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Pilot-Scale Bioremediation of PAH-Contaminated Soils

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ABSTRACT

The Institute of Gas Technology (IGT) conducted a pilot-scale study at a former manufactured gas plant (MGP) site in New Jersey. The objective of the study was to determine the effectiveness of an innovative chemical/biological treatment process (MGP-REM process) to remediate soils contaminated with polynuclear aromatic hydrocarbons (PAHs). In order to identify the benefits of the MGP-REM process, the system was also operated in the conventional bioremediation mode.

Results showed that the MGP-REM process can effectively treat PAH-contaminated MGP site soils, and it reduced the toxicity of the soil by a factor of 50, as indicated by the Microtox Toxicity Test. The MGP-REM process was 70% more efficient than conventional bioremediation in the removal of the PAHs from the soils. Air emissions data suggest that minimal air pollution control and monitoring are required for the slurry-phase application of both the MGP-REM process and the conventional biological treatment. Process economics indicate that the MGP-REM process in a slurry-phase mode has an estimated treatment cost of $100/cubic yard for remediation of PAH-contaminated soils.

Index Entries: Pilot-scale study; polynuclear aromatic hydrocarbons; slurry-phase mode; chemical/biological treatment (MGP-REM process); Fenton's reaction; manufactured gas plant site.

INTRODUCTION

A pilot study was conducted in Elizabeth, New Jersey to evaluate the slurry-phase bioremediation of former manufactured gas plant (MGP) site soils contaminated with polynuclear aromatic hydrocarbons (PAHs). The

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remedial technologies evaluated to treat the soil at this site were Institute of Gas Technology's (IGT's) innovative chemical/biological treatment process (MGP-REM process) and conventional bioremediation. The effect of the treatments on contaminant concentrations, soil microbiology, and toxicity was examined. Air emissions from the system were monitored to ensure compliance with the regulatory limits set by New Jersey Department of Environmental Protection (NJDEP).

Background

In 1950, natural gas replaced manufactured gas as the major gaseous fuel, and hence, the production of manufactured gas came to an end. Operations and residuals management practices of many former manufactured gas plants resulted in the contamination of their site soils with hazardous organic compounds. One of the main contaminants of concern are PAHs. Some of these PAHs are known carcinogens and pose an environmental hazard. As a result, these MGP sites may require cleanup to ensure environmental safety.

IGT has been developing engineering processes to remediate waste media, such as sediment, soil, sludge, ground water, and surface water, at former MGP sites contaminated with hazardous organic compounds *(1–3)*. The ultimate goal is to provide cost-effective waste treatment technologies that furnish an efficient alternative to incineration and landfilling.

After identifying the limitations of conventional bioremediation, IGT has developed approaches to overcome these limitations. As a result of extensive bench-scale studies carried out since 1987, IGT has developed a process for PAH-contaminated soils that is a combination of biological and chemical treatment—the MGP-REM process.

Technology Description: MGP-REM Process

The MGP-REM process combines two remedial steps: (1) biological treatment and (2) chemical treatment. These steps can be applied in different sequences depending on the nature and degree of contamination, and the contaminated matrix.

Biological treatment harnesses the ability of microorganisms to break down or transform organic compounds into less hazardous forms. The two-, three-, and some of the four-ring PAHs are mostly biodegradable and can support the growth of bacteria. However, biodegradation of most of the higher ring (four- to six-ring) PAHs is often slow, incomplete, and/or insufficient *(2,4,5)*. This is when the chemical treatment is beneficial.

