SUPERCRITICAL EXTRACTION OF POLYCHLORINATED BIPHENYLS FROM SOILS AND SEDIMENTS: REMEDIATION AND POSSIBLE RISKS

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INTRODUCTION

It is estimated that there exists about 350 million pounds of polychlorinated biphenyls (PCBs) in landfill and other storage, and another 24 million pounds in sediments, soil, vegetation and animals (1). The potential environmental threat of the large amount of PCBs has called for the development of effective PCB cleanup techniques. Although some PCB remediation technologies such as incineration and in-situ vitrification have been commercial available, many efforts are still being conducted in order to develop more economic and social acceptable methods (1-3). Among these efforts, the application of supercritical fluid extraction (SFE) in the removal of toxic organics from environmental samples is receiving much attention due to the unique properties of supercritical fluids (SCFs) such as low viscosity, high diffusivity, and easily tunable solvent power (2-5). A process concept advanced at Syracuse University will be presented here.

The process to treat PCB contaminated soils with supercritical technique may involve some risks. These risks could include additional contamination of underground waters due to fracture and permeation through underground structure when contaminated soils are excavated; removal of organic matter from soil and rendering it inert; hazardous operation of large scale high pressure mobile apparatus; and hazards in surface transportation of PCB soil extracts to a central site for supercritical water oxidation (SCWO) destruction. These issues will be discussed.

METHODOLOGY

We are developing a new generation of soil remediation technology at Syracuse University to clean soils and sediments contaminated with chlorinated hydrocarbons such as PCBs as well as polycyclic aromatic hydrocarbons (PAHs). The two-stage concept advanced is shown in Figure 1. First (Figure 1a), the toxic PCBs or PAHs are extracted from the sediments or soils using SFE with high-pressure carbon dioxide fluids. The clean soils/sediments are returned to the site, the concentrated toxic organics are separated from the supercritical fluids for further processing, and the supercritical fluids are recycled. In the second process step (Figure 1b), SCWO, the concentrated toxic organics are destroyed by wet oxidation to form harmless carbon dioxide, water and hydrochloric acid.

A laboratory scale extraction unit is employed to obtain desorption data for PCB removal from laboratory-spiked and native contaminated soils with supercritical carbon dioxide and cosolvents. Various conditions of extraction for a variety of soils/sediments have been studied. A flowsheet of the unit is shown in Figure 2. The fixed-bed unit can be operated at pressures and temperatures as high as 680 atm and 100 °C.
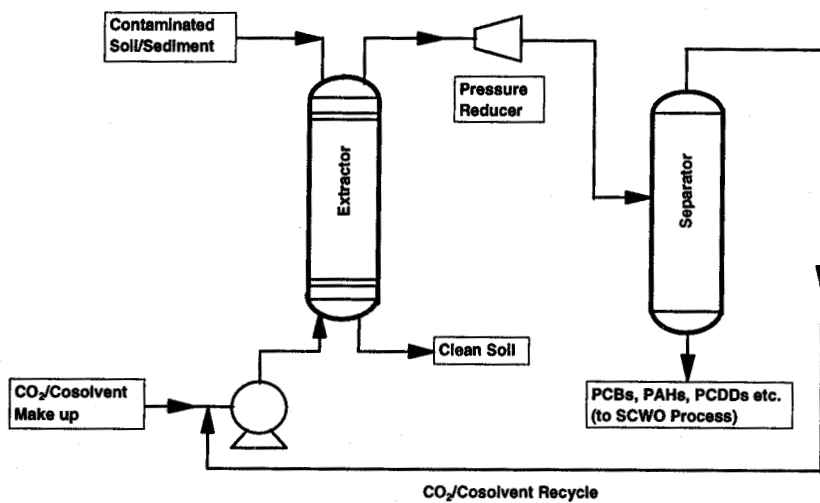
(a) Supercritical Fluid Extraction(SFE)
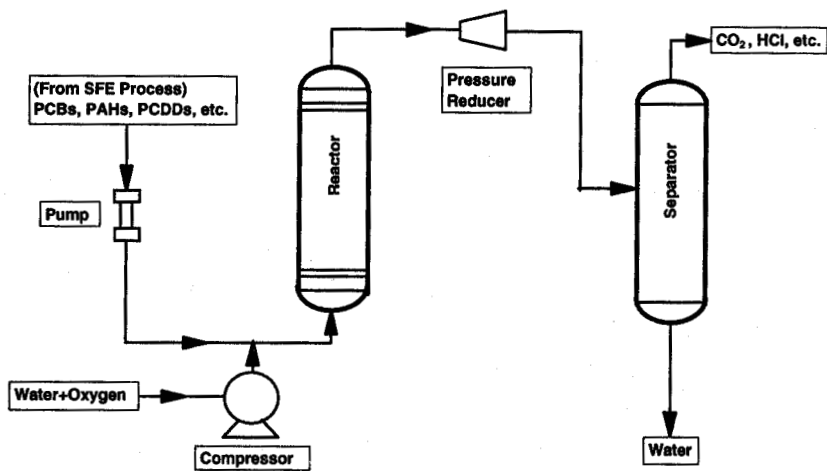
(b) Supercritical Water Oxidation(SCWO)

