

Project # 64979

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

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Problem Area: Decontamination and Decommissioning

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Project Director: Mr. Edward A. Hamilton, 864-656-1564, hamilte@clemson.edu

Lead Principal Investigator: Dr. Michael A. Matthews, 803-777-0556, matthews@engr.sc.edu

Major Collaborator(s): Dr. Lawrence Oji, Savannah River Technology Center, 803-725-5328, lawrence.oji@srs.gov

Co-investigators: Dr. David A. Bruce, Clemson University, 864-656-5425, dbruce@clemson.edu
Dr. Mark C. Thies, Clemson University, 864-656-5424, mcths@clemson.edu
Dr. Thomas A. Davis, University of South Carolina, 803-777-7540, davisth@engr.sc.edu
Dr. John W. Weidner, University of South Carolina, 803-777-3207, weidner@engr.sc.edu
Dr. Ralph E. White, University of South Carolina, 803-777-3270, rew@sc.edu
Dr. John B. Pickett, Westinghouse Savannah River Company, 803-725-3838, john.pickett@srs.gov
Nancy Lowry, Westinghouse Savannah River Company, 803-725-7305, nancy.lowry@srs.gov

Research Objective

Large quantities of mixed low level waste (MLLW) that fall under the Toxic Substances Control Act (TSCA) exist and will continue to be generated during D&D operations at DOE sites across the country. Currently, the volume of these wastes is 23,500 m³, and the majority of these wastes (*i.e.*, almost 19,000 m³) consist of PCBs and PCB-contaminated materials. No proposed process for the recovery and/or destruction of these persistent pollutants has emerged as the preferred choice for DOE cleanup.

Collaborating researchers at the University of South Carolina (USC), Clemson University (Clemson University), and the Savannah River Technology Center (SRTC), under the direction of the South Carolina Universities Research and Education Foundation (SCUREF), have performed initial research and development on a combined PCB extraction/destruction process for the PCB-contaminated solids that are generated during D&D activities. Extraction is

performed using either supercritical carbon dioxide (CO₂) or hot, pressurized water. Destruction is accomplished by oxidation in supercritical or near-critical water. Two key aspects of the proposed process are that it isolates and concentrates the PCBs from the solid matrices (thereby reducing waste volume greatly), and little if any secondary solvent or solid wastes are generated.

Highlights for Annual Report:

Diffusion coefficients for model contaminants -- phenol, 1,2,4-trichlorobenzene, phenanthrene, and benzoic acid -- in near-critical CO₂ have been measured, and two papers on this topic have been published. Work on this task is concluded.

We have finished the extraction work of 1,2,4-trichlorobenzene (a surrogate of PCBs) 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 effects of temperature, pressure and cosolvents have been investigated, and the extraction efficiency of supercritical fluid extraction (SFE) has been compared with Soxhlet extraction and sonication. According to our extraction results, SFE can be a valuable extraction technology for extracting chlorinated aromatics from this job control waste and other DOE matrices.

We developed a low-cost reactor and electrode system for rapid screening of electrochemical reactions under high pressure. Initial high-pressure electrochemical tests were performed in supercritical carbon dioxide (scCO₂) and synthesized novel CO₂-soluble supporting electrolyte tetrakis(decyl)ammonium tetraphenylborate (TDATPhB) system at 70° C and 3000psi.

We have constructed a continuous-flow supercritical water oxidation apparatus (shown in Figure 3) in which to conduct hydrothermal oxidation of PCBs. Chemical analysis is performed with a new GC/electron capture detector system. We have conducted SCWO screening tests with methanol as a tuning compound for the continuous-flow supercritical water oxidation reactor. Methanol was chosen not only because it is easy to work with, but also because the supercritical water oxidation behavior of methanol is well documented in the literature. Hydrogen peroxide was chosen as the oxidant, as it outperforms oxygen as indicated by the literature. The reactor has the capability to obtain conversions of methanol and PCBs in excess of 99%.

