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SUPERCRITICAL EXTRACTION/LIQUID-PHASE OXIDATION OF WASTES

by

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EXECUTIVE SUMMARY

This final report presents the work performed by the Institute of Gas Technology (IGT) during the period from September 29, 1994 through May 31, 1998, under a Cooperative Agreement (No. CR-822701-01-0) with the U.S. Environmental Protection Agency (EPA) for the project "Supercritical Extraction/Liquid-Phase Oxidation of Wastes." The program was co-sponsored by IGT's Sustaining Membership Program (IGT/SMP).

The overall objectives of this program were to develop and test IGT's Supercritical Extraction/Liquid-Phase Oxidation (SELPhOx) process for hazardous wastes and contaminated soils. Prior to the initiation of the experimental program, IGT prepared and submitted a Quality Assurance Project Plan (Task 1) to the EPA. The EPA subsequently approved the QAPP.

The experimental results and achievements made during the project are described below.

During the experimental program, IGT conducted a series of laboratory-scale supercritical CO_2 extraction tests to evaluate the effects of CO_2 flow rate, temperature, and the addition of a modifier on the extraction of polynuclear aromatic hydrocarbons (PAHs) from soil. These tests were conducted in IGT's laboratory- and bench-scale supercritical extraction equipment. The laboratory-scale tests were conducted with supercritical CO_2 in once-through mode. The bench-scale tests were conducted in CO_2 recirculation mode with activated carbon adsorption of the PAHs. Overall, the results of these tests show that the extent of PAH extraction from soil increases with temperature to a maximum at about 65°C. At temperatures above 65°C the extent of PAH extraction decreases.

In PAH adsorption tests with activated carbon; the results showed that lower, rather than higher temperatures of the activated carbon increased the capture of PAHs from supercritical CO_2. A temperature of about 45°C yielded the highest recovery of PAHs. The results of tests conducted with modifier (methanol) showed that a concentration of three percent yielded the highest PAH extractions in the range of methanol concentrations, up to 10 percent in CO_2.

IGT also prepared the laboratory-scale batch WAO equipment for testing. Tests were conducted with samples of contaminant-laden activated carbon slurry from the laboratory-scale tests (Task 4).

IGT also designed and constructed a SELPhOx Field Test Unit (FTU) for testing with samples of contaminated manufactured gas plant soil. IGT conducted shakedown tests in the FTU. The FTU is skid-mounted and consists of a supercritical CO_2 extraction vessel, an activated carbon contaminant absorption vessel, a recirculating booster compressor, flow meters, on-board computer data acquisition system, and a wet air oxidation vessel. The WAO vessel is constructed with an agitator, means for sparging air through the system and means for condensing water vapor back to the WAO reactor.

The results of the supercritical CO_2 extraction shakedown tests showed that total petroleum hydrocarbons (TPH) compounds were extracted from the soil. However the extent of extraction was much lower than demonstrated in the laboratory-scale tests. Similarly, the collection of the extracted TPHs by the activated carbon was lower than expected.

These results demonstrate that the SELPhOx process requires additional development work. Fluctuations in the flow meter readings were significant which caused uncertainty in the accuracy of the flows. This must be confirmed. Also, the actual flow pattern of the supercritical CO_2 flowing through the bed of contaminated soil must be determined. Supercritical CO_2 may have been flowing through the extraction cell at the prescribed flow rate; however, it may have channeled through the contaminated soil in the bed with much of the contamination not intimately contacting the CO_2. A supercritical CO_2 flow distributor may be required in the extractor as well as the activated carbon collector vessels. Both of these factors may have contributed to the low extractions as well as the low carbon collection by the activated carbon.

IGT prepared a preliminary design and cost estimate for the SELPhOx Process. The preliminary design and cost estimate was for a SELPhOx process plant with a capacity of about 300 tons per day (12½ ton/hour) of contaminated soil. The commercial plant consists of three trains of extractors and one train of a wet air oxidizer. The total plant investment for this plant was determined to be $16,300,000. Based on a 10-year equipment amortization and 6.0 percent cost of capital, the yearly operating cost was estimated to be $9,333,000. This relates to a unit processing cost ranging from $150 to $250 per ton.

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INTRODUCTION

The overall objectives of this project, initiated September 29, 1994, were to develop and test the Institute of Gas Technology's (IGT) Supercritical Extraction/Liquid-Phase Oxidation (SELPhOx) process for hazardous wastes and contaminated soils. The data obtained during the laboratory-scale tasks of the program were to be used in the design and construction of a transportable SELPhOx Field Test Unit (FTU). The FTU was to be tested in Phase II to obtain operational and performance data on the SELPhOx process. The results would then be used for evaluating the process economics and for engineering design of commercial-scale units. The SELPhOx process technology will be available for permanent cleanup of Superfund site soils, soils from manufactured gas plant (MGP) sites, and other organic-contaminated soils.

The SELPhOx process, shown schematically in Figure 1, combines two proven processing steps --

Supercritical Extraction (SCE) of organic contaminants with carbon dioxide (CO_2)

- Highly efficient and effective
- Uses environmentally acceptable CO_2 with or without modifiers as solubilizing agent
- Extraction leaves much of the original soil organic matter in place
- Produces no gaseous emissions
- Transportable unit can be developed

Wet Air Oxidation (WAO) destruction of the contaminants.

- Flameless oxidation generates no fly ash, smoke, or oxides of sulfur or nitrogen
- Organic sulfur and chloride are converted to H_2SO_4 and HCl (or salts), which are present and subsequently processed in the liquid phase
- Destruction levels exceeding 99 percent are routinely achieved
- Process is proven and thermally efficient
- Cost of treatment is low and less than other technologies, i.e., activated sludge treatment
- Heat generated by WAO can be utilized to increase thermal efficiency.

The two-stage SELPhOx process, linked by a separation step, offers great flexibility in the removal and destruction of both high and low concentrations of organic contaminants. The two distinct technologies are well suited for use in a single environmental remediation process.

The primary goals of the two phases of the project were to:

- Evaluate the effectiveness of the SELPhOx process on contaminated soils.
- Determine the conditions of extraction that achieve the best economic efficiency.
- Determine the best method and materials for separating extracted organics from CO_2 and conveying them to the WAO stage.
- Determine the effectiveness of WAO to degrade contaminants extracted from the soil
- Demonstrate operation of both SELPhOx process steps in a specially constructed transportable field test unit (FTU).
- Perform an economic assessment of SELPhOx process.

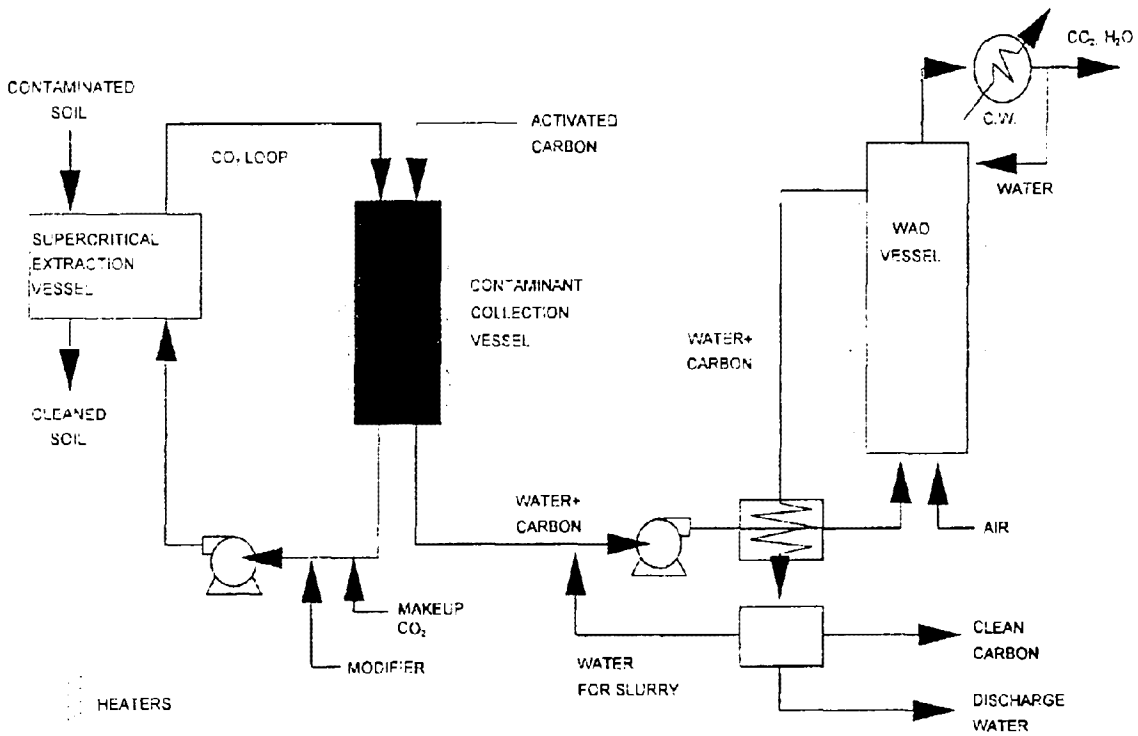

Figure 1. IGT's SUPERCRITICAL EXTRACTION/LIQUID-PHASE OXIDATION (SELPhOx) PROCESS

An overview of planned activities for Phases I and II is presented below.

PHASE I

During Phase I, contaminated soil from a manufactured gas plant (MGP) site was to be tested. IGT had a limited quantity of contaminated soil from an MGP site, which was used for Phase I tests. These supercritical extraction tests were to be conducted on the soil samples using CO_2 recirculated around the extraction circuit (at pressure). Activated carbon was to be tested as

a means for removing contaminants from the recirculating supercritical CO_2 stream. Contaminant-laden activated carbon was to be subjected to wet air oxidation (WAO) to determine the extent of contaminant destruction and potential activated carbon recovery.

A preliminary design and economic evaluation was also to be made for a commercial-scale SELPhOx process plant based on previously obtained laboratory-scale data. Also during Phase I, the design and construction of the SELPhOx Field Test Unit (FTU) was to be completed. Shakedown testing of the FTU was to follow in Phase II.

PHASE II

In Phase II of the program, shakedown testing of the FTU was to be completed. Tests were to be conducted in the FTU tests to evaluate the performance of the FTU with contaminated soil depending upon availability of resources. The skid-mounted FTU could be transported to Superfund or MGP sites for testing. FTU tests would determine the effects of temperature, pressure, solvent-to-contaminant ratio, and modifier on extraction efficiency. The preliminary design and economic evaluation performed in Phase I was also to be revised as necessary based on the laboratory-scale and FTU test results.

The results from the SCE tests would be employed to reduce the cost of supercritical extraction technology and would also extend the database for SCE. Results from the WAO step would demonstrate destruction of hazardous compounds from SCE and provide data for SELPhOx process design efforts. A key task of the project was to demonstrate the intermediate separation step between the SCE and the WAO in which extracted contaminants were separated from the supercritical CO_2 via adsorption onto activated carbon.

The SELPhOx process can be used to extract and destroy the types of organic compounds present at many Superfund and other contaminated sites. The SELPhOx process can be applied to a wide range of organic pollutants including aliphatic and aromatic compounds, such as gasoline, jet fuel, benzene, toluene, ethyl benzene, and xylene (BTEX). However, the process is targeted toward sites contaminated by high concentrations of high-molecular weight 4- to 6-ring PAHs, which are difficult to remove by other means.

The program is co-sponsored by the U.S. Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation program under Cooperative Agreement No. CR-822701-01-0 and IGT's Sustaining Membership Program. The EPA cooperative agreement was approved on September 29, 1994. The IGT/SMP program was initiated on November 28, 1994.

This final report describes the results of the work conducted by IGT from September 29, 1994 through May 31, 1998.

ACHIEVEMENTS MADE DURING THE PROJECT

The achievements made during the project are summarized below for each of the six experimental program tasks. The results are discussed in chronological order.

- Quality Assurance Project Plan
- Supercritical Extraction Tests
- SELPhOx Field Test Unit
- Field Test Unit and Data Analysis
- Wet Air Oxidation Tests
- Process Design and Economics

Quality Assurance Project Plan

The objective of this task was to prepare the quality assurance project plan (QAPP). The QAPP includes a detailed project description, quality assurance objectives, site selection and sampling procedures, analytical procedures and calibration, data reduction, validation, and reporting procedures, internal quality control checks, performance and systems audits, calculation of data quality indicators, corrective action, and quality control reports to management. The data quality indicators that were used to meet the quality assurance objectives for the critical measurements included precision, accuracy, completeness, method detection limit, representativeness, and comparability.

IGT's draft QAPP was submitted to EPA, which suggested comments and modifications. IGT revised and resubmitted the QAPP. EPA subsequently approved the revised QAPP.

