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PROJECT SUMMARY

REPORT ON DECONTAMINATION OF PCB-BEARING SEDIMENTS

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by

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PROJECT SUMMARY

Introduction:

Polychlorinated biphenyls (PCBs) have in the past been widely used as a dielectric fluid in transformers and capacitors as well as in hydraulic and heat-transfer fluid systems because of their stability and heat resistance. During the 50 years that PCBs were manufactured and used in this country, an estimated 400 million pounds of these chemicals entered the environment. Because of the broad use of PCBs (ranging from transformer dielectric oils to carbonless paper production), they are widespread in the modern environment, especially the aqueous environment.

Although PCBs are a suspected carcinogen, their acute toxicity is considered to be non-to slightly toxic by the LD50 Method. A more significant health impact has been linked to the incomplete combustion (burning) of PCBs. Under certain circumstances, oxidation of PCBs form dioxins and furans, most toxic of all man-made substances. While PCBs have long been known to be toxic, they have only recently been acknowledged to be a general threat to the environment. The characteristics that make PCBs such a problem is their stability and therefore, persistence in the environment. These chemicals have been found in measurable concentrations in waterways and sediments through the world and are widely spread contaminants of fish and wildlife resources. The PCBs contamination results from an era when industrial wastes were disposed of by flushing them directly into waterways, local sewage plants or landfills.

The PCB contamination problems in New Bedford, Massachusetts (EPA Region I), the Hudson River in New York (EPA Region II), and in Waukegan, Illinois (EPA Region V) are reported to be the worst in the United States in terms of concentration and total quantity of PCBs. It is estimated that 290,000 kg of PCBs are contaminating 382,000 M^3(500,000 yd^3) of sediments of the Hudson River. During the 70's approximately 907,000 kg of PCBs were used in the New Bedford area annually, of which an estimated 45,500 kg were improperly disposed. Also, there are numerous industrial lagoons contaminated with large quantities of PCBs. For example, EPA Region III reports three sites in Pennsylvania and two in West Virginia where over 3200 2447 m^3 yd^3 of soil/sediments are contaminated with PCBs. The PCBs contamination problems pose threats to both drinking water and the fishing industry.

The only available proven technology is dredging and expensive incineration. Land disposal of the untreated sediments has legal restrictions. Biodegradation is a possibility, but sufficient information does not exist to design and operate such a system. There is little experience in the application of encapsulation technology to PCB-contaminated sediments.

Although a great amount of work has been done by many research groups in the area of PCB-contaminated liquids, relatively little effort has been directed toward PCB-contaminated sediments and sludges. The EPA Regional and Program

Offices are being asked to comment on the technical and economic feasibility of chemical/ biological processes for clean-up of these sediments and sludges. These Offices do not have adequate data to recommend any of a number of processes proposed or being tested/evaluated for the decontamination of sediments containing PCBs.

Assessment of Processes

Because there is little known about the application of chemical and biological processes to the decontamination of PCBs in sediments, Research Triangle Institute (RTI) was engaged by EPA to undertake a study to identify the most technically feasible processes that have been proposed by research concerns for the removal of PCBs from sediments; to identify their extent of development, effectiveness, limitations and probable costs; and to determine needs for their further development. The study involved three phases: identification of the most promising processes and their further development needs; evaluation of the unit operations involved in the processes against engineering, health, and environmental criteria for further testing and evaluation; and definitive assessment of the recommended treatment processes using pilot systems and contaminated sediments.

