

SUPERCRITICAL FLUID TECHNOLOGY FOR REMEDIATION OF PCB/PAH-CONTAMINATED SOILS/SEDIMENTS

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ABSTRACT

A two-stage technology employing green solvents such as supercritical CO₂ (SC-CO₂) and supercritical water (SCW) for the extraction and destruction of polychlorinated biphenyls (PCBs)/polycyclic aromatic hydrocarbons (PAHs) from contaminated soils/sediments is proposed. Results of our laboratory and bench-scale investigations indicate that SC-CO₂ modified with 5% methanol, is an effective solvent and conditions have been defined to achieve sub 5 ppm in 45-60 minutes for 99.8% removal. Comprehensive data on PCB/PAH solubilities in SC-CO₂/MeOH, partition equilibria, and desorption provide a solid basis to develop models regarding the extraction of these pollutants from solid matrices. Further, the supercritical water oxidation (SCWO) stage, coupled to the extraction process with three possible configurations, would provide clean effluent materials. The ultimate products of the proposed technology are mainly clean soil/sediments and inorganic species such as H₂O, CO₂, and small amounts of chlorides. Our SCWO studies indicate that 5245 ppm Aroclor 1248 in methanol-simulated soil extract solutions can be oxidized to 99.95% conversion in less than one minute at 550°C. An economic analysis based on three possible configurations of the technological process indicates that the expected cost of \$198-318 per m³ of soil processed is economically competitive.

Key words: *soil/sediments remediation technology, supercritical fluids, PCBs, PAHs*

INTRODUCTION

The objective of this study is to develop an economical technology based on supercritical fluids (SCFs) to remediate contaminated soils and sediments. Chlorinated xenobiotics, such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzo-furans (PCDFs), and polycyclic aromatic hydrocarbons (PAHs) are major pollutants at hazardous waste sites.

Despite great efforts and expenditure of resources to develop both technically and economically effective cleanup processes of PCB/PAH-contaminated soils/sediments, no widely accepted methods have been found and further research is still needed (GAO/RCED-96-13, 1996). Nevertheless, recent developments show that the number of available treatment methods will probably increase in the near future (Akgerman et al., 1997; Ekhtera et al.,

1997). Engineering know-how concerning unit operations, hazardous waste treatment, and transport and handling of soil is needed for development and implementation. A short overview of processes that have been applied in practice or which are currently the subject of intense research for a scale-up design is shown in Table 1.

The main advantages and disadvantages, status of development, and limited economic evaluation of these processes are given. These PCB/PAH remediation technologies for soils/sediments can be grouped into three general categories: (1) extraction/removal, (2) destruction after separation, and (3) *in situ* processes. Although EPA is considering the possibility of "natural" processes for remediation of soils/sediments contaminated by organic pollutants like PCBs (Renner, 1998; Cooney, 1996), we think that an effective remediation strategy

should combine “natural” processes for broad and lightly contaminated areas and aggressive technologies such SCF-based processes for quick removal and destruction of heavily contaminated “hot spots.”

BACKGROUND

Supercritical fluid technologies (supercritical fluid extraction, SFE, and supercritical water oxidation, SCWO) are drawing much attention as emerging techniques

for soil remediation due to the following attractive features: (a) Cleanliness. A supercritical fluid process employs environmentally benign solvents (CO₂ and water) to extract/destroy pollutants in contaminated soils/sediments without destroying the structure and altering the major properties of the treated soils/sediments. (b) Quickness. The cleanup can be achieved in a relatively short processing time (10 - 60 min). (c) Wide range of application. The SFE process

Table 1. Comparison of relevant processes for remediation of PCB/PAH-contaminated soils/sediments.