Supercritical Extraction Tests

The objectives of this task were 1) to determine the optimum conditions for removing organic contaminants from selected soils, 2) to provide a baseline for comparison with tests to be conducted in the FTU, and 3) to generate contaminant-laden activated carbon samples for testing in the **Wet Air Oxidation** task. Other objectives included determining the effects of recycling CO_2 through the extraction equipment on extraction efficiency and evaluating different types of activated carbon to collect contaminants from the CO_2 in the separation stage.

For the tests planned in this task, an air-driven reciprocating piston pump was selected for recirculating supercritical CO_2 around the extraction circuit. A piston pump is compatible with the high pressure of the system. While a piston pump is appropriate for the system from an operational point of view, each stroke of the piston causes a pulse in the pressure of the system. To dampen the pressure variation of the system, two pressure dampers (each 2 liters in volume) were installed in the unit during the previous reporting period. Installation of those pressure dampers reduced the pressure variations to less than about 100 psig per stroke. In addition to the

pressure dampers, a back-pressure regulator (BPR) was installed downstream from the recirculating pump on its bypass. Installation of the BPR has reduced the pressure fluctuation of the system to less than about 50 psig per stroke.

The flow rate of recirculating CO_2 in the system is measured using an orifice meter system. At a given system pressure, the differential pressure across the orifice is proportional to the flow of supercritical CO_2. In order to control the CO_2 flow rate around the SCE circuit, actual measurements of the CO_2 flow rate through the orifice were needed at supercritical conditions. The pressure of the CO_2 in the system was reduced in three steps from supercritical conditions to atmospheric pressure before the CO_2 passed through the dry test meter for measurement. The exit lines were equipped with electric heaters and a temperature controller to avoid freezing and blocking of the lines by CO_2 as a result of Joule-Thomson cooling. Thus, for a given differential pressure across the orifice, the flow rate of CO_2 flowing through the orifice could be determined.

To study the effect of temperature on the amount of contaminants adsorbed by the activated carbon, the line connecting the supercritical extractor and the activated carbon adsorption bed was equipped with a heating tape and temperature controller. The length of the process lines was reduced to minimize the quantity of materials that might be deposited in the lines. The entire system was insulated.

Flow Calibration of Laboratory-Scale SCE Equipment

The objective of the laboratory-scale SCE equipment calibration was to obtain a correlation for calculating the flow rate of supercritical CO_2 within the recirculation circuit. The resultant correlation is a function of three parameters, namely the absolute pressure and temperature at the orifice, and the pressure drop across the orifice. Since the flow rate of CO_2 through the contaminated soil is a critical measurement, its accuracy is very important. A number of tests were performed on the laboratory-scale SCE equipment to calculate the parameters of the flow rate equation. In these tests, the flow rate was measured while holding two of the variables (pressure, temperature, or pressure drop) constant and varying the other one. The flow rate correlation is in the following form:

$$Q = k \text{ sqrt } [(P \Delta P / T)]$$

where Q is the CO_2 flow rate (SCF/h), k is the instrumentation coefficient, P is absolute pressure (psia), ΔP is pressure drop (inches H_2O), and T is absolute temperature. The coefficient k was found to have the following relationship with absolute pressure of the CO_2:

$$k = 5.25 + 0.0625 \text{ sqrt } (P)$$

Experiments, Results, and Data Analysis

A total of 25 tests were performed on two different soils each containing 572 and 1300 mg/kg of a suite of 16 PAH compounds, respectively. Eighteen of the SCE tests were conducted in an analytical supercritical extraction unit (Hewlett-Packard, Model HP 780T SCF unit). The other seven tests were conducted in IGT's SCE equipment modified for CO_2 recirculation and contaminant adsorption on activated carbon. The objectives of these tests were to:

- Determine the effects of supercritical CO_2 flow rate, extraction time, temperature, and concentration of modifier (methanol) in CO_2 on PAH extraction.
- Evaluate different conditions of extraction and activated carbon adsorption on extracting and capturing PAHs and total petroleum hydrocarbons (TPH) from soil with supercritical CO_2 and supercritical CO_2/methanol mixture.

Analyses were conducted to determine a suite of 16 PAHs in the feed soil, extracted soil, and contaminant-laden activated carbon. In addition, total petroleum hydrocarbon (TPH) analyses were conducted for some test samples to reduce laboratory expenses.

Analytical Laboratory Extraction Tests:

Tests 1 through 18 were conducted in the analytical laboratory SCE equipment with 1 to 2 gram samples each of contaminated soil. The extractions were dynamic with no static (or holding) period employed. Tables 1 through 4 summarize the experimental conditions, experimental results, and data analyses for these tests. Based on these results, the following conclusions can be drawn.

The level of PAH extraction by supercritical CO_2 is affected by temperature. Higher temperatures increase the percentage removal of PAHs (see Figure 2). The effect is more pronounced for PAH numbers 1 through 6. For PAH numbers 8 through 16, increasing the temperature from 45° to 145°C appears to decrease extraction slightly. Over the temperatures tested (45° and 145°C), the number of moles of PAHs extracted per mole of CO_2 passing through the soil increases with increasing temperature (Figure 3). This is clearly evident for PAH numbers 1 through 8. The extraction of PAH numbers 9 through 16 does not appear to be affected significantly by temperature. (Specific PAH compounds are numbered in the tables.)

The total efficiency of extraction declines with increasing extraction time (Figure 4). For the same CO_2 flow rate and temperature, the number of moles of PAHs extracted per mole of CO_2 declines as the extraction time increases. This behavior of the efficiency-time curve suggests that PAHs in the soil exist in two different states: deposited and adsorbed. The rate of removal of deposited PAHs is relatively fast and is controlled by local solid-supercritical fluid equilibria. The rate of removal of adsorbed PAHs is relatively slow and is controlled by adsorption-desorption isotherms.

Table 1. EFFECT OF TEMPERATURE, FLOW RATE, AND EXTRACTION TIME ON THE EXTRACTION OF PAHS FROM SOIL 1

Experimental Conditions:

	Test#						
	1	2	3	4	5	6	7
Flow rate (ml/min)	0.5	1.5	4	0.5	0.5	4	4
P (psi)	2000						
T (°C)	45						145
Density (gm/ml)	0.72						0.25
Extraction time (min)	50	16.7	6.25	25	100	12.5	6.25
Weight of dry sample (gm)	0.8773	0.8459	0.9516	0.7783	0.7395	0.8925	0.9934

Experimental Results:

			PAH (mg/kg soil) Removed From Soil 1						
			Test #						
Compound	PAH#	Soil 1	1	2	3	4	5	6	7
Naphthalene	1	8.8	8.8	5.4	5.8	4.4	6.5	7.7	9.5
Acenaphthylene	2	10.8	1.7	1.8	2	1.3	2.5	2.7	5.1
Acenaphthene	3	3.1	2.8	2.5	2.5	1.9	2.7	3.6	3.4
Fluorence	4	11.4	11.3	9.6	9.8	7.2	10.5	12.7	13.2
Phenanthrene	5	35.1	33.9	29.3	29.3	19.1	36.4	40.7	37.1
Anthracene	6	9.7	6.6	4.8	5.3	3.2	6.8	7.7	7.2
Fluoranthene	7	91.9	23.8	26.9	27.7	14.3	39.3	42	27.5
Pyrene	8	112	27.4	30.8	31.3	16	48.5	49.4	29.6
Benz(a)anthracene	9	52.8	7	7.9	9.4	3.5	14.5	14.1	5.3
Chrysene + Triphenyle...	10	57.1	6.7	7.6	9.2	3.7	14.4	13.6	5.2
Benzo(b)fluoranthene	11	41.1	2	2.6	3.2	1	5.2	4.7	1.2
Benzo(k)fluoranthene	12	40.8	2.4	2.9	4.1	1.1	5.7	5.2	1.4
Benzo(a)pyrene	13	40.5	1.5	1.9	2.8	0.7	3.8	3.5	0.8
Indeno(1,2,3-cd)pyrene	14	24.9	0.4	0.5	0.9	0.1	1.2	1.1	0.1
Dibenz(a,h)anthracene	15	9.8	0.1	0.2	0.4	0.1	0.5	0.5	0.1
Benzo(ghi)perylene	16	22.2	0.2	0.3	0.6	0.1	0.7	0.7	0.1
Total (mg/kg soil)		572	136.6	135	144.3	77.7	199.2	209.9	146.8

Table 1 (continued). EFFECT OF TEMPERATURE, FLOW RATE, AND EXTRACTION TIME ON THE EXTRACTION OF PAHS FROM SOIL 1

Data analysis:

		PAH (mol/mol CO2) Removed From Soil 1						
		Test #						
Compound	PAH#	1	2	3	4	5	6	7
Naphthalene	1	1.47E-7	8.66E-8	1.05E-7	1.30E-7	4.56E-8	6.52E-8	4.39E-7
Acenaphthylene	2	2.40E-8	2.44E-8	3.06E-8	3.25E-8	1.48E-8	1.93E-8	2.00E-7
Acenaphthene	3	3.89E-8	3.35E-8	3.77E-8	4.69E-8	1.58E-8	2.55E-8	1.31E-7
Fluorence	4	1.46E-7	1.19E-7	1.37E-7	1.65E-7	5.71E-8	8.33E-8	4.73E-7
Phenanthrene	5	4.08E-7	3.39E-7	3.82E-7	4.08E-7	1.85E-7	2.49E-7	1.24E-6
Anthracene	6	7.94E-8	5.56E-8	6.92E-8	6.83E-8	3.45E-8	4.71E-8	2.41E-7
Fluoranthene	7	2.52E-7	2.74E-7	3.18E-7	2.69E-7	1.75E-7	2.26E-7	8.09E-7
Pyrene	8	2.90E-7	3.14E-7	3.59E-7	3.01E-7	2.16E-7	2.66E-7	8.70E-7
Benz(a)anthracene	9	6.58E-8	7.14E-8	9.58E-8	5.83E-8	5.74E-8	6.74E-8	1.38E-7
Chrysene + Triphenylene	10	6.29E-8	6.87E-8	9.37E-8	6.17E-8	5.70E-8	6.50E-8	1.36E-7
Benzo(b)fluoranthene	11	1.70E-8	2.13E-8	2.95E-8	1.51E-8	1.86E-8	2.03E-8	2.83E-8
Benzo(k)fluoranthene	12	2.04E-8	2.37E-8	3.78E-8	1.66E-8	2.04E-8	2.25E-8	3.31E-8
Benzo(a)pyrene	13	1.28E-8	1.55E-8	2.58E-8	1.06E-8	1.36E-8	1.51E-8	1.89E-8
Indeno(1,2,3-cd)pyrene	14	3.11E-9	3.74E-9	7.58E-9	1.38E-9	3.93E-9	4.34E-9	2.16E-9
Dibenz(a,h)anthracene	15	7.71E-10	1.48E-9	3.34E-9	1.37E-9	1.62E-9	1.96E-9	2.14E-9
Benzo(ghi)perylene	16	1.55E-9	2.24E-9	5.05E-9	1.38E-9	2.29E-9	2.76E-9	2.16E-9
Total moles of PAH's/mole of CO2		1.57E-6	1.45E-6	1.74E-6	1.59E-6	9.19E-7	1.18E-6	4.76E-6

		PAH Percentage Removal From Soil 1						
		Tset#						
Compound	PAH#	1	2	3	4	5	6	7
Naphthalene	1	100.0	61.4	65.9	50.0	73.9	87.5	108.0
Acenaphthylene	2	15.7	16.7	18.5	12.0	23.1	25.0	47.2
Acenaphthene	3	90.3	80.6	80.6	61.3	87.1	116.1	109.7
Fluorence	4	99.1	84.2	86.0	63.2	92.1	111.4	115.8
Phenanthrene	5	96.6	83.5	83.5	54.4	103.7	116.0	105.7
Anthracene	6	68.0	49.5	54.6	33.0	70.1	79.4	74.2
Fluoranthene	7	25.9	29.3	30.1	15.6	42.8	45.7	29.9
Pyrene	8	24.5	27.5	27.9	14.3	43.3	44.1	26.4
Benz(a)anthracene	9	13.3	15.0	17.8	6.6	27.5	26.7	10.0
Chrysene + Triphenylene	10	11.7	13.3	16.1	6.5	25.2	23.8	9.1
Benzo(b)fluoranthene	11	4.9	6.3	7.8	2.4	12.7	11.4	2.9
Benzo(k)fluoranthene	12	5.9	7.1	10.0	2.7	14.0	12.7	3.4
Benzo(a)pyrene	13	3.7	4.7	6.9	1.7	9.4	8.6	2.0
Indeno(1,2,3-cd)pyrene	14	1.6	2.0	3.6	0.4	4.8	4.4	0.4
Dibenz(a,h)anthracene	15	1.0	2.0	4.1	1.0	5.1	5.1	1.0
Benzo(ghi)perylene	16	0.9	1.4	2.7	0.5	3.2	3.2	0.5
Total Removal, %		23.9	23.6	25.2	13.6	34.8	36.7	25.7