The first phase involved four steps: data acquisition, screening and selection of most technically feasible processes, development of criteria for process assessment, and process assessment. Under step one, three major sources of data were: EPA's file of proposals and correspondence concerning problems of PCB contamination and possible approaches to alternative solutions; the open literature; and direct contacts with proponents of treatment technologies. In step two, the processes were categorized according to their generic technology so that their potential performance could be judged appropriately. Processes with undesirable aspects, for example lack of tolerance for water, were rejected from further assessment. Criteria for assessment, step three, were chosen which relate to a broad range of principles of operation of diverse applied technologies, yet can be used effectively in comparing one treatment process with another. Additional factors, specific to a technology, were included to help portray the inherent strengths and limitations of a process. The seven criteria used and three additional factors were: estimated residual PCB; available capacity; conditions/limitations; concentration range handled; status of development; test and evaluation data needs; estimated cost; unit operations; RCRA waste generated; and estimated destruction/detoxification/removal efficiency. In the final step, the processes were assessed by characterization and ranking. Characterization provided for objective comparison of the processes. Ranking provided a subjective comparison of the processes based on the seven criteria.

In the first phase eleven emerging alternative treatments of the sixty four processes considered for PCB contaminated sediments were compared and ranked. Eight candidate treatment processes showed potential as alternatives to chemical waste landfill and to incineration. Some had been tested on soils; but none were tested specifically on PCB contaminated sediments. Sediments of concern differ from soils in several properties that influence the performance of unit operations involved in the treatment processes.

The second phase built upon the first phase of the assessment so that EPA may have more complete information before evaluating any technology in the field. This second phase involved three steps: consulting with the treatment process developers, technical assessment of the process, and the selection of three of the processes for thorough test and evaluation. Consultations included visits to the developers' facilities where further information was developed. The most recent performance data were reviewed. The availability of the system was determined. The visits included a checklist of needed information and criteria for assessment of the processes. The Technical assessment was based upon the projection of the performance and cost of a large-scale treatment system of sufficient capacity to treat an estimated 380,000m^3 of PCB-contaminated Hudson River sediments in 2.5 years. Specific sample data from Hudson River sediments were used to guide the projection of operating conditions required for treatment by each process assessed. The processes were compared and rated using the results of the assessment. Based on composite ratings, three processes showing the highest rating were recommended for test and evaluation.

The objective of the proposed third phase is to provide EPA with a defensible thorough test and evaluation of the three alternative treatments selected in Phase 2. In carrying out this phase, EPA will arrange to have PCB-contaminated sediments treated in pilot-scale processing systems selected in Phase 2. The pilot tests will evaluate performance under field conditions, and will be supported by laboratory tests. Confirmation of treatment process effectiveness will make these processes very viable and cost-effective methods of treating these hazardous wastes.

The following processes were studied by RTI on Phase 2 of the study:

B.E.S.T.

The Basic Extraction Sludge Treatment (B.E.S.T.) process has been developed by the Resources Conservation Co. (RCC), 3101 N.E. Northup Way, Belleview, WA 98004. The process uses a solvent having an inverse critica solution point in water to remove water and oily material from solid matter. It has been applied to clean-up PCB-contaminated oily sludges at a CERCLA site (General Refining Site, Savannah, Georgia).

Ultrasonics/Hydrogen - Ozone/UV Technology

The process is based upon simultaneous extraction and treatment of a sediment slurry with ultrasound (above 20KHz) added to increase rates of dissolution of the PCB contaminants and reduce coalescence of bubbles of gs reactants. The treatment is achieved by either ozone/ultraviolet irradiation or hydrogen/ultraviolet irradiation. The sediments are fed as a slurry containing about 20 wt. percent solids into a mixing tank where predetermined amounts of detergent and sodium hydroxide are added. The conditioned mix is pumped to the reactor where the solids are maintained in suspension while the mixture is exposed to ultraviolet irradiation and ozone (or hydrogen) is added. During this treatment, microscopic turbulence is produced through ultrasonics. The treated slurry is

fed into a cyclone where the solids are removed, sampled, and tested to certify them for discharge. The separated water is neutralized and also tested before discharge.

Bio-Clean Naturally-Adapted Microbial

The Bio-Clean Naturally-Adapted Microbial process has been developed by Bio-Clean, Inc. Bio-Clean is a company engaged in developing process systems to clean-up, remove or destroy hazardous chemicals in the environment. The process utilizes Arthrobacteria sp and/or other naturally-adapted microbes to destroy PCBs (and related organics) under aerobic conditions.

