



SITE
SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION



Emerging Technology Summary

Innovative Methods for Bioslurry Treatment

The tests reported herein were conducted by IT Corporation (IT), Knoxville, TN, to investigate the feasibility of combined biological and chemical treatments to treat polycyclic aromatic hydrocarbons (PAHs). Bioslurry treatment of PAH-contaminated soils was demonstrated under the Superfund Innovative Technology Evaluation - Emerging Technology Program (SITE ETP) as an extension of research previously funded by IT (Brown and Sanseverino 1993) and additional investigations supported by the U.S. Environmental Protection Agency (U.S. EPA) (Dávila et al. 1994). All testing was initiated in September 1994.

During the demonstration, IT operated two 60-liter (L) TEKNO Associates bioslurry reactors (Salt Lake City, UT) and a 10-L reactor in series under semicontinuous, plug-flow mode for a 7-month period. The first 60-L reactor received fresh feed daily and supplements of salicylate and succinate to enhance PAH biodegradation.

Slurry from the first reactor was fed to the second 10-L reactor, where Fenton's reagent ($\text{Fe}^{++} + \text{H}_2\text{O}_2$) was added to accelerate chemical oxidation of 4 to 6-ring PAHs. The third reactor in series was used to biologically oxidize contaminants remaining following addition of Fenton's reagent. This reactor received no additions of salicylate and succinate and was aerated, nutrient amended, and pH adjusted only.

During operation, the reactor system demonstrated total PAH and carcinogenic PAH (CPAH) transformation up to 95% and 84%, respectively.

This Summary was developed by EPA's National Risk Management Research Laboratory, Cincinnati, OH, to announce key findings of the SITE emerging technology project that is fully documented in a separate report of the same title (see ordering information at back).

Introduction

Among the types of organic contaminants present in Superfund soils, complex PAH constitute one of the more challenging class to remediate. Sites that contain PAH contamination include coal gasification sites, wood-treating facilities, petrochemical facilities, and coke plants. Soil contamination by PAH is a large environmental problem in the United States and, using traditional biological and chemical treatments separately, desirable target levels for PAH cleanup may not be reached in a timely desirable manner. Therefore, this investigation focussed on increasing the rate and extent of PAH oxidation using a combination of biological and chemical treatments.

PAHs are characterized by high organic partition coefficients, low aqueous solubility, and low vapor pressures. These characteristics result in the highly sorptive nature of PAH and their subsequent limited availability to microbial populations.



IT's past experience with PAH-contaminated soils indicated that contaminant desorption from soil is the rate limiting factor in bioremediation (Sanseverino et al. 1993). Manipulation of parameters such as pH, agitation, and temperature, as well as the addition of surfactants or solvents, can be used to enhance the rate of desorption, increasing the rate of biodegradation.

Bioslurry reactors can provide rapid biodegradation of contaminants due to enhanced mass transfer rates and increased contaminant-to-microorganism contact. These units are capable of treating high concentrations of organic contaminants in soils and sludges, with demonstrated biodegradation of selected contaminant concentrations ranging from 2,500 to 250,000 milligrams per kilogram (mg/kg). In general, the percent removal of PAH in these systems ranges from 70% to 95%, with 30% to 80% reduction of the carcinogenic PAH (CPAH) fraction (EPA 1990). The primary objective of this SITE project was to achieve greater than 80% CPAH transformation with subsequent increases in PAH transformation.

Process Description

The primary objective of reactor 1 (R1) operation was to increase the biological transformation of organic carbon. Salicylate was used to induce the naphthalene degradation operon on NAH plasmids. It was assumed that NAH plasmids were naturally occurring in microbial populations indigenous to subject soils. This operon has also been shown to degrade phenanthrene and anthracene (Sanseverino et al. 1993). The naphthalene pathway may also play a role in CPAH metabolism. Succinate, a by-product of naphthalene metabolism, served as a general carbon source in R1 which removed easily degradable carbon and increased biological activity against more recalcitrant PAH (i.e., 4-ring compounds and higher).

