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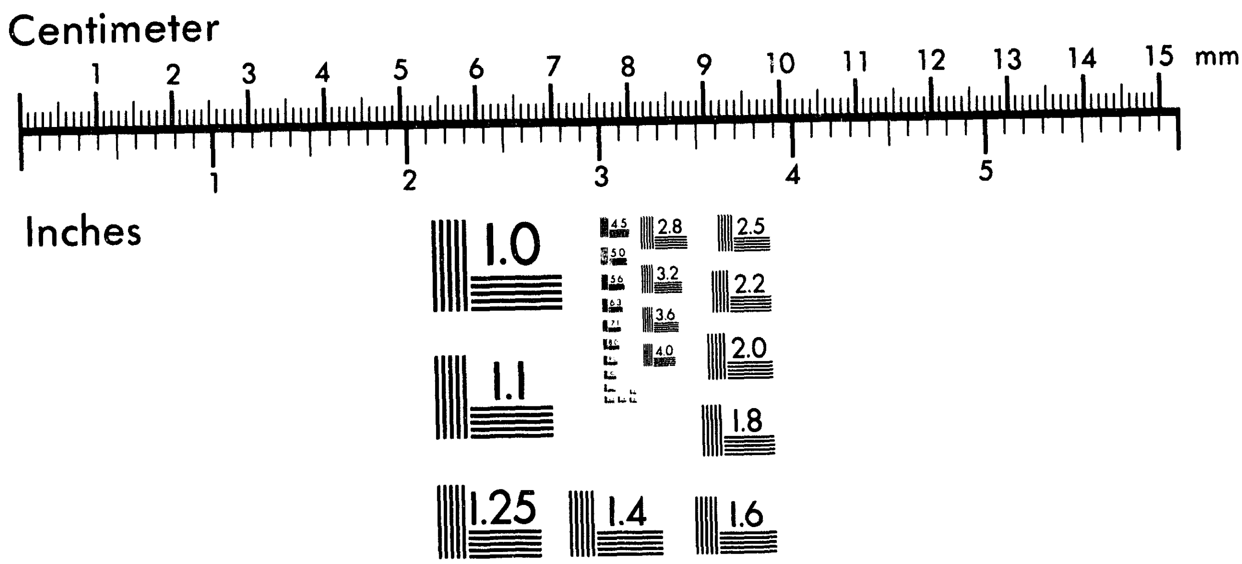

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MANUFACTURED GAS PLANT SITES: CHARACTERIZATION OF WASTES AND IGT's INNOVATIVE REMEDIATION ALTERNATIVES

by

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ABSTRACT

Manufactured gas plants (MGP) – often referred to as town gas plants – have existed in many parts of the world, including the United States, during the nineteenth and twentieth centuries. Consequently, many of these plants disposed of process wastes and less valuable by-products onsite, contaminated the soils with coal-tar wastes, light oils, naphthalene, etc. Polynuclear aromatic hydrocarbons (PAHs) are components of coal-tar wastes and other wastes that remain at many of these town gas sites. PAH-containing soils, as a result, represent the largest waste type at most MGP sites. Also, certain PAHs are recognized today as being potential animal and/or human carcinogens and, as such, represent an environmental hazard.

The Institute of Gas Technology (IGT) has developed and/or evaluated several techniques/processes to improve the biodegradation of PAHs present at MGP sites. As a result of extensive studies, IGT has successfully developed and demonstrated an integrated Chemical/Biological Treatment (CBT) process that is capable of enhancing the rate as well as the extent of PAH degradation. This process combines two complementary as well as powerful remedial techniques: 1) chemical pretreatment using Fenton's reagent and 2) a biological system using native aerobic microorganisms.

This paper presents the general characteristics of MGP sites and wastes and the innovative IGT processes at various stages of development and demonstration. This paper also discusses the IGT/GRI treatability protocol that can be used to determine the potential of bioremediation for any MGP site soil within a 2 to 3-month period.

INTRODUCTION

History of Manufactured Gas Plants

It has been estimated that more than 1500 manufactured gas plants (MGP) were in existence in the United States during the nineteenth century and the first half of the twentieth century.

The first manufactured gas (town gas) plant was built in England in 1812 by London and Westminster Chartered Gas, Light and Coke Company, although the first record of experimental manufactured gas production from coal dates back to seventeenth century England.[2] North America's first manufactured gas plants were built in Baltimore in 1816, in Boston in 1822, and in New York in 1825.[7] The early processes involved the "carbonization," or destructive distillation of bituminous coal at temperatures of 600° to 800°C in small cast iron retorts,[9] producing "retort gas" or "coal gas." Over the next hundred years, a variety of gas manufacturing processes were developed, with different fuels and processes used under the varying circumstances of geography, demography, transportation, and fuel availability.[5] These processes included coal carbonization, carburetted water gas, oil gas, coke oven gas, and product and blast furnace gas. Table 1 presents the approximate breakdown of gas-making operations of 87 sites evaluated under a Gas Research Institute (GRI) contract.[6]

Table 1. GENERAL CLASSIFICATION OF GAS-MAKING OPERATIONS

Process Type	Approximate Percentage of Total Number of Sites Evaluated
Coal Carbonization	30
Carburetted Water Gas	36
Oil Gas	7
Coal Carbonization/Carburetted Water Gas	17
Other	10

The types of manufactured gas may be divided into three major categories: coal gas, water gas, and oil gas. The coal gas processes, described above, yielded a gas high in hydrogen and methane with a heating value of 400 to 500 Btu/ft^3. The main by-products were coke, tar, and ammonia.[6] Water gas was produced by passing steam through hot coke, forming a gas of mainly hydrogen and carbon monoxide. "Gasification" referred to the heat treatment of coke or oil to produce gas, whereas "carbonization" referred to the use of coal. Water gas had a heating value of 300 Btu/ft^3 and was nonbituminous; therefore, "carburetted water gas" was often produced by the addition of gas produced from the cracking of coal. The "oil gas" had a heating value of greater than 1000 Btu/ft^3 before being added to the water gas. Generally, less coke, tar, and ammonia were produced via the water gas process than the coal gas process. The major by-products of oil gas were oil derivatives, tar, and naphthalene.