Process ^a	Advantages	Disadvantages	Status ^b	Cost (\$/m ³)	Reference
Supercritical Fluid Extraction ¹	High extraction efficiency Suitable conc. range Cleaned soils unmodified	Further PCB treatment High-P devices Soil excavation required	L	198-318 SFE+SCWO	Tavlarides et al., 1999 ^c
<i>In situ</i> Thermal Desorption ¹	<i>In situ</i> (no excavation) Applicable to heterog. soil Broad applicability	Further PCB treatment High temperatures Slow process	C	100-380	Caruana, 1998
Liquid Solvent Extraction ¹	High extraction efficiency Low T-P conditions Portability	Diffic. to separate PCB Further PCB treatment Secondhand pollution	P	250-1169	Meckes et al., 1997
Incineration ²	High destruction efficiency Continuous flow system Broad applicability	High cost, high temp. Emission of toxic gas/ash Irrev. soil degradation	C	>> 360	GAO/RCD 1996 EPA Report 1993
Supercritical Water Oxidation ²	High destruction efficiency Continuous flow system Portable, closed system	High corrosion Requires an extr. step High P-T conditions	L	198/318 SFE+SCWO	Tavlarides et al., 1999 ^c
Chemical Dechlorination ²	Low T-P conditions Portability Continuous flow system	Low destr. efficiency Requires an extr. step Low PCB/H ₂ O soly.	P	350-360	Caruana, 1997
Gas Phase Chemical Reduction ²	High destruction efficiency Continuous flow system Portability	Uses high-risk H ₂ High temperature Requires excavation	C	350	Caruana, 1997
Bio-remediation ³	No secondhand pollution Broad area of land applic. Ambient conditions	Low destr. efficiency Very slow process Inactive for ortho-PCBs	L	245-474	Carpenter, 1985

^a Category of: (1) extraction/removal, (2) destruction after separation, (3) in situ process; ^b L = Laboratory, P = Pilot, C = Commercial; ^c this work.

is able to clean up PCB-contaminated soils/sediments with PCB concentrations in the range of 10-10,000 ppm, which represents the PCB levels in most contaminated sites, and is particularly effective to remediate soils with high PCB concentrations. Finally, the concentrated PCBs collected after the extraction can be easily destroyed using other available methods such as incineration or SCWO.

The unique property of SCFs that makes them technically enticing is that they show enhanced ability to dissolve organic compounds, and this solvent ability can be easily tuned by changing temperature and/or pressure (McHugh and Krukonis, 1994; Akgerman et al., 1993; Brennecke, 1996). This sensitivity to temperature and pressure leads to simple solute-solvent separation schemes. Other attractive features of SCFs include low viscosity and high diffusivity that are essential to reduce mass transfer resistance during the desorption processes. The two most popular fluids are supercritical CO₂ (SC-CO₂) and water (SCW) because they are non-toxic, non-flammable, readily available, and inexpensive.

SFE of contaminated soils has been studied by a number of investigators (Modell, 1987; Hawthorne et al., 1989, 1992, 1993, 1994, 1995; Langenfeld et al., 1993, 1995; Dooley et al., 1987, 1990; McNally et al. 1993; McNally, 1995; Brady et al., 1987; Yang et al., 1995; Markowz, 1996; Koinecke et al., 1997; Schantz et al., 1998; Monterro et al., 1996; Holst et al., 1992; Madras et al., 1994; Zhou et al., 1997). We investigated PCB desorption rates and efficiencies from several

spiked soil samples and native Hudson and St. Lawrence river sediments (Chen et al., 1997; Chen, 1997). Effects of pressure, temperature, cosolvent, soil moisture content, and initial concentration on PCB desorption efficiencies are reported. It is found that cosolvent and soil moisture are the two most important factors affecting PCB extraction efficiencies. Significant differences between spike samples and native samples also are found in this research. Similar studies were conducted by Morselli et al. (1998) and Liu et al. (1991). The structure and properties of PCB congeners are also found to have a significant effect on PCB desorption (Reutergardh, 1998). Becnel et al. (1998) studied the effects of supercritical fluid density, temperature, and cosolvents on PAH extraction. Lutermann et al. (1998) investigated effects of various binary and ternary SCFs on extraction of PAHs from real soils. Eaton et al. (1997), Akgerman et al. (1996), Lee et al. (1995), Knaff et al. (1997), Olesik et al. (1991), and Madras et al. (1993) have made substantial contributions to quantify mass transfer, diffusion coefficient, and desorption rate in SFE processes. All of these studies have shown promise of SFE as an effective remediation process.