Solubilities of various chlorinated organic compounds (chlorobenzene; 1-monochlorobiphenyl; 1,2-dichlorobiphenyl; and 2,3,4,5-tetrachlorobiphenyl) in water have been determined at temperatures ranging from 25° C to 180° C. Data obtained for chlorobenzene (a test compound) agree with established literature values and have a precision of 3%. These data were obtained using a high pressure, high temperature equilibrium cell and magnetic recirculation pump that uses a novel, noninvasive, fiber optic UV spectrophotometer to measure concentration. This apparatus has been used to measure the first PCB solubilities ever obtained at above-ambient temperatures. Given the practically nonexistent database for PCB-water solubilities at any temperature, our new technique is capable of providing an invaluable service to the environmental science community.

We will conduct a bench-scale test of the new process during June-August 2001. For the bench-scale task, it was originally intended to use actual PCB-contaminated radioactive waste samples generated during D&D operations at the Savannah River Site (SRS). However, most recently we were informed that DOE-SR Waste Management will not release any of the PCB-

contaminated radioactive waste to our research team for the planned tests since they have finalized a burn plan with the TSCA incinerator at Oak Ridge to incinerate the stored SRS radioactive PCB wastes. All of the PCB-contaminated waste at SRS must be characterized and shipped to Oak Ridge by the end of August. Thus, at this point it is our intention to run the extraction and oxidation experiments with Toxi-Dry spiked with PCBs. We believe the results will be essentially the same as if we had been able to use actual PCB-contaminated radioactive waste from SRS.

Research Progress and Implications

This report summarizes work through thirty-three months of the three-year project. This project involves personnel from two universities and the SRS; 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, especially polychlorinated biphenyl (PCBs) samples.
2. Find cosolvents and CO₂-soluble surfactants to enhance PCB extraction rate and recovery.
3. To develop new processes for the extraction of PCBs from DOE matrix materials generated during D&D operations.

Experimental approach:

In this work, 1,2,4-trichlorobenzene (TCB) was used as a surrogate for PCBs. A spiked TCB Toxi-dry sample was prepared. Baseline analytical method comparing Soxhlet extraction and sonication for the Toxi-dry was used. About one-gram samples were packed into an extraction cell. Membrane filters (five micron) were placed at each end inside the cell to prevent small particles from reaching the restrictor. After the extraction cell was placed in the extractor, the temperature was set using the temperature controller of the extractor. The outlet valve of the syringe pump was opened and the extraction cell was pressurized quickly. Static pressure was maintained for 20 minutes, after which the outlet valve was opened and dynamic extraction occurred. To collect the TCB extract, we used solvent trapping with chilled acetone as the solvent. The TCB-impregnated Toxi-dry samples were extracted for 2 hours. Flow rates (0.2 – 0.3 ml/min) were controlled by an ISCO integral restrictor. The experimental pressures examined were 2,000, 4,000 and 6,000 psia, and the temperature was either 40° C or 80° C. Acetone or ethanol was used as a cosolvent (5wt%).

Table 1 gives representative results from extraction with pure CO₂, CO₂ +5 weight percent acetone, or CO₂ + 5 weight percent ethanol. All extractions lasted two hours. The metric is the percentage recovery of TCB from the Toxi-dry matrix, where 100% recovery is defined by Soxhlet extraction using acetone.

Tables 1a, 1b, and 1c show that increasing pressure at 40° C was found to have little effect on recovery, while the extraction yield increased with pressure at 80° C. Complete recovery of TCB was not achieved using pure CO₂ . It was necessary to use pressures near 6000

psi to achieve TCB recoveries in excess of 90% using pure CO₂. The extraction of trace amounts of TCB from this spiked sample is clearly not solubility controlled, but TCB in this spiked sample is almost certainly not absorbed as strongly as that in an aged environmental sample. The effect of extraction temperature is complex, and is a combination of the effects on thermodynamic properties (solute vapor pressure, fluid density, and desorption isotherm) as well as dynamic properties (viscosity, desorption kinetics, mass transfer coefficients). It is clear that the recoveries of TCB from the Toxi-dry samples are greatly affected by the extraction temperature. For a temperature increase from 40° C to 80° C, the vapor pressure of 1,2,4-TCB changes from 102.4 to 1038 Pa, while the density of CO₂ decreases only from 0.880 to 0.687 g/ml. The solute vapor pressure increase is substantial, and the density decrease of the supercritical CO₂ is relatively low, so the positive effect of temperature is clear. It is believed that temperature enhances the diffusion coefficients and reduces solvent viscosity and superficial tensions. These two effects can contribute to faster mass transfer. At the same time, increasing temperature can also facilitate the breaking of the analyte-matrix interaction.

