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SITE
SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

Technology Demonstration Summary

Pilot-Scale Demonstration of a Slurry-Phase Biological Reactor for Creosote-Contaminated Soil

In support of the U.S. Environmental Protection Agency's (EPA) Superfund Innovative Technology Evaluation (SITE) Program, a pilot-scale demonstration of slurry-phase bioremediation was performed May 1991 at the EPA's Test & Evaluation Facility in Cincinnati, OH.

In this 12-wk study, a creosote-contaminated soil from the Burlington Northern (BN) Superfund site in Brainerd, MN, was used to test the slurry-phase bioreactors. During the demonstration, five 64-L stainless-steel bioreactors, equipped with agitation, aeration, and temperature controls, were used. The pilot-scale study employed a 30% slurry, an inoculum of indigenous polynuclear aromatic hydrocarbon (PAH) degraders, an inorganic nitrogen supplement in the form of NH_4-N, and a nutrient broth containing potassium, phosphate, magnesium, calcium, and iron.

During the course of the study, levels of soil-bound and liquid-phase PAHs, total petroleum hydrocarbons (TPHs), nutrients, pH, dissolved oxygen (DO), temperature, toxicity, and microbial populations were monitored. The percent reduction of soil-bound PAHs over 12 wk of testing ranged from greater than 72% for 4- through 6-ring PAHs to greater than 98% for 2- and 3-ring PAHs; the reduction of total PAHs exceeded 87%.

This Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the pilot-scale SITE demonstration of slurry-phase biological treatment that is fully documented in two separate reports (see ordering information at back).

Introduction

In response to the Superfund Amendments and Reauthorization Act of 1986 (SARA), the EPA Office of Solid Waste and Emergency Response and Office of Research and Development established a formal program called the SITE Program to promote the development and use of innovative technologies to clean up Superfund sites across the country. The primary purpose of the SITE Program is to enhance the development and demonstration of innovative technologies applicable to Superfund sites so as to establish their commercial availability.

The SITE Program comprises four major elements:

- Demonstration Program
- Emerging Technologies Program
- Measurement and Monitoring Technologies Program
- Technology Transfer Program

The objective of the SITE Demonstration Program is to develop reliable engineering performance and cost data on selected technologies so that potential users can evaluate each technology's applicability to a specific site and compare it with the applicability of other alternatives. Demonstration data are used to assess the performance and reliability of the technology, the potential operating problems, and approximate capital and operating costs.

Technologies are selected for the SITE Demonstration Program through annual requests for proposals (RFPs). EPA reviews proposals to determine the technologies with the most promise for use at Superfund sites. To qualify for the program, a new technology must have been developed to pilot- or full-scale and must offer some advantage over existing technologies. One of the selected technologies was pilot-scale slurry-phase biological treatment, performed by IT Corporation in conjunction with ECOVA Corporation, Redmond, WA.

The technology demonstration was conducted at EPA's Test and Evaluation (T&E) Facility in Cincinnati, OH, during May through July 1991. In this process, the soil was suspended in water to obtain a pumpable slurry, then pumped into a 64-L, continuously stirred tank reactor (CSTR). The CSTR was supplemented with air, nutrients, and an inoculum of microorganisms to enhance the biodegradation process. The objectives of the technology demonstration were:

1. Evaluate the ability of slurry-phase bioreactor to degrade polynuclear aromatic hydrocarbons (PAHs) present in the creosote-contaminated soil from the Burlington Northern (BN) Superfund site in Brainerd, MN.
2. Evaluate the performance of the slurry-phase bioreactor and its removal efficiencies for PAHs and soil toxicity.
3. Determine the air emissions resulting from the volatilization in the reactor.
4. Provide technical data to assist EPA in establishing best demonstrated available technology (BDAT) standards for the level of treatment required before land disposal.
5. Develop information on capital and operating costs for the full-scale treatment system.