The solubility of a solute in a SCF is one of the most important properties (along with the mass transfer coefficients) that must be determined and modeled in order to design effective SFE processes. Among the factors responsible for the limited acceptance of the SFE process to date, a lack of solubility data has been frequently cited. A number of investigators have published equilibrium solubility data of various

individual solids in SCFs (reviewed by Bartle et al., 1991; also Andrews, 1990; Johnston et al., 1982; Yu et al., 1995; Miller et al., 1996 and 1997; Anitescu and Tavlarides, 1997a, 1997b, and 1999a). However, according to our present knowledge, the solubility data for individual PCB congeners and Aroclor mixtures have been limited (Akgerman et al., 1997; Yu et al., 1995) until recently (Anitescu and Tavlarides, 1999a). A great effort has been devoted to develop reliable models for solubility calculations (Bartle et al., 1991; Bush and Eckert, 1997; Kwon and Mansoori, 1993; Kumar and Johnston, 1998). Unfortunately, the critical properties required for both solvent and solute when an equation of state is used are, in most cases, unavailable. So, other models such as a dilute two-region solution theory (Wang and Tavlarides, 1994), solubility enhancement-based correlations (Miller et al., 1997), and other semiempirical and empirical relationships have been proposed (Vetere, 1998; Guigard and Stiver, 1998; Buchwald and Kauschus, 1997; Engelhardt and Jurs, 1997). Our solubility studies on PCB/PAH compounds (Anitescu and Tavlarides, 1997a,b; 1998; 1999a-c) provide an adequate database and semiempirical relationships to select optimum conditions for design of large-scale SFE apparatus.

Solute partition equilibrium data which determine the driving force of desorption processes are key elements in the modeling and design of full-scale apparatuses. Adsorption equilibrium models and experimental data have been reported for several volatile organics in supercritical environments (2,4-dichlorophenol-

water-CO₂, Akgerman et al., 1994; phenol-water-CO₂, Brudi et al., 1996; phenol-activated carbon-CO₂, Akman et al., 1991). The partition equilibrium of a phenolic mixture and a PAH mixture in a soil-water-CO₂ system was studied by Green et al. (1996). Madras et al. (1994) and Erkey et al. (1993) investigated the adsorption equilibrium of naphthalene, phenanthrene, hexachlorobenzene, and pentachlorophenol between SC-CO₂ and activated carbon. The phenanthrene partition equilibrium data between SC-CO₂ and two soils were reported by Young et al. (1997). No data has been found for PCB partition equilibrium between soils and SCFs. A new sorption apparatus developed in our laboratories provides data between organic solutes (PCBs/PAHs) sorbed on soil matrices and SCFs at pressures up to 400 bar and temperatures up to 353K (Zhou and Tavlarides, 1999). Reliable PCB partition equilibrium data have been obtained between real St. Lawrence River sediments and two SCFs (SC-CO₂, and SC-CO₂/5 mol% methanol).

This strong activity in the field of SFE of contaminated soils underscores the interest generated for the potential of this technology to deal with the widespread soils/sediments contamination problems caused by pollutants like PCBs. However, a major gap exists between the laboratory results and the demonstration of the technical feasibility to remediate the contaminated soils and the economic viability of the process. Further, the database is still insufficient for the design of a full-scale remediation unit.

Using “green” supercritical water solvent instead of organic solvents in a wide variety of chemical processes offers environmental advantages and may lead to pollution prevention. Most of the recent work has dealt with waste treatment. Two reviews in the field give a comprehensive account of research in SCW up to 1999 (Savage et al., 1995; Savage, 1999). Of all the articles published in this field in the last 12 years (more than 250), over half have appeared since 1995. SCWO of organic compounds is the process that has undoubtedly received the most attention. The technology takes advantage of the complete miscibility of organic compounds and oxygen with SCW, eliminating the slow mass transfer process which occurs in multiphase systems. Moreover, essentially complete conversion of organic carbon to carbon dioxide occurs on the time scale of a few minutes.