KPEG with DMSO

Nucleophilic substitution with the KPEG process and the Galson Research Corp. version (Terraclean-Cl process) was looked at as a means of decontaming PCB-bearing sediments. The potassium polyethylene glycolate (KPEG) process has two potential applications in the treatment of PCB-contaminated sediments: The treatment of the sediments themselves, or the treatment of concentrated PCBs resulting from extraction processes. The former is assessed in terms of the Galson Modified KPEG process, that is with dimethyl sulfoxide (DMSO). The latter application would require treatment of a relatively concentrated solution of PCBs in a non-aqueous solvent (triethylamine, kerosene, etc.).

CFS Propane Extraction

The CFS Propane Extraction Process is a technology available from C. F. Systems Corporation, 25 Acorn Park, Cambridge, Massachusetts 02140. The company is a subsidiary of Arthur D. Little. As applied to PCB-contaminated sediments, the process uses propane at ambient temperature and 1378 kPa (200 lb/in^2) to extract PCBs along with other oily organics from a water slurry of the sediment. The treated slurry is discharged after separation from the liquid propane which contains dissolved contaminant. The propane solution is fed to a separator where the solvent is removed by vaporization and recycled. The contaminants are drawn off as a concentrate for final treatment. The process has been tested for PCB-containing refinery sludge. The PCB content of the solids component of the sludge was reduced to 5 ppm.

Modar Supercritical Water - Oxidation

The process has been developed by MODAR, Inc., 3200 Wilcrest, Suite 220, Houston, Texas 77042. The process utilizes water above critical conditions (374°C and 22.1 MPa) to increase the solubility of organic materials and oxygen and effect a rapid oxidation, destroying organic contaminants. It has been applied to destroy PCBs in oils, and to decontaminate dioxin tainted soil. The company has a laboratory test unit and a skid-mounted pilot test unit having a nominal organic material flow capacity of 190 Liters/day. This unit has bee operated at MODAR's research facility in Natick, Massachusetts and at the CECOS International Niagara Falls site.

In Situ Vitrification

In Situ Vitrification was previously discussed as a process developed to treat radionuclide-contaminated wastes, and subsequently tested for possible adaptation to the treatment of PCB-contaminated soils. Submerged sediments would be dredged before treatment. The process stabilizes contaminated soils by melton into a durable glass and crystalline form. Four electrodes are inserted into the sediments in a square array. A path for electric current is made by placing a mixture of graphite and glass frit between the electrodes. Dissipation of power through the starter materials creates temperatures high enough to melt a layer of sediment, which establishes a conductive path. The molten zone grown downward through the contaminated soil At the high temperatures created (<1700°C) organic materials pyrolyze, diffuse to the surface, and combust. Off-gases are collected, monitored, and treated.

Solvent Extraction Process

In a separate study, scientists at the New York University's Department of Applied Science have been carrying on a three year EPA supported investigational program on the development and evaluation of a low energy process technology for the solvent extraction and subsequent chemical destruction of PCBs from contaminated sediments and sludges. This is also one of the processes which was assessed by RTI in Phase 2. This program involves experimental studies on potentially more cost-effective PCB disposal alternatives to currently accepted practices. The research activities during the first year of this program comprised the investigation of suitable solvent extraction and supporting equipment, identification of candidate solvents for extraction and concurrently developed application and verification of analytical methodology for quantitative determination of PCBs in contaminated sediments. Exploratory experiments were also carried out on the extraction of PCBs from contaminated sediments obtained from Waukegan Harbor, Illinois.