Table 2. EFFECT OF EXTRACTION TIME ON THE EXTRACTION EFFICIENCY OF PAHS FROM SOIL 2

Experimental Conditions:

	Test#				
	8	9	10	11	12
Flow rate (ml/min)	4				
Tempearture (°C)	45				
Pressure (psi)	2000				
Density (g/ml)	0.72				
Extraction time (min)	6.25	12.5	25	50	100
Weight of dry sample (gm)	0.5297	0.6733	0.709	0.6205	0.5662

Experimental Results:

			PAH (mg/kg soil) Removed From Soil 2				
			Test#				
Compound	PAH #	Soil 2	8	9	10	11	12
Naphthalene	1	23.4	1.5	3.3	2.8	7.8	4.1
Acenaphthylene	2	51.6	4	5.6	4.9	7.3	6.6
Acenaphthene	3	9.5	7.4	10.1	9.8	11.9	10.1
Fluorene	4	4.5	4.87	7.8	4.8	5.9	4.1
Phenanthrene	5	26.9	12.4	35.6	22.3	24.9	18.6
Anthracene	6	26.2	15.5	26.2	22.5	32.6	26.6
Fluoranthene	7	242	63.1	87.2	113	160	168
Pyrene	8	318	69.5	94.2	125	182	202
Benz(a)anthracene	9	127	15.8	20.8	32.6	53.7	71.1
Chrysene + Triphenylene	10	128	13	17.5	26.6	45.3	61.2
Benzo(b)fluoranthene	11	54.6	2.7	3.3	5.3	10	18
Benzo(k)fluoranthene	12	72.5	3.2	4.2	7.7	12.9	20.9
Benzo(a)pyrene	13	113	3.7	4.3	8.5	15	29.4
Indeno(1,2,3-cd)pyrene	14	39.8	1.6	1.4	1.4	2	5.4
Dibenz(a,h)anthracene	15	14.4	1.6	1.4	1.4	1.6	2.6
Benzo(ghi)perylene	16	45.1	1.6	1.4	1.4	1.7	4.8
Total (mg/kg)		1296.5	221.47	324.3	390	574.6	653.5

Table 2 (continued). EFFECT OF EXTRACTION TIME ON THE EXTRACTION EFFICIENCY OF PAHS FROM SOIL 2

Data Analysis:

		PAH (mol/mol CO2) Removed From Soil 2				
		Test#				
Compound	PAH#	8	9	10	11	12
Naphthalene	1	1.5E-8	2.1E-8	9.4E-9	1.2E-8	2.8E-9
Acenaphthylene	2	3.4E-8	3.0E-8	1.4E-8	9.1E-9	3.8E-9
Acenaphthene	3	6.2E-8	5.4E-8	2.8E-8	1.5E-8	5.7E-9
Fluorene	4	3.8E-8	3.9E-8	1.3E-8	6.7E-9	2.1E-9
Phenanthrene	5	9.0E-8	1.6E-7	5.4E-8	2.7E-8	9.0E-9
Anthracene	6	1.1E-7	1.2E-7	5.5E-8	3.5E-8	1.3E-8
Fluoranthene	7	4.0E-7	3.5E-7	2.4E-7	1.5E-7	7.2E-8
Pyrene	8	4.4E-7	3.8E-7	2.7E-7	1.7E-7	8.6E-8
Benz(a)anthracene	9	9.0E-8	7.5E-8	6.2E-8	4.5E-8	2.7E-8
Chrysene + Triphenylene	10	7.4E-8	6.3E-8	5.1E-8	3.8E-8	2.3E-8
Benzo(b)fluoranthene	11	1.4E-8	1.1E-8	9.1E-9	7.5E-9	6.2E-9
Benzo(k)fluoranthene	12	1.6E-8	1.4E-8	1.3E-8	9.7E-9	7.2E-9
Benzo(a)pyrene	13	1.9E-8	1.4E-8	1.5E-8	1.1E-8	1.0E-8
Indeno(1,2,3-cd)pyrene	14	7.5E-9	4.2E-9	2.2E-9	1.4E-9	1.7E-9
Dibenz(a,h)anthracene	15	7.5E-9	4.1E-9	2.2E-9	1.1E-9	8.1E-10
Benzo(ghi)perylene	16	7.5E-9	4.2E-9	2.2E-9	1.2E-9	1.5E-9
Total mol PAHs/mol CO2		1.4E-6	1.4E-6	8.4E-7	5.4E-7	2.7E-7

		PAH Percentage Removal From Soil 2				
		Test#				
Compound	PAH#	8	9	10	11	12
Naphthalene	1	6.41	14.10	11.97	33.33	17.52
Acenaphthylene	2	7.75	10.85	9.50	14.15	12.79
Acenaphthene	3	77.89	106.32	103.16	125.26	106.32
Fluorene	4	108.22	173.33	106.67	131.11	91.11
Phenanthrene	5	46.10	132.34	82.90	92.57	69.14
Anthracene	6	59.16	100.00	85.88	124.43	101.53
Fluoranthene	7	26.07	36.03	46.69	66.12	69.42
Pyrene	8	21.86	29.62	39.31	57.23	63.52
Benz(a)anthracene	9	12.44	16.38	25.67	42.28	55.98
Chrysene + Triphenyle...	10	10.16	13.67	20.78	35.39	47.81
Benzo(b)fluoranthene	11	4.95	6.04	9.71	18.32	32.97
Benzo(k)fluoranthene	12	4.41	5.79	10.62	17.79	28.83
Benzo(a)pyrene	13	3.27	3.81	7.52	13.27	26.02
Indeno(1,2,3-cd)pyrene	14	4.02	3.52	3.52	5.03	13.57
Dibenz(a,h)anthracene	15	11.11	9.72	9.72	11.11	18.06
Benzo(ghi)perylene	16	3.55	3.10	3.10	3.77	10.64
Total Removal, %		17.08	25.01	30.08	44.32	50.40

Table 3. EFFECT OF CONCENTRATION OF METHANOL IN SUPERCRITICAL CO_2 ON THE EXTRACTION OF PAHS FROM SOIL 2

Experiments Conditions:

	Test#			
	11	13	14	15
Flow rate (ml/min)	4			
Temperature (°C)	45			
Pressure (psi)	2000			
Extraction time (min)	50			
%me-OH in CO2	0	3	5	10

Experimental Results:

PAH (mg/kg soil) Removed From Soil 2

			Test#			
Compound	PAH#	Soil	11	13	14	15
Naphthalene	1	23.4	7.8	0.6	0.9	0.8
Acenaphthylene	2	51.6	7.3	10.2	8.9	11.1
Acenaphthene	3	9.5	11.9	0.6	0.9	0.8
Fluorence	4	4.5	5.9	5.2	0.9	0.8
Phenanthrene	5	26.9	24.9	42.4	12.4	10.2
Anthracene	6	26.2	32.6	37.5	16.7	14.4
Fluoranthene	7	242	160	261	210	175
Pyrene	8	318	182	302	258	218
Benz(a)anthracene	9	127	53.7	119	104	97
Chrysene + Triphenylene	10	128	45.3	115	99.1	95.1
Benzo(b)fluoranthene	11	54.6	10	36.7	29.4	40.4
Benzo(k)fluoranthene	12	72.5	12.9	46	41.8	45.1
Benzo(a)pyrene	13	113	15	61.8	52.2	72.7
Indeno(1,2,3-cd)pyrene	14	39.8	2	13.4	11.1	20.1
Dibenz(a,h)anthracene	15	14.4	1.6	5.4	5.4	8
Benzo(ghi)perylene	16	45.1	1.7	11.3	9.7	19.2

Table 3 (continued). EFFECT OF CONCENTRATION OF METHANOL IN SUPERCRITICAL CO_2 ON THE EXTRACTION OF PAHS FROM SOIL 2

PAH's Percentage Removal From Soil 2 Using 0, 3, 5, and 10% Methanol in Supercritical CO2

		Test#			
Compound	PAH#	11	13	14	15
Naphthalene	1	33.3	2.6	3.8	3.4
Acenaphthylene	2	14.1	19.8	17.2	21.5
Acenaphthene	3	125.3	6.3	9.5	8.4
Fluorence	4	131.1	115.6	20.0	17.8
Phenanthrene	5	92.6	157.6	46.1	37.9
Anthracene	6	124.4	143.1	63.7	55.0
Fluoranthene	7	66.1	107.9	86.8	72.3
Pyrene	8	57.2	95.0	81.1	68.6
Benz(a)anthracene	9	42.3	93.7	81.9	76.4
Chrysene + Triphenylene	10	35.4	89.8	77.4	74.3
Benzo(b)fluoranthene	11	18.3	67.2	53.8	74.0
Benzo(k)fluoranthene	12	17.8	63.4	57.7	62.2
Benzo(a)pyrene	13	13.3	54.7	46.2	64.3
Indeno(1,2,3-cd)pyrene	14	5.0	33.7	27.9	50.5
Dibenz(a,h)anthracene	15	11.1	37.5	37.5	55.6
Benzo(ghi)perylene	16	3.8	25.1	21.5	42.6
Total PAH Removal, %		44.3	82.4	66.4	63.9

Table 4. EFFECT OF TEMPERATURE ON THE EXTRACTION OF PAHS FROM SOIL 2 USING 5% METHANOL IN SUPERCRITICAL CO_2

Experimental Conditions:

Test#	14	16	17	18
Flow rate (ml/min)	4			
Extraction Time (mi...	50			
Temperature (°C)	45	60	100	140
Pressure (psi)	2000			2020
%me-OH in CO2	5			

Experimental Results:

			PAH (mg/kg soil) Removed From Soil 2			
			Test#			
Compound	PAH#	Soil	14	16	17	18
Naphthalene	1	23.4	0.9	0.5	0.9	0.7
Acenaphthylene	2	51.6	8.9	12	3.6	5.9
Acenaphthene	3	9.5	0.9	0.5	0.9	0.7
Fluorence	4	4.5	0.9	0.9	0.9	0.9
Phenanthrene	5	26.9	12.4	25	18	50.3
Anthracene	6	26.2	16.7	23.3	19	35.9
Fluoranthene	7	242	210	230	211	246
Pyrene	8	318	258	280	252	285
Benz(a)anthracene	9	127	104	120	65.3	75.3
Chrysene + Triphenyle...	10	128	99.1	119	60.2	69.5
Benzo(b)fluoranthene	11	54.6	29.4	38.7	14.8	16.8
Benzo(k)fluoranthene	12	72.5	41.8	54	17.3	19.8
Benzo(a)pyrene	13	113	52.2	70.6	21.1	23.5
Indeno(1,2,3-cd)pyrene	14	39.8	11.1	16.1	2.9	2.8
Dibenz(a,h)anthracene	15	14.4	5.4	7.6	1.8	1.4
Benzo(ghi)perylene	16	45.1	9.7	13.9	2.3	2.4

Table 4 (continued). EFFECT OF TEMPERATURE ON THE EXTRACTION OF PAHS FROM SOIL 2 USING 5% METHANOL IN SUPERCRITICAL CO_2

Data Analysis:

PAH Percentage Removal USing 5% Methanol in Supercritical CO2 at 45°C, 60°C, 100°C, and 140 °C

		Test#			
Compound	PAH#	14	16	17	18
Naphthalene	1	3.8	2.1	3.8	3.0
Acenaphthylene	2	17.2	23.3	7.0	11.4
Acenaphthene	3	9.5	5.3	9.5	7.4
Fluorence	4	20.0	20.0	20.0	20.0
Phenanthrene	5	46.1	92.9	66.9	187.0
Anthracene	6	63.7	88.9	72.5	137.0
Fluoranthene	7	86.8	95.0	87.2	101.7
Pyrene	8	81.1	88.1	79.2	89.6
Benz(a)anthracene	9	81.9	94.5	51.4	59.3
Chrysene + Triphenyle...	10	77.4	93.0	47.0	54.3
Benzo(b)fluoranthene	11	53.8	70.9	27.1	30.8
Benzo(k)fluoranthene	12	57.7	74.5	23.9	27.3
Benzo(a)pyrene	13	46.2	62.5	18.7	20.8
Indeno(1,2,3-cd)pyrene	14	27.9	40.5	7.3	7.0
Dibenz(a,h)anthracene	15	37.5	52.8	12.5	9.7
Benzo(ghi)perylene	16	21.5	30.8	5.1	5.3
Total PAH Removal %		66	78	53	65