In May 1994, the first commercial SCWO waste processing facility was implemented in Austin, Tex., by Eco Waste Technologies (McBrayer, 1995). The performance of this unit demonstrates the large-scale viability of the SCWO process. For wastewater-treated sludges, the effluent meets stringent environmental standards at cost considerably less than fluidized-bed incineration (Modell et al., 1995). Oe (1998) reported a complete decomposition of PCBs feed up to 7% using a bench-scale apparatus, and Hatakeda et al. (1997) reported SCWO of 3-chlorobiphenyl. Recently, Aki and Abraham (1998) made an economic evaluation of SCWO and a comparison with alternative waste treatment technologies.

These results demonstrate the feasibility for SCWO destruction of environmentally harmful chemicals including PCBs. However, there is a gap in available data to determine the feasibility of SCWO of PCBs/PAHs in general and in particular for PCBs/PAHs dissolved in solutions extracted from soils. Further, no kinetic studies have been reported on PCB oxidation in SCW to determine reactor optimum conditions and the nature and concentrations of reaction by-products.

EXPERIMENTAL

To secure the experimental data necessary for a design of a SFE/SCWO process, we have designed, built, and commissioned laboratory-scale experimental units for solubility data acquisition (Anitescu and Tavlarides, 1997a-b), screening partition equilibrium and desorption studies (Zhou et al., 1998), and SCWO kinetic studies (Anitescu et al., 1999). The laboratory-scale desorption studies and the partition equilibrium studies on the samples have been conducted to support the bench-scale experiments.

A bench-scale SFE unit equipped with a two-liter fixed-bed extractor has been built and installed in our laboratory. The unit employs a low-pressure separator (31 bar) to separate PCBs from CO₂. The regenerated CO₂ is then re-pressurized for reuse. Both pure CO₂ and CO₂ with a cosolvent can be used as SCFs. The system is controlled by a computer and is designed to operate at a pressure range of 80–650 bar and temperature range of 40–80 °C. The unit has been fully tested using blank samples.

Due to the finding that significant differences exist between spiked and real-world samples, three real-world St. Lawrence River sediment samples have been obtained to conduct bench-scale studies. Cohesive studies for a comprehensive systematic evaluation of the SFE process PCB require contaminated sediment samples with similar properties and PCB congener distribution patterns but different PCB concentration levels. The three real-world St. Lawrence River sediment samples obtained from a contaminated site near Massena, N.Y., meet these requirements. The three sediments were prepared by air-drying and sieving through a No.30 screen. Mineral properties, total organic carbon (TOC), and initial PCB concentrations of the three sediments given in Table 2 indicate that the three samples have similar soil properties yet different levels of PCB concentrations. PCB congener distribution patterns in the three sediments are relatively similar (compared to Aroclor 1248) and have shifted to the light chlorinated congeners from the original pattern of Aroclor 1248, probably due to naturally occurring dechlorination processes.

RESULTS AND DISCUSSION

Bench-Scale Desorption Study

Bench-scale experiments were needed to validate extraction efficiencies achieved in the laboratory-scale desorption studies, provide information for the scaleup of the process, and provide information for improving economic analysis. Bench-scale desorption experiments were conducted on St. Lawrence River sediment #3 (Table 2). Based on the results of laboratory desorption and partition equilibrium studies on the real-world St. Lawrence River sediments, the conditions of bench-scale desorption studies were determined as SCFs are CO₂ and CO₂/5 mol% methanol; sample size is ~1.500 kg; CO₂ flow rates are 450 g/min and 250 g/min; temperature is 50 °C; SCF density is in the range of 10.5-15.0 mole/L.

Experimental data were for extractions of St. Lawrence River samples with initial concentration of 1840 ppm. We noted the rapid desorption in the first 20 minutes to 6-9 ppm for both cases. After 40 minutes, we achieved less than 5 ppm for both flows. The lower flow rate of 2.2 mol/min compared to 4.4 mol per min

Table 2. Properties of real-world St. Lawrence River sediments.