Technology Description

Biological treatment entails degradation of organic compounds by microorganisms. The desired end products of aerobic biodegradation are carbon dioxide, water, inorganic salts, and other relatively harmless products of microbial metabolism. In treating hazardous wastes or remediating contaminated soil, nutrients and microorganisms are often added to enhance biodegradation.

This treatment method has several advantages because an optimal environment for biodegradation of the organic contaminants can be maintained with a high degree of reliability. Biological reactions can proceed at an accelerated rate in a slurry system because limiting nutrients can be supplied and contact between contaminants and microorganisms can be increased by effective mixing and maintenance of high bacterial populations.

A slurry-phase process can also be operated as a continuous-flow system since the impact of toxic waste levels is reduced by the instantaneous dilution of the feed stream as it enters the reactor. In addition, toxic end products of microbial metabolism, which may repress bacterial activity, typically do not accumulate to inhibitory levels in the continuous-flow mode.

Specifications of Slurry-Phase Reactor Used During SITE Demonstration

The EIMCO Biolift™ Reactor * (nominal volume of 64-L) used during the SITE demonstration, shown diagrammatically in Figure 1, is of stainless steel and is equipped with agitation, aeration, and temperature controls.

Specifications for the 64-L EIMCO Biolift™ reactor are:

- Reactor is made of 304 stainless-steel plate, 3/16-in. thick. Interior tank diameter is 15 in. Total height is 36 in. Usable volume is approximately 60 L.
- Two airlift pipes and rake arm mechanisms are made of 304 stainless steel.
- Two elastomeric membrane diffusers are mounted on rake arm. Diffuser membrane consists of NBR rubber; other rubber materials are available depending on application.
- Air to diffusers is supplied via a rotary air valve. Air to airlift is supplied through a connection in the bottom plate of reactor.
- Drive motor for the rake arm is a Dayton, permanent-magnet, DC gear motor: power input 1/12 hp; 0.83 amps; 9.9 rpm; gear ratio 167:1; 228 in. lb torque; a Dayton Motor Speed Control 3 amps (max). Power transmission is by a timing belt.
- Drive motor for the impeller is a Dayton, permanent-magnet, DC gear motor: power input 1/10 hp; 0.89 amps; 110 rpm; gear ratio 37:1; 34 in. lb torque; a Dayton Motor Speed Control 3 amps (max). Power transmission is by timing belt.
- Reactor is heat traced electrically: chromolox™ on/off proportional temperature controller with digital indicator.
- Axial flow impeller with pitched blades is mounted on drive shaft.
- Flowmeters for airlift and diffusers are Dwyer Instruments RMB type.
- All the necessary tabs, fittings, and plugs allow insertion of DO, pH, and temperature probes.
- The single stage, single-cylinder, oilless, diaphragm compressor is Thomas Industries Model 917CA22: 1/8 hp shaded pole motor, single phase; 110v, 60 Hz; or alternatively, a filter regulator for hook-up to high pressure house air.
- A mechanical foam breaker with 1/6 hp variable speed motor is optional.

The reactor's contents are agitated by three mechanical methods. First, a rake mechanism moves the settled material from the bottom of the reactor to the second agitation mechanism, an airlift circulation system, which circulates the material to the top of the reactor. The third agitation mechanism is a low-shear impeller located approximately in the center of the central shaft of the reactor. Aeration is supplied by a set of air diffusers attached to the rake arm at the bottom of the reactor. Temperature is maintained by a heat tape system equipped with a digital readout.

The contents of the EIMCO Biolift™ Reactor can be sampled in two ways. An opening at the front top of the reactor allows access at the top surface of the liquid. This permits visual inspection of the mechanical actions within the reactor as well as data collection with hand-held instruments that can be inserted into the slurry from the top. Samples can also be collected from the three sampling ports located along the side of the reactor at three vertical positions along the reactor wall. Each port represents a distinct zone of the slurry: the bottom sampling port provides material from within the rake mixing zone where the heaviest particles are

*Mention of tradenames or commerical products does not constitute endorsement or recommendation for use.