It is estimated that from 1880 to 1950, the gas plants produced approximately 15 trillion cubic feet of gas and the by-product of approximately 11 billion gallons of tar. Some of these tars were sold or consumed at the plant site, and the remainder were discarded along with other by-products such as coke and ammonia. Some of the wastes left behind at these town gas plant sites may be regulated under the Resource Conservation and Recovery Act (RCRA); the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA and Superfund); and the Superfund Amendment and Reauthorization Act (SARA). Because many manufactured gas plants were located near waterways to provide access to the large quantities of coal necessary for their processes, it is not surprising that aromatic hydrocarbon contamination of a number of streams and rivers has been traced back to town gas sites.[1] Contaminants have also caused problems when abandoned town gas plant sites have been sold for parkland or for construction.[1,8]

Manufactured Gas Plant Site and Soil Characteristics

Most of the MGP sites are 10 acres or less, and approximately 90% of the evaluated sites are located in an urban setting.[6] Figure 1 presents the general characteristics of MGP sites. It is also evident that most sites are located within 100 feet of a water body such as a river or lake and are generally adjacent to light industrial or commercial facilities. As a result, most of these sites are relatively flat or gently sloping. Also, due to the proximity to the water body, the groundwater depth at most sites is less than

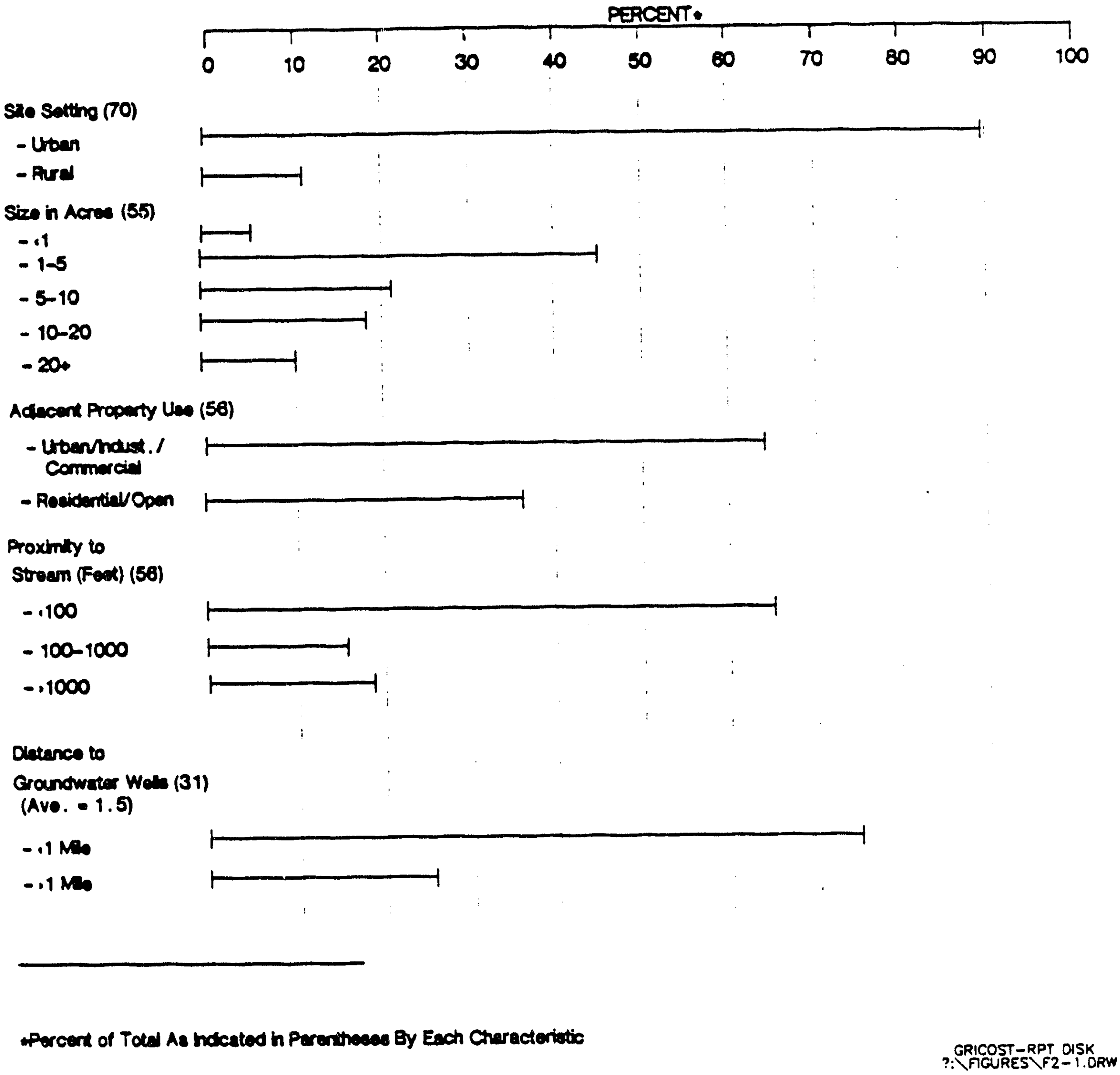

Figure 1. GENERAL CHARACTERISTICS OF MGP SITES[6]

20 feet, many within 10 feet. Consequently, many sites have several feet of fill at the surface. The fill material is generally some combination of gravel, sand, and clay. Peat has also been used at a few sites. Because of the use of fill material, most sites are generally permeable to depths of 30 to 50 feet from the surface.

Manufactured Gas Plant Waste Characteristics

Manufactured gas plants, as mentioned earlier, produced large quantities of tar and related by-products. Although there are some similarities among these sites, the sites often vary significantly in the specific types and quantities of wastes present, depending upon the types of processes used (coal, water, or oil gas) and the era in which the plant operated. Polynuclear aromatic hydrocarbons (PAHs) are components of all kinds of tars, and tars are a by-product of all of these plants. The physical and chemical characteristics of these tars vary, however, according to the process employed.[5,9] Oxide wastes from purifier boxes may contain ferrocyanide and varying amounts of arsenic, chromium, copper, lead, nickel, and zinc (all of which appear on the Environmental Protection Agency priority pollutants list). Lamp black, clinker, cinders, and ash may also be present.

The MGP wastes can be categorized into five major types:

- Free tars, oils, and lamp black
- Organic waste or tar-contaminated soils
- Organic waste or tar/oil-contaminated waters
- Purifier box (or spent oxide) wastes
- Mixed wastes and fills.

Specifically, the contaminants of interest present at MGP sites can also be divided into five categories: inorganics, metals, volatile aromatics, phenolics, and polynuclear aromatic hydrocarbons. Table 2 presents the types of contaminants under each category.

The organic-contaminated or PAH-containing soils represent the largest waste type at most sites. Some of the PAHs are suspected or potential carcinogens (Table 3) and, therefore, must be removed or treated to reduce

Table 2. CHEMICALS OF INTEREST AT MGP SITES

Inorganics	Metals	Volatile Aromatics	Phenolics	PAHs
Ammonia	Aluminum	Benzene	Phenol	Acenaphthene
Cyanide	Antimony	Ethyl Benzene	2-Methylphenol	Acenaphthylene
Nitrate	Arsenic	Toluene	4-Methylphenol	Anthracene
Sulfate	Barium	Total Xylenes	2,4-Dimethylphenol	Benzo(a)anthracene
Sulfide	Cadmium			Benzo(a)pyrene
Thiocyanates	Chromium			Benzo(b)fluoranthene
	Copper			Benzo(g,h,i)perylene
	Iron			Benzo(k)fluoranthene
	Lead			Chrysene
	Manganese			Dibenzo(a,h)anthracene
	Mercury			Dibenzofuran
	Nickel			Fluoranthene
	Selenium			Fluorene
	Silver			Naphthalene
	Vanadium			Phenanthrene
	Zinc			Pyrene
				2-Methylnaphthalene

Table 3. SUMMARY OF ANALYTES COMMONLY DETECTED AT MGP SITES

PAH – Potential Carcinogens	PAH – Noncarcinogens
Benzo(a)anthracene	Naphthalene
Benzo(a)pyrene	2-Methylnaphthalene
Benzo(b)fluoranthene	Acenaphthene
Benzo(g,h,i)perylene	Anthracene
Benzo(k)fluoranthene	Fluoranthene
Chrysene	Dibenzofurans
Dibenzo(a,h)anthracene	Fluorene
Indeno(1,2,3-cd)pyrene	Phenanthrene
	Pyrene

their concentrations so that they do not pose a risk to humans and/or animals. These risks may be due to the direct contact with soils (ingestion, dermal contact, inhalation, etc.) as well as direct and/or indirect effect associated with the groundwater and surface water.