Chemical treatment uses Fenton's reagent to transform the organic compounds in the waste matrix into environmentally benign end products. The Fenton's reaction, interaction of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}), involves formation of highly reactive free hydroxyl radicals that oxidize the recalcitrant contaminants, such as the higher-ring PAHs, into

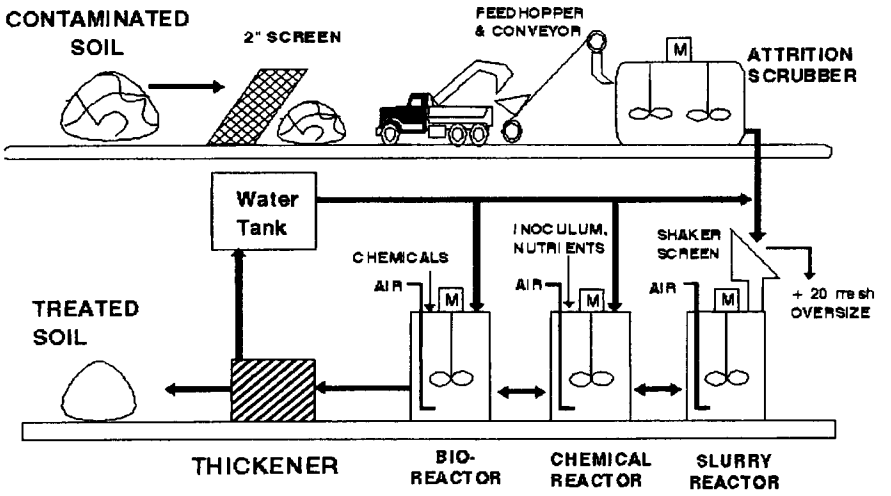

Fig. 1. Schematic of the slurry-phase MGP-REM process.

more readily biodegradable and water-soluble compounds *(1,6)*. Thus, the chemical treatment enhances the rate and extent of degradation of the PAHs in the soil.

METHODS

Process Description

A schematic diagram of the pilot plant is shown in Fig. 1. The treatment train included the following sections: feed preparation, reactor operation, and solids dewatering.

Feed Preparation

Excavated soil was screened to remove objects >2 in. The screened soil was then transported to an attrition scrubber, where soil was mixed with water to make a 50% soil slurry. Slurry from the attrition scrubber was sent to a 20-mesh vibrating screen to remove particles >1 mm, which were sent to the reject stockpile.

Reactor Operation

The reactor system was comprised of a slurry reactor, a bioreactor, and a chemical reactor; each with an identical capacity of 2100 gal. Slurry passing through the 20-mesh vibrating screen was diluted to the desired solids content in the slurry reactor and then pumped to the bioreactor. A startup run was used to promote and develop naturally occurring microbial population in the soil. The supernatant from this run that contained the active microorganisms was used as part of the makeup water to slurry the soil for subsequent tests. During the biological treatment, appropriate conditions for microbial growth were maintained as outlined in Table 1.

Table 1
Operating Conditions During
Biological Treatment

Parameter	Operating Range
pH	6.5 - 7.5
Temperature, °F	65 - 85
Dissolved Oxygen (DO), mg/l	2 - 6
Nitrogen, mg/l	≥ 50
Phosphorus, mg/l	≥ 10

For chemical treatment, the slurry was transferred to the chemical reactor. Prior to chemical addition, the slurry was allowed to settle, and the supernatant (about 20% of the total volume) was decanted. This procedure served as a way to oxidize only the contaminants in the soil and to keep the microbial population in the supernatant unaffected. The remaining thick slurry in the chemical reactor was mixed with predetermined concentrations of ferrous sulfate (range of 1–100 m*M* in slurry) and hydrogen peroxide (range of 0.5–2% by volume of slurry). In order to prevent excessive foam formation, the aeration was temporarily stopped. Following the chemical treatment, the pH of the slurry was adjusted to 7.0, the supernatant with active microbial population was added back for subsequent biological treatment, and aeration was restarted.

Solids Dewatering

Following the termination of each test run, the treated soil slurry was pumped to a thickener for solid/water separation. The overflow from the thickener was transferred to the water management tank for reuse in subsequent tests, and the underflow was discharged to the drying bed.

Operating Protocol

The two test runs were operated in a batch mode. The treatment conditions in the reactor system are shown in Table 2. The MGP-REM process used a treatment sequence of biological followed by chemical and a final biological step. The MGP-REM process was compared with the Conventional Bioremediation Test, which included only biological treatment of the soil.