Slurry from R1 was fed to reactor 2 (R2) where Fenton's reagent was continuously introduced, resulting in chemical oxidation being the primary mechanism for PAH transformation in this reactor. The pH in R2 was maintained at 2.0 following the addition of R1 slurry. Fenton's reagent (hydrogen peroxide in the presence of reduced iron salts) produces free radicals, effective in extensively oxidizing multiring aromatic hydrocarbons in both soil and water systems (Gauger et al. 1991; Kelley et al. 1991; Elizardo 1991; Frisbie 1992). Because hydroxylation of high-molecular-weight PAHs is generally the rate-limiting step in biological oxidation, the objective of adding Fenton's reagent was hydroxy-

lation of PAH, not mineralization. Reactor 3 (R3) was used for biological oxidation of R2 slurry. R3 received no additions of salicylate and succinate. The reactor was aerated, nutrient amended, and pH adjusted following the introduction of R2 feed.

This study differs from other investigations in the reactor configuration which allowed for evaluation of biological treatment followed by chemical oxidation, and chemical oxidation followed by biological treatment. In addition, the introduction of organic supplements to increase biological oxidation of PAH, and minimization of Fenton's reagent addition were evaluated.

Bioslurry reactors can aerobically biodegrade aqueous slurries created through the mixing of soils or sludges with water. The most common state of bioslurry treatment is batch; however, continuous-flow operation can be achieved. Continuous-flow operation is preferred over batch due to the maintenance of a higher average reaction rate (Benefield and Randall 1985). Aeration is provided through floating or submerged aerators or compressors and spargers. Mixing may be achieved through aeration alone or in conjunction with mechanical mixers. Nutrient addition and pH adjustment are accomplished through metered chemical addition to the reactor. Following aeration, the treated slurry is dewatered via standard dewatering equipment, such as clarifiers or filter presses.

The residual streams created during bioslurry treatment include treated solids, process water, and possible air emissions. The process water collected during the solids/liquid separation phase is recycled for influent waste stream slurring or discharged under permit. Air emissions may be controlled through air pollution control devices.

Full-scale commercial bioslurry units require approximately 0.5 to 1 acre per million gallons of reactor volume (EPA 1990). Reactor size is determined based on the hydraulic retention time (HRT) required for treatment. Retention times are established based on the biodegradability of the waste, level of treatment required, influent contaminant concentration, and physical/chemical nature of the waste.

Major issues of concern during bioslurry treatment system design include reducing system HRT and increasing the rate and extent of contaminant biodegradation.

Test Procedures

PAH and CPAH-contaminated soils were collected from a southeastern wood-treatment facility. The soils, sand (30%) with silt and clay (70%), were wet-sieved on site through a 30 mesh screen and submitted to IT's Biotechnology Applications

Center (BAC) located in Knoxville, TN, for bioslurry testing. Oversized material was disposed of on site. Blended slurry PAH and CPAH maximum concentrations were 6,120 and 434 mg/kg, respectively. Wet sieving the soils increased the uniformity of the slurry, thereby reducing the potential for sampling variability.

All reactors were loaded to establish 40% total solids (TS) slurry of the screened soil and operated as batch reactors for 2 weeks prior to the initiation of semicontinuous flow. The 40% solids loading was required to suspend the sandy slurry. Following 3 months of operation, the initial 40% solids loading was decreased to a set point of 30% to reduce the total mass of organic carbon loaded to the system. Additionally, in order to maintain suspension of the slurry, the silt and clay content of the feed was increased to greater than 75% by blending clean, clayey soils with the highly impacted screened material.

No microbial cultures were added to the reactors during the project. All reactors were operated at approximately 25°C. During treatment, several operational difficulties were encountered, including significant foaming and tar ball formation. To reduce foaming, antifoaming agents were manually added, diffused air sparging decreased, and mixing intensity reduced. Tar balls were physically removed prior to continuous-flow operation.

During semicontinuous flow, 6 L/day of influent slurry was manually introduced to R1, resulting in a HRT of 10 days. To induce biological activity for PAH biodegradation, salicylate and succinate were added on a weekly basis to achieve final reactor concentrations of 86 and 4.4 mg/L, respectively. This addition rate was increased to 3 times per week after 4 weeks of operation to increase PAH transformation in R1. Salicylate and succinate addition was discontinued following four months of operation to evaluate its effect on biological oxidation and to reduce the amount of organic carbon in the system.