The use of mixed solvent, sc-CO₂ and 5 weight percent of either acetone or ethanol improved the extraction of TCB, especially at 80° C. TCB recoveries in excess of 90% and approaching 100% (within experimental uncertainty) are obtained at pressures as low as 2000 psia. This is a significant benefit because both capital costs and operating costs will be substantially lower if the extraction process can be operated at lower pressures.

We are installing and testing the 3-liter extractor system (Fig. 1) to be used for extraction and recovery of PCBs from Toxi-dry with supercritical CO₂ and ethanol. It consists of a 3-liter extraction vessel, a 1-liter separation vessel, feed pumps for CO₂ and ethanol, two back pressure regulator valves, and appropriate valves, pressure gauges and temperature sensors. We expect to finish the testing quickly, so that we can start the testing with actual PCB-contaminated waste matrices by the end of June.

Table 1a. Representative results for extraction of 1,2,4-trichlorobenzene (TCB) spiked onto Toxi-dry samples. Pure CO₂ is the extraction solvent.

	T (°C)	P (psia)	Dense CO ₂ Flowrate (ml/min)	Extraction Time (min)	% TCB Extracted[1]
3	40	2000	0.07	120	33
7	40	4000	0.14	120	31
9	40	6000	0.3	120	42.9
12	80	2000	0.07	120	60
16	80	4000	0.25	120	75.2
17	80	6000	0.3	120	96.3

Table 1b. Representative results for extraction of 1,2,4-trichlorobenzene (TCB) spiked onto Toxi-dry samples. The extraction solvent is CO₂ + 5% acetone.

	T (°C)	P (psia)	Dense CO2 Flowrate (ml/min)	Extraction Time (min)	% TCB Extracted[1]
1	40	2000	0.07	120	61.9
2	40	2000	0.07	120	50.3
3	40	4000	0.25	120	58.3
4	40	6000	0.25	120	61.6
5	80	2000	0.25	120	94.2
6	80	2000	0.25	120	98.5
7	80	4000	0.25	120	100.4

Table 1c. Representative results for extraction of 1,2,4-trichlorobenzene (TCB) spiked onto Toxi-dry samples. The extraction solvent is CO₂ + 5% ethanol.

	T (°C)	P (psia)	Dense CO2 Flowrate (ml/min)	Extraction Time (min)	% TCB Extracted[1]
1	80	2000	0.4	120	87.3
2	80	2000	0.4	120	102.1
3	80	4000	0.4	120	109.7
4	40	2000	0.25	120	68.2
5	40	2000	0.25	120	74.58
6	40	4000	0.3	120	71.77

Plans:

1. Sufficient runs of SFE need be conducted this summer to get the optimal extraction conditions of PCB-contaminated wastes from SRS.
2. Additional solid matrices (representative of the broad spectrum of PCB-contaminated wastes generated during D&D activities) could be tested using the equipment and techniques that we have developed.
3. Kinetics of PCB extraction and retention on the solid matrices will be modeled.

