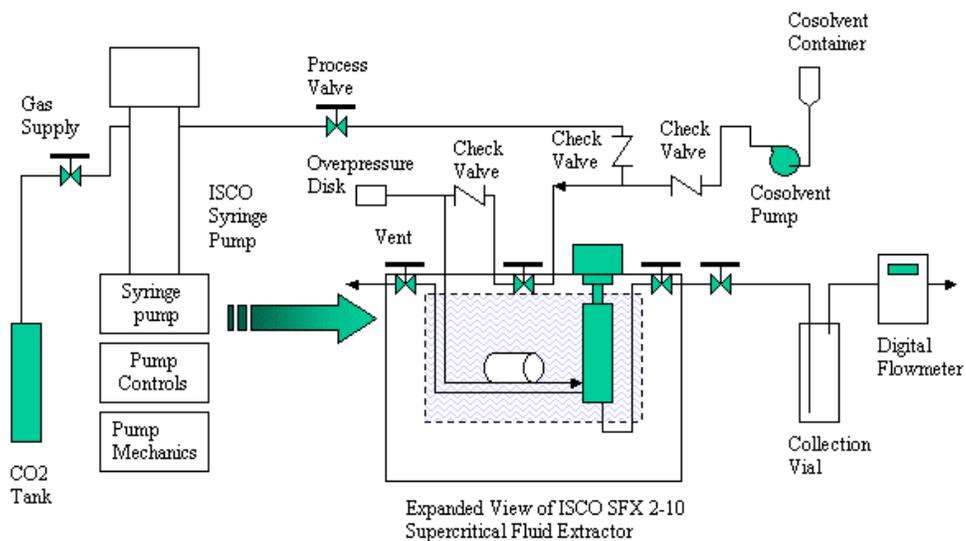


Figure 1. - Schematic of supercritical CO₂ extraction apparatus at University of South Carolina

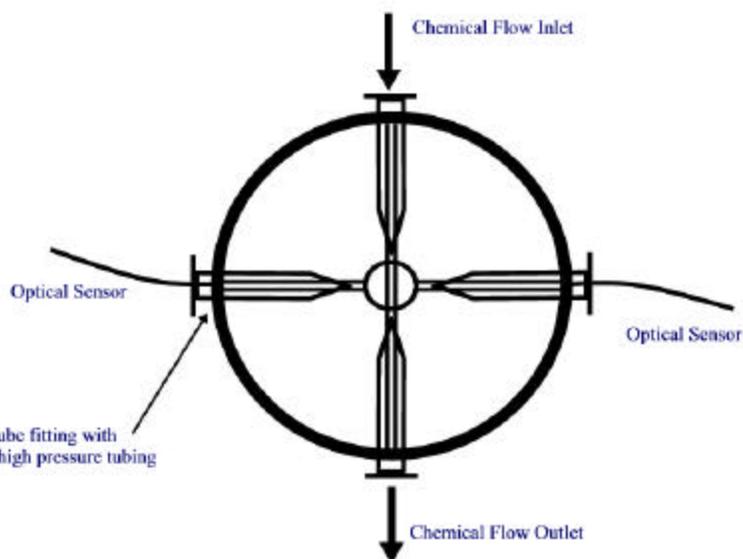


Figure 2. Design of fiber-optic UV probe in a high pressure cross for use with the supercritical CO₂ extraction apparatus.