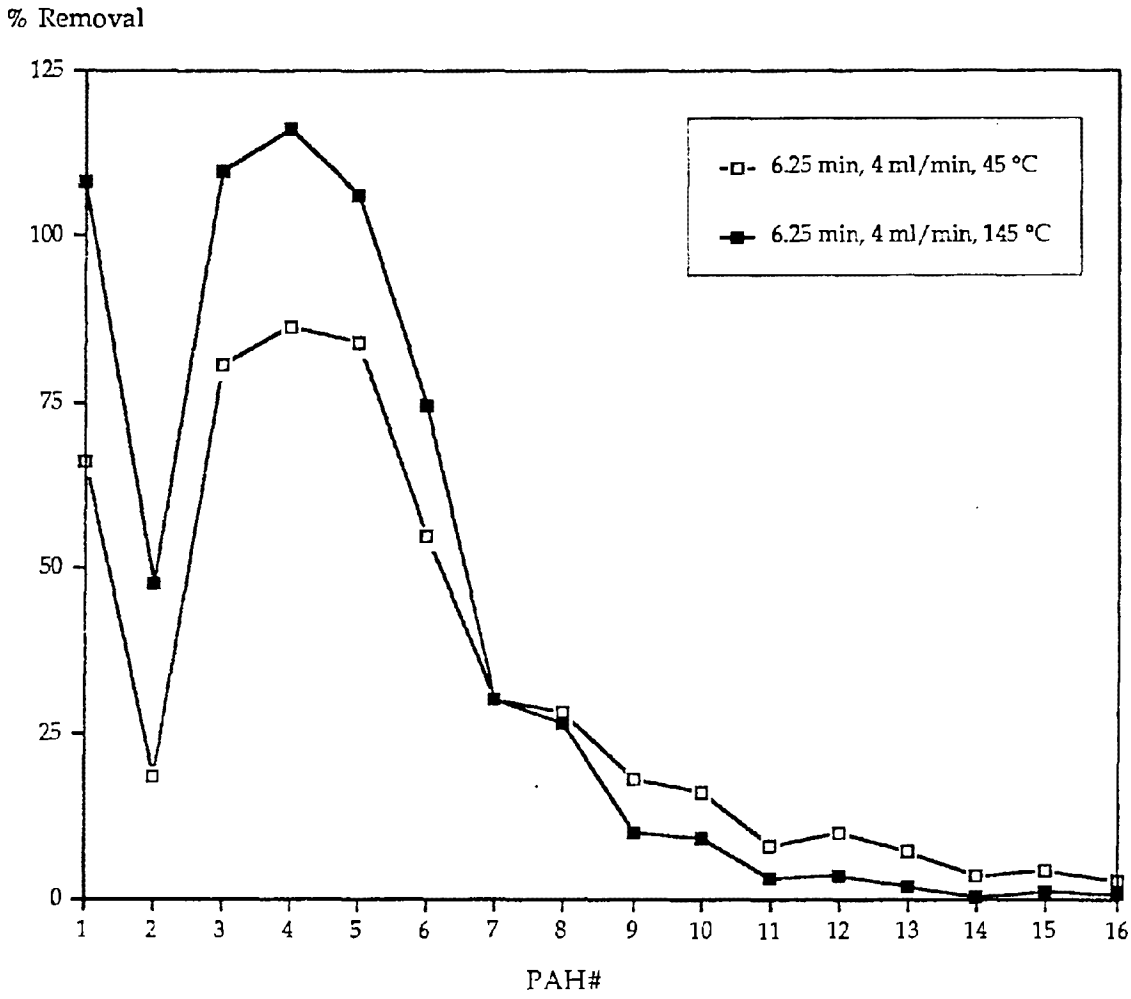

Figure 2. PERCENTAGE REMOVAL OF PAHS FROM SOIL 1

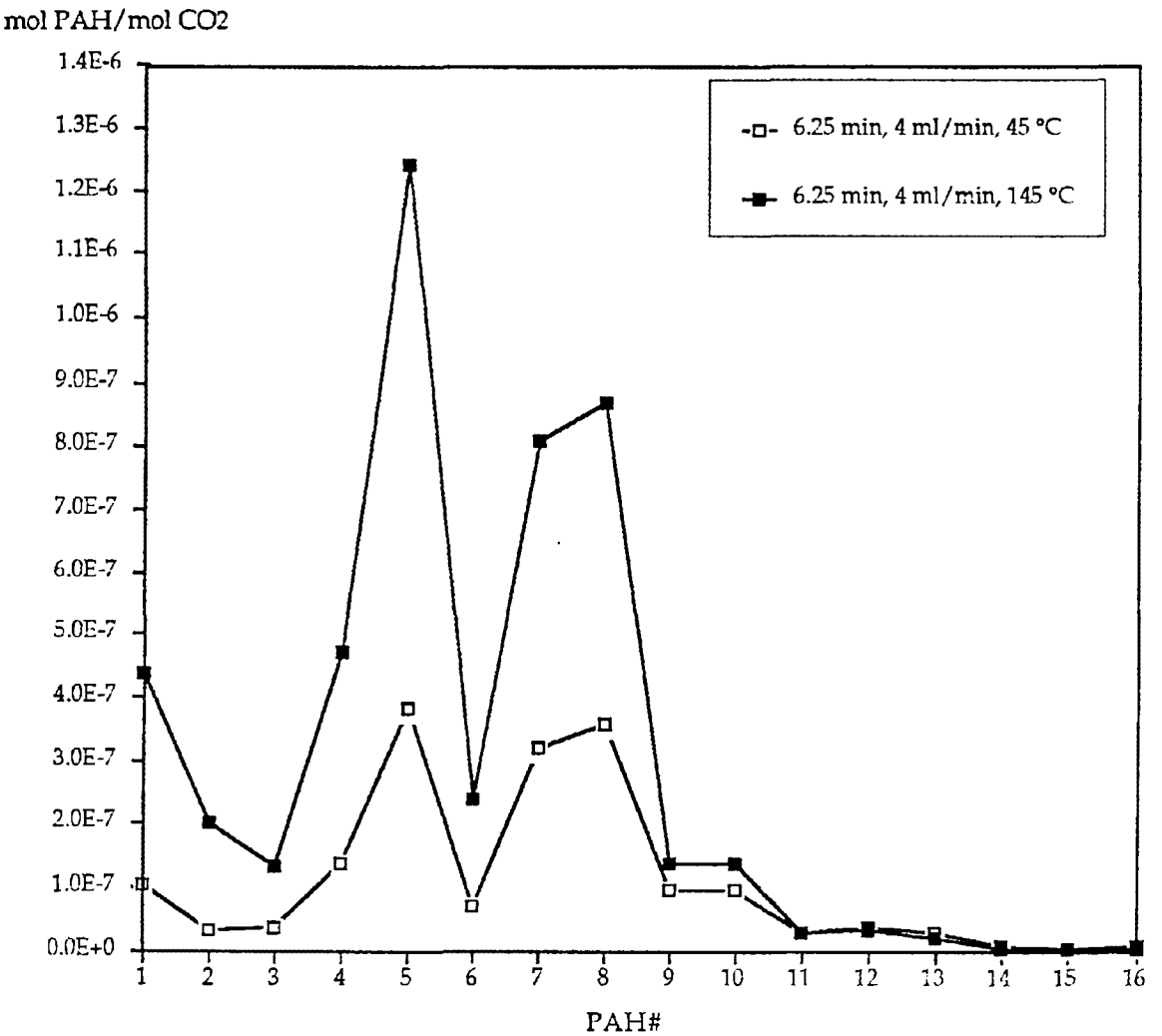

Figure 3. NUMBER OF MOLES OF PAHS EXTRACTED FROM SOIL 1 PER MOLE OF CO_2

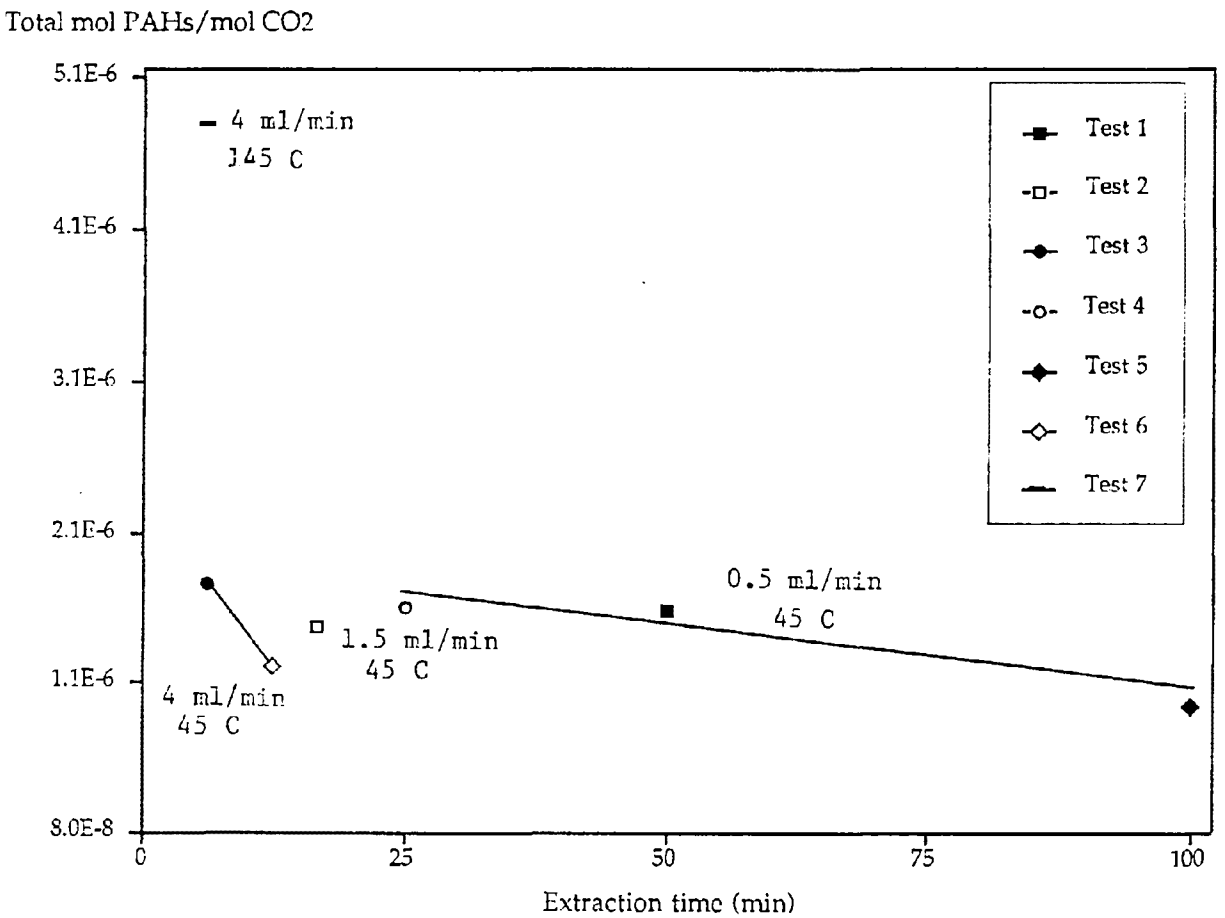

Figure 4. EFFECT OF EXTRACTION TIME ON THE TOTAL EXTRACTION EFFICIENCY OF PAHS FROM SOIL 1 AT DIFFERENT FLOW RATES AND TEMPERATURES

Considering these two rate limiting steps one should expect to observe a sharp decrease in the slope of the mole fraction curve for short extraction times (when deposited PAHs are being extracted) and a small decrease in the slope of the same curve for longer extraction times. Tests 8 through 12 were conducted at 4 ml/min of supercritical CO_2 at 45°C and 2000 psig for different extraction times on a soil with 1296 mg/kg PAH concentration. In Figure 5, the moles of PAHs per mole of CO_2 declines fairly rapidly for extraction times up to about 25 minutes. From 25 to 100 minutes, the extraction efficiency decreases more slowly. These results are consistent with those of Tests 1 through 7, which were conducted on a different soil and different flow rates and temperatures.

In Figure 6, the efficiency of extraction of each individual PAH compound decreases with increasing extraction time from 6¼ to 100 minutes. The total (cumulative) percentage removal of PAHs increases with extraction time. The increase is fast initially (for short extraction times) and continues to increase with a smaller slope for longer extraction times (Figure 7).