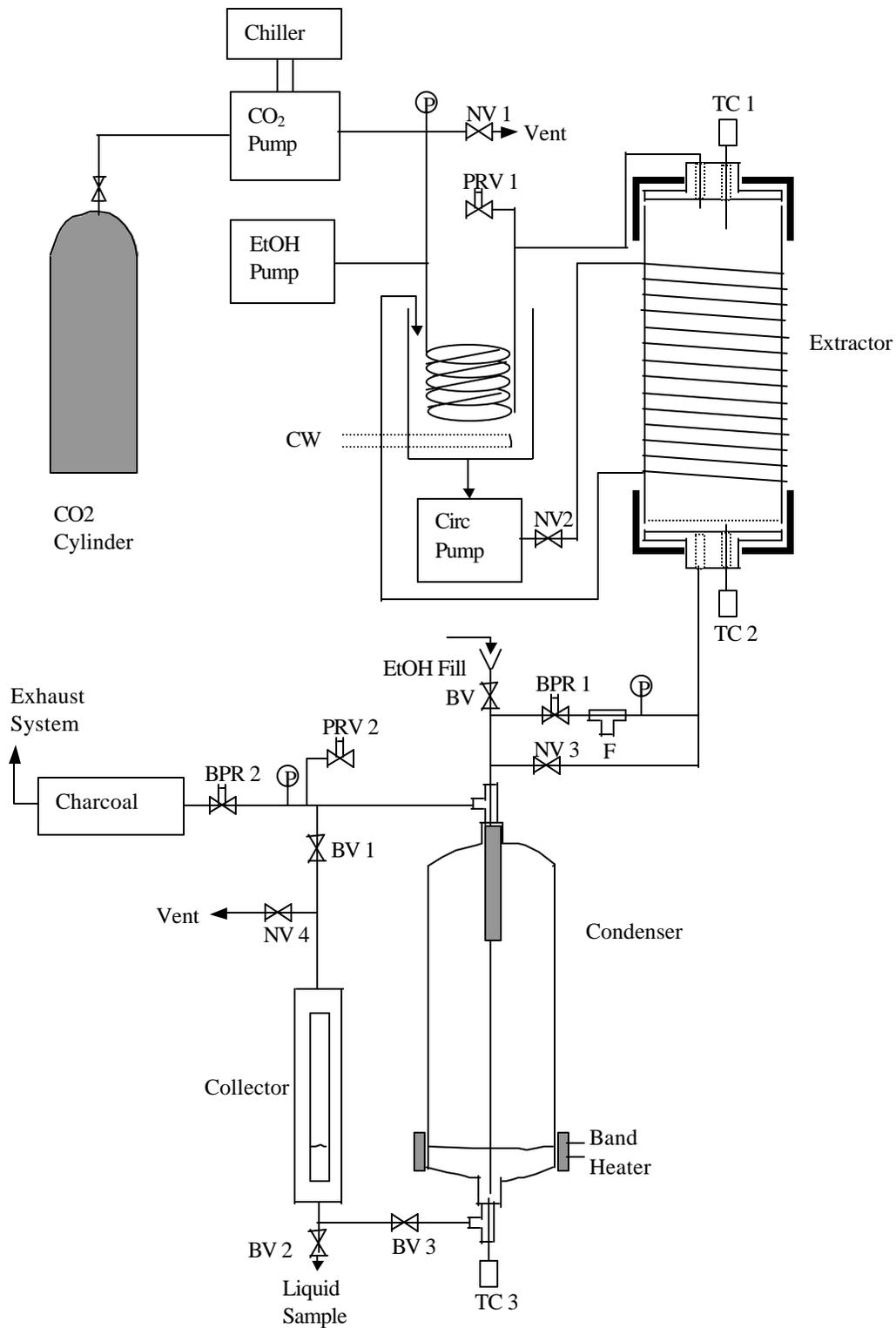


Figure 1. - Schematic of 3-liter supercritical CO₂ extraction apparatus at USC

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 developed a low-cost reactor and electrode system for rapid screening of electrochemical reactions under high pressure. Initial high-pressure electrochemical tests were performed in supercritical carbon dioxide (scCO₂) and a synthesized novel CO₂-soluble supporting electrolyte tetrakis(decyl)ammonium tetraphenylborate (TDATPhB) system at 70°C and 3000psi. Unfortunately, sufficient conductivities could not be achieved. Therefore, an aprotic solvent acetonitrile with supporting electrolyte tetraethylammonium perchlorate (TEAP, 0.1M) was tested. Oxygen pressures of 160 psig, with and without CO₂ overpressures of 40 psig were added to the high-pressure cell. Superoxide ion (O₂^{•-}), the destruction agent, was electrochemically generated under these conditions. This work was presented to the International Society of Electrochemistry.