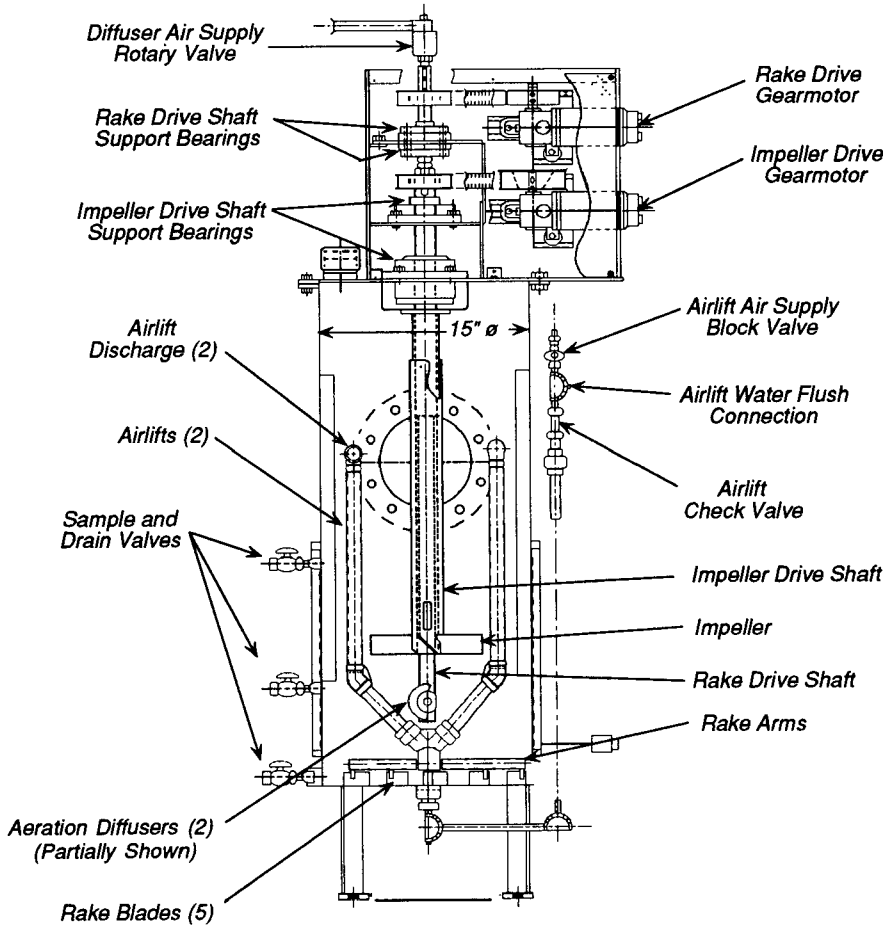

Figure 1. *EIMCO Biolift™ Reactor.*

likely to be present; the middle sampling port, from within the most well-mixed zone of optimal grain size; the top sampling port, from the layer containing the finest particles. Samples of contaminated material can be taken from each of these three ports to permit an evaluation of the mixing efficiency of the reactor.

Overview of the SITE Demonstration

Five 64-L EIMCO Biolift™ reactors, operated in series mode, were used to test the degradation of soil-bound PAHs in a slurry-phase, biologically active matrix.

Creosote-contaminated soil from the BN site was passed through a 1/2-in. screen to remove oversized material. After screening, the soil was mixed with water to form a 30% slurry. The slurry was then poured into a ball mill to reduce the particle size and was screened on exit from the ball mill through a No. 8 sieve to produce a slurry with a grain size distribution suitable for charging EIMCO Biolift™ reactors. Following milling, 66 L of the soil slurry was transferred into each of the five reactors.

After the reactors were charged with the soil slurry, a concentrated inoculum of indigenous bacteria was added to each of the reactors. For optimal microbial activity, nutrient amendments, including ammonia, phosphate, magnesium, calcium, iron, and ammonium molybdate, were added to the reactors.