Table 2
Treatment Conditions in the Reactor System for Pilot-Scale Study

Parameter	Treatment Range
Slurry Volume, gals.	1800 - 2100
Total Solids, %	25 - 35
Slurry Residence Time, days	10 - 20
Air Flow Rate, SCFM	0 - 25
Hydrogen Peroxide, % (vol./vol.)	0.5 - 2.0
Treatment Scheme	1. MGP-REM Process (Biological-Chemical-Biological Treatment) 2. Conventional Bioremediation (Biological Treatment)

Sampling and Analyses

Sampling and analytical methods were consistent with the NJDEP-approved methods. Soil and slurry samples, corresponding to each step of the MGP-REM Process, were collected at suitable time-points.

PAHs in the samples were determined using a modified United States Environmental Protection Agency (USEPA) SW-846 Method 8270B analysis of soxhlet extracts. Soxhlet extraction was performed by EPA SW-846 Method 3540 using a 1:1 mixture of acetone and hexane as the extraction solvent. The modifications of Method 8270B involved a 30-m long XTI-5 (Restek) column (0.25-mm id and 0.5-μm film) installed in a Hewlett Packard 5890 II gas chromatograph/5971 mass selective detector. The injector temperature was 270°C, and the following temperature program was used: 40°C, for 4 min followed by an increase to 300°C at a rate of 10°C/min isothermal at 300°C for 20 min. The PAH analysis was done by Analab, Edison, NJ.

Microbiology tests (total heterotrophic bacterial counts) were conducted on samples using the Method of Most Probable Numbers, at IGT, Des Plaines, IL. The Microtox Test was used to determine the toxicity of the samples. The Microtox Test was used to determine the toxicity of the soil samples. This test system measures the light output of the luminescent bacteria after they have been challenged by a sample of unknown toxicity and compares it to the light output of a control (reagent blank) that contains no sample. The degree of the toxicity of the sample is indicated by the degree of light loss, which is a measure of the metabolic inhibition of the

Table 3
Air-Monitoring Procedures for the Pilot Study

Analytical Parameter	USEPA Method	Air Flow Rate	Cartridge
BTEX	TO-10	25 cc/min	Carbotrap-300
PAHs	TO-1	1000 cc/min	XAD-2 Resin

test organisms. Toxicity levels in the samples were tested at MSL Inc., Pendleton, SC.

Air-Monitoring System

The entire process, which included the feed preparation, biological, and chemical treatment, was conducted in closed systems: attrition scrubber, slurry reactor, bioreactor, and chemical reactor. In order to prevent organic emissions, off-gas from these units was passed through two granular activated carbon (GAC) canisters operated in series.

Air samples were collected before and after the GAC units, and were analyzed by Aqua Air Analytical, Raritan, NJ, for benzene, toluene, ethyl benzene, and xylene (BTEX) and PAHs. The procedures used for collecting and analyzing the air samples are shown in Table 3.

RESULTS AND DISCUSSION

Results of the pilot study are summarized in this section. PAHs were the main contaminants of concern, and hence, the reduction in PAH concentrations in the soil was used to evaluate the performance of the remedial technology.

PAH Results

MGP-REM Process

The complete results of the MGP-REM test are plotted in Fig. 2. PAH concentrations of samples taken at days 0, 20, and 40 are summarized in Table 4. Day 20 sample corresponds to the last day of the reactor operation, and the day 40 sample was taken from the thickener, 20 d after the treatment was completed. Table 4 shows that a 95% removal efficiency was achieved for total PAHs, and the noncarcinogenic and carcinogenic PAHs showed a reduction of 97 and 90%, respectively. Table 4 also shows that PAHs with fewer (2, 3, and 4) aromatic rings were degraded more effectively than those with more (5 and 6) aromatic rings. However, the 87 and 88% removal efficiency of five- and six-ring PAHs, respectively, is notable. Figure 3 compares the carcinogenic PAH concentrations before and after the MGP-REM