SITE REMEDIATION EFFORTS AT IGT

The Institute of Gas Technology (IGT) has been developing processes to treat soils and water at former MGP sites that are contaminated with wastes such as PAHs, cyanides, and metals. Remediation technologies are also being developed for other gas industry wastes such as halogenated hydrocarbons, including polychlorinated biphenyls (PCBs) and perchloroethylene (PCE). This paper will discuss only two processes that are based on biological principles and are very suitable for PAH-contaminated soils.

PAH-Contaminated Soil Remediation

The research associated with the MGP site remediation at IGT has been primarily funded by the IGT Sustaining Membership Program (SMP – a consortium of gas companies) and GRI. The United States Environmental Protection Agency (U.S. EPA) and a few gas companies have also co-funded the process demonstration projects. The ultimate goal of this technology development program is to provide a cost-effective waste treatment technology alternative to conventional options that include containment, land filling, chemical fixation, soil washing, thermal treatment, conventional bioremediation, etc. The limitations of the conventional options include either limited/incomplete/insufficient waste degradation, considerable expense, or both. IGT's approach has been to identify the treatment-limiting steps and then develop approaches to overcome those limiting steps. As a result of extensive bench-scale studies conducted since 1987, IGT has developed and demonstrated two processes for PAH-contaminated soils that are a combination of biological treatment and physical/chemical treatment: 1) the integrated Chemical/Biological Treatment (CBT) or MGP-REM Process and 2) the Fluid-Extraction/Biological Degradation (FEBD) process.

MGP-REM or Chemical/Biological Treatment Process

The MGP-REM or Chemical/Biological Treatment (CBT) process combines two complementary remedial techniques: 1) chemical oxidation as the pretreatment for hard-to-degrade contaminants and 2) biological treatment using an aerobic biosystem. The CBT process uses mild chemical treatment with Fenton's reagent (H_2O_2 + Fe^{++}) that produces hydroxyl radicals that start the chain reaction with the organic contaminants, resulting in modification and degradation of organics to biodegradable and environmentally benign products. These products and other organics are later degraded in the biological step. Figure 2 shows the conceptual MGP-REM (or CBT) process scheme, and Figure 3 shows the potential advantage of this process over the conventional bioremediation. Results from bench-scale studies conducted with approximately 25 MGP soil samples show that the CBT process is capable of enhancing the rate as well as the extent of PAH degradation. The results indicate that when a soil is dominated by 4 to 6-ring PAHs, chemical treatment is performed as a pre-treatment step. However, when a soil is dominated by 2 to 3-ring PAHs, chemical treatment is used as a co-treatment step. In other words, when initial soil screening indicates that a soil contains 2 and 3-ring PAHs in significant amounts, biological treatment is recommended as the initial step to remove as many of these compounds as possible. This is then followed by chemical treatment using Fenton's reaction to reduce the remaining persistent PAHs. This was demonstrated using the highly contaminated soil, TGS-7, which was much different in terms of soil/waste matrix from the other soils that have been studied. TGS-7 soil was used in experiments involving Fenton's reaction applied after an initial period of aerobic biological treatment. Figure 4 shows that the initial period of aerobic biological treatment reduced total PAHs by 76% from 35,000 to about 8400 ppm. When Fenton's reaction was used as a post-treatment, PAH levels dropped by an additional 18% to 2200 ppm; and when coupled with a second round of biological treatment, the total PAH