The second reactor in series (R2) received dilute concentrations of Fenton's reagent to accelerate chemical oxidation of PAH. Fenton's reagent was prepared by mixing a 1:1 volumetric ratio of 30% hydrogen peroxide and 8.4 millimolar (mM) iron sulfate solution. The iron sulfate solution and the hydrogen peroxide were individually applied to R2 below the slurry surface at a combined rate of 2.0 L/day. The introduction of Fenton's components was simultaneous. The influent feed rate to R2 was 6 L/day, resulting in a substrate HRT of 1 day. The addition of Fenton's reagent maintained the reactor pH at 2.

The last reactor in series (R3) was used for the transformation of any partially oxidized contaminants remaining following addition of Fenton's reagent. PAH and CPAH concentrations following chemical oxidation in R2 averaged 947 and 140 mg/kg, respectively. The system received 8.0 L/day of influent feed from R2, resulting in an HRT of 7.5 days. All operational parameters were maintained similar to R1, however, no salicylate and succinate additions were made. The pH was buffered in the reactor due to the addition of R2 contents. Table 1 illustrates the initial operating set points for all reactors.

After four months of operation, the HRT in R1 and R3 was increased to 20 days. R2 HRT was increased to 2 days. This change was initiated to decrease the amount of total carbon introduced to the reactors and extend the microorganism-contaminant contact time.

Reactor pH, dissolved oxygen, ammoniacal nitrogen, and ortho-phosphate concentrations were monitored weekly during system operation. During operation, slurry in R1, R2, and R3 was monitored weekly for TS, volatile solids (VS) concentrations, and slurry density. Microbial enumeration of total heterotrophs and naphthalene degraders was also conducted on the same schedule, using spread plate techniques.

Aqueous- and solid-phase PAH concentrations in R1, R2, and R3 were also monitored once per week. Grab slurry samples were collected from the middle sample port on each reactor, centrifuged, and the solid- and aqueous-phases submitted for analysis using high performance liquid chromatography. Volatilization of constituents was monitored monthly in R1 off-gas

through the analysis of XAD sorbent media. All PAH concentrations in aqueous phase, solid phase, or in sorbent media were determined using modified EPA Method 8310.

Results

The bioslurry reactor system demonstrated up to 95% and 84% transformation of PAH and CPAH, respectively. Transformation was determined through comparison of influent and effluent PAH and CPAH concentrations adjusted for abiotic losses. Figure 1 illustrates the overall reduction in concentration of all PAH compounds. Overall, the biologically active reactors (R1 and R3) illustrated a decreasing effectiveness in PAH transformation as a function of compound molecular weight.

Prior to operational changes initiated in March (following 5 months of treatment), R1 demonstrated 62% \pm 15% transformation of PAH, with approximately 27% \pm 18% transformation of CPAH. R2 demonstrated comparable transformation of PAH and CPAH (approximately 40% \pm 16%), as expected during chemical oxidation. R3 CPAH and PAH transformations averaged approximately 25% \pm 19% and 34% \pm 24%, respectively. The total system PAH and CPAH transformations averaged 85% \pm 6% and 65% \pm 8%, respectively. No significant volatilization of PAH was evident in R1.

Following operational changes initiated in March 1995, including increasing the HRT from 10 to 20 days, overall PAH and CPAH transformation rates increased up to 95% and 84%. R1 demonstrated 87% \pm 1% transformation of PAH, with 65% \pm

4% transformation of CPAH. R2 demonstrated comparable transformation of PAH and CPAH (greater than 45%), as expected during chemical oxidation. R3 PAH and CPAH transformations were decreased averaging 4% \pm 6% and 0.4% \pm 1%, respectively. The total system PAH and CPAH transformations increased to 91% \pm 4% and 75% \pm 11%, respectively. All data is presented in Tables 2 and 3.

During optimal operation, the influent PAH concentration was decreased from 6,210 mg/kg to 325 mg/kg. Influent CPAH concentrations were decreased from 422 mg/kg to 65 mg/kg.

R1 and R3 pH averaged 7.0, with R2 pH reduced to an average of 2. Dissolved oxygen in R1 and R3 varied depending on foaming and mechanical upsets; however, during optimal periods of operation the dissolved oxygen concentrations in these reactors were greater than 2 mg/L. Ammoniacal nitrogen was added to R1 to maintain an average concentration throughout the system of approximately 80 mg/L. Phosphate addition to the system was not required due to the naturally high concentrations in the soil. The average ortho-phosphate concentration in all reactors was 150 mg/L. Total heterotrophic counts in R1 and R3 ranged from 10⁸ to 10⁹ colony forming unit per milliliter (CFU/mL). Despite severe conditions maintained in R2, total microbial counts ranged up to 10⁴ CFU/mL.