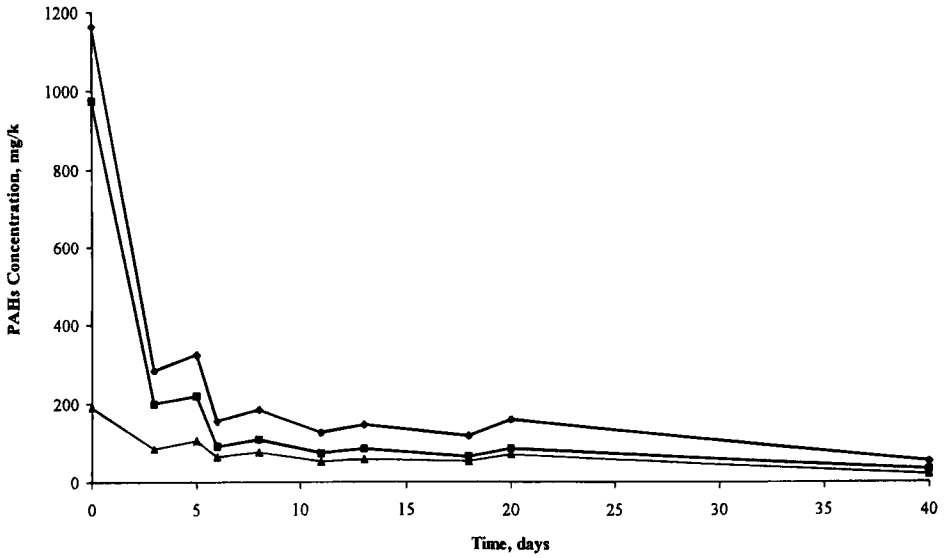

Fig. 2. Time plot of total, noncarcinogenic, and carcinogenic PAHs during the MGP-REM process. -◆- Total, -■- noncarcinogenic, -▲- carcinogenic.

Table 4
PAHs Degradation Data for MGP-REM Process

PAHs, (mg/kg)	Day 1	Day 20	Day 40*	% Degraded
Total	1164	157	53	95
Non-Carcinogenic	974	86	33	97
Carcinogenic	191	71	20	90
Individual Ring PAHs				
2-ring	202	21	7.6	96
3-ring	516	29	13.2	97
4-ring	337	41	18.2	95
5-ring	85	46	11.3	87
6-ring	24	21	2.8	88

*Samples taken from thickener.

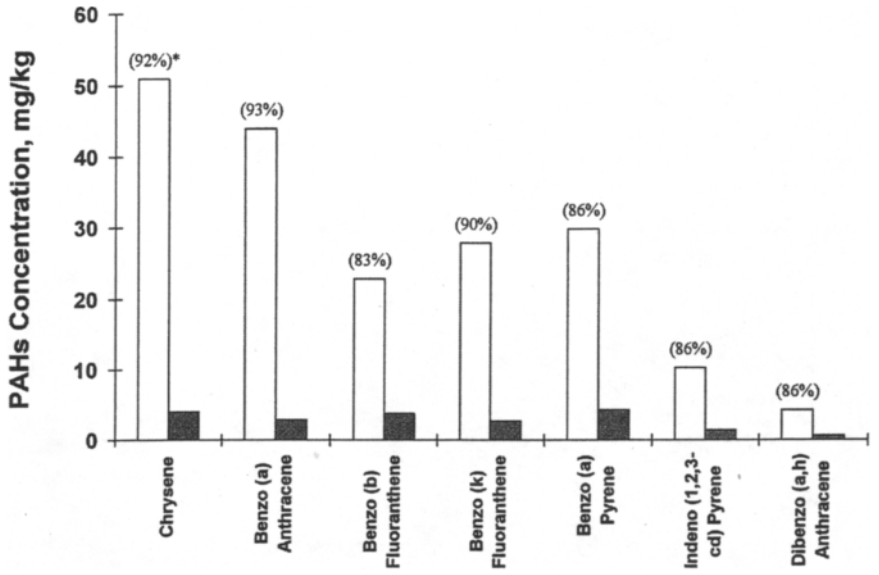

Fig. 3. Comparison of initial and final concentrations of carcinogenic PAHs during the MGP-REM process. □ Day 0, ■ day 40 (thickener). *Percent reduction is shown in parentheses.