Sediments	Composition (%)			TOC (%)	PCB Conc. (ppm)
	Sand	Clay	Silt		
St. L. R. Sediment #1	37.67	32.72	29.60	1.34	130
St. L. R. Sediment #2	55.73	23.21	21.06	1.21	710
St. L. R. Sediment #3	58.38	22.10	19.53	1.76	2200

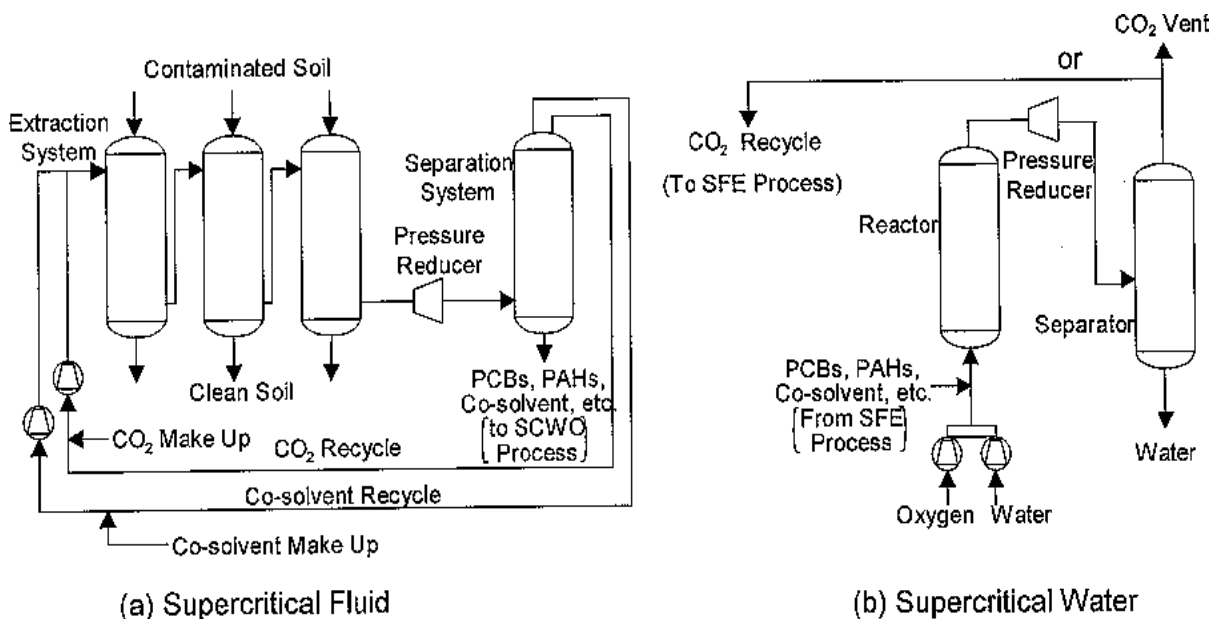


Figure 1. Supercritical fluid technology process for soil cleanup.

was less than the rate per kg of soil than in the laboratory-scale experiments, and suggests an economic savings of SCF to achieve this level of separation at 40 minutes.

The processing cost of SFE heavily depends on the flow rate of the SCF and the processing time needed to achieve the desired level of decontamination. It took 60 minutes to reduce PCB concentration from ~2000 ppm in real-world St. Lawrence River sediment to less than 5 ppm with 5% methanol as cosolvent. It also was noted that more than 98% of PCBs in the sediment were removed in the first 10 minutes. The final 50 minutes of processing time only removed less than 2% of the total PCBs in the sediment. To reduce the processing time per unit of sediment and improve cost efficiency, a multi-bed configuration was proposed as shown in Figure 1.

The proposed bench-scale configuration consisted of three high-pressure extractors of two-liter capacity. At any moment, two of them

were coupled together while the third one was idle for load and reload. Such a system will run continuously by switching extractors at appropriate processing times. The outlet SCF of the upper stream vessel, which has very low PCB levels, goes to the second vessel which contains freshly loaded soil with high PCB concentration to desorb more PCBs before going into the separation vessel. The proposed three-bed system will roughly reduce the processing time for unit mass of soil by one-half. Additional beds will further reduce the processing time and improve SCF utilization but will increase capital cost of the system and complexity of operation. An optimization needs to be pursued to achieve best overall cost based on this study.