Sampling and analysis activities performed during the pilot-scale demonstration involved collecting composite samples from each of the reactors for pre- and posttreatment analyses and sampling throughout the demonstration to monitor system operation. During the demonstration, soil-bound and liquid-phase PAHs, TPHs, nutrients, pH, DO, temperature, toxicity, and microbial activity and phenotype were monitored. Composite samples were collected from the three sampling ports located along the side of each reactor at three different vertical locations. Soil-slurry samples were taken from the reactors over a 12-wk period. In the ninth week of operation, four of the bioreactors were reinoculated with an additional 125 mL of the inoculum to stimulate the PAH degradation process.

SITE Demonstration Results

In addition to IT's sampling and analyses described above, ECOVA performed PAH analyses of soil samples. IT analyzed samples taken during Weeks T_0, T_9, and T_{12} to determine PAH concentrations by use of a gas chromatography/mass spectroscopy (GC/MS) method. ECOVA used a high performance liquid chromatography (HPLC) method in the analysis of samples taken during Weeks T_0, T_1, T_2, T_3, T_4, T_6, T_9, T_{10}, T_{11}, and T_{12}. The results obtained from each method are described and compared in the following subsections.

Results of Pretreatment and Posttreatment Soil Samples Analyzed by Gas Chromatography/Mass Spectroscopy (GC/MS) Method

The pre- and posttreatment soil and liquid samples were analyzed for critical contaminants PAHs and TPH. The air samples were analyzed for volatile and semivolatile organics (VOCs and SVOCs) and total hydrocarbons (THCs). All the PAH analyses on soil and liquid samples were performed by the EPA-approved GC/MS method (SW-846, Method 8270).

The pretreatment samples were collected at the start of testing (Week T_0) to determine the baseline concentration of the critical semivolatile contaminants in the soil treatment. The posttreatment samples were collected 9 wk (T_9) and 12 wk (T_{12}) after the start of testing to determine the levels of the critical contaminants remaining in the soil after treatment.

The concentrations of the PAH contaminants in the pretreatment soil samples ranged from 5.5 to 840 mg/kg. The concentration of total, 2- and 3-ring, and 4- through 6-ring PAH level and the degradation rates determined by GC/MS are given in Tables 1 and 2. The concentrations of the PAHs in posttreatment samples indicated a significant reduction of PAHs in the soil matrix. The percent reduction of total PAH for Week T_{12} samples for the five reactors ranged from >72.4% in Re-

Table 1. *Concentrations of Total, 2- and 3-Ring, and 4- through 6-Ring PAH Levels in Soil Samples, Determined by GC/MS, mg/kg*

Reactor	Week 0	9	12
2- and 3-Ring PAHs			
Reactor 1	2299	<31.4	<49.5
Reactor 2	1418	5.5	<23.8
Reactor 4	390.5	<32.3	8.1
Reactor 5	2644	31.5	<46.3
Reactor 6	718 6	18	<44.7
Total	1494 0	<23.7	<34.5
4- through 6-Ring PAHs			
Reactor 1	1410	<273.7	316.4
Reactor 2	775	<65.2	<267.5
Reactor 4	288	<357.9	<91.3
Reactor 5	1836	<308.9	404.6
Reactor 6	502	182.3	<291.8
Total	962.2	<237.6	274.3
Total PAHs			
Reactor 1	3709	<305.1	<365.9
Reactor 2	2193	<70.7	<291.3
Reactor 4	678.5	<390.2	<99.4
Reactor 5	4480	<340.4	<450.9
Reactor 6	1220.6	200.3	<336.5
Total	2456.2	<261.3	308.8

Table 2. *Percent Degradation of Total, 2- and 3-Ring, and 4- through 6-Ring PAH Levels in Soil Samples, Determined by GC/MS*