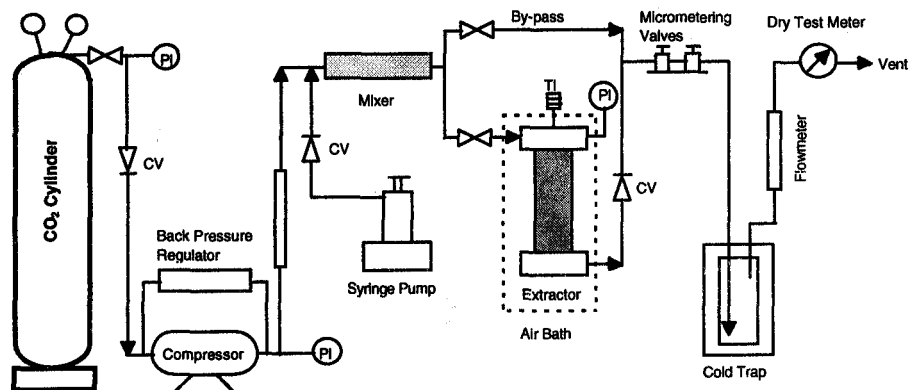Figure 1. Supercritical Methods for Soil Clean-up

Figure 2. Schematic of Laboratory SFE System

RESULTS

Experiments have been executed with the laboratory scale unit in a wide range of experimental conditions such as temperature, pressure, cosolvent type and concentrations, soil type and initial PCB concentration. A summary of results are shown in Table 1 which shows the contact times necessary to achieve sub 10 ppm removal of PCB congeners (Aroclor 1248) from various soil types at specific initial concentration.

TABLE 1. SUMMARY OF EXPERIMENTS WITH SUB 10 PPM REMOVAL OF AROCLOR 1248

Soil	Initial Conc. (ppm)	Pressure (atm)	Temp. (°C)	Cosolvent (mol%)	Moisture (wt.%)	Contact Time (min.)	Residual Conc. (ppm)
		P1	T1	5	10	60	2.6
Till	1150	P2	T2	5	10	45	3.2
		P2	T3	5	10	30	3.0
		P2	T1	0	10	120	3.4
Sediment		P1	T2	5	0	60	18.9
(Native, St.	370	P1	T2	5	10	60	15.1
Lawrence							
River)							
		P1	T2	5	0	45	6.5
Sediment		P1	T2	5	20	45	5.7
(Native,	71	P1	T3	5	0	60	4.3
Hudson River)		P1	T3	5	20	60	3.2
		P2	T2	5	10	60	4.4
Surficial	4200	P2	T3	5	10	30	6.7
(4" - 12")		P2	T2	5	0	30	8.0
Sand	950	P1	T2	5	10	15	1.2