The major corresponding modifications in the existing bench-scale SFE unit included replacing the current one-bed extractor system with a three-bed system and a low-pressure flash tank separator, and updating the automatic control system to support a three-bed opera-

tion. The bed design will be specified to facilitate quick disconnection of the vessel top and loading/reloading of soils with a canister insert. A six-port valve will be added at the outlet of each vessel to get effluent SCF samples readily. A side-view gauge will also be added to the flash tank separator to better monitor liquid level in the vessel.

Supercritical Water Oxidation (SCWO) Studies

SCWO studies were initiated to understand the kinetics of methanol oxidation (solvent for PCBs since they are insoluble in liquid water) and to determine the conditions for complete oxidation of several single PCB congeners and the Aroclor 1248 mixture in methanol. With appropriate models, this information will permit evaluation of the feasibility and cost of SCWO of PCB extracts from soils. A study on SCWO of methanol (Anitescu et al., 1999) was conducted to determine the capability of the experimental unit and to use the methanol SCWO kinetic models for PCBs/MeOH studies. Experimental conditions covered a temperature range of 400-500 °C at 253 bar and residence time range of 3-50 s. For this system, our data may be compared with those previously reported (Brock et al., 1996; Rice et al., 1996; Tester et al., 1993). Two kinetic models were successfully developed to correlate the experimental data. Also, a GC/TCD analysis was conducted for CO and CO₂ formation, and a pathway analysis was conducted for the formation of these by-products.

Kinetic SCWO data were obtained for individual PCB congeners such as 4-

chlorobiphenyl (253 bar, 380-600 °C, 2.0-46.3 s, 40-540 ppm in MeOH) and 3,3',4,4' tetrachlorobiphenyl (253 bar, 400-500 °C, 5-26 s, 500 ppm in MeOH). The results for the latter show that an oxidation level of near 100% can be achieved. Effect of temperature and residence time on oxidation of the above organic compounds was also studied. The ratio of oxygen to organic reactants for these experiments was kept the same at 1.8 (20 % excess of O₂) after a parametric study conducted on SCWO of methanol.

An important finding resulted in the oxidation study of Aroclor 1248 in methanol at 253 bar, 450-550 °C, 4-62 s, and 5245 ppm (Anitescu and Tavlarides, 2000). Congener specific analysis was made and the conversion patterns of ~50 components were determined simultaneously. The production of the lowest chlorinated congeners (which are not significantly present in the initial composition of Aroclor 1248) by an incomplete dechlorination process of higher chlorinated congeners at 500 °C and lower residence times was observed. Therefore, a shift in the congener pattern of Aroclor 1248 occurred between the feed material and the product. At 550 °C and 54.4 s, 99.95% conversion for Aroclor 1248 feed of 5245 ppm in methanol was obtained.

A preliminary investigation has been conducted to identify the oxidation reaction by-products of 4-chlorobiphenyl and 3,3',4,4' tetrachlorobiphenyl. The unreacted organics and by-products were extracted from the effluent liquid-phase samples and analyzed by GC/MS and GC/IR methods. The results positively