Although the feasibility of electrochemically generating the superoxide was demonstrated, the use of acetonitrile introduces a secondary waste stream. Therefore, electrochemical oxidation of PCBs in CO₂ does not appear promising. However, this work led us to investigate alternative, more environmentally benign solvents, namely room temperature ionic liquids (RTILs). The USC investigators recently received funding from the National Science Foundation to continue to pursue this work. Our preliminary results have been submitted to the Journal of the Electrochemical Society. If successful, electrochemistry in RTILs could be coupled with dense CO₂ extraction to produce a process for destroying PCBs.

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. Demonstrate effectiveness of apparatus on actual DOE mixed low level waste.
2. Understand and model the effects of process variables (i.e., temperature, pressure, flow rates, etc.) on PCB conversion.
3. Determine destruction efficiencies and kinetics of destruction of PCB congeners.

Experimental approach:

At Clemson University, the supercritical water oxidation (SCWO) reactor has been modified to incorporate state-of-the-art features and to address various problems encountered in the course of performing experiments. The number and severity of the problems encountered only serve to reinforce the assertion that fundamental kinetic data is required for intelligent reactor design of a process designed to destroy PCB-contaminated wastes. The SCWO reactor, shown in Figure 2, will be used to oxidize aqueous solutions of representative (i.e., of those encountered on DOE sites) PCB congeners. Special attention will be paid to the effect of degree-of-chlorination and position of chlorine substitution. Kinetic parameters crucial to reactor design and scale-up will be calculated, and the optimum reaction conditions will be determined. Beginning immediately, experiments with surrogate DOE waste will be performed to demonstrate the effectiveness of the SCWO reactor at decomposing hazardous DOE mixed low-level waste (MLLW).