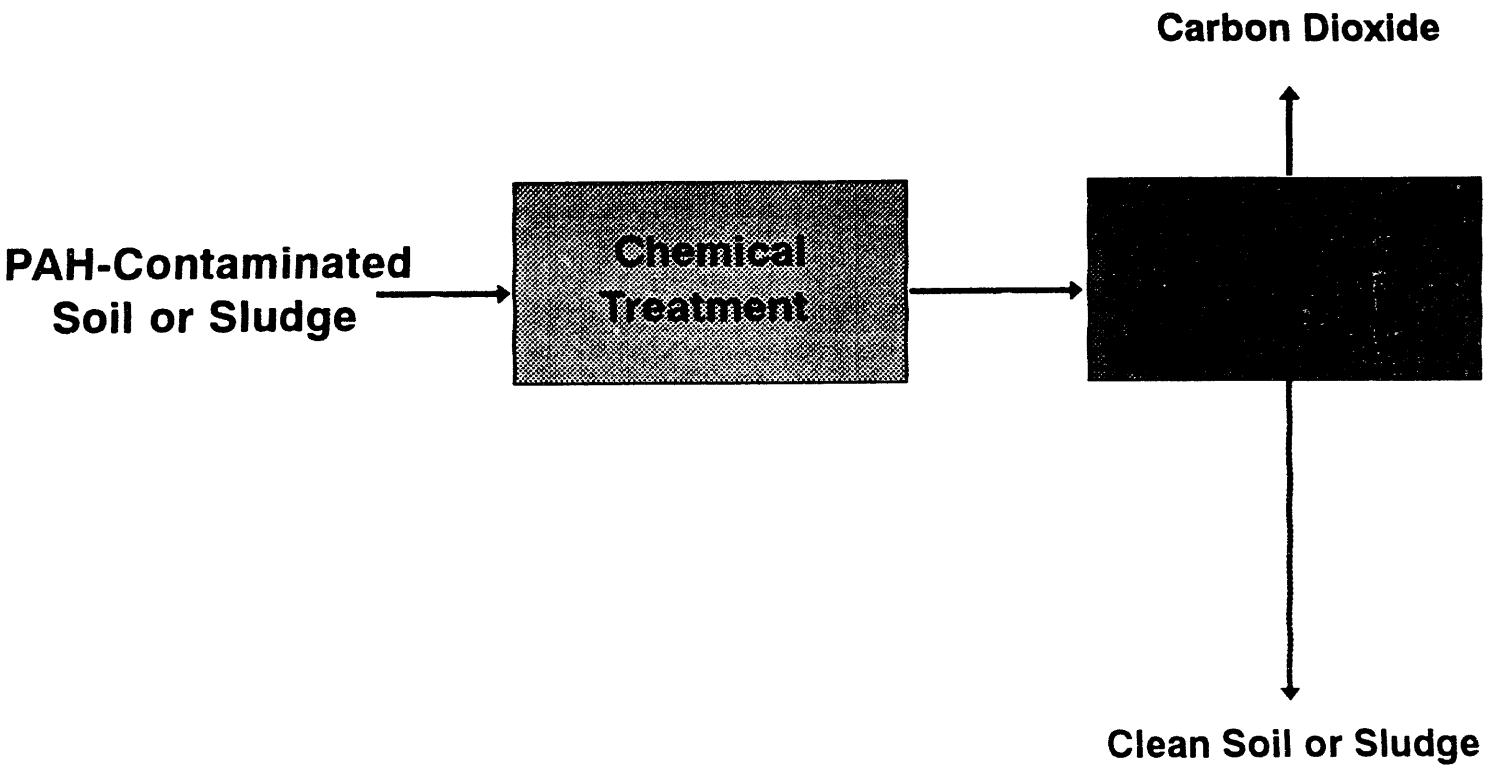

Figure 2. CHEMICAL/BIOLOGICAL TREATMENT (CBT)
PROCESS FOR PAH-CONTAMINATED SOILS

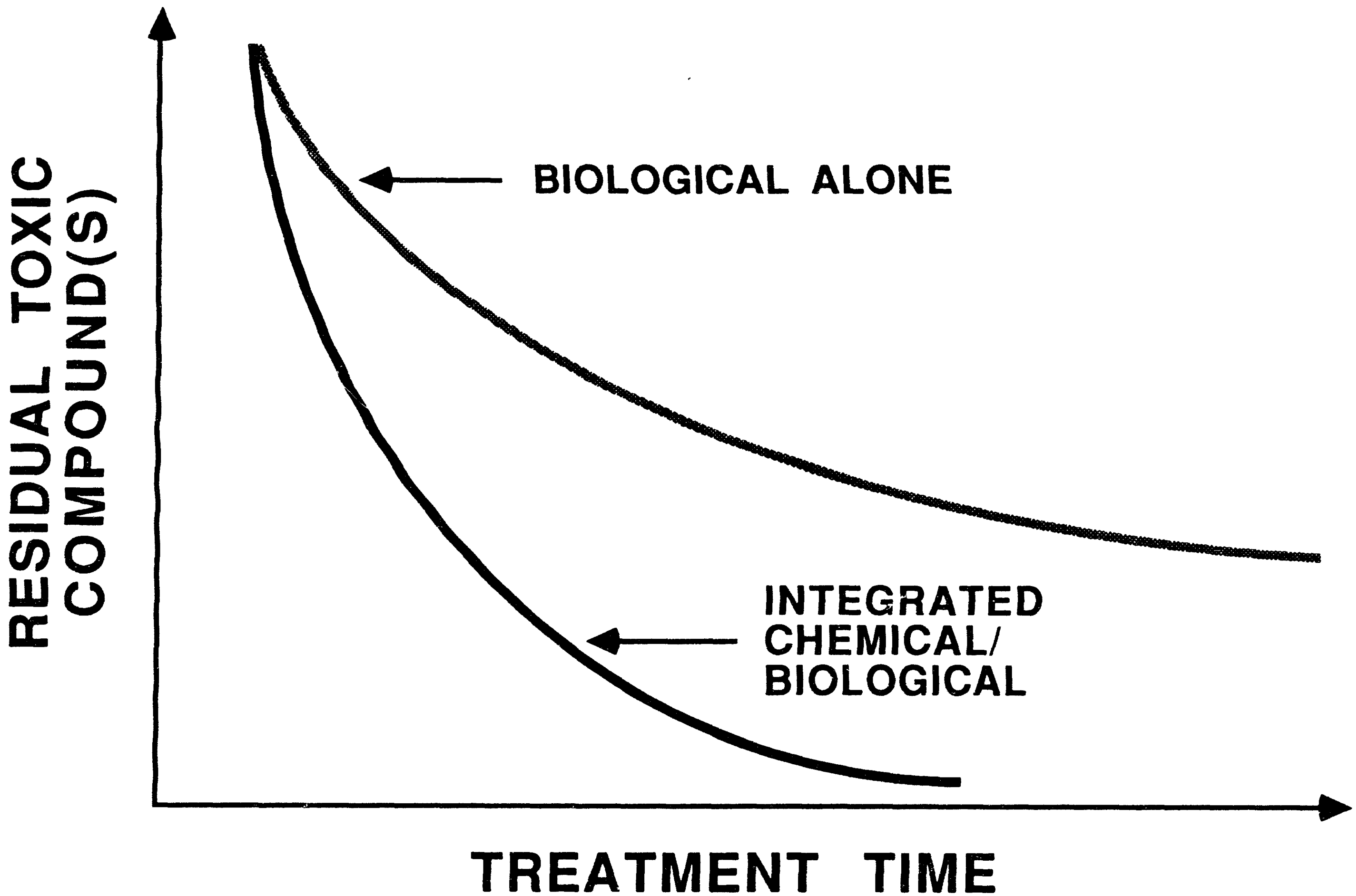

Figure 3. ADVANTAGES OF THE CBT PROCESS OVER CONVENTIONAL BIOREMEDIATION

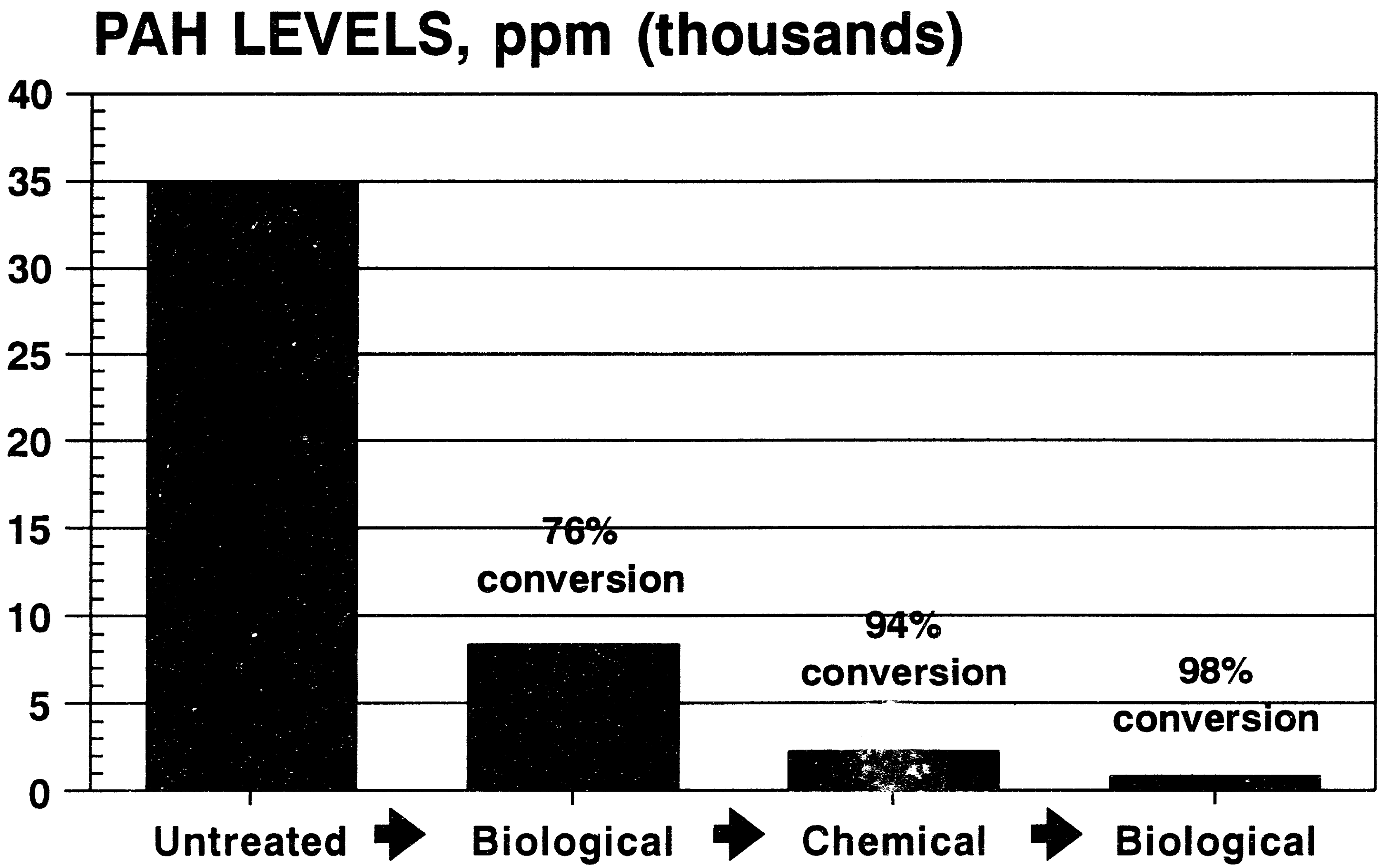

Figure 4. TOTAL PAHS IN TGS-7 SOIL AFTER SEQUENTIONAL BIOLOGICIAL-CHEMICAL-BIOLOGICAL TREATMENT

reduction approached 98%. Added cycles of combined chemical and biological treatments could be implemented as deemed necessary to reduce the end point further. The aerobic biological treatment alone could reduce PAHs to only just under 80% after a long treatment duration.

The merits of the MGP-REM (or CBT) process was verified in a field experiment conducted with the soils from an MGP site that is also a Superfund site in the state of Iowa.[4] Figure 5 presents the results of the field test conducted in the landfarming mode of the CBT process. In this figure, the residual PAH concentrations in the soil are compared with control plots that did not receive any nutrients, conventional bioremediation plots that received nutrients, and CBT treatment plots. Because this particular soil naturally contained nutrients, the control plots also exhibited some degradation of PAHs. Therefore, this figure is intended to show the PAH reductions over and above those observed in control plots. The integrated treatment reduced PAHs at a higher rate and to a greater extent than the conventional bioremediation. The treatment goals for this soil were met within the first 28 days when using the CBT process. Table 4 summarizes the preliminary economic evaluations for this site. Results show that this site can be cleaned at $60/cu yd or less when using the landfarming mode of soil treatment using the CBT process. Process optimization results as well as the initial PAH concentration and final treatment goals would affect the soil remediation costs for other sites.

Accelerated Site Treatability Protocol for the CBT Process

If site characterizations indicate that bioremediation might be appropriate for any part of the site, the soil treatability potential is evaluated by performing what is termed a treatability study. A treatability protocol, summarized in Figure 6, has been developed to determine the potential of conventional bioremediation as well as the CBT process within a 2 to 3-month period.[3] See Phase I of the three-phase protocol. This phase consists of the following five major steps:

- Soil Characterization – The composite soil samples are characterized for physical, chemical, microbiological, and geotechnical properties
- Abiotic Waste Extraction – The soil samples are extracted with Soxhlet extraction using EPA protocols and an organic solvent such as dichloromethane or a 1:1 mixture of acetone and hexane. This provides a measurement of the maximum amount of PAHs bound to the solid matrix.