These results show that sub 10 ppm residual concentrations can be achieved at fixed-bed contact times of 15 to 60 minutes.
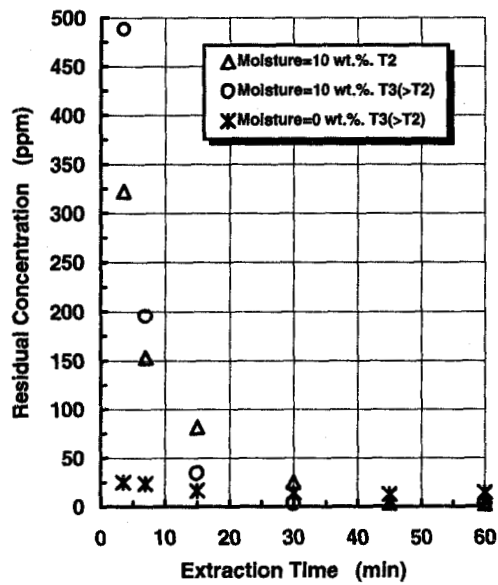
Figure 3. Temperature and Moisture Effects on SFE of Arolor 1248 from Lab-spiked Till Conditions: P2, MOD1=5 mol%, Initial Concentration=1150 ppm.
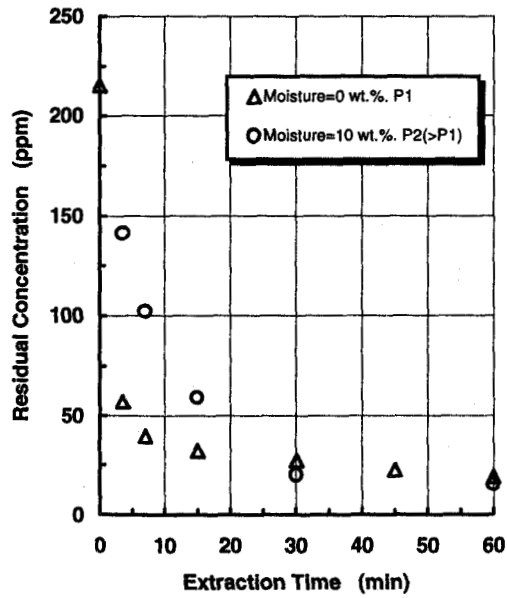
Figure 4. Moisture Effects on SFE of PCBs from Contaminated Sediment of St. Lawrence River Conditions: T2, MOD1=5 mol%, Initial Concentration=370 ppm.

Figures 3 and 4 are the experimental results whereby the residual Aroclor 1248 concentration is plotted versus time of extraction during which the supercritical carbon dioxide with cosolvent is passed through the bed of contaminated soil. In Figure 3, the results for till are illustrated. Higher temperature of T3 is preferred to remove Aroclor 1248 from wet till to sub 5 ppm. At T2, it takes 45 minutes, but 30 minutes at T3. It is also seen that a rapid drop occurs without moisture present, to about 25 ppm after 3.5 minutes of contact, however, an equilibrium value is reached and the final concentration is 12 ppm.

In Figure 4, it is seen that the residual concentration drops to 19 ppm between 30 to 45 minutes for extraction of Aroclor 1248 from contaminated, St. Lawrence River sediment of initial concentration of 370 ppm for either dry or 10 wt.% moisture content sediment. These results occur although the dry samples were extracted at a lower pressure. The residual concentrations remain at the same level even after 60 minutes of extraction which indicates the achievement of equilibrium value. Desorption rate models are being applied to correlate these data.

Economic estimates have been made comparing treatment costs for supercritical extraction of PCBs from soil with other competing technologies. This comparison is based on an up-date of work by Carpenter (15) and has built into it the soil handing costs and shown in Table 2.

The comparison shows the favorable economics for SFE/SCWO of PCBs from soils.

CONCLUSIONS

The results of laboratory scale SFE clearly indicate that supercritical carbon dioxide/cosolvent fluids can remove PCBs in various contaminated soil matrices to sub 10 ppm level under proper conditions of contact.

An economic analysis based on laboratory scale unit results shows that the SFE/SCWO of PCBs from soils to be a favorable process.

Despite the advantages of the supercritical technology for remediation of contaminated soils, risks may still occur during the processing procedures. The risks involved would be disturbing underground structure and causing dispersion of contaminants beyond the hazardous waste site; removal of organic matter from soil and producing an inert soil which may be unsuitable for reuse; hazards in transporting PCB laden extracted hydrocarbons to a central site for SCWO destruction; and hazardous operation of large scale high pressure mobile apparatus. These risks do not appear insurmountable, however.