The concept of using kerosene as an extraction solvent for removing PCBs from sludges and sediments was based on two factors: 1) the low cost of kerosene and 2) some work conducted on extraction of PCBs from soils (M. B. Saunders at Oak Ridge National Laboratory, 1985). While the cost factor is a driving force in any development, it alone cannot overcome technical impracticalities. It became quite evident early in this study that the presence of large quantities of water in the contaminated samples presented an insurmountable barrier to the use of kerosene in this application. A new approach to this difficult problem was needed and is herein presented.

The first step of the process takes advantage of the extremely low solubility of PCBs in water. In a typical PCB contaminated sediment or sludge composed primarily of water with generally 20% total solids, virtually all of the PCBs are associated with the sediment. Thus, the first processing step is a physical separation of water and solids. In the second step, the PCB contaminated oil is disociated from the sediment substrate. This is accomplished by a multistage counter-current leaching with a hydrophyllic solvent. The third step is a stripping operation in which the PCB-containing stream from above is contacted in a liquid-liquid extractor with a hydrophobic solvent and additional water. The two streams which leave this step are the PCBs concentrated in stripping

solvent which proceeds to appropriate methods for final destruction, and the hydrophyllic solvent/water mixture containing trace PCBs. The solvent/ water mixture goes next to a distillation column in which the solvent is separated and returned to the leaching process. The water contaminated with trace amounts of PCBs is recycled to the front of the stripping process to close the cycle.

Conclusions

Various experimental and supporting activities were carried out during the first year of the EPA-supported research in order to develop an adequate data base for achieving an effective low energy process for the extraction of PCBs from contaminated sediments and sludges. Achievements from these investigations are summarized as follows:

1. Selection of extraction and supporting equipment for a specific extraction.
2. Identification of candidate solvent systems for extraction.
3. Development of an appropriate analytical methodology for the determination of PCBs in contaminated sediments and sludges.
4. Development of an innovative process scheme for the extraction of PCBs from sediments and sludges.

Emerging treatment processes for decontamination of sediments containing PCBs that show potential as alternatives to incinceration and chemical waste landfill have been identified in Phase One of an assessment study. Eleven alternative treatments were compared and ranked using technical performance, status of development, test and evaluation data needs, and cost as factors. The first eight processes show potential for reduction of PCB concentrations to the desired background levels (1-5ppm) or less, with minimum environmental impacts and low to moderate cost. The sediments must be dredged for application of these treatments. Based on the weighted ratings of Phase One, eleven processes ranked as follows from highest to lowest: KPEG, LARC, Acurex, Bio-Clean, Modar-Supercritical Water, Advanced Electric Reactor, Vitrification, OHM Extraction, Soilex, Composting, and Sybron Bi-Chem 1006.

At the start of the final assessment study before field tests, some former developers indicated their processes should not be considered and some new processes became available. Thus, in the next assessment study-Phase Two, eight emerging treatment processes for decontamination of PCB-contaminated sediments were evaluated as candidates for thorough test and evaluation using a test system of sufficient size to provide performance, cost, and scale-up data for a large commercial plant. The processes assessed and listed in relative desirability of test and evaluation include: (1) Basic Extraction Sludge Treatment (B.E.S.T.) developed by Resources Conservation Co.; (2) UV/Ozone or Hydrogen/Ultrasonics Technology of Ozonic Technology, Inc.; (3) Bio-Clean Naturally-Adapted Microbial Process of Bio-Clean, Inc.; (4) KPEG (Galson) Process modified by Galson Research Corp.; (5) Low Energy-Acetone-Kerosene Extraction Process developed by the Applied Science Dept. of New York University; (6) Modar Supercritical Water Oxidation Process of Modar, Inc.; (7) CFS Propane Extraction Process of C. F. Systems Corp.; and (8) In-Situ Vitrification Process by Battelle Pacific Northwest Research Laboratories.

Recommendations

While all the processes except In Situ Vitrification appear to merit further development for this application, those three with the highest comparative ratings are recommended for EPA-supported thorough test and evaluation. These are the Basic Extraction Sludge Treatment, UV/Ozone or Hydrogen/Ultrasonics Technology, and Bio-Clean Naturally-Adapted Microbe processes.