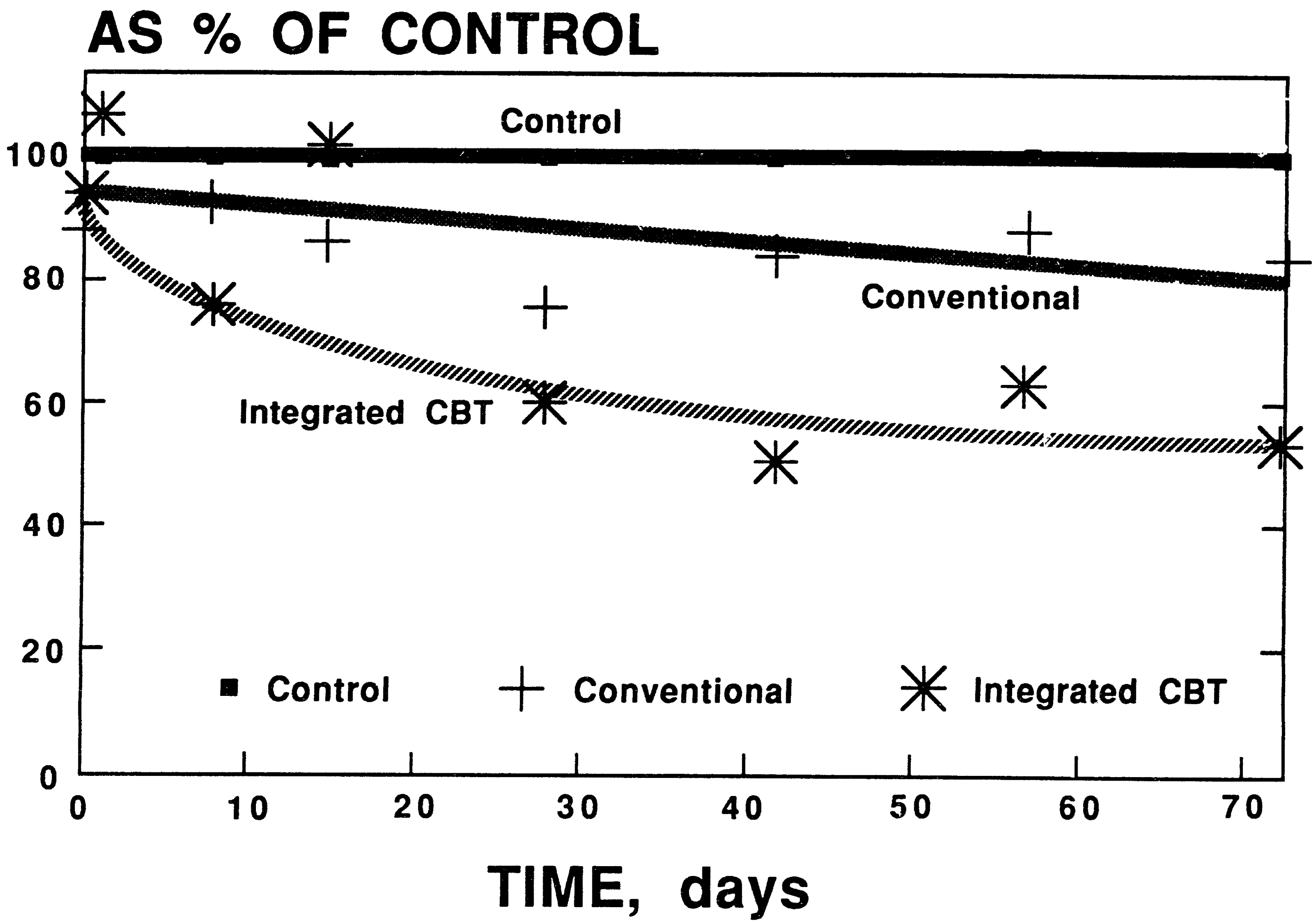

Figure 5. PAH CONCENTRATIONS IN MIDWEST GAS SOIL DURING FIELD TEST IN 1991

Table 4. PRELIMINARY ECONOMIC ANALYSIS: LANDFARMING AT IOWA SITE 1991*

Chemical Concentration, wt %	Treatment Cost, $ per cu yd
0.5	48
1.0	60
1.5	72
2.0	85
3.0	110

* A 1% chemical addition was the minimum dosage that resulted in the successful attainment of the treatment goals. The 2% and 3% additions also reached the goals.

- Abiotic Waste Desorption – Soil samples are gently mixed in an aqueous solution, and the periodic water samples are measured for PAHs desorbed from the solid matrix into the aqueous solution. This provides a measurement of bioavailability of solids-bound PAHs for microbial degradation.

- Liquid Culture Reactor Studies – Extracted PAHs are resolubilized in methanol and added to the bioreactor for biodegradation. The PAH concentration in the reactor should represent the PAHs in the contaminated soil in a solids slurry system. The bioreactor is inoculated with a high concentration of PAH-degrading organisms. This gives a measurement of the extent to which PAHs present in a particular soil can be biodegraded.

- Soil-Slurry Reactor Studies – Contaminated soils at 10% to 30% solids concentrations are treated in a variety of conditions representing controls, conventional bioremediation, and the CBT process for 4 to 8 weeks. Periodic samples are analyzed for PAHs bound to the solid matrix as well as present in the aqueous phase to determine the rate as well as the extent of PAH degradation in each bioreactor. The results of these investigations provide an indication of how effective a bioremediation process is likely to be for a given site.

The results of Phase I of the treatability protocol can be used to assess the potential of bioremediation. If the results are encouraging, Phase II is initiated where the process is optimized either in soil-slurry systems, if the entire site soils are to be treated in such a system, or in soil pans if the site soils are to be treated in the landfarming mode.

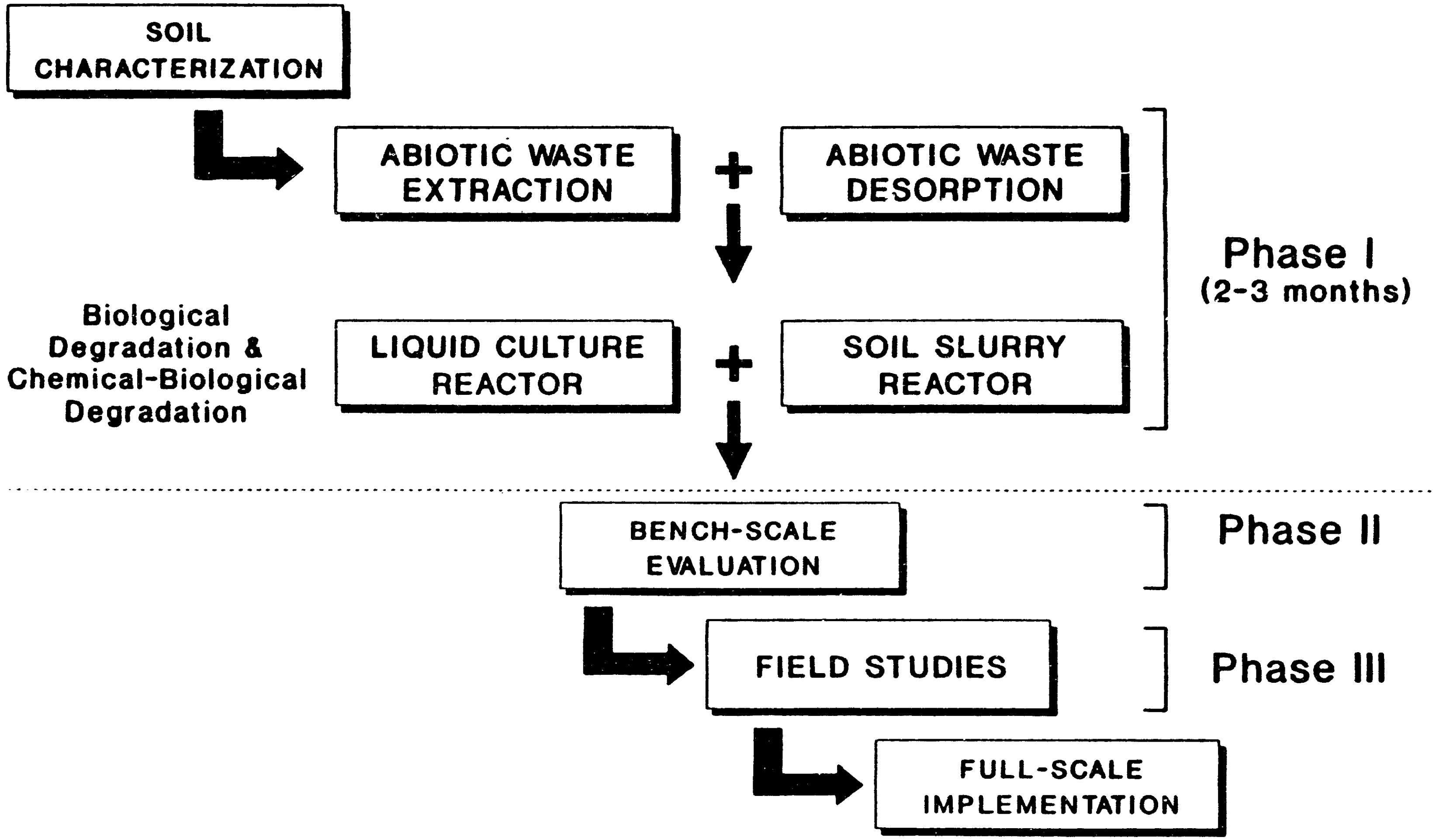

Figure 6. IGT/GRI TREATABILITY PROTOCOL FOR EFFECTIVE REMEDIATION OF MGP SOILS

Phase III is the field-scale demonstration prior to the full-scale implementation.

Fluid-Extraction/Biological-Degradation Process

The Fluid Extraction/Biological-Degradation (FEBD) process is a three-step process for the effective remediation of organic contaminants from soil. (See Figure 7.) It combines three distinct technologies: 1) fluid extraction, which removes organics from contaminated solids; 2) separation, which transfers pollutants from the extract to a biologically compatible solvent; and 3) biological treatment, which degrades organic pollutants to innocuous end products.