process. The 86% reduction of benzo(a)pyrene is of special significance, since it is considered one of the most toxic and recalcitrant PAH moieties.

Conventional Bioremediation Test

The complete results of the Conventional Bioremediation Test are plotted in Fig. 4. PAH concentrations of samples taken at days 0, 13, and 35 are summarized in Table 5. Day 13 corresponds to the last sample taken during the reactor operation, and the day 35 sample was taken from the thickener. Table 5 shows that a 60% removal efficiency was achieved for total PAHs, and the noncarcinogenic and carcinogenic PAHs showed a reduction of 68 and 36%, respectively. Surprisingly, the two-ring PAHs showed a relatively lower removal efficiency of 31% compared to the three- and four-ring PAHs, which showed 76 and 69% reduction, respectively. The five-ring PAHs showed a very low removal of 22%, whereas the six-ring PAHs were not removed at all. Higher concentrations of PAHs were observed in the samples for day 35 compared to day 13, probably because of sampling and analytical variations. Figure 5 compares the carcinogenic PAH concentrations, before and after the conventional biological treatment. No reduction in concentration of benzo(a)pyrene was observed.

MGP-REM vs Conventional Bioremediation

The percent reductions in the total, noncarcinogenic, and carcinogenic PAHs for both the MGP-REM Process and conventional biological treatment are presented in Fig. 6. The comparison is made for day 40 and

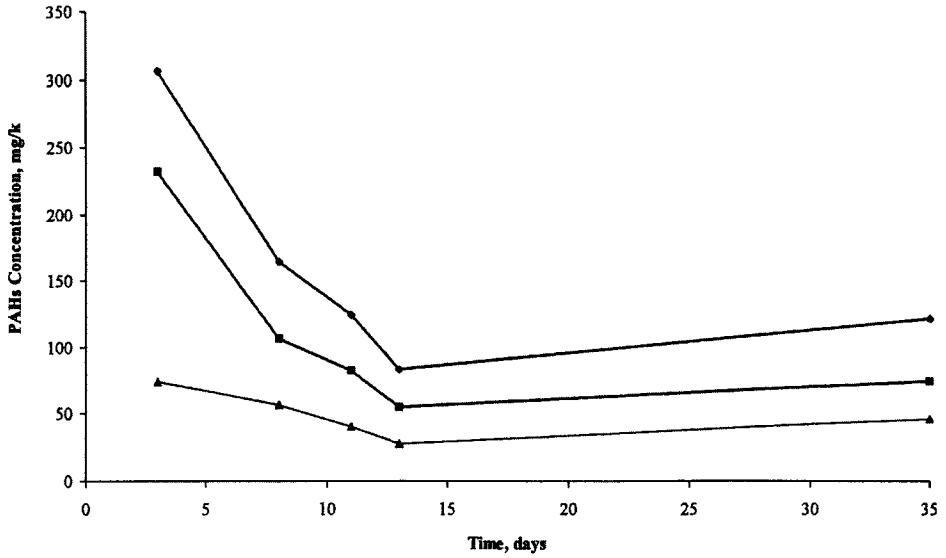

Fig. 4. Time plot of total, noncarcinogenic, and carcinogenic PAHs during the conventional bioremediation process. ◆ Total, ■ noncarcinogenic, ▲ carcinogenic.