Reactor	Week 9	12
2- and 3-Ring PAH Degradation Rate		
Reactor 1	>98.63	>97.85
Reactor 2	99.61	>98.32
Reactor 4	>91.73	97.93
Reactor 5	98.81	>98.25
Reactor 6	97.50	>93.78
Mean Percent	>98.41	>97.69
4- through 6-Ring PAH Degradation Rate		
Reactor 1	>80.59	77.56
Reactor 2	>91.59	>65.48
Reactor 4	>-24.3	>68.30
Reactor 5	>83.18	77.96
Reactor 6	63.69	>41.87
Mean Percent	>75.31	>71.49
Total PAH Degradation Rate		
Reactor 1	>91.77	>90.10
Reactor 2	>96.77	>86.72
Reactor 4	>42.50	>85.35
Reactor 5	>92.40	>89.94
Reactor 6	83.59	>72.43
Mean Percent	>89.36	>87.43

actor 6 to >90.1% in Reactor 1. Results indicate that an average of greater than 87% of total PAHs were degraded over all five operating reactors after the 12th week of the demonstration period.

Initial levels of the hazardous component of creosote PAHs were 2460 mg/kg, as determined by GC/MS. After 12 wk of treatment, the concentration of the easily-degraded 2- and 3-ring compounds had declined by >98% from 1490 mg/kg to <35 mg/kg (average of five reactors). The concentration of the much more intractable 4-, 5- and 6-ring compounds declined >72% from 960 mg/kg to <270 mg/kg (average of five reactors).

The more complete degradation of the lower molecular-weight PAHs may reflect higher bioavailability of 2- and 3-ring PAHs than of 4- through 6-ring PAHs. Four- and higher-ring PAHs are considerably less soluble than simpler ring-PAHs.

The degradation rates of the different PAHs varied appreciably during the course of the study and reflect changes in the reactor environments. After 9 wk of testing, Reactors 2 and 4 were inoculated with fresh bacterial populations, and Reactors 5 and 6 were both reinoculated and amended with the surfactant Tween 80. Reactor 1 was not amended in any way. Results from Week 12 indicate that additional spiking during Week 9 did not assist in further degradation of the complex PAHs. On the contrary, the level of contamination due to the presence of the more complex PAHs was greater in Week 12 than in Week 9. The lower level of PAH contamination in Week 9 soil samples may have resulted from laboratory procedures. To extract PAHs, the analytical laboratory used a sonication method (EPA Method 3550) that calls for a 2-min sonication period. This may not have been enough time for the entire soil sample to intimately contact the extraction solvents and may have led to some inconsistent results for higher ring PAHs.

IT monitored TPH by infrared spectroscopy analysis over the course of the study. The concentration of TPH declined by 89.3% after 12 wk of treatment. The data for soil-bound TPH indicate that, as with the PAH data, variations occurred in TPH levels in the slurry (Table 3) during the 12-wk treatment. As with the PAHs, the greatest decline in TPH occurred in the first 2 wk of the study. A rise in the levels of TPH occurred at Week T_6; however, this is 2 wk after total PAHs rose in the slurries. This delay could reflect the actual production of TPH compounds as metabolic products of the biodegradation of the PAHs. It could also reflect a simple rise in extraction efficiency resulting from soil particle comminution.

GC/MS Analytical Results of Pretreatment and Posttreatment Liquid Samples

The concentrations of the PAH contaminants in the pretreatment liquid samples ranged from 0.006 to 18 mg/L. The concentrations for the majority of PAHs in the posttreatment samples were below the established method detection limits (MDLs) for the instruments. After 9 wk of treatment, only the more recalcitrant complex PAHs remained in the liquid matrix. These contaminants ranged in concentration from 0.013 to 0.14 mg/L. Results from Week 12 indicated a further reduction in liquid phase contaminants as the levels of PAHs in the soil were further diminished, and the MDLs for the contaminants from Week 12 were lower than those for Week 9.