The naphthalene-degrading bacterial population in the influent slurry was 10⁵ CFU/mL slurry at the initiation of the demonstration. Following 7 months of treatment, the influent feed population had decreased to 10⁴ CFU/mL. Populations in R1 and R3 measured 10⁶ and 10⁸ CFU/mL slurry, respectively.

Conclusions

The investigation illustrated the potential effectiveness of combined bioslurry treatment and chemical oxidation for the treatment of PAH-impacted soils. Overall, the following conclusions were made.

The 80% CPAH transformation goal had been achieved with CPAH transformation following operational changes ranging up to 84%.

An HRT of approximately 20 days increased system performance.

Due to the increased transformation of PAH in R1 and R2 during optimal performance, transformation rates in R3 were significantly decreased. This result may indicate that R3 is not required for effective treatment and biological treatment following chemical oxidation may be preferred.

Table 1. Initial Operational Setpoints

Parameter	R1	R2	R3
Feed Flow	6 L/day	6 L/day	8 L/day
Hydraulic Retention Time	10 days	1 day	7.5 days
Temperature	25°C \pm 5°C	24°C \pm 5°C	25°C \pm 5°C
Dissolved Oxygen	3 mg/L	---	3 mg/L
pH	7.0 \pm 0.5	<5.0	7.0 \pm 0.5
Agitation	500 rpm	250 rpm	500 rpm
Working Volume	57 L	6 L	57 L
Ammoniacal Nitrogen	50 mg/L	---	---
o-phosphate	10 mg/L	---	10 mg/L
Sodium Salicylate	100 mg/L	---	---
Sodium Succinate	10 mg/L	---	---
Fenton's Reagent Addition	---	2 L/day	---

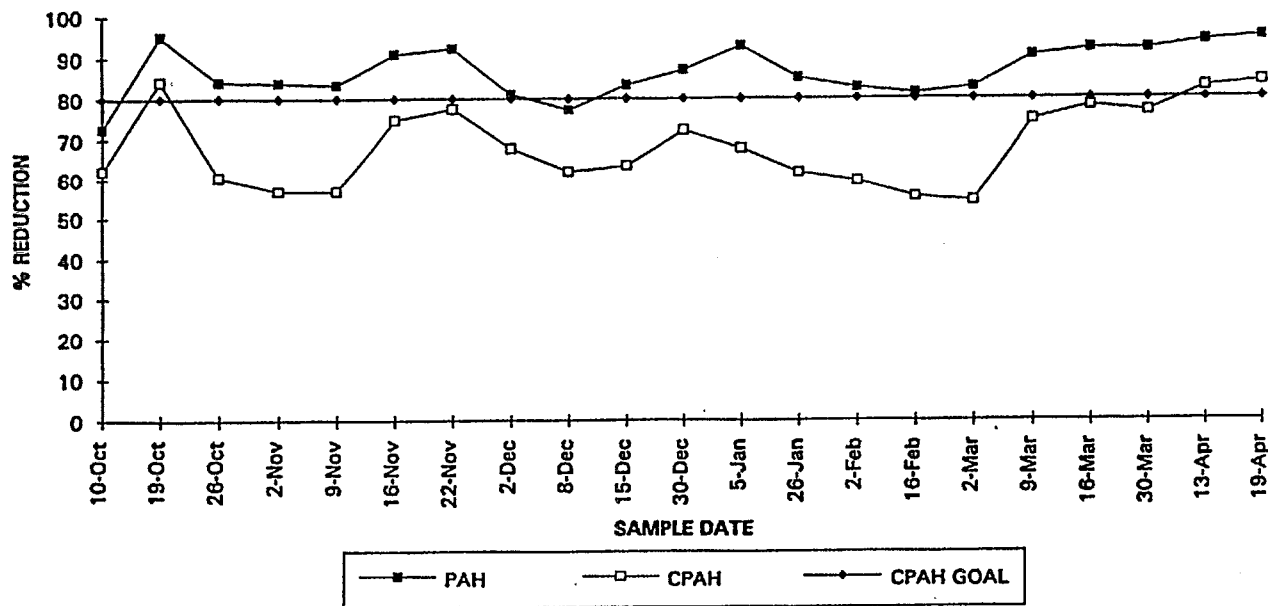


Figure 1. Percent reduction - overall.