SCWO studies are in progress to determine conditions for acceptable PCB destruction efficiencies, kinetics of the reaction, and economic estimates of this process step.

A bench scale unit has been fabricated and installed for experiments to confirm the laboratory conditions and to establish suitable extractor geometry and contacting schemes for a viable process.

TABLE 2* COMPARISON OF TREATMENT PROCESSES

Process (order of rank)	Cost Range ($/m³ processed)
O.H.M. Methanol Extraction	$513 to $658
Advanced Electric Reactor (thermal treatment)	$1063 to $1206
Acurex Solvent Wash (hexane/trichlorotrifluoro-ethane extraction	$251 to $728
Bio-Clean	$245 to $474
Vitrification	$326 to $702
LARC (isopropanol extraction and radiation treatment)	$286 to $430
Modar Supercritical Water	$320 to $938
Soilex Solvent Extraction (kerosene extraction)	$1096 to $1169
SFE/SCWO (estimate in this work)#	$220 to $270

* First eight process costs taken from Carpenter (15); 1985 dollars updated to 1994 dollars using 1.35 M&S factor.
# Assumptions for this estimate are given in the text.

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INTRODUCTION

Supercritical water oxidation (SCWO) is an emerging technology for the ultimate destruction of organic wastes. Organic compounds and oxygen can be intimately mixed in a single homogeneous aqueous phase at supercritical conditions ($T_c = 374°C$, $P_c = 218$ atm). Thus, the rapid oxidation reactions are unhindered by inter-phase transport limitations that could occur at subcritical conditions where multiple phases exist. Savage et al. (1) describe current research into SCWO reactions in their review of reactions at supercritical conditions.

The rational design, optimization, control, and analysis of SCWO processes requires a knowledge of SCWO kinetics and potential byproducts formed from the oxidation of real pollutants. Our research group has focused on the oxidation of phenolic compounds (2-10), and this presentation will provide an overview of our most recent work.

METHODOLOGY

All oxidation experiments were performed in a reactor that nominally operated isothermally, isobarically, and in plug flow. Aqueous solutions of O_2 and the phenol were prepared separately and used as the reactor feed streams. The feed streams were pressurized and pumped through the reactor using two liquid chromatography pumps. The phenol and oxygen streams were preheated in separate coils of Hastelloy C-276 tubing. These preheater lines meet in a mixing union, where the temperature was measured by a thermocouple and the mixed feed streams enter the 4 m. long by 0.125 in. O.D. Hastelloy reactor. The preheater lines, mixing tee, and reactor coil are housed in an isothermal fluidized aluminum-oxide bath equipped with a temperature controller.

The reactor effluent was cooled in two consecutive tube-in-tube heat exchangers and decompressed in a back pressure regulator. The exiting stream was separated into gas and liquid phases (at ambient conditions) in a liquid trap. The gas flow rate was measured with a bubble meter at the outlet of the system, and the gas stream was then sent to an on-line gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). The liquid flow rate was measured, and samples of the liquid phase were retained for analysis.

A reverse-phase high-performance liquid chromatograph (HPLC) was used to determine the concentration of phenolics in the liquid effluent samples. Analyses were performed isocratically with a mobile phase of water/acetonitrile in a 5:2 v/v ratio flowing at 1 ml/min. The UV absorbance at a wavelength of 210 nm was monitored, and detector response factors were determined experimentally.

Before additional products in the liquid phase were analyzed, the samples were concentrated because many products were present in low concentrations. 20 mL of the reactor effluent was extracted with three successive 10 mL aliquots of dichloromethane. The 30 mL volume of this organic phase was subsequently reduced to 1 mL using a Kuderna-Danish concentrator in a water bath at 50°C. 10 mL of a dichloromethane solution containing a standard was added to each sample prior to concentration.

Reaction products in these concentrated samples were identified by GC-MS. The reaction products were quantified by GC with a flame ionization detector (FID). When a suspected reaction product was available commercially, we positively identified that product by matching both the mass spectrum and retention time with those of the authentic sample. The FID response factor was then determined experimentally for these compounds. Other suspected products, for which the authentic compound was not available commercially, were tentatively identified by inspecting the mass spectra and