Results of Pretreatment and Posttreatment Soil Samples Analyzed by HPLC Method

The ECOVA Laboratory employed HPLC (ECOVA modified EPA SW-846, Method 8310) to analyze for PAHs. The baseline soil (Week T_0) characterization showed that naphthalene, acenaphthene, and fluoranthene are the constituents present at the highest levels (range of 2170 ± 250 ppm), followed by fluorene and benzo(a)anthracene (range of 960 ± 8 ppm). Total PAH levels in these soils are 10,970 ppm. The 2- and 3-ring PAHs constitute 5890 ppm of the total, and the 4- through 6-ring PAHs account for 5080 ppm.

The PAH degradation rates over all five operating reactors during the 12-wk study are presented in Table 4. As seen in Table

Table 3. *Concentrations of Total Petroleum Hydrocarbons (TPH) in Soil, mg/kg*

Reactor	Week 0	2	4	6	9	11	12
1	35000	7200	1800	3100	1800	1900	1700
2	17500	2600	1800	2300	3200	1700	1800
4	13000	2700	1600	2100	1800	1700	1900
5	16000	3600	2300	2900	1700	3700	2700
6	19500	2400	2400	3600	2200	4900	2700

4, after the initial 2 wk of slurry-phase treatment, 90% of the total PAHs were degraded. Degradation rates (mg/kg/wk) for 2- and 3-ring PAHs were somewhat higher at 2 wk (96%) than they were for 4- through 6-ring PAHs (83%). The final levels at Week T_{12} were 653.5 mg/kg for total PAHs, 152.1 mg/kg for 2- and 3-ring PAHs, and 501.4 mg/kg for 4- through 6-ring PAHs.

Comparison of Analytical Results Obtained by GC/MS and HPLC Methods

The GC/MS results indicate total PAHs were degraded by more than 87% for all reactors during a 12-wk study. Degradation rates for 2- and 3-ring PAHs (over 98%) were much higher than they were for 4- through 6-ring PAHs (72%). These observations (based on GC/MS data) agree with those obtained in the ECOVA HPLC study. The HPLC results show 94% reduction of total PAHs, 97% reduction of 2- and 3-ring PAHs, and 90% reduction of 4- through 6-ring PAHs. Figures 2 and 3 compare the mean total PAH concentration at Weeks T_0, T_9, and T_{12}, as determined by GC/MS and HPLC.

Results of Air Monitoring

Air monitoring of THCs, SVOCs, and VOCs was performed continuously for the first few days of the demonstration. The VOCs and SVOCs were monitored periodically through the ninth week. THC emissions data show high emissions the first 2 days of process operation, followed by a steady decline to baseline recordings by the fifth day of operation. The VOC volatilization was high the first 2 days of operation, decreasing to near analytical detection limits by the third day of operation. The SVOC emissions (naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, dibenzofuran, fluorene, phenanthrene, and anthracene) were detectable during the first 4 days of sampling. Beginning the sixth day of operation, very small quantities (at or below detection) of semivolatiles were found.

Slurry Toxicity Reduction

Microtox™ analysis was performed over the course of the study to monitor toxicity levels of the slurried soil to determine if soil toxicity decreased during slurry-phase biological treatment. The general trend in toxicity declined over the 12 wk. After 4 wk of treatment, some toxicity was still present in all the reactor slurries; and by Week 9, Reactors 5 and 6 still appeared to have some residual toxicity. By Week 10, either marginal or no toxicity was associated with the slurries.