There is, in an evaluation of processes such as this, much uncertainty. Additional research of the other processes is very important to fill in the data gaps. The other processes, for example, may be more cost effective on a smaller scale than what the study assumed or with other unit processes. The results of the EPA funded study at the New York University have led to a novel approach to treatment of PCB-contaminated sediments and sludges. It is recommended that a study is needed to model, engineer and otherwise fully characterize this process so that its full potential might be realized.

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NOTICE

This report has been reviewed by the Hazardous Waste Engineering Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. It's products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local government and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes an in-depth assessment of emerging alternative treatment processes that show potential for decontaminating polychlorinated biphenyl (PCB)-contaminated sediments and the selection of processes for thorough test and evaluation. The comparison of these processes as to their technical performance, the availability of a test system, the test and evaluation effort required, the projected time to commercial availability, and the probable cost of their application should be useful to EPA Regional Offices, to those concerned with developing hazardous waste treatment regulations, and to those interested in the development of new and innovative treatments.

For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser, Director
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ABSTRACT

In recent years, polychlorinated biphenyls (PCBs) have been discovered as contaminents in sediments throughout the country. Conventional and emerging waste management methods have not been evaluated for decontamination of PCB-bearing sediments.

The EPA has initiated a research program to identify chemical/biological methods as alternatives to incineration and to chemical land disposal for clean-up of PCB contaminated sediments. The overall objective of the program is to identify, validate, and demonstrate effective and economical chemical/biological processes for removal/destruction of PCBs in sediments. This report summarizes research progress on chemical/biological methods development for the detoxification/destruction of PCBs in sediments.

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SECTION I
INTRODUCTION

Polychlorinated biphenyls (PCBs) are a class of compounds that have 209 combinations of chlorine atoms attached to the biphenyl molecule. When they were first introduced into the United States by the Monsanto Company in 1929, PCBs were considered a "wonder" chemical. PCBs are clear, odorless liquids which have thermal, biological and chemical stability, plus high dielectric constants. These characteristics made PCBs have widespread use. Initially, PCBs were used as dielectric fluids in capacitors and transformers. A small amount was used in electromagnets, heat transfer and hydraulic systems. PCBs applications spread to plasticizers in paint, adhesives, dry caulking compounds, carbonless paper, flame retardants and fillers of all sorts.

Between 1929 and 1975, over 1.25 billion pounds of PCBs have been manufactured and used in the U.S., primarily in mixtures with chlorobenzenes (mostly trichlorobenzene or TCB) known as askarel (typical 40% PCB and 60% TCB). Askarels were used as dielectric fluids for electrical equipment and consisted of about 77% or 965 million pounds of the PCBs produced. It is estimated that 328 million pounds remain in service in electrical systems.

These compounds were not discovered in the environment until 1966 in Sweden and 1967 in the U.S. despite their use commercially for about 40 years. Interest in PCBs arose because they were frequently found in fish, bird, water, sediment and other environmental samples when such samples were examined for chlorinated pesticide residues.

Although PCBs have long been known to be toxic, only in recent years have they been acknowledged to be a general threat to the environment. Extensive research has shown a link between PCBs and chronic (longterm) effects in many species at less than 10ppm. There are well-documented tests on laboratory animals that show PCBs cause developmental toxicity, reproduction abnormalities, and tumors. Even though PCBs are a suspected carcinogen, their acute toxicity is considered to be non- to slightly-toxic by the LD50 Method. Recently, there have been additional concerns brought on by the finding of other toxic contaminants in PCBs and askarel fluids or linked to their incomplete combustion (burning). These toxic compounds include polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), chlorinated benzenes and other chlorinated substances. These compounds are among the most toxic of all man made substances. Because of these concerns, in 1971, the Monsanto Company, the sole United States producer, terminated sales of PCBs for all but closed electrical systems uses.