Table 2. PAH Removal Efficiencies (Percent)

Date	Reactor 1	Reactor 2	Reactor 3	Overall
10/10	85	0	36.1	72.6
10/19	65	58.2	67	95.2
10/26	29	45.2	59.3	84.2
11/2	55.5	37.7	42	83.9
11/9	59.2	26.7	44.8	83.5
11/16	61.7	41	59.6	90.9
11/22	55.3	42.9	69.5	92.2
12/2	30.4	62	28.9	81
12/8	56.9	44.1	5.7	77.2
12/15	68.6	22	31.7	83.3
12/30	71.6	51.1	6.5	87
1/5	63.6	64	44.8	92.8
1/26	69.3	44.8	12.1	85.1
2/2	71.6	38	1.2	82.6
2/16	79.8	22.3	0	81.3
3/2	85.9	33	0	82.8
3/9	87.9	39.1	0	90.4
3/16	86	37	10.3	92
3/30	85.8	65.9	0	91.9
4/13	88.6	37	12.9	93.8
4/19	88.3	55.4	0	94.7
Total Operational Period Average	69.17 ± 17.9	41.4 ± 15.7	25.35 ± 24.81	86.59 ± 6.17
Average Prior to 3/2	61.5 ± 15.45	40 ± 16.93	33.95 ± 24.27	84.85 ± 6.05
Average Following 3/2	87.08 ± 1.32	44.6 ± 13.04	3.87 ± 6.05	90.93 ± 4.26

Recommendations

Continued investigation under the process set points maintained during the final month of system operation is recommended to consistently achieve greater than 80% CPAH transformation. As demonstrated by the increase in PAH and CPAH transformation during this period, reduced solids loading, increased clay content, and extended HRT set points proved beneficial to the treatment process.

Modifications to the pilot-scale reactor design should be investigated to decrease the incidence of foaming. Additional optimization of the addition of Fenton's reagent to reduce foaming is also recommended. Process foaming, particularly when operating on the full-scale, will result in poor system performance, reactor overflow, and the inability to effectively aerate the system.

During the spring of 1995 results of this project were presented at the following conferences.