Table 4. Percent Total, 2- and 3-Ring, and 4- through 6-Ring PAH Degradation Rates in Soil Samples Analyzed by HPLC[a]

	Week								
Reactor	1	2	3	4	6	9	10	11	12
2- and 3-Ring PAH									
Reactor 1	98.53	92.87	99.14	84.41	99.28	98.56	98.71	86.28	98.21
Reactor 2	84.25	97.39	99.10	95.98	96.54	98.11	98.82	92.00	98.45
Reactor 4	56.64	97.17	99.38	97.76	95.02	98.15	95.41	91.77	98.43
Reactor 5	81.82	95.52	97.74	90.43	98.16	97.74	91.54	97.87	93.36
Reactor 6	88.79	96.40	98.29	97.15	99.39	97.83	99.22	99.50	97.25
Mean Percent		96.14				98.06			97.42
4- through 6-Ring PAH									
Reactor 1	35.54	70.41	87.37	50.80	88.15	93.23	86.65	85.11	86.16
Reactor 2	34.10	83.46	91.56	77.56	80.13	91.86	90.30	91.16	92.41
Reactor 4	-79.11	87.28	93.79	90.22	72.28	93.19	92.37	92.72	94.32
Reactor 5	28.65	80.83	83.36	60.76	64.95	83.65	86.64	80.54	82.34
Reactor 6	47.60	85.90	83.35	83.35	93.53	95.59	91.99	88.50	90.07
Mean Percent		82.89				92.22			90.13
Total PAH									
Reactor 1	61.86	82.86	93.89	69.42	94.31	96.18	93.33	85.76	92.83
Reactor 2	60.15	90.70	95.48	87.13	88.65	95.10	94.73	91.60	95.55
Reactor 4	-10.75	92.26	96.61	94.02	83.73	95.69	93.90	92.24	96.39
Reactor 5	56.72	88.58	90.95	76.43	82.48	91.09	89.23	89.69	88.16
Reactor 6	71.34	91.95	91.96	91.30	96.91	96.88	96.16	94.84	94.21
Mean Percent		90.00				95.35			94.04

[a]*HPLC = High performance liquid chromatography.*

Conclusions

Based on results of the slurry-phase biological treatment SITE demonstration, the following conclusions can be made regarding the performance of the technology:

- The percent reduction of soil-bound PAHs (analyzed by GC/MS) over 12 wk of testing demonstrated an average reduction of >72% for 4-through 6-ring PAHs to >98% for 2- and 3-ring PAHs; the reduction of total PAHs exceeded 87%.
- The average percent reduction of TPH was 89.3% after 12 wk of treatment.
- Emissions data show high emissions of THC the first 2 days of process operation, followed by a steady decline to baseline recordings by the fifth day of operation. The VOC volatilization was high the first 2 days of operation, decreasing to near analytical detection limits by the third day of operation. The SVOC emissions were detectable during the first 4 days of sampling. Beginning the sixth day of operation, very small quantities (at or below detection) of semivolatiles were found.
- Slurry toxicity decreased to marginal or no toxicity by the tenth week of treatment.
- The total cost incurred by IT and ECOVA during the demonstration was approximately $333,800. Because of the BDAT status of this demonstration, extensive chemical analyses were required. In an actual site operation, this cost could be greatly reduced by limiting the analytical goals. Based on available full-scale cost data, the cost of full-scale remediations typically range from $50-$250/yd^3.