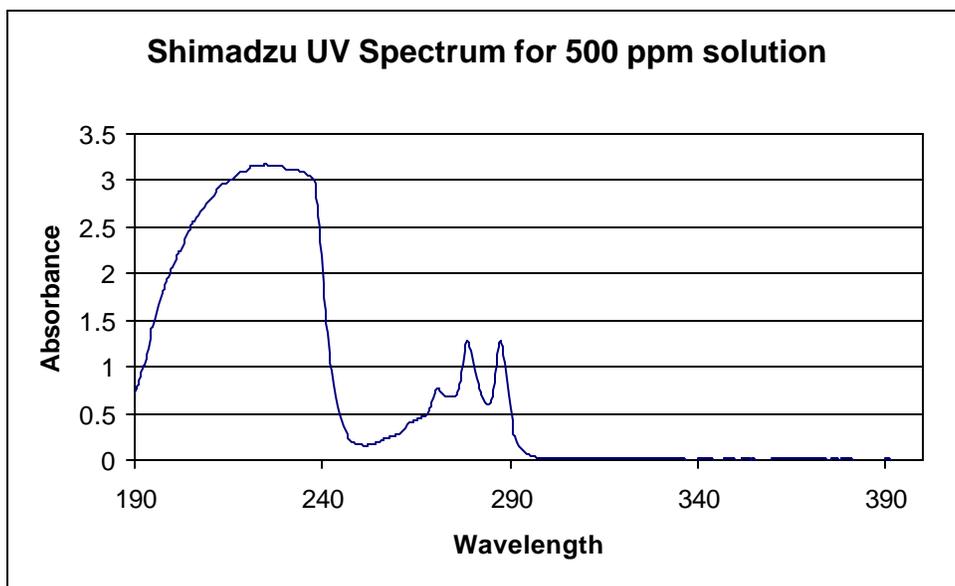


Figure 3. Shimadzu absorbance spectrum, 500 ppm 1,2,4-trichlorobenzene in hexane

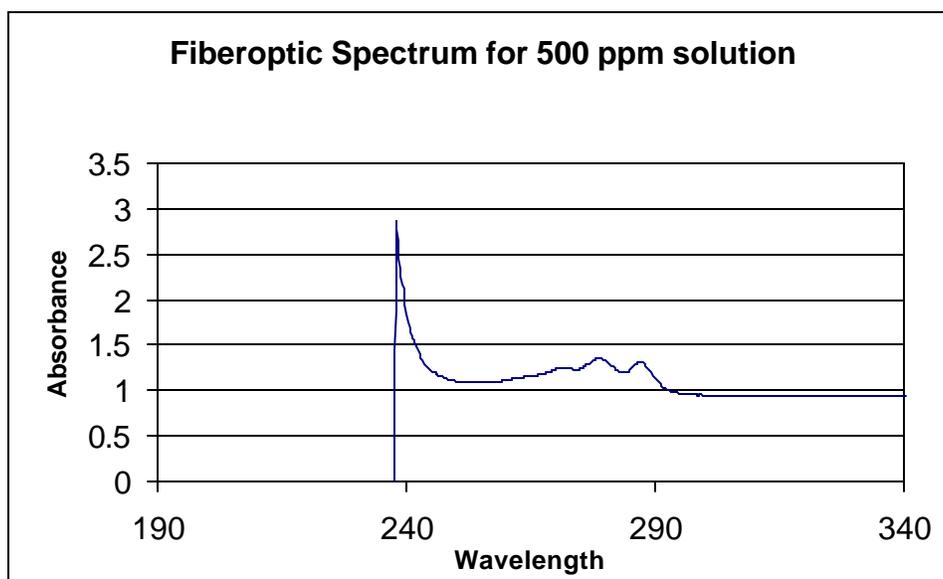


Figure 4. Ocean Optics absorbance spectrum, 500 ppm 1,2,4-trichlorobenzene in hexane

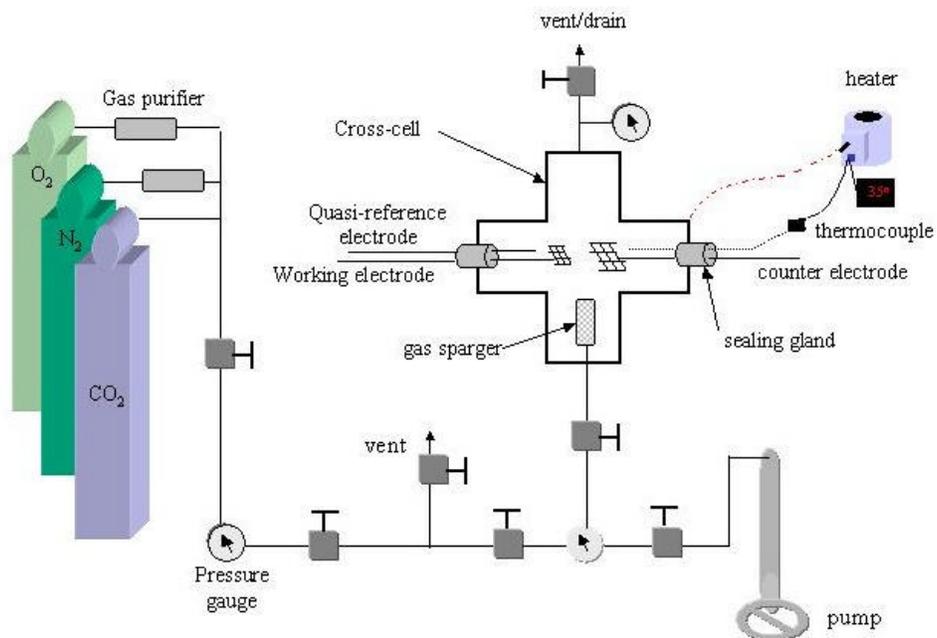


Figure 5. - Schematic of High-Pressure Electrochemical Cell at University of South Carolina