The addition of methanol as a modifier always enhances extraction of heavier PAHs (PAH numbers 7 through 16) from soil. A high concentration of methanol (ten percent) in the CO_2 enhances the extraction of fluoranthene (No. 7) and heavier PAHs while reducing the extraction of lighter PAHs. A low concentration of methanol (three percent) in supercritical CO_2 enhances the recovery of both heavy and light PAHs (Figure 8).

For the same concentration of methanol (five percent) in supercritical CO_2, increasing the temperature from 45° to 60°C enhances the extraction of PAHs from soil. Increasing the temperature to 100° and higher (140°C) decreases the extraction efficiency (Figure 9).

Laboratory-Scale Tests

Tests 19 through 25 were conducted in the SCE laboratory-scale equipment in CO_2 recirculation mode. The results of these tests are presented in Tables 5 and 6. For Tests 19 through 21, the soils were analyzed for a suite of 16 PAHs; for Tests 22 through 25, the soils were analyzed for Total Petroleum Hydrocarbons (TPH). The following conclusions can be drawn from these experimental results.

The results shown in Figure 10 indicate that increasing the temperature from 110° to 155°F (43° to 68°C) and the pressure from 1700 to 1850 psi increases the percentage removal of PAHs from soil (compare Tests 19 and 20). At the same temperature (155°F or 68°C), increasing the pressure from 1850 to 2025 psi with a higher CO_2/soil ratio also increases PAH removal (Tests 20 and 21).

In Figure 11, the results show that the efficiency of capturing PAHs on the activated carbon increases by reducing the temperature of the activated carbon bed. At adsorption temperatures of 145° and 155°F (63° and 68°C) (Tests 21 and 20, respectively), PAH capture is fairly low. At an adsorption temperature of 110°F (43°C) (Test 19), PAH capture is significantly increased. For the activated carbon used in these experiments (Sargent-Welch 8-12 mesh

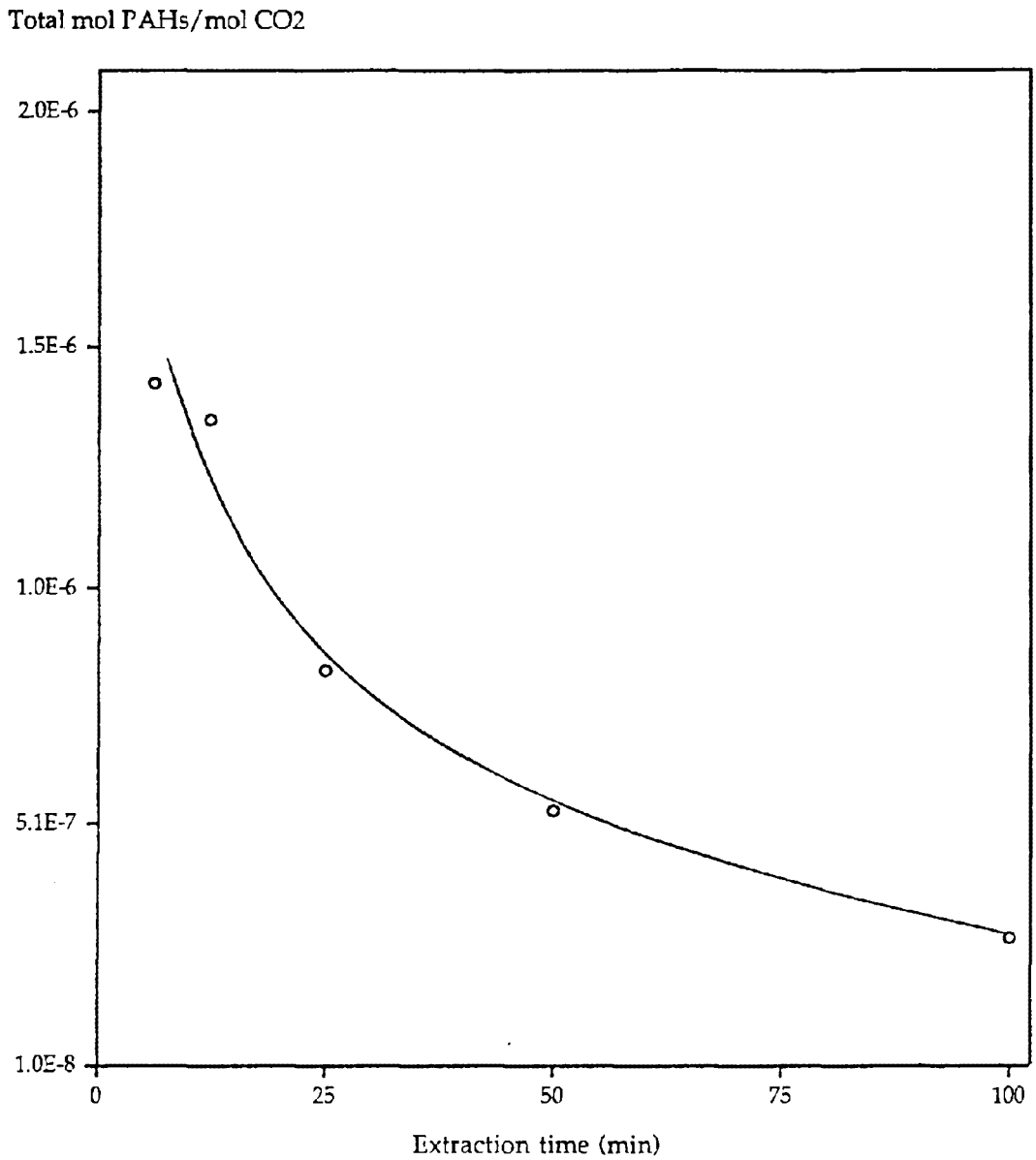

Figure 5. EFFECT OF EXTRACTION TIME ON THE TOTAL EXTRACTION EFFICIENCY OF PAHS FROM SOIL 2
(Extraction conditions - 4 ml/min. 45°C, 2000 psi)

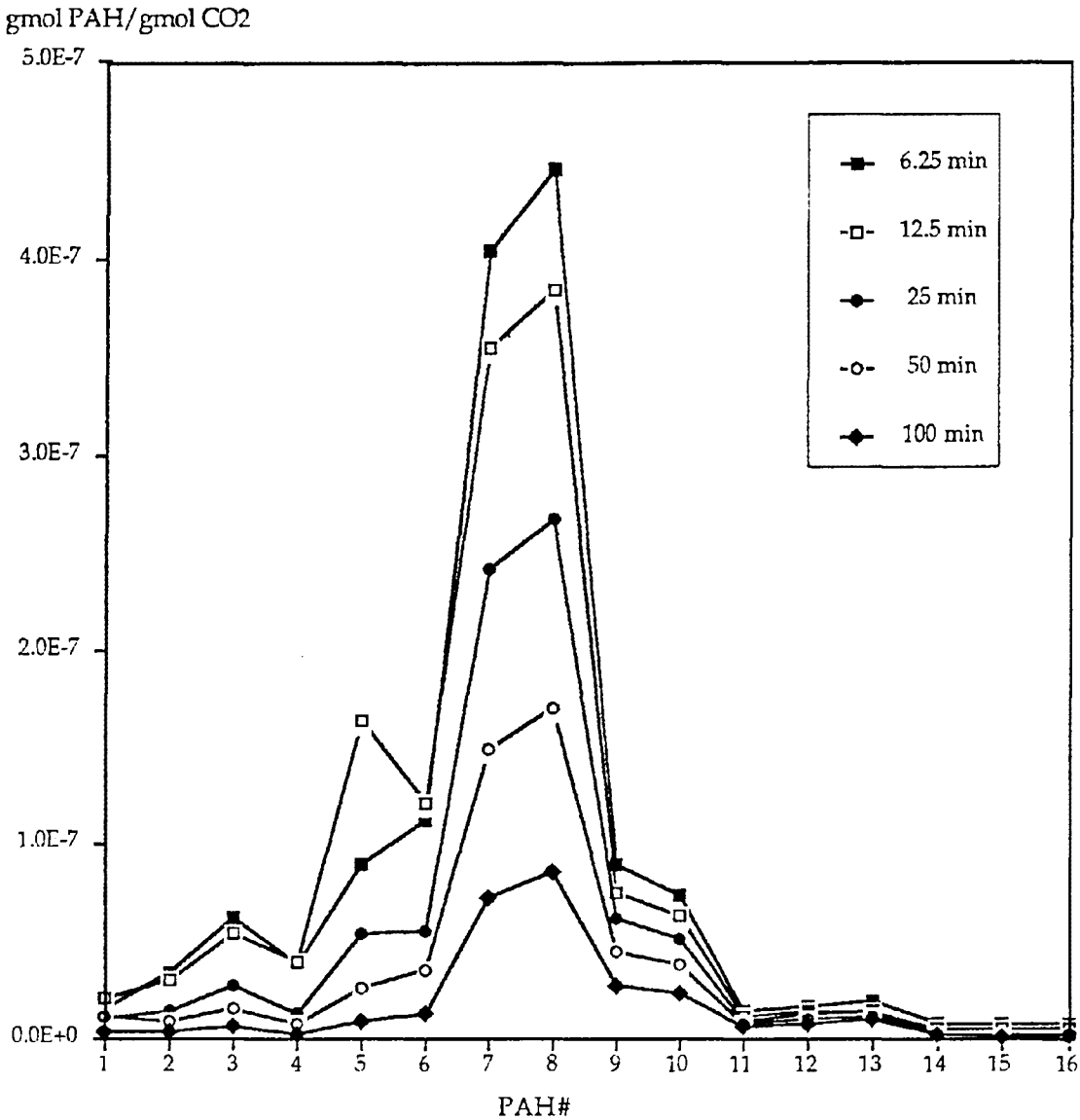

Figure 6. EFFECT OF EXTRACTION TIME ON THE EXTRACTION EFFICIENCY OF PAHS FROM SOIL 2
(Extraction conditions - 2000 psi, 45°C, 4 ml/min)

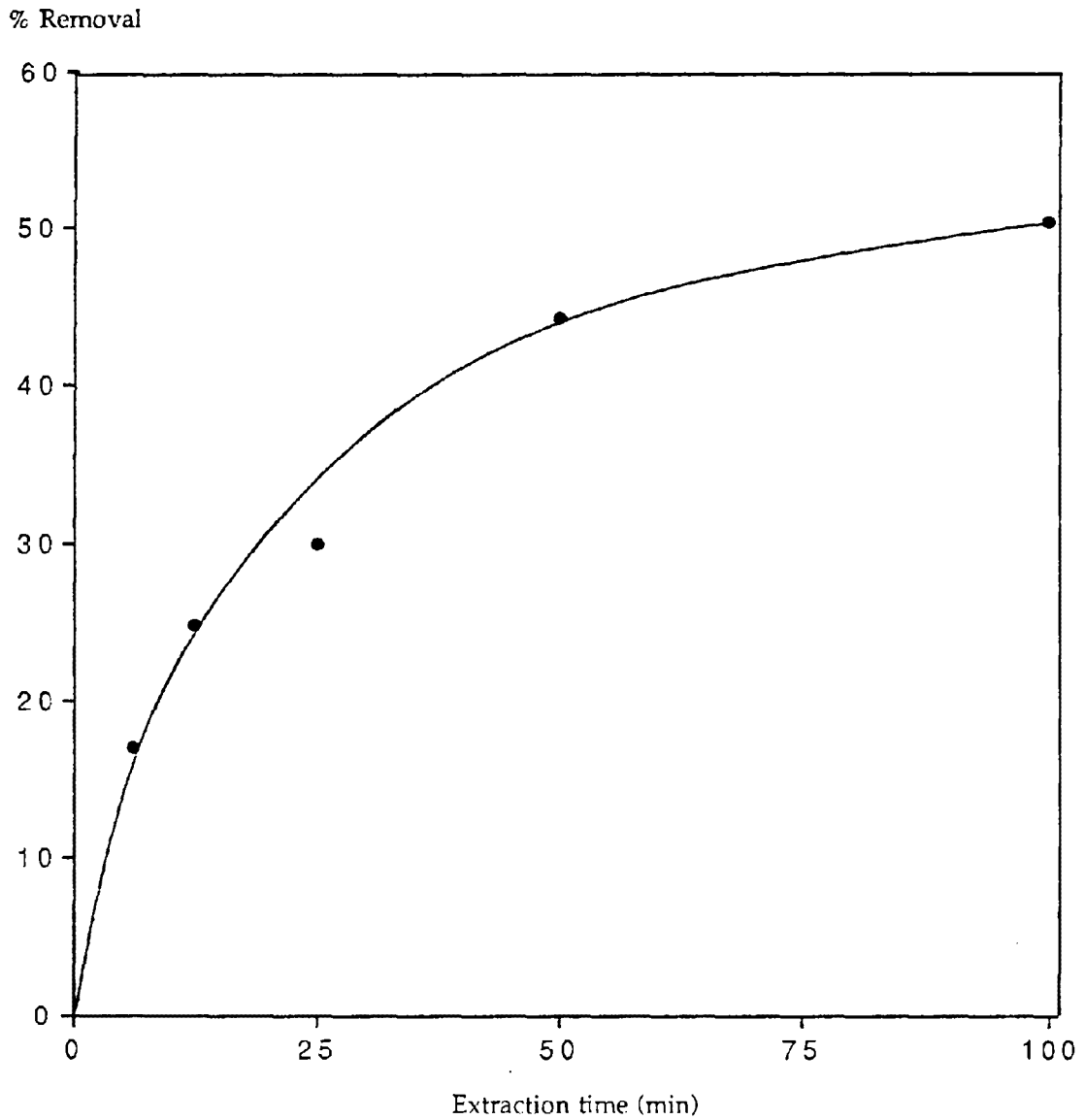

Figure 7. EFFECT OF EXTRACTION TIME ON TOTAL PERCENT REMOVAL OF PAHS FROM SOIL 2
(Extraction conditions - 2000 psi, 45°C, 4 ml/min)