Table 5
PAH Degradation Data for Conventional Biological Treatment

PAHs, mg/kg	Day 3	Day 13	Day 35*	% Degraded
Total	306	83	123	60
Noncarcinogenic	232	55	75	68
Carcinogenic	74	28	47	36
Individual Ring PAHs				
2-Rings	26	16	18	31
3-Rings	121	19	29	76
4-Rings	112	25	35	69
5-Rings	40	16	31	22
6-Rings	8	8	10	0

*Samples taken from thickener.

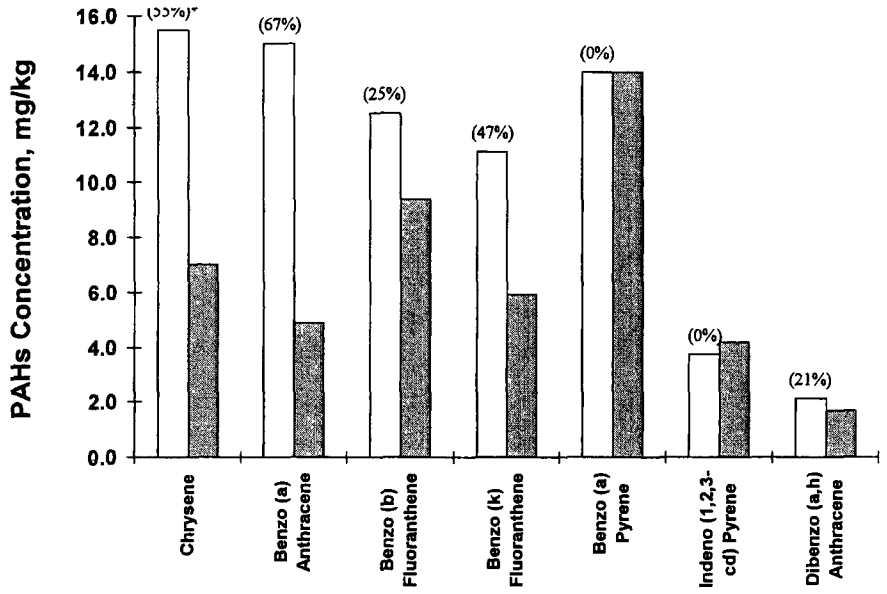

Fig. 5. Comparison of initial and final concentrations of carcinogenic PAHs during the conventional bioremediation process. □ Day 3, ■ day 35 (thickener). *Percent reduction is shown in parentheses.

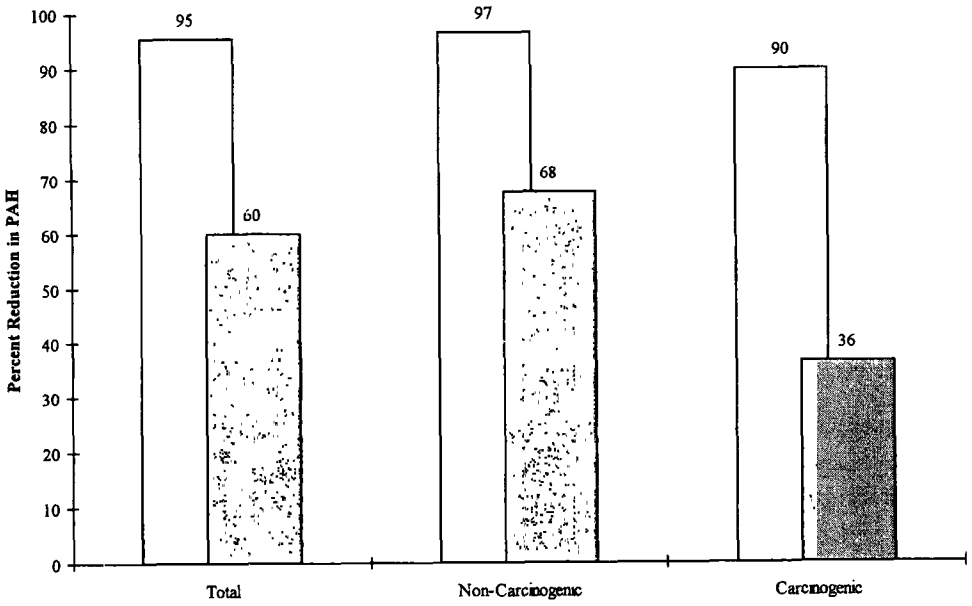

Fig. 6. Comparison of percent reductions in total, noncarcinogenic, and carcinogenic PAHs between the MGP-REM process and conventional bioremediation process. □ MGP-REM (day 40), ■ conventional bioremediation (day 35).