Federal regulations of PCBs took several years to develop. In 1976, Congress enacted the Toxic Substances Control Act (TSCA), Pl 94-469, and included special provisions, Section 6e, for the regulation of PCBs. In the May 31, 1979 Federal Register 44 (106), the EPA promugated rules which prohibited the manufacture of PCBs and their use in almost all nonenclosed applications. Since 1979, many regulations, rules, modifications to existing regulations, additional rules, clarification, and re-evaluated EPA positions have been issued. The position has moved toward the direction of tighter regulatory control. The Chemical & Biological Staff conducted a regional survey in early 1987 on the acceptable PCBs

levels in soils and sediments. There existed some variation between the EPA Regional Offices on the clean-up policies for spills of PCBs on soils and sediments. On April 2, a new policy for cleaning spills of PCBs that sets the same standards for every region in the country was released by EPA, after two years of negotiations among the Agency, environmental groups and industry (40 CFR, Part 761, April 2, 1987, pp 10688-10710). The policy calls for decontamination of soil down to 10ppm PCBs by weight in residential areas. This soil would then be covered by a clean-soil cap. Less restricted areas calls for clean-up down to 25ppm or 50ppm. Disposal of treated soils/sediments must meet the criteria of less than 2ppm PCBs concentration. The regulations permit PCBs to be landfilled or burned only in special incinerators, cement kilns or boilers. They also allow the EPA Regional Administrator to approve other alternative technologies to be used if he finds they do not "present an unreasonable risk of injury to health or the environment", and if their "level of performance is equivalent to Annex I incinerators or high efficiency boilers". However, the March 30, 1983 procedural rule on authority over alternative methods is still in effect. Under this ruling, incinerators and alternate methods that are mobile or of identical design and intended to be used in more than one region must obtain approval from the Assistant Administrator for Pesticides and Toxic Substances. Also included are certain research and development methods that dispose of more than 500lbs of total PCBs or PCB contaminated material. This report discusses several alternative technologies and their abilities to meet these regulations.

PCBs in Sediments

Polychlorinated biphenyls (PCBs) are widely used industrial chemicals that were never intended for release into the environment, but they have nonetheless been found in rainwater, in human tissue, and in many species of birds and fish. PCBs are released into the environment by several means. Sewage outfalls and industrial disposal into waterways are major sources of PCB-contamination. Rivers and streams are primary means of transport for PCBs within the environment, although the atmosphere also is a means of dispersal. It is estimated that from 1000 to 2000 tons per year escaped into the atmosphere in the 1960s from plasticized materials containing PCBs, and that about 4000 tons per year entered waterways from dumping and leakage of lubricants, hydraulic fluids, and heat transfer fluids. Other sources include leaching from dumps and landfills, where about half of the PCBs produced eventually end up. Once in the environment, PCBs persist for a long time. Their physical property of low water solubility caused the PCBs present in waterways to accumulate in sediments.

Reported the worst PCBs-sediment contamination sites in the United States, in terms of concentration and total quantity, are: New Bedford, Massachusetts (EPA Region I); Hudson River, New York (EPA Region II); and Waukegan, Illinios (EPA Region V). It is estimated that 290,000 kg of PCBs are contaminating 382,000 m^3(500,000 yd^3) of sediments of the Hudson River. During the 70s, approximately 907,000 kg of PCBs were used in the New Bedford area annually, of which an estimated 45,500 kg were improperly disposed. Also, there are numerous industrial lagoons contaminated with large quantities of PCBs. For example, the following is a partial list of PCBs removals which have occurred in EPA Region III:

Site Name	Site Location	Approx. cu.yd. Contaminated
Interstate Transformer	Lawrence Co., PA	200
Paoli Railroad	Paoli, PA	800
Sandonelle	Mercer Co., PA	600
Shaffer Equipment	Minden, WV	1600
Frazier's Bottom	Putnam Co., WV	unknown

These PCB contaminated sites pose threats especially to both drinking water and the fishing industry. The only available proven technology for PCB contaminated sediments is to remove them by dredging and using incineration which is costly. Land disposal of the untreated sediments is an option; but, as previously noted, this option has many legal restrictions and concentration limitations. Biodegradation is a possibility, but sufficient information does not exist to design and operate such a system. There is little experience in the application of encapsulation technology to PCB-contaminated sediments, plus the large volumes involved may make it cost prohibitive.