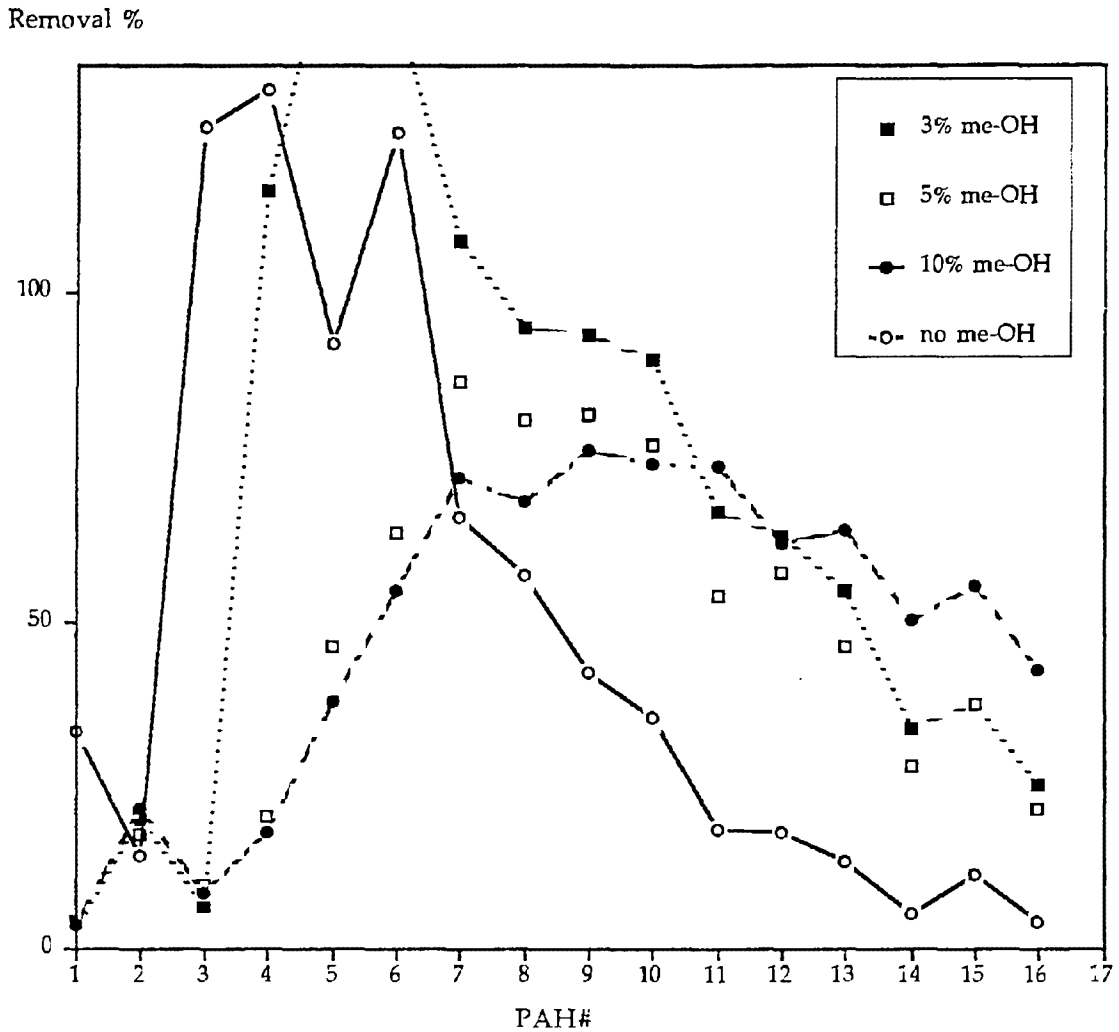

Figure 8. EFFECT OF CONCENTRATION OF METHANOL ON THE EXTRACTION OF PAHS FROM SOIL 2
(Extraction conditions - 2000 psi, 45°C, 4 ml/min)

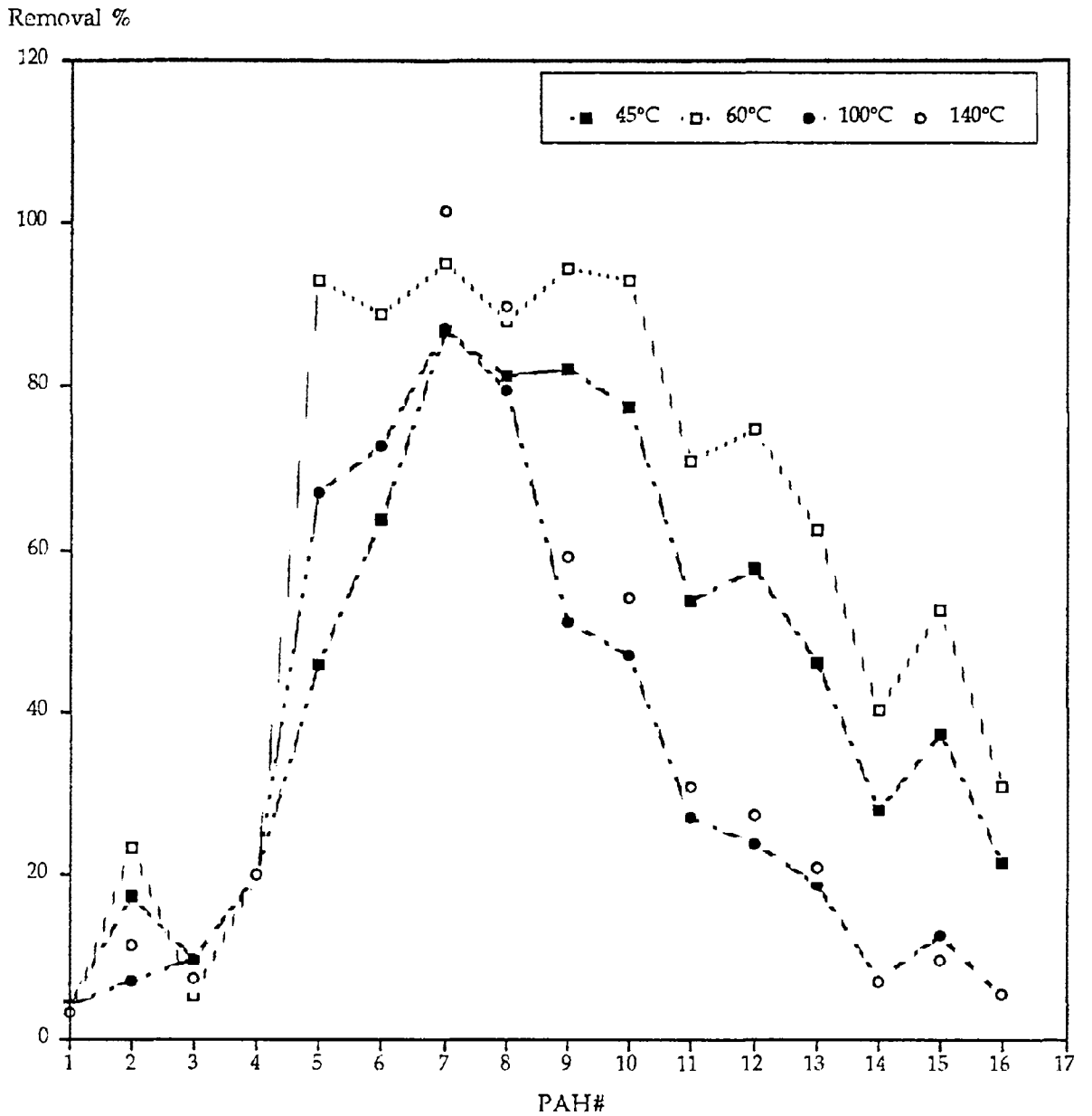

Figure 9. EFFECT OF TEMPERATURE ON PERCENTAGE REMOVAL OF PAHS FROM SOIL 2
(Extraction conditions - 2000 psi, 4 ml/min, 5 wt % methanol in CO_2)

Table 5. RESULTS OF SUPERCRITICAL CO_2 EXTRACTION TESTS CONDUCTED IN CO_2 RECIRCULATION MODE

Experimental Conditions:

	Test#		
	19	20	21
Weight dry soil (gm)	26.1	30.9	34.7
Weight dry carbon (gm)	12.4	11.9	11.2
Extraction temperature (°F)	110	155	155
Extraction pressure (psi)	1700	1850	2025
Adsorption temperature (°F)	110	145	155
Adsorption pressure (psi)	1700	1850	2025
Extraction time (min)	50	60	64
Ratio of CO2/soil (scf/gm)	1.214	1.034	1.672
Activated carbon	GAC (Surgent-Welch), Cocoanut, 8-12		

Experimental Results:

Concentration of PAHs (mg/kg) Remained in Soil and Activated Carbon After Each Experiment

			Test #					
			19		20		21	
Compound	PAH#	Soil 3*	Soil	AC	Soil	AC	Soil	AC
Naphthalene	1	46.0	38.70	15.30	16.02	36.33	7.33	42.45
Acenaphthylene	2	109.6	60.40	102.00	44.43	124.29	35.67	123.24
Acenaphthene	3	17.5	2.70	31.10	0.91	56.42	0.67	61.67
Fluorence	4	14.3	9.40	8.90	2.95	52.14	1.00	69.22
Phenanthrene	5	120.5	62.30	107.00	29.55	129.80	7.44	100.88
Anthracene	6	82.9	38.20	34.30	21.48	42.14	9.78	33.14
Fluoranthene	7	198.7	175.00	42.70	125.11	57.22	35.33	69.31
Pyrene	8	251.1	224.00	44.50	176.93	53.33	53.44	56.14
Benz(a)anthracene	9	123.4	122.00	1.40	120.57	1.76	49.56	3.17
Chrysene + Triphenylene	10	138.0	136.00	2.80	130.57	2.13	62.33	3.66
Benzo(b)fluoranthene	11	66.1	66.00	0.30	61.70	0.19	42.00	0.59
Benzo(k)fluoranthene	12	76.9	76.80	0.30	72.05	0.19	48.44	0.40
Benzo(a)pyrene	13	133.2	133.00	0.40	121.14	0.00	89.11	0.50
Indeno(1,2,3-cd)pyrene	14	62.6	61.90	0.00	53.98	0.00	50.56	0.20
Dibenz(a,h)anthracene	15	19.2	17.80	0.00	21.14	0.00	14.56	0.20
Benzo(ghi)perylene	16	70.2	69.50	0.00	59.77	0.00	57.11	0.20
Total (mg/kg soil)		1530.1	1293.70	391.00	1058.30	555.93	564.33	564.94

* Calculated based on PAH's left in the system and CO2.