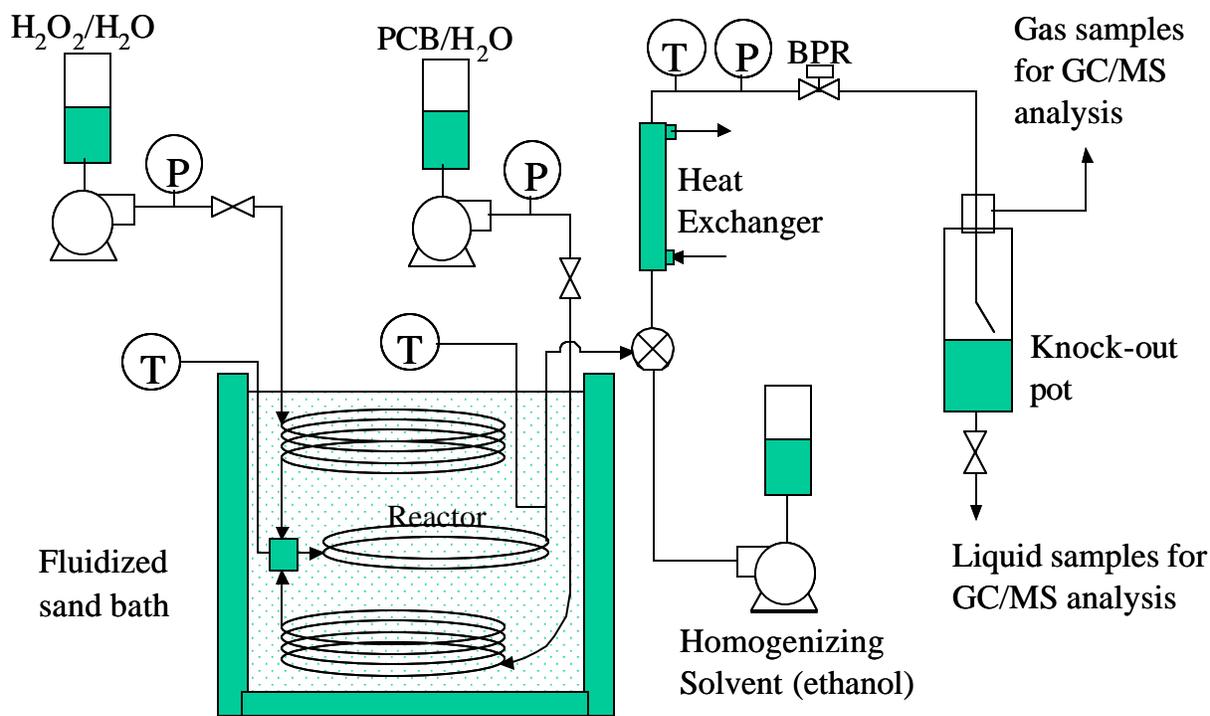


Figure 2. – Supercritical Water Oxidation Reactor at Clemson University

Plans:

1. Continue SCWO experiments with PCB simulants, PCBs, and MLLW.
2. Examine reaction kinetics.
3. Determine the effects of organic cosolvents (e.g., ethanol) on PCB degradation.
4. Evaluate increased chlorine content of PCB congeners on oxidation efficiency.

Task 4: Solubility of PCBs in hot water:

Task 4 Objectives:

1. Obtain solubility-temperature relationships for all PCB congeners that are to be examined in the SCWO reactor.
2. Obtain solubility data on several PCB congeners and correlate with a thermodynamic model.

Experimental Approach:

The high-pressure equilibrium cell (Figure 3) is being used for in-situ measurements of PCB solubilities in ambient and hot water. The design features an inline magnetically actuated recirculation pump that can operate at elevated temperatures. Prior to its use in the SCWO experiments, each new congener will be studied in the solubility apparatus. Operation of the solubility apparatus has proven successful, so obtaining additional solubility measurements should be accomplished with routine efficiency. Once a suitable complement of data is obtained, a predictive model will be developed.