Contaminants must first be extracted from the soil. Excavated soils are placed in a pressure vessel and extracted with a recirculated stream of supercritical or near supercritical carbon dioxide. An extraction co-solvent such as methanol can improve the removal of many contaminants. Figure 8 presents the results of extraction for three different soils.

Following extraction, organic contaminants are collected in a biologically compatible separation solvent. Clean extraction solvent is recycled to the extraction stage. The separation solvent containing the contaminants is sent to the final stage of the process, where bacteria are used to degrade the waste to carbon dioxide and water.

Biodegradation is achieved in above-ground aerobic bioreactors, using mixtures of bacterial cultures capable of degrading the contaminants. Selection of cultures is based on site characteristics. For example, if a site is contaminated mainly with polynuclear aromatic hydrocarbons, such as naphthalene, phenanthrene, fluorene, pyrene, and others, cultures able to grow at the expenses of these hydrocarbons or capable of degrading these and other hydrocarbons are used in the biological treatment stage. Results of one of these biodegradation studies are shown in Figure 9.

The FEBD process is especially suitable for those soils that contain high levels of metals or cyanides where in-situ biodegradation in the presence of these compounds would not be feasible. The CBT process treatability protocol can be modified to evaluate the FEBD process as well.

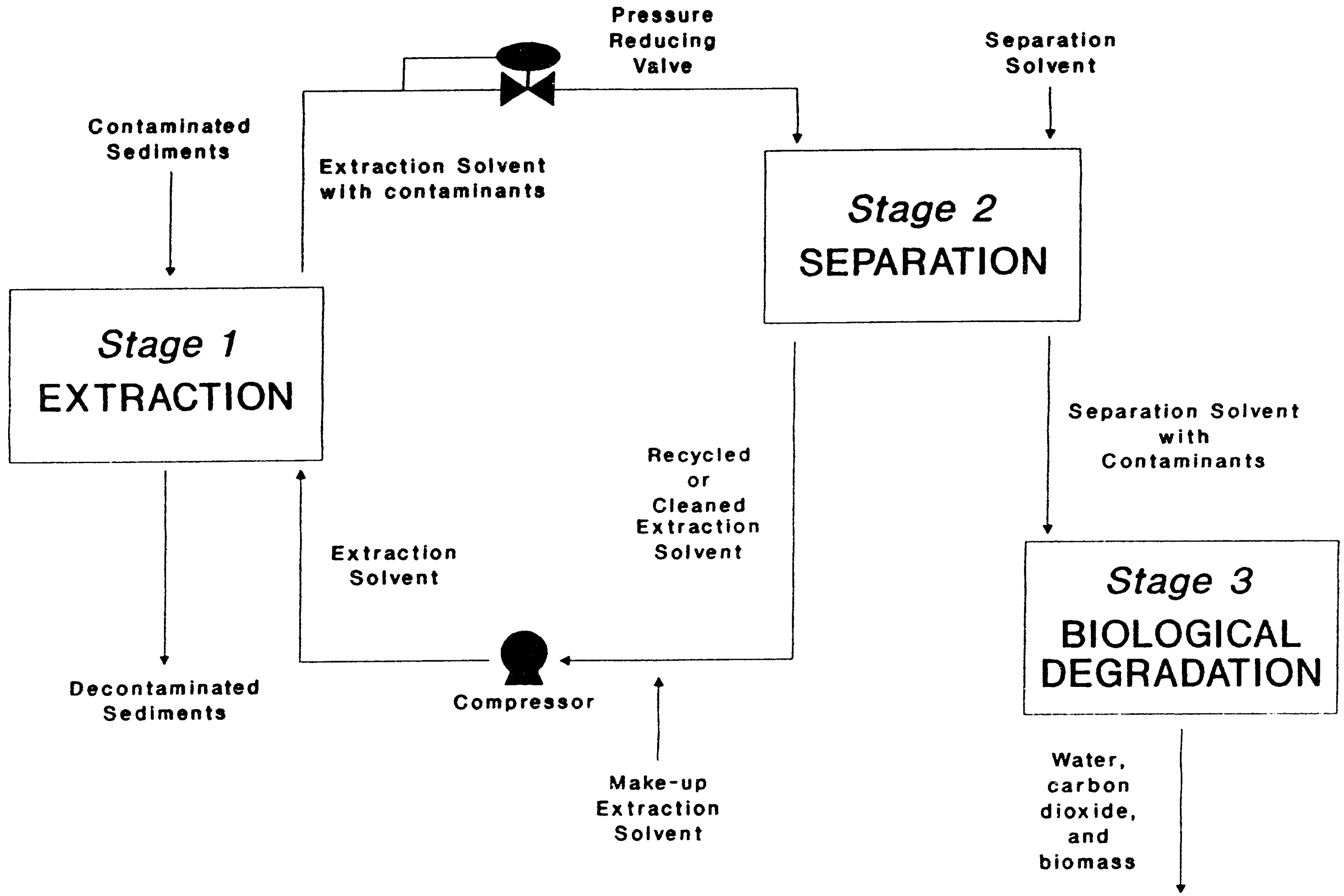

Figure 7. OVERVIEW OF THE FLUID-EXTRACTION/BIOLOGICAL-DEGRADATION PROCESS

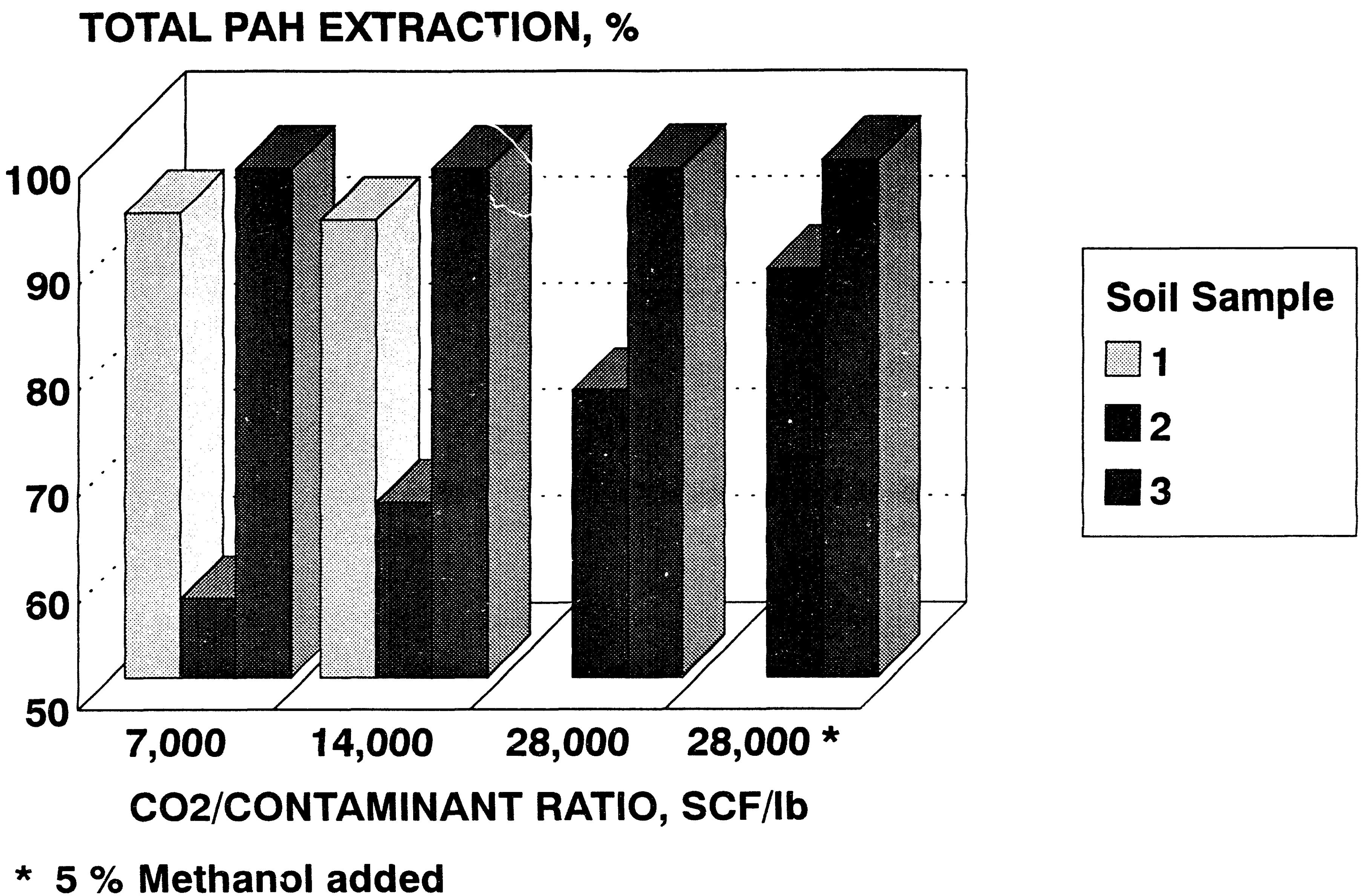

Figure 8. SUPERCRITICAL FLUID EXTRACTION OF PAHs FROM SOIL AT A PRESSURE OF 2000 psig

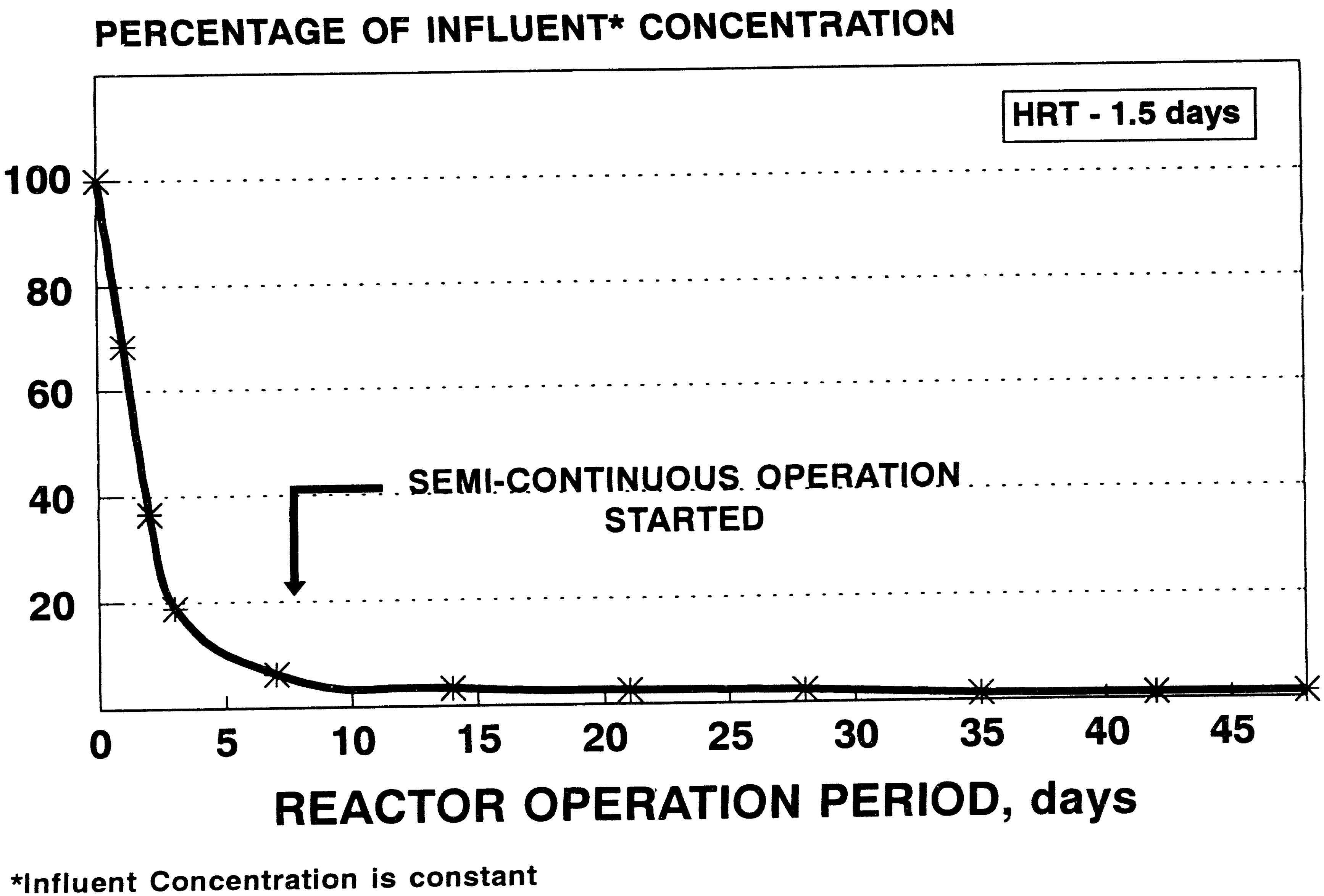

Figure 9. PAH DEGRADATION IN BIOREACTORS SOIL

SUMMARY

The manufactured gas plant sites are nonhomogeneous in soil and waste types and concentrations of contaminants. PAH-contaminated soils represent the largest fraction of the contamination at the MGP sites. Studies conducted by IGT show that –

- Bioremediation is effective in removing PAHs from MGP soils.
- Integrated Chemical/Biological Treatment improves the rate as well as the extent of PAH removal.
- MGP soils can be effectively cleaned in the landfarming mode of the CBT process.
- Soils with high sand content are easier to clean. Also, soil-slurry reactors are an effective and efficient system for contaminated soil bioremediation.
- Integrated Chemical/Biological Treatment is also effective for soils with high silts and clay contents.
- Fluid-Extraction/Biological-Degradation is effective for soils that contain high levels of metals, cyanides, and/or PAHs.

Finally, IGT also continues to develop, optimize, and demonstrate innovative and accelerated contaminated-soil treatment technologies. A field evaluation of the integrated treatment in the soil-slurry treatment system is being planned.

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