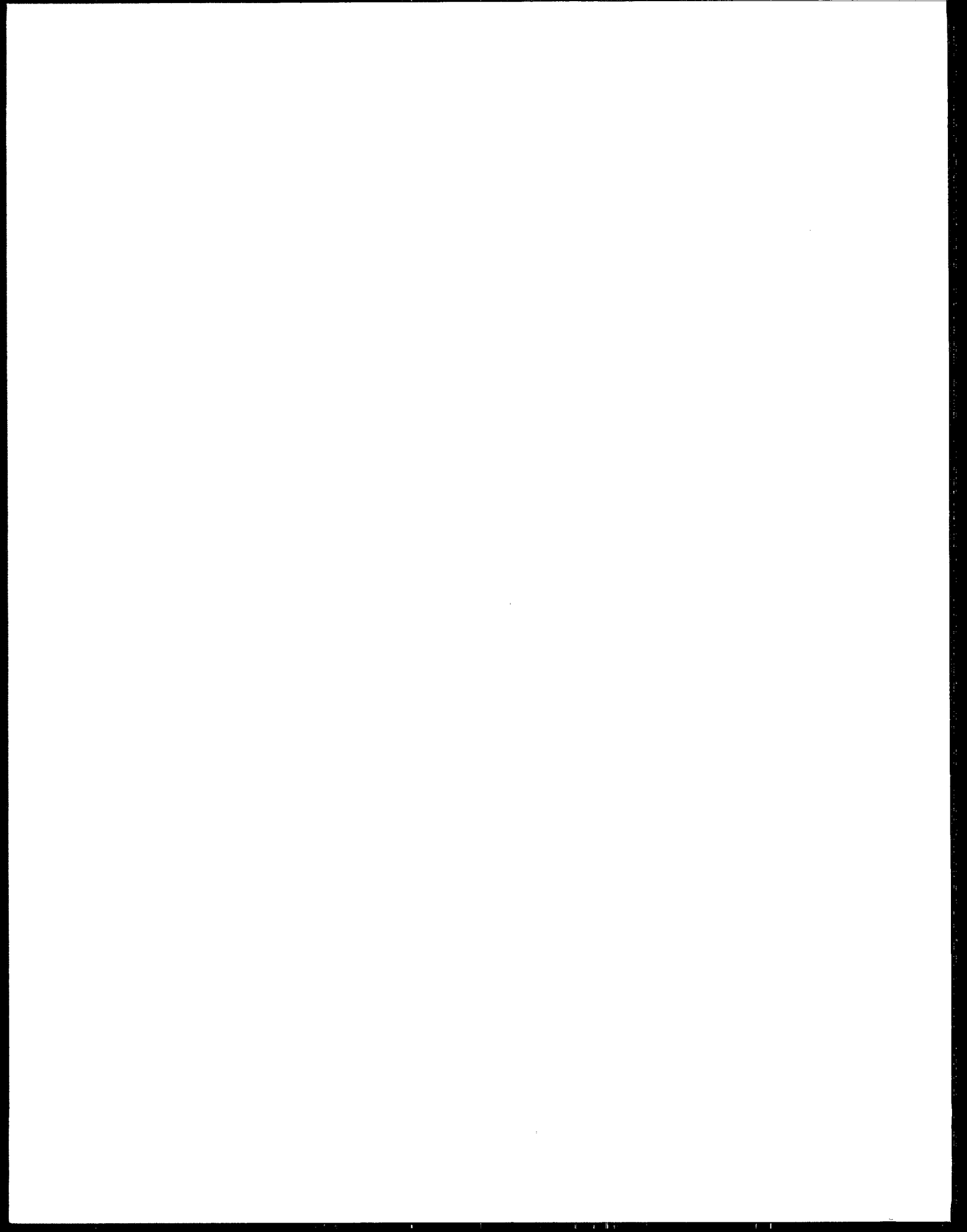
- Brown, K.L., B. Dávila, and J. Sanseverino. "Combined Chemical and Biological Oxidation of Slurry-Phase Polycyclic Aromatic Hydrocarbons." *Proceedings of HAZMACON '95*, San Jose, CA, 1995.

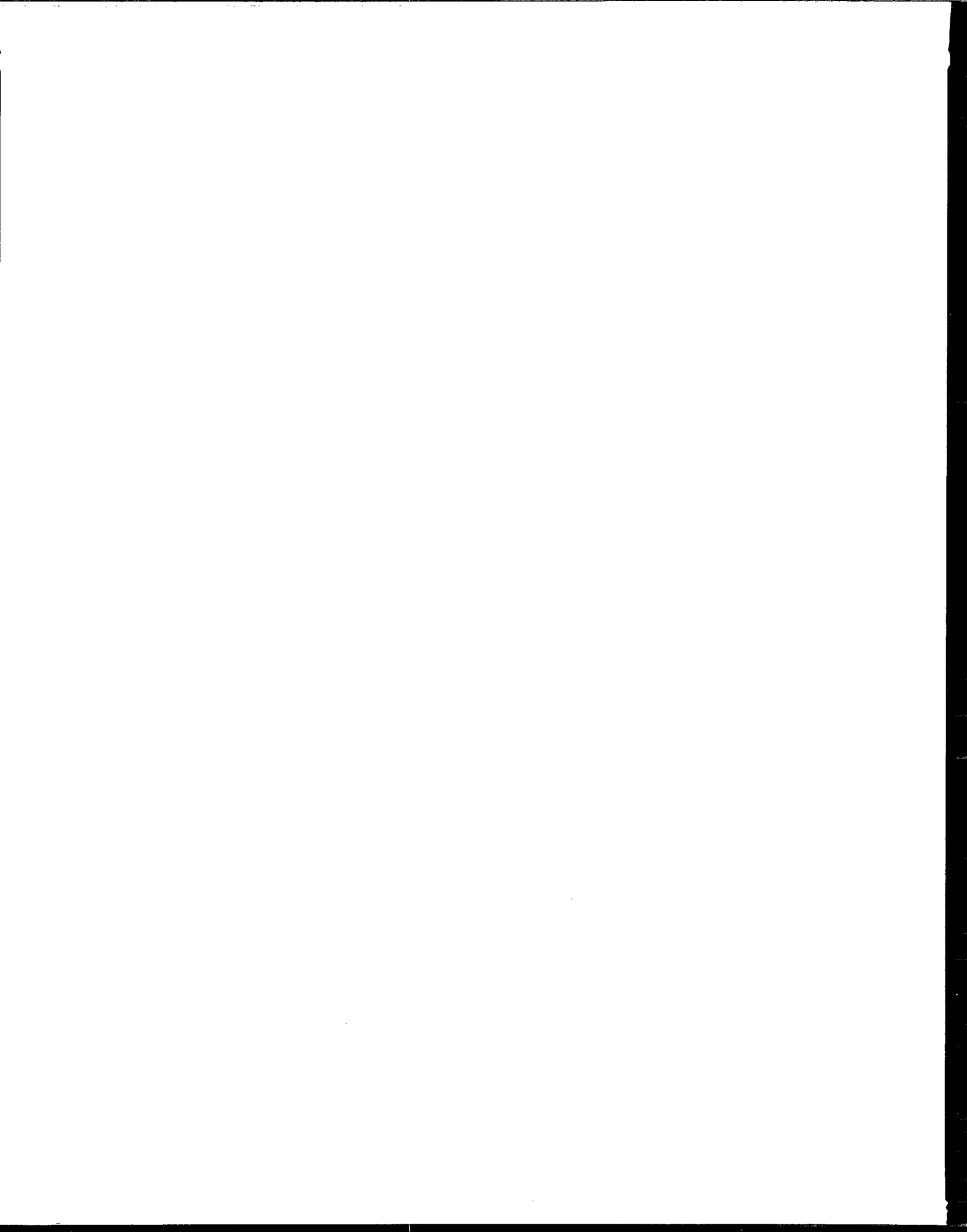
Table 3. CPAH Removal Efficiencies (Percent)