Although a great amount of work has been done by many research groups in the area of PCB-contaminated liquids, relatively little effort has been directed toward PCB-contaminated sediments and sludges. The EPA Regional and Program Offices are being asked to comment on the technical and economic feasibility of chemical/biological processes for clean-up of these sediments and sludges. These Offices do not have adequate data to recommend any of a number of processes proposed or being tested/evaluated for the decontamination of sediments containing PCBs. The Hazardous Waste Engineering Research Laboratory (HWERL) past and current research in the area of decontamination of PCB-bearing sediments is addressed to these Agency needs.

Solvent Extraction Process

Extraction of PCBs from sediments is viewed as an attractive alternative to either incineration or burial. Solvent extraction processes are defined to be separation processes in which two immiscible or partially soluble liquid phases are brought in contact for transfer of one or more components. For PCBs removal from sediments, one phase will be the sediments containing various amounts of PCBs. A key element in extraction, the ability of a solvent to extract a particular solute, is measured by the distribution coefficient. Choice of solvent must be optimized for maximum separation effectiveness. Low energy requirements and low/moderate capital costs are some advantageous features of extraction processes.

PCBs are soluble in most organic solvents and insoluble in water and polyhydroxy liquids. Because of their polar nature, PCBs are more soluble in many polar solvents than various hydrocarbons. The characteristics of a good extraction solvent should include high solubility for the PCBs, also a low solubility for oils and a considerable solvent power for water. Using these concepts, experimental studies were initiated about 1980-84 at the Union Carbide Corp. Nuclear Division, Oak Ridge, TN, on the extraction of PCBs from contaminated sludges in a lagoon using a hydrocarbon as the extraction solvent. It is understood that solvents such as hexane, furfural, triethylphosphate, etc. have been investigated in the laboratory. Ultimate disposal of the extracted PCBs was achieved by incineration. This extraction was used essentially only for PCBs contamination in a smaller oil volume.

During early 1985, exploratory experimental studies being conducted at HWERL showed that kerosene is a good solvent for extraction of PCBs from sediments. The Department of Applied Science, New York University, was engaged to conduct extensive experimental studies which will develop and optimize the extraction process. They are to demonstrate both its technical effectiveness and economic viability with a pilot plant operation. The research activities during the first year of this program comprised the investigation of suitable solvent extraction and supporting equipment, identification of candidate solvents for extraction and concurrently develop application and verification of analytical methodology for quantitative determination of PCBs in contaminated sediments. Exploratory experiments were also carried out on the extraction of PCBs from contaminated sediments obtained from Waukegan Harbor, IL.

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In a separate study, scientists at the New York University's Department of Applied Science have been carrying on a three year EPA supported investigational program on the development and evaluation of a low energy process technology for the solvent extraction and subsequent chemical destruction of PCBs from contaminated sediments and sludges. This is also one of the processes which was assessed by RTI in Phase 2. This program involves experimental studies on potentially more cost-effective PCB disposal alternatives to currently accepted practices. The research activities during the first year of this program comprised the investigation of suitable solvent extraction and supporting equipment, identification of candidate solvents for extraction and concurrently developed application and verification of analytical methodology for quantitative determination of PCBs in contaminated sediments. Exploratory experiments were also carried out on the extraction of PCBs from contaminated sediments obtained from Waukegan Harbor, Illinois.