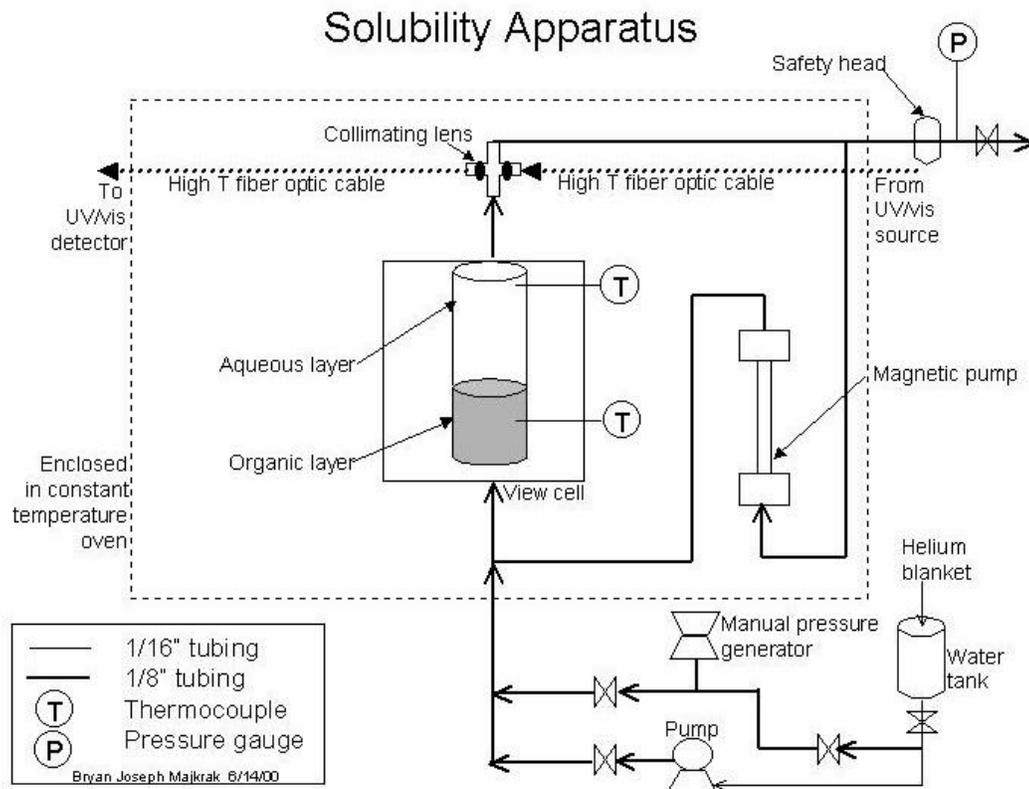


Figure 3. Apparatus for determining PCB solubilities in ambient and hot water

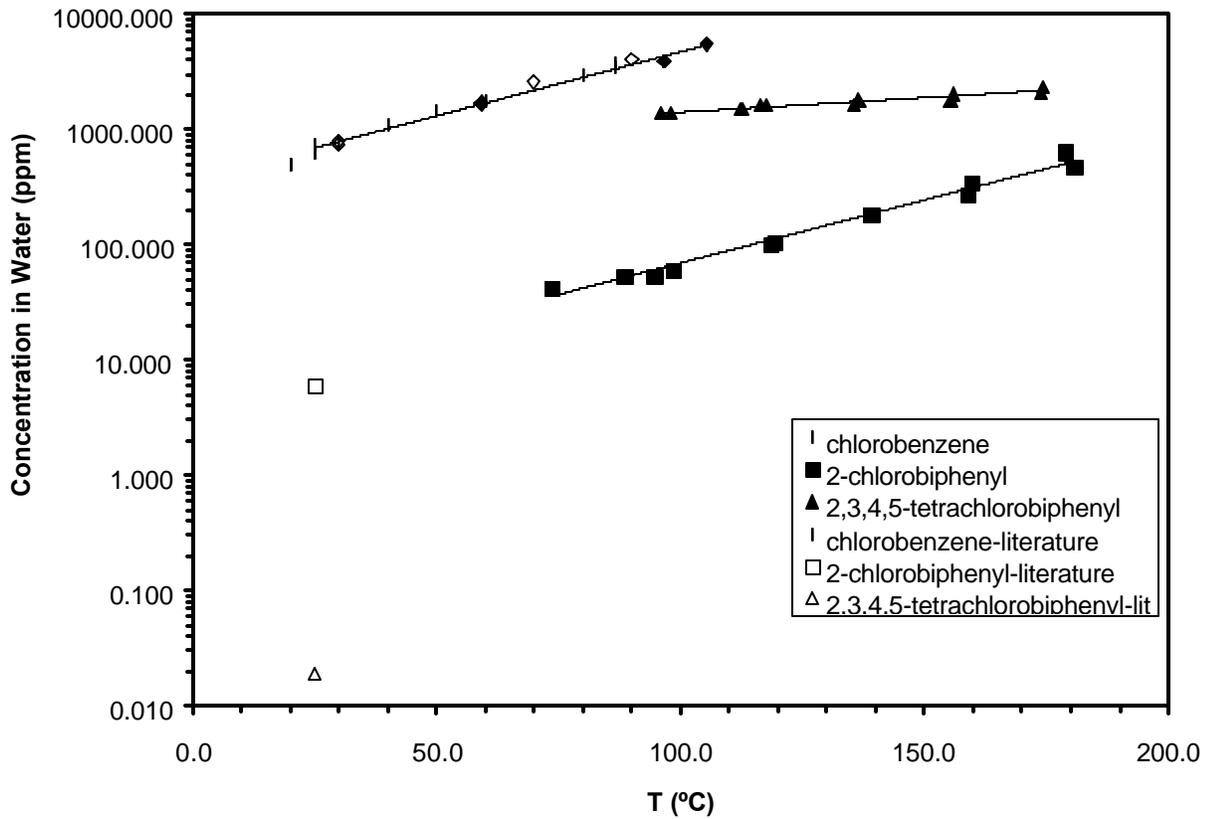


Figure 4. Solubility of various chlorinated organic compounds

Plans:

1. Continue measuring solubilities of additional PCB pure components (e.g., hexachlorobiphenyl).
2. Develop model to predict solubility of PCB mixtures in water as a function of temperature and degree-of-chlorination.