Date	Reactor 1	Reactor 2	Reactor 3	Overall
10/10	60	0	40.9	62.2
10/19	28.2	56.9	49	84.3
10/26	0	48.5	33.9	60.5
11/2	2.5	40.5	26	56.9
11/9	0	23.9	44	56.9
11/16	9.3	50	44.5	74.7
11/22	30.4	33.4	51.2	77.4
12/2	10.4	51	26.3	67.7
12/8	30.9	48.3	0	61.8
12/15	32.7	15	36.1	63.4
12/30	43.5	43.3	12.9	72.1
1/5	38	59	0	67.7
1/26	30.7	35.3	14.4	61.6
2/2	37.6	40	0	59.4
2/16	44.4	23.3	0	55.2
3/2	66.4	34	0	54.2
3/9	71	46.3	0	74.7
3/16	59.9	44	2.5	78
3/30	60.9	69	0	76.6
4/13	69	44	0	82.6
4/19	64.8	55.9	0	84
Total Operational Period Average	37.65 ± 23.61	41.03 ± 15.86	18.18 ± 19.84	68.19 ± 9.92
Average Prior to 3/2	26.57 ± 18.16	37.89 ± 16.44	25.28 ± 19.31	65.45 ± 8.42
Average Following 3/2	65.33 ± 4.39	48.87 ± 12.08	0.42 ± 1.02	75.02 ± 10.79

- Brown, K.L., B. Dávila, J. Sanseverino, M. Thomas, C. Lang, K. Hague, and T. Smith. "Combined Chemical and Biological Oxidation of Slurry-Phase Polycyclic Aromatic Hydrocarbons." *Proceedings of the Third International In Situ and On-Site Bioreclamation Symposium*, San Diego, CA, 1995.
- Brown, K.L., B. Dávila, and J. Sanseverino. "Combined Chemical and Biological Oxidation of Slurry-Phase Polycyclic Aromatic Hydrocarbons." *Proceedings of the Air and Waste Management Association 88th Annual Meeting and Exhibition*, San Antonio, TX, 1995.

The full report was submitted by IT in fulfillment of Cooperative Agreement No. CR821186-01-01 under the sponsorship of the EPA.





This Emerging Technology Summary was prepared by the staff of IT Corporation, San Bernardino, CA 92408.

Brunilda Dávila is the EPA Project Manager (see below).

The complete report, entitled "Innovative Methods for Bioslurry Treatment," (Order No. PB97-176820; Cost: \$21.50, subject to change) will be available only from:

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