35 samples for the MGP-REM process and conventional biological treatment, respectively. The MGP-REM process reduced the total and noncarcinogenic by more than approx 30% over that achieved by the conventional biological treatment. More significant was the 54% higher reduction of the carcinogenic PAHs achieved by the MGP-REM process, compared to the conventional biological treatment, as shown earlier in Tables 4 and 5, respectively. The five- and six-ring PAHs were reduced 87 and 88%, respectively, for the MGP-REM process compared to the only 22 and 0% reduction observed for the conventional biological treatment. Also, more than 95% removal was observed for the two- to four-ring PAHs compared to much lower efficiencies obtained by conventional biological treatment. Thus, the MGP-REM process was clearly superior in the extent of removal of the PAHs from the soil. This is also indicated by the treatment end points of 53 and 123 mg/kg achieved for the total PAHs in the soil by the MGP-REM process and conventional biological treatment, respectively.

The pilot-scale study demonstrated that the MGP-REM process can effectively treat PAH-contaminated soils in slurry-phase bioremediation, and improves the extent (by 70%) of biodegradation of the PAHs (especially the carcinogenic) over the conventional biological treatment.

Microbiology Results

The results of the microbiological testing for the MGP-REM process and conventional biological treatment are shown in Fig. 7. The colony-forming units (CFU)/mL of slurry for the MGP-REM process were in excess of 10^6 through the entire treatment. The data for conventional biological treatment are available only up to day 8. The rest of the data were not generated because of improper sample storage. However, the CFU/mL were above 10^7 up to day 8, indicating a healthy bacterial population. A healthy bacterial population suggests that the chemical treatment did not annihilate the microorganisms during the MGP-REM process.

Toxicity Test Results

Soil samples were analyzed using the Microtox Toxicity Test to determine the effectiveness of the MGP-REM process to reduce the toxicity level in soil. The samples tested were soils before and after treatment. The toxicity results are presented in Table 6. The measure of toxicity used here is EC_{50}, meaning the percentage of soil slurry that will inhibit 50% of a known bacterial activity. Therefore, the lower the EC_{50} reading, the higher the toxicity in the soil. As seen from Table 6, the soil prior to testing was very toxic, and the MGP-REM process decreased the toxicity by more than 50 times.