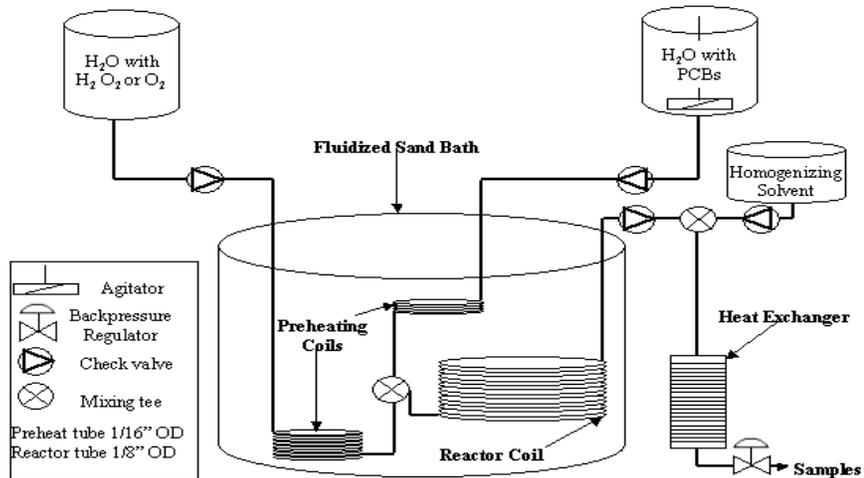


Figure 6. - Supercritical Water Oxidation Test Stand at Clemson University

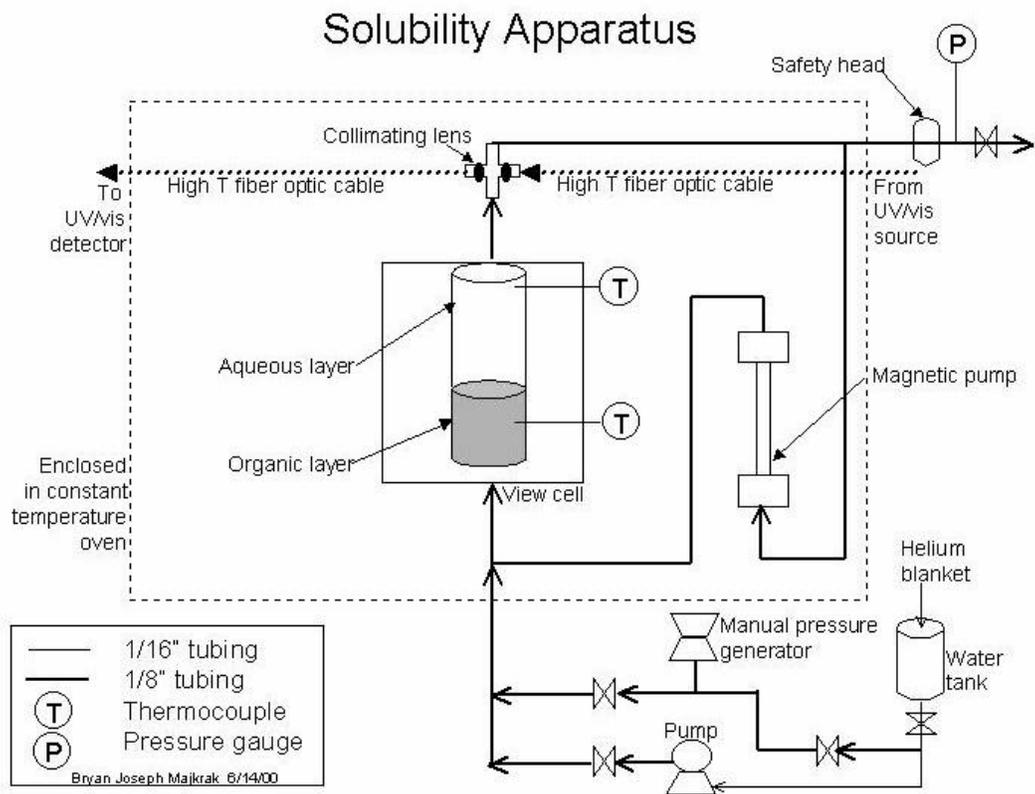


Figure 7. Apparatus for determining PCB solubilities in hot water

Table 1. Results from extraction of 1,2,4-trichlorobenzene contaminated Toxi-Dry Samples

	T (°C)	P (psia)	Dense CO2 Flowrate (ml/min)	Extraction Time (min)	% TCB Extracted[1]	% Material Balance of TCB[1]
1	40	2000	0.07	120	41.9	84
2	40	2000	0.07	120	27.7	104
3	40	2000	0.07	120	33	109
4	40	4000	0.14	120	20	81.6
5	40	4000	0.14	120	20.6	91.6
6	40	4000	0.14	120	29.4	87.4
7	40	4000	0.14	120	11	67
8	40	4000	0.25	120	23.8	106.5
9	40	6000	0.3	120	17.9	84.8
10	80	2000	0.07	120	49	72
11	80	2000	0.07	120	40	71
12	80	2000	0.07	120	42	66
13	80	2000	0.07	120	67.8	75.8
14	80	4000	0.25	120	110	113
15	80	4000	0.25	120	75.2	84.2

(1) Estimated uncertainty $\pm 15\%$