Table 5 (continued). RESULTS OF SUPERCRITICAL CO_2 EXTRACTION TESTS CONDUCTED IN CO_2 RECIRCULATION MODE

Data analysis:

Percentage of Extracted PAH's Adsorbed on Activated Carbon From Soil 3

		Test#		
Compound	PAH#	19	20	21
Naphthalene	1	100	46.72	35.46
Acenaphthylene	2	99	73.50	53.83
Acenaphthene	3	100	131.16	118.41
Fluorence	4	86	176.60	167.65
Phenanthrene	5	87	54.98	28.81
Anthracene	6	36	26.42	14.63
Fluoranthene	7	86	29.95	13.69
Pyrene	8	78	27.70	9.17
Benz(a)anthracene	9	49	24.25	1.39
Chrysene + Triphenylene	10	66	10.99	1.56
Benzo(b)fluoranthene	11	100	1.61	0.79
Benzo(k)fluoranthene	12	100	1.46	0.45
Benzo(a)pyrene	13	100	0.00	0.36
Indeno(1,2,3-cd)pyrene	14	0	0.00	0.53
Dibenz(a,h)anthracene	15	0	-0.00	1.38
Benzo(ghi)perylene	16	0	0.00	0.49

PAH's Percentage Removal From Soil 3

		Test#		
Compound	PAH#	19	20	21
Naphthalene	1	15.8	65.1	84.0
Acenaphthylene	2	44.9	59.4	67.4
Acenaphthene	3	84.5	94.8	96.2
Fluorence	4	34.4	79.4	93.0
Phenanthrene	5	48.3	75.5	93.8
Anthracene	6	53.9	74.1	88.2
Fluoranthene	7	11.9	37.0	82.2
Pyrene	8	10.8	29.5	78.7
Benz(a)anthracene	9	1.1	2.3	59.8
Chrysene + Triphenylene	10	1.5	5.4	54.8
Benzo(b)fluoranthene	11	0.2	6.7	36.5
Benzo(k)fluoranthene	12	0.2	6.4	37.0
Benzo(a)pyrene	13	0.1	9.0	33.1
Indeno(1,2,3-cd)pyrene	14	1.1	13.8	19.2
Dibenz(a,h)anthracene	15	7.3	-10.1	24.2
Benzo(ghi)perylene	16	1.0	14.9	18.6
Total PAH Removal, %		15.5	30.8	63.1

Table 6. EXTRACTION OF PETROLEUM HYDROCARBONS FROM SOIL IN CO_2 RECIRCULATION MODE

Experimental Conditions:

	Test #			
	22	23	24	25
Weight dry soil (gm)	34.6	33.1	14.9	16.68
Weight dry carbon (gm)	13.3	13.4	5.5	6.33
Extraction temperature (°F)	160	175	180	150
Extraction pressure (psi)	1900	2000	1930	1880
Adsorption temperature (°F)	155	170	132	165
Adsorption pressure (psi)	1900	2000	1930	1880
Extraction time (min)	60	47	30	30
Ratio of CO2/soil (scf/gm)	1.488	1.099	1.68	1.378
% of me-OH in Soil	0	7.2	0	0

Experimental Results:

	Total petroleum concentration (mg/kg)			
Soil before extraction	17900	17900	17900	17900
Soil after extraction	8500	8100	10500	8900
Activated carbon after extraction	3400	3200	5600	3400

Data Analysis:

TPH extracted/mol CO2 (mg/mol)	5.0	7.1	3.5	5.2
Percentage of Extracted TPH Adsorbed on AC	13.9	13.2	27.9	14.3
Total % TPH removal	52.5	54.7	41.3	50.3

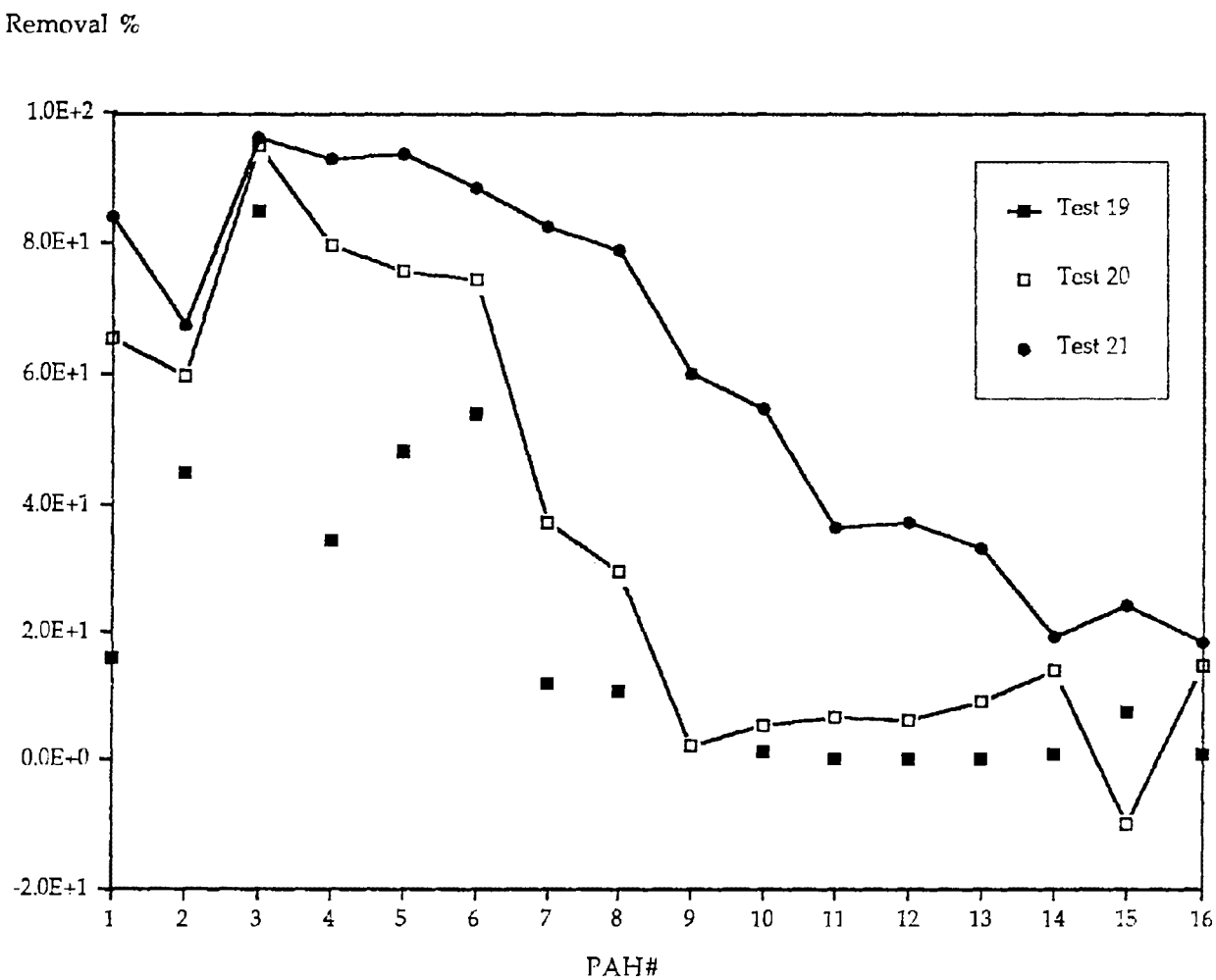

Figure 10. REMOVAL PERCENTAGE OF PAHS FROM SOIL 3 IN RECIRCULATING MODE
(Extraction temperature in Tests 20 and 21 are the same. Higher removal percent in Test 21 is due to higher ratio of CO_2 to soil)

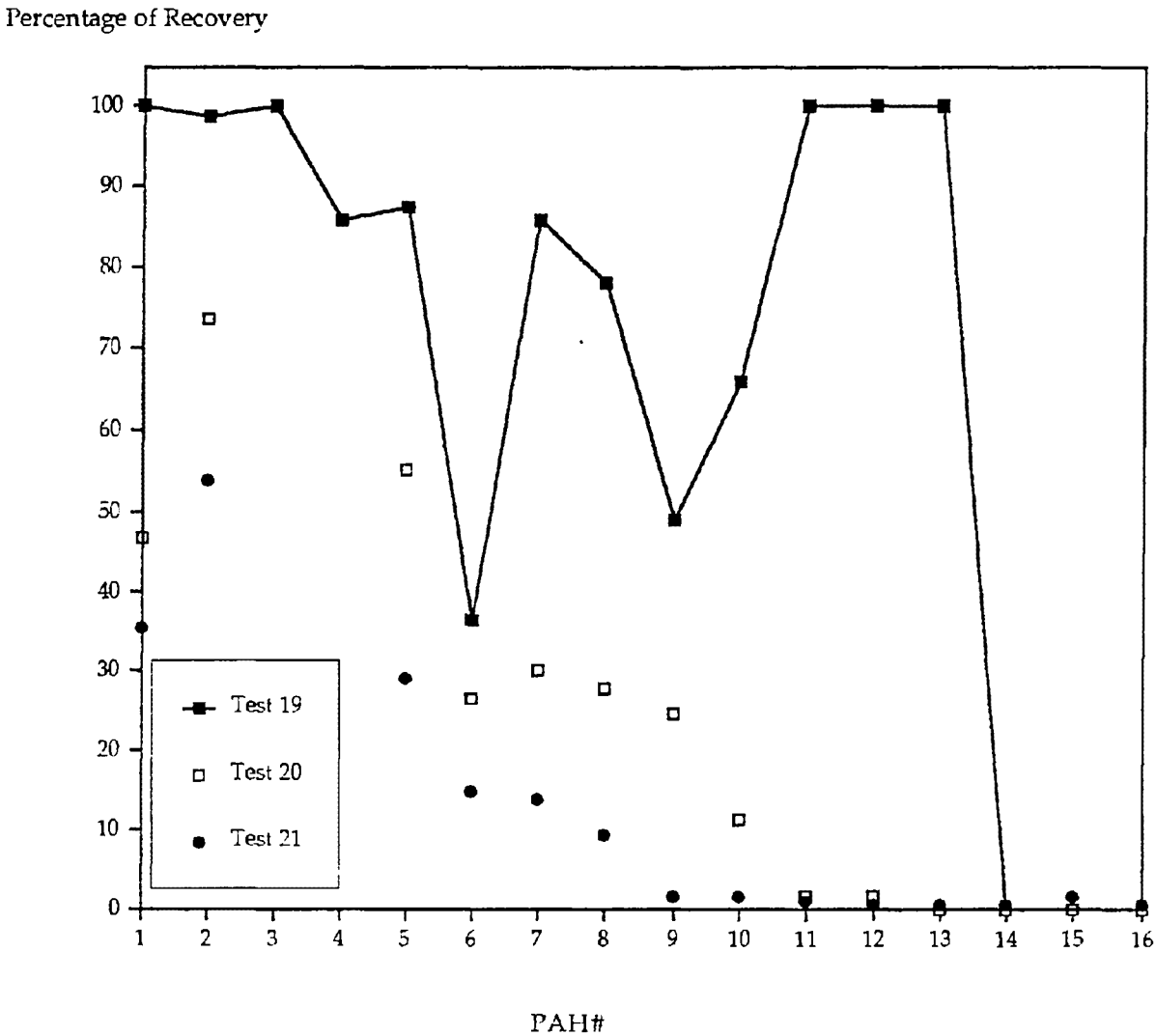

Figure 11. PERCENTAGE OF EXTRACTED PAHS ADSORBED ON THE ACTIVATED CARBON
(At lower temperature, PAHS are adsorbed better on the activated carbon)

granular activated carbon from coconut shells), the percentage recovery was very sensitive to the temperature of the activated carbon bed.

Tests 22 and 23 were conducted to determine the effect of modifier (methanol) on extraction of TPHs. Addition of methanol to the soil directly (before extraction) increased the ratio of TPHs extracted from soil to the number of moles of CO_2 from 5.0 mg/mol to 7.1 mg/mol. The ratio of TPH extracted by supercritical CO_2 to TPH adsorbed by activated carbon was slightly decreased by addition of methanol (Table 6).

The results of Tests 24 and 25 show the effect of activated carbon bed temperature on the adsorption power of activated carbon. The data indicates that organic contaminants capture (as measured by TPH) is improved using supercritical CO_2 at lower temperatures.

SELPhOx Field Test Unit

The overall objective of this task was to build a field test unit (FTU) based on the SELPhOx process. This task was comprised of subtasks to design, construct, and conduct initial shakedown testing of the FTU. For the FTU, the original SELPhOx process concept was simplified to reduce the number of pressure vessels and process complexity.

The SELPhOx FTU design incorporated CO_2 recirculation in the SCE stage, contaminant collection in an activated carbon vessel, and a wet air oxidation (WAO) reactor with off-gas condenser. Contaminant-laden activated carbon from the contaminant collection vessel was collected after each SCE cycle. The activated carbon was weighed and manually loaded into the WAO vessel and slurried with a weighed quantity of water. High-pressure cylinders provided air for the WAO reactor. Temperatures in each vessel were controlled by local temperature controllers and recorded by a dedicated computer-based data acquisition system. Means for adding modifiers, such as alcohols, to the SCE stage could be provided in the FTU. Also, high-pressure cylinders containing liquid CO_2 blended with a small amount of modifier could be used as in the laboratory-scale batch tests.