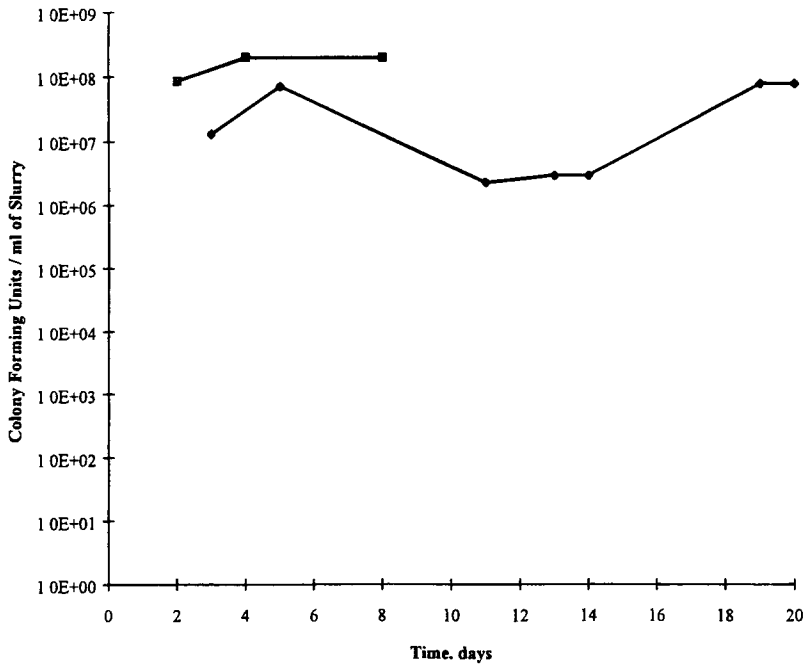

Fig. 7. Total heterotrophic counts in the slurry during the MGP-REM process and conventional bioremediation process. -◆- MGP-REM, -■- conventional bioremediation.

Table 6
Toxocity Test Results for the MGP-REM Process

Soil Sample Description	EC50	Interpretation
Before Treatment	0.212	Very toxic
After Treatment (day 20)	>10	Non toxic

Air-Monitoring Results

The compounds detected in the air emissions included BTEX, and naphthalene, acenaphthene, fluorene, and phenanthrene among the PAHs. These compounds together are termed as total hydrocarbons.

The highest emission rates of benzene and total hydrocarbons (BTEX + PAHs) in the exit airstream observed during the two test runs are shown in Table 7. These numbers are compared with the maximum emission rates permitted by the NJDEP. These results indicate that at any time during the pilot study, the emissions prior to and after the carbon treatment were significantly lower (by five orders) than the NJDEP limits of 0.05 and 0.5 lbs/h for benzene and total hydrocarbons (BTEX + PAHs), respectively.

Table 7
Maximum Emission Rates Obtained During the Pilot Study

Test Description	BTEX and PAHs, lbs/hr	Benzene, lbs/hr
MGP-REM Process	3.4×10^{-7}	Not detected
Conventional	8.1×10^{-6}	4.0×10^{-7}
NJDEP Limits	**0.5**	**0.05**

Table 8
Total Hydrocarbons (BTEX and PAHs) in the Soil During the Pilot Study

Test Description	Cumulative Air Emissions, lbs	Volatilization, %
MGP-REM Process	6.8×10^{-5}	0.003
Conventional Bioremediation	1.3×10^{-3}	0 8

The cumulative air emissions and percent volatilization of total hydrocarbons (BTEX + PAHs) for both the test runs are shown in Table 8. The percent volatilization of the total hydrocarbons was 0.003 and 0.8% for the MGP-REM process and the conventional bioremediation test, respectively. These results suggest that the air emissions from both test runs do not pose a health hazard, and therefore, this process requires minimal air pollution control and monitoring.

Process Economics

The economic evaluation for this pilot-scale soil remediation slurry-phase system was performed as an independent study (*7*). This evaluation was based on specific site characteristics, which were estimated for a soil volume of 71,500 cubic yards. Shorter treatment times were assumed for the MGP-REM process compared to Conventional Bioremediation. The treatment costs are summarized in Table 9.

SUMMARY OF THE RESULTS

- The pilot study demonstrated that the MGP-REM process can effectively treat MGP site soils and reduce the total PAHs concentration in the soil by 95%.
- The MGP-REM process reduced the toxicity levels present in the soil by approx 50 times, as indicated by the Microtox Toxicity Test.

Table 9
Treatment Costs for Slurry-Phase Bioremediation

Test Description	Cost in $/cubic yard
MGP-REM Process	100-135
Conventional Bioremediation	125

- The MGP-REM process is superior to conventional bioremediation in the extent (by approx 70%) of PAH removal from the soil.
- Microbiological data suggest that sufficient microbial levels were present during both the MGP-REM process and the conventional biological treatment.
- Negligible air emissions were detected during the slurry-phase operation, and off gas emissions from both processes were well in compliance with the NJDEP limits.
- Process economics study indicates that the MGP-REM process has an estimated cost of $100–135/cubic yard for remediation of soil.

Acknowledgments

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