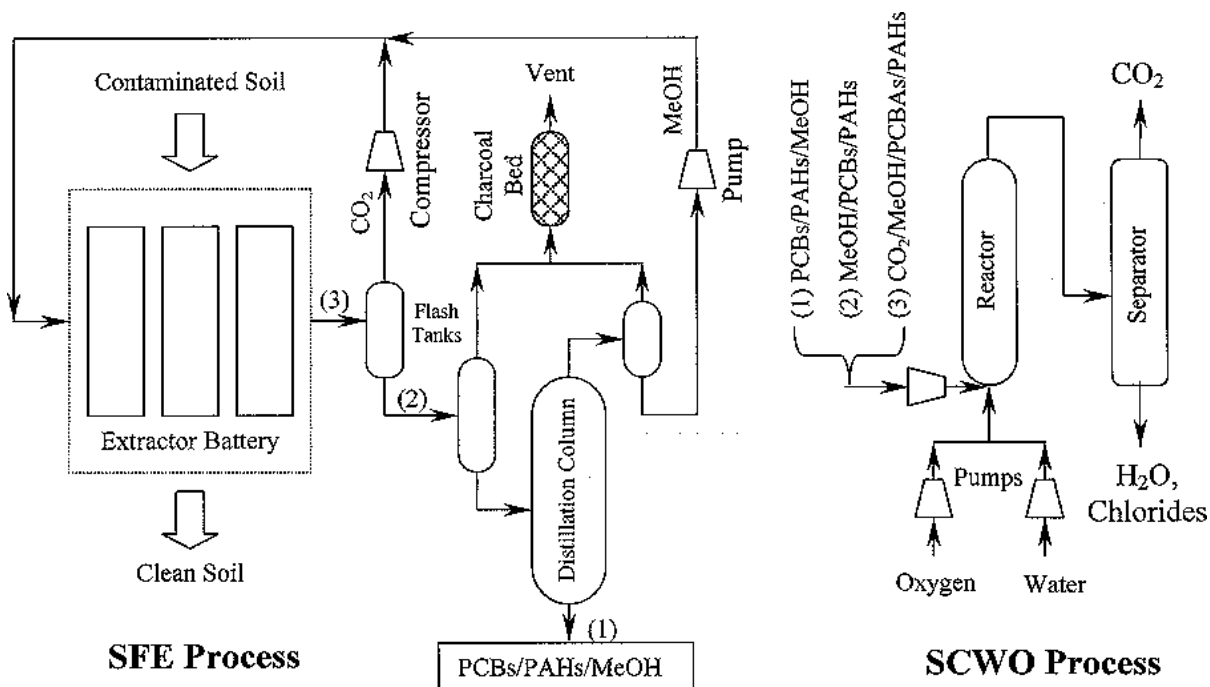


Figure 2. Possible configurations for the two-stage process.

showed biphenyl as a major by-product and several benzene derivatives for lower temperatures and residence time values. However, there were no dioxins among them. The positive identification and quantification of these compounds was not fully accomplished at this stage of the project and needed to be further researched.

The need for future study includes kinetic data acquisition for larger scale reactor design and a selective study for optimal reaction conditions for satisfactory degradation to harmless discharge waters. A pathway analysis of specific congeners to explain a degradation mechanism in order to optimize thermoconditions for maximum and safe conversion is also required.

Proposed Schematic of SFE/SCWO Technology

Based on our current investigations and

coupled with results in the literature, several alternative configurations of our proposed soil remediation process are suggested conceptually in Figure 2.

(1) Extraction; flashing, recompression, and recycle of CO_2 ; distillation to recovery and recycle the bulk of methanol; and recovery of concentrated PCBs/PAHs and organics in methanol for destruction by SCWO (on or off site) or other methods.

(2) Extraction; flashing, recompression, and recycle of CO_2 ; SCWO of PCB/PAH/MeOH stream from flash tank.

(3) Extraction; direct destruction of PCB/PAH in the SCF by SCWO; recycle of conditioned CO_2 .

The alternatives for the SCF regeneration and extracted PCB disposal sub-system are also shown in Figure 2. A decision will be made to select a proper alternative based on the

results of proposed experiments described above which define the technical feasibility and results of economic analysis which define the economic feasibility.

Economic Analysis

Soil remediation cost depends on operational conditions and system configurations. Our proposed research will provide a three-soil-system database which can be used to suggest a range of operational conditions for soil remediation. The process configuration can be categorized into three sub-systems: the SCF delivery sub-system, the extraction sub-system, and the SCF regeneration and extracted-PCB disposal sub-system.

The key aspect of the process is the extraction sub-system where PCBs/PAHs are removed from soils and dissolved in the SCF phase. For a given site cleanup, factors such as SCF flow rates, processing time, and size and number of extraction vessel need to be optimized using the results of the bench-scale studies and an economic analysis to achieve lowest total cost.