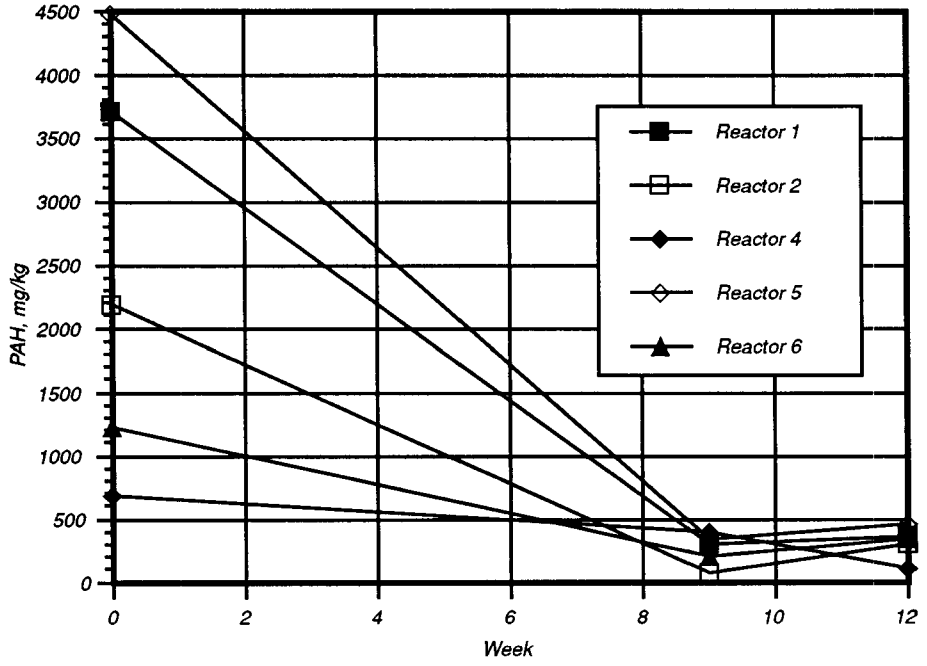

Figure 2. *Total PAH levels in reactor soil samples as determined by GC/MS*

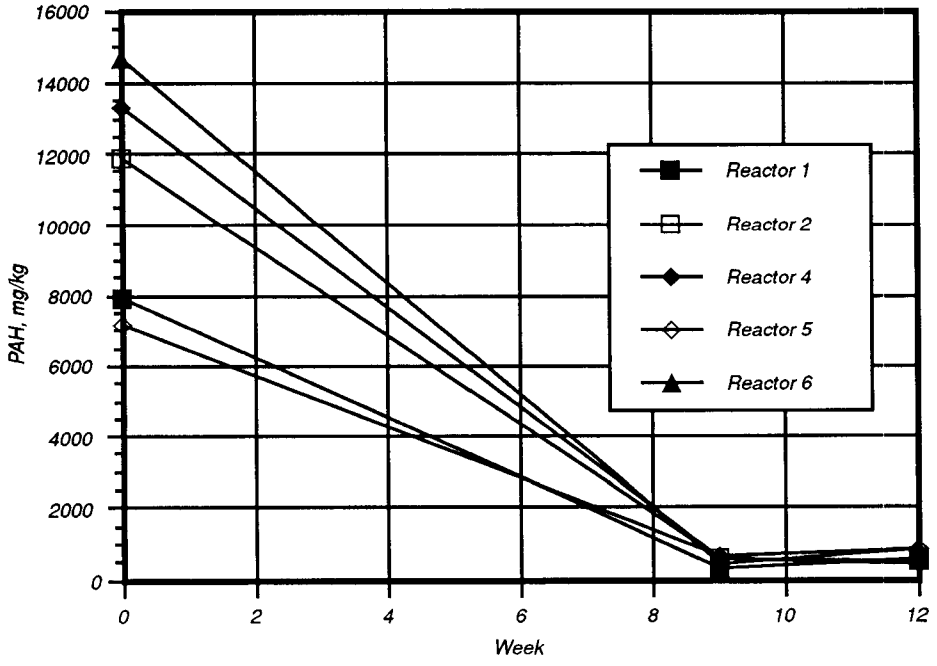

Figure 3. *Total PAH levels in reactor soil samples as determined by HPLC.*

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Ronald Lewis *(the EPA Project Officer, see below) is with the Risk Reduction Engineering Laboratory, Cincinnati, OH .*

The complete report, entitled "Technology Evaluation Report: Pilot-Scale Demonstration of a Slurry Phase Biological Reactor for Creosote-Contaminated Soil," (Order No. PB93-205 532/AS; Cost: $27.00, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

A related report, entitled "Applications Analysis Report: Pilot-Scale Demonstration of a Slurry Phase Biological Reactor for Creosote-Contaminated Soil," discusses the applications of the demonstrated technology.

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