As the FTU is an experimental unit, several aspects of a commercial-scale plant are not included. In a commercial unit, after each extraction cycle is completed, supercritical CO_2 is pumped to a high-pressure holding tank for the next cycle. The CO_2 is not depressurized during the process, which saves considerable expense in recompression. Also in the commercial design, CO_2 is separated from the WAO product gas and recycled to the supercritical extraction cycle. Separation and recycle of regenerated activated carbon from the WAO unit is an important consideration of the commercial design. However, at this stage of process development, we do not consider this necessary to demonstrate the SELPhOx process.

The FTU was constructed and installed at IGT's Research Center in Des Plaines, Illinois. The base and frame for the FTU is constructed of high-strength Unistrut® beams. The FTU floor is made from ¾-inch thick plywood. The nominal dimensions of the FTU are 5½ feet wide by 6 feet tall by 8 feet long. The computer, controls, supercritical extraction unit, activated carbon vessel, and high-pressure recirculation pump are positioned along one side of the frame. The

WAO unit as well as CO_2 and air cylinder storage are on the other side of the FTU frame. Three-phase (220 V) power is required to operate the high-pressure piston pump for initially charging the CO_2 to the extraction unit. Single-phase (115 V) power operates the computer, strip-chart recorder, line and vessel heaters, temperature controllers, and pressure transducers.

In the WAO vessel, a backpressure regulator (BPR) controls air pressure. The BPR is set manually for the desired pressure. The oxidizer pressure is monitored and recorded by the computer. A mass flow controller (MFC) is used to control the flow rate of the air into the WAO. A check valve installed after the MFC ensures one-way flow of air into the oxidizer. The air is introduced from the bottom of the oxidizer through a simple sparger. An agitator is used to continuously mix the slurry of activated carbon and water. Two graphite-impregnated gaskets are used to seal the head of the oxidizer vessel and maintain pressure. An electric heater heats the oxidizer vessel. A local temperature controller controls temperature.

Product gas from the oxidizer consists predominantly of CO_2, nitrogen (from sparged air), and water vapor. This effluent flows to a condenser where the bulk of the water vapor is removed from the stream. An in-line check valve ensures one-way flow of product gas to the condenser. The level of accumulated water in the condenser (which also acts as a reservoir) is observed by a visual level indicator. A pressure regulator controls the pressure of the reservoir. Cooled effluent gases exit the WAO unit from the top of the condenser. Condensed water is recirculated to the WAO vessel by a metering pump as needed.

For the temperature control circuits in the supercritical extractor and wet air oxidizer, a solid-state relay was added to accommodate the electric current requirement of the heaters. For the temperature control circuit for the extractor vessel lines, the built-in capacity of 2½ amps was sufficient. Since computer records the temperatures, the output from each thermocouple is sent in parallel to the data acquisition system and to the temperature controller.

The main components of the WAO unit include the oxidizer vessel, heater, connecting lines, air sparger, condenser, reservoir, pressure control system, temperature control system, heater, blanket insulation, make-up water pump, agitator and variable-speed motor, and level indicator. A motor for the agitator, mass flow controller for air, and air pressure control system were also installed.

A condenser to condense water vapor exiting the WAO was installed downstream of the BPR. The condenser was constructed as two sections: 1) a shell-and-tube heat exchanger with vapor on the shell side and chilled fluid on the tube side, and 2) a vertical cylindrical vessel with a cooling coil wrapped around its upper part. The heat exchanger is constructed using ¼-inch stainless steel tubing with ½-inch stainless steel tubing for the shell. The cooling coil for the cylindrical vessel was constructed with ¼-inch copper tubing.

The chilled fluid (ethylene glycol) enters the heat exchanger at -9°C. The cold fluid leaving the heat exchanger enters the cooling coil of the cylindrical vessel. The effluent from the oxidizer, which consists essentially of water vapor and CO_2, enters the heat exchanger at about 250°C. Most of the water is expected to condense in the heat exchanger; the remaining water

will condense in the vessel, which is cooled at the top. The condensed water is collected in the lower half part of the vessel. The level of the water in the vessel is observed through a glass sight tube, which is installed in parallel with the vessel.

Cylinders of liquid CO_2 provided the on-board supply of fluid for supercritical tests. Cylinders of high-pressure air provided air for the WAO stage. Utilities included electricity, water, and instrument air.

Field Test Unit and Data Analysis

The objectives of this task were to conduct integrated supercritical extraction/liquid-phase oxidation tests with contaminated soils using the SELPhOx FTU and to analyze the data generated during these tests. Operating conditions were based on laboratory-scale tests results.

The results of the three shakedown tests conducted in the FTU are summarized in Table 7 below. The tests were conducted with contaminated soil containing from 3200 to 3400 mg/kg of TPH (total petroleum hydrocarbons). The nominal conditions for the tests were a system pressure of 2000 psig, extraction temperature of 70° to 82°C, absorption temperature of 68° and 71°C, and extraction time of 1 to 2 hours. The ratio of activated carbon in the absorption vessel to the quantity of contaminated soil charged to the extraction vessel was 1 to 3 (wt/wt).

Table 7. SUMMARY OF CONDITIONS AND RESULTS OF SHAKEDOWN TESTS CONDUCTED IN THE SELPhOx FTU WITH CONTAMINATED SOIL

Test No.	1	2	3
Feed, grams	2911.5	3000	1932.7
TPH Concentration, mg/kg	3400	3300	3200
Moisture Content, wt %.	9	12	11
Pressure, psig	2000	2000	2000
Extraction Vessel Temperature, °C	70	82	71
Absorption Vessel Temperature, °C	68	71	71
Extraction Time, hours	1	1	2
Soil/Carbon ratio, wt/wt basis	3	3	1
Extracted Soil, grams	2911.5	3000	1932.7
Concentration, mg/kg	2300	3000	2300
Moisture Content, wt %.	7	10	11
Activated Carbon, grams	998.2	1000	1933
Concentration, mg/kg	320	100	540
Moisture Content, wt %.	3	3	4
% Extracted from the soil	30.9	7.0	28.1
% Collected by the activated carbon	3.4	1.1	18.2
Overall TPH material balance, %	72.6	94.1	90.1

The results of these shakedown tests show that TPH compounds were extracted from the contaminated soil with the recirculating supercritical CO_2. However, the extent of extraction was lower than expected based on the results of the laboratory-scale tests. Extractions of about 30 percent were achieved in Tests 1 and 3. In Test 2, the extraction was less than 10 percent. The temperature of the extraction does not appear to have affected the extent of extraction significantly.

The quantity of the TPH compounds that were collected by the activated carbon was very low. The best recovery was about 18 percent in Test 3. This test also had the highest ratio of activated carbon to soil (1 wt/wt) than the other tests. It also had the lowest quantity of soil charged to the extraction vessel (~2 kilograms). The quantity of soil charged and the ratio of soil/activated carbon appear to have more impact on the results than the extraction and absorption temperatures.

The results of the shakedown tests indicate two significant aspects of FTU operation that require additional experimental confirmation: 1) the flow rate of supercritical CO_2 that is actually being recirculated through the extraction vessel via the recycle compressor needs to be quantified more rigorously. The flow meter readings taken during the tests indicate that supercritical CO_2 was being recirculated through the extraction vessel. However, fluctuations in the flow meter readings were significant which caused uncertainty in the accuracy of the flow meter calibration. The supercritical CO_2 flow meter calibration must be confirmed. 2) the flow pattern of the supercritical CO_2 flowing through the bed of contaminated soil must be determined. Supercritical CO_2 may have been flowing through the extraction cell at the prescribed flow rate; however, it may have channeled through the contaminated soil in the bed with much of the contamination not intimately contacting the CO_2. A supercritical CO_2 flow distributor may be required in the extractor as well as the activated carbon collector vessels. Both of these factors may have contributed to the low extractions as well as the low carbon collection by the activated carbon.

Wet Air Oxidation Tests

The objective of this task is to determine the effectiveness of wet air oxidation (WAO) on destroying/degrading contaminants adsorbed onto activated carbon obtained from SCE. Up to three samples will be subjected to WAO using a batch autoclave unit at IGT. Samples of contaminant-laden activated carbon were generated in the FTU as described above. Results of this work will be used to scale the WAO portion of the SELPhOx process and assist in a preliminary materials evaluation. Results of this work will also be used to evaluate the economics of the WAO portion of the SELPhOx process.

A shakedown test was conducted in the WAO unit installed on the SELPhOx FTU with contaminant-laden activated carbon from supercritical extraction test No. 1. A 10 weight percent slurry of the activated carbon sample and deionized water was prepared and charged to the WAO vessel. Operating conditions for the WAO test were a nominal temperature of 240° to 250°C, a pressure of 700 to 800 psig, and an air sparge (bubbling) rate through the WAO vessel of 6 to 7

ml/minute. The slurry of activated carbon and water was held at conditions for one hour. The activated carbon samples were analyzed before and after the WAO test. The extent of TPH destruction via WAO for this shakedown test was about 15 percent. It appears that more severe conditions will be required to accomplish the desired TPH destruction.

Process Design and Economics

A facility design and cost estimate was made for a transportable unit to process contaminated soil from a typical site. The approach will be to size the SCE equipment for the transportable unit to achieve a high degree of extraction of the principal organic hazardous constituent (or POHC). Similarly, the WAO equipment will be sized for achieving a high degree of destruction of the same POHC. The effect of lower or higher extraction and destruction criteria on the economics of the transportable unit will be determined in parametric studies.

The overall objective of this work is to determine if the capital and operating costs of the SELPhOx process are competitive with other soil remediation technologies with which it must compete. The criterion of competitiveness for the process is soil remediation costs of less than about $200 per ton. Further, in order to estimate the economics of the process, a fairly detailed process design must be prepared. Problems and concerns that arise during the design process can be addressed in a timely manner, rather than waiting toward the end of the project.

The total capital cost for a commercial-scale SELPhOx plant consisting of 3 supercritical extraction trains and one WAO train with intermediate CO_2 storage was estimated for the project. The nominal throughput capacity for a commercial-scale plant is 100,000 tons of soil per year. The total plant investment for a SELPhOx plant to process 100,000 tons per year of contaminated soil was determined to be $16,300,000. Based on a 10-year equipment amortization and 6.0 percent cost of capital, the yearly operating costs were estimated to be $9,333,000. This relates to a unit processing cost ranging from $150 to $250 per ton.

Project Management

The objective of this task was to ensure that a coordinated program is maintained among the EPA and IGT, and that all program requirements are met.

During the project period, IGT oversaw the experimental and process design work of the program. The University of Illinois (Chicago campus) participated in the project with the involvement of a doctoral candidate under the tutelage of Professor G. Ali Mansoori. One paper was prepared for the American Chemical Society meeting held in New Orleans on March 23-25, 1996. This paper was entitled "SELPhOx Process for Remediation of Contaminated Soil." A second paper entitled "Design and Construction of a Supercritical Fluid Extraction Process for Remediation of Contaminated Soil" was presented at the 1996 Midwest Thermodynamics and Statistical Mechanics Conference held on May 3 (Madison, WI).

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn from the experimental results

- The extent of PAH extraction from soil by supercritical CO_2 increases with temperature to a maximum at about 65°C. At temperatures above 65°C the extent of PAH extraction decreases.

- In PAH adsorption tests with activated carbon; the results showed that lower, rather than higher temperatures of the activated carbon increased the capture of PAHs from supercritical CO_2. A temperature of about 45°C yielded the highest recovery of PAHs.

- The results of tests conducted with modifier (methanol) showed that a concentration of three percent yielded higher PAH extractions than any other higher methanol concentration (up to 10 percent methanol in CO_2 was tested).

It is recommended that the concerns described above for the operation of the SELPhOx FTU be addressed and that additional supercritical CO_2 extraction and WAO tests be conducted in the FTU to develop design data to scale up the FTU to commercial scale.

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15. SUPPLEMENTARY NOTES

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16. ABSTRACT

During the experimental program, IGT conducted a series of laboratory-scale supercritical CO_2 extraction tests to evaluate the effects of CO_2 flow rate, temperature, and the addition of a modifier on the extraction of polynuclear aromatic hydrocarbons (PAHs) from soil. These tests were conducted in IGT's laboratory- and bench-scale supercritical extraction equipment. The laboratory-scale tests were conducted with supercritical CO_2 in once-through mode. The bench-scale tests were conducted in CO_2 recirculation mode with activated carbon adsorption of the PAHs. Overall, the results of these tests show that the extent of PAH extraction from soil increases with temperature to a maximum at about 65°C. At temperatures above 65°C the extent of PAH extraction decreases.

In PAH adsorption tests with activated carbon, the results showed that lower, rather than higher, temperatures of the activated carbon increased the capture of PAHs from supercritical CO_2. A temperature of about 45°C yielded the highest recovery of PAHs. The results of tests conducted with modifier (Methanol) showed that a concentration of three percent yielded the highest PAH extractions in the range of methanol concentrations, up to 10 percent in CO_2.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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