One difficulty of the SFE process is to measure and control the flow rate of SCFs at high pressure. To avoid this difficulty, one alternative is to let the delivery sub-system control the flow rate of SCFs by pumping liquid CO₂. A key factor to the control of the CO₂ flow rate is to ensure that CO₂ inside the pump head is liquid instead of CO₂ vapor. One option to achieve this state is to sub-cool the inlet CO₂ to a temperature much lower than its corresponding phase-equilibrium temperature using a chiller (this is the configuration of our bench-

scale unit). Another option is to use an auxiliary pump to increase the CO₂ fluid pressure before the main CO₂ pump so that one is assured that the CO₂ is liquid at that process temperature. The configuration and design of this sub-system solely depend on the economic analysis.

The proposed economic analysis weighed all the above options in order to evaluate capital costs, labor costs, and processing costs. The objective of this economic analysis is to suggest an optimized configuration for a given remediation task.

An updated preliminary process economic analysis has been conducted based on our solubility data and laboratory-scale design data using the real-world, PCB-contaminated St. Lawrence River sediments discussed above. The process schematic shown in Figure 1 indicates a three-stage extraction battery: one extractor is unloaded/loaded and the process fluid flows through the other two units. These units are cycled appropriately. The extract solution undergoes a high-pressure flash to recover CO₂ for recompression and recycle. Subsequently, methanol is recovered and recycled, and a PCB concentrate is produced for SCWO.

The key assumptions for a commercial-size unit for SFE of chlorinated organics from soil are (1) the extraction unit processes 1 m³ every half-hour; (2) 12,000 m³/yr are processed during 250 days/yr. for 24 hr./day operation; (3) the initial soil/sediment concentration is 2500 ppm PCB dried to <1% moisture; (4) final soil/sediment concentration is <5 ppm PCB; (5) soil excavation and replacement costs \$50/m³; and (6) SCWO processing to destroy extracted

chlorinated hydrocarbons adds \$15/m³ to the total cost of processing the soil/sediment. This cost of SCWO is an updated price based on the cost of \$0.352/gal estimated by Modell (1989) and Aki and Abraham (1998).

The comparison in Table 1 shows that the cost of \$198-\$318/m³ for SCE/SCWO of PCBs from soils competes very favorably with other processes and underscores the importance of vigorously pursuing the demonstration of this technology.

The two-stage supercritical fluid technology process we advance at Syracuse University consists of SFE of PCBs/PAHs from the contaminated soil and SCWO of the extracts. Figure 1 depicts the first step wherein the PCBs/PAHs-contaminated soils are contacted in a multistage SFE system, and the extracted PCBs/PAHs are separated from the supercritical fluids by pressure let-down and could be concentrated by distillation. The cleaned soils are returned to the site. The second stage oxidizes the extracted PCBs/PAHs, cosolvent and other soil extracts in a SCWO unit to harmless oxidation products. The oxidation can occur at the end or at intermediate points in the separation step to recover high pressure CO₂ as dictated by process merits and economics.

CONCLUSIONS

The significance of our work is that we have demonstrated that the SFE of CO₂ - 5 mol% methanol can achieve sub 5 ppm residual PCBs in real-world St. Lawrence River sediments and soils from initial concentrations of

~2200 ppm (4300 ppm with lab-spiked soils) in 45-60 minutes processing time for 99.8% removal. Supercritical water oxidation studies indicate 5245 ppm of Aroclor 1248/methanol simulated soil extract solutions can be oxidized to 99.95% conversion with higher conversions possible. An updated preliminary economic analysis indicates this SCF technology cost of \$198-318/m³ soil processed is economically competitive.

Fundamental process data and appropriate models obtained define

(a) solubilities of PCBs and PAHs in supercritical CO₂ with and without cosolvents, (b) effects of process and soil conditions on desorption efficiencies of sediments and supercritical fluids, (c) sorption equilibria of PCBs between supercritical CO₂ with and without cosolvents and contaminated soils, and (d) kinetic data for oxidation of Aroclor 1248 and several congeners. Confirmatory bench-scale studies (ca 2.0 liter extractor volume) will demonstrate the basic concept with real SLR sediments.

These studies suggest that a multistage semi-batch process with CO₂ and methanol recycle and SCWO of the PCB extract is an efficient process configuration. Other downstream process configurations may prove more effective. Additional process information is needed to define an operable and economic process configuration to implement this technology. Completion of this project from basic research to implementation makes eminent strategical sense.

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