The concept of using kerosene as an extraction solvent for removing PCBs from sludges and sediments was based on two factors: 1) the low cost of kerosene and 2) some work conducted on extraction of PCBs from soils (M. B. Saunders at Oak Ridge National Laboratory, 1985). While the cost factor is a driving force in any development, it alone cannot overcome technical impracticalities. It became quite evident early in this study that the presence of large quantities of water in the contaminated samples presented an insurmountable barrier to the use of kerosene in this application. A new approach to this difficult problem was needed and is herein presented.

The first step of the process takes advantage of the extremely low solubility of PCBs in water. In a typical PCB contaminated sediment or sludge composed primarily of water with generally 20% total solids, virtually all of the PCBs are associated with the sediment. Thus, the first processing step is a physical separation of water and solids. In the second step, the PCB contaminated oil is disociated from the sediment substrate. This is accomplished by a multistage counter-current leaching with a hydrophyllic solvent. The third step is a stripping operation in which the PCB-containing stream from above is contacted in a liquid-liquid extractor with a hydrophobic solvent and additional water. The two streams which leave this step are the PCBs concentrated in stripping

ination and possible approaches to alternative solutions proved invaluable in directing the contacts for further information.

A bibliography was prepared, which included approximately 100 references containing information useful in defining potential treatment technologies and in analyzing treatment process performance data. This bibliography was expanded to 171 references by addition of treatment feasibility study reports, process test and evaluation reports, process development proposals, and patents. As processes were identified, direct contacts were made with the investigators for details of their process studies.

Alternative (non-incineration) destruction/detoxification/removal (D/D/R) processes were subjected to screening to identify those to be assessed further. The processes were categorized according to their generic technology so that appropriate technical screening criteria could be applied for each. This screening yielded 11 emerging processes for further assessment. The selected processes represent six different generic technologies.

Criteria used to assess the identified emerging technologies included: residual PCB concentration in treated sediments, available capacity, conditions/limitations (including range of PCB concentration handled), the developmental status, test and evaluation (T and E) data needs, and estimated cost of treatment.

The assessment of the different processes required consideration of the characteristics inherent in the criteria. Their capability to remove PCBs adequately from wet contaminated sediments, the required processing time, and process controllability were all considered. Available data were examined for limits on the range of PCB concentrations that could be adequately reduced by the process to yield a treated sediment eligible for delisting. The status of development, whether laboratory-scale or pilot-scale, was identified. The extent of available data - whether showing only tests of the concept or lists of the unit processes of a pilot-scale process system - was identified. A preliminary estimate of the cost of applying the process was developed in conjunction with the Developer.

Because the processes identified were at various stages of development, data deficiencies exist, and engineering judgement was used to supplement available information.

Using the information obtained and developed, the characteristics for each process were given subjective ratings relative to an arbitrarily-defined perfect process. These ratings were then weighted and summed to give a single number that could represent the overall relative rating of each process.

The product or report from this study is entitled "PCB Sediment Decontamination-Technical/Economic Assessment of Selected Alternative Treatments", 600/2-86-112, Dec. 1986 (PB87-133112/AS). Section 3 of this report describes

the screening of alternative technologies for technical feasibility to treat PCB-contaminated sediments. Section 4 describes the development of criteria to assess selected processes. Section 5 describes the assessment of the processes, including descriptions, analyses of performance potential, and cost estimates. Section 6 summarizes the characteristics of the selected processes and ranks them subjectively. Section 7 presents a bibliography of references used and other relevant sources. Contacts with developers of the processes are noted throughout the text.

In November of 1986, HWERL funded a second phase study with RTI. The purpose of this study is to establish suitable factors for further assessment of the candidate processes that have been identified, to review these processes against these factors and identify additional data needs, and to provide a basis for the selection of three processes for a defensible, thorough technical assessment (including laboratory experiments and field validation) in a third phase of assessment.

This study builds upon the first phase of the assessment so that EPA may make better use of funds by having more complete information before evaluating any technology in the field. Factors considered include: (a) combinations of unit processes, for example, a solvent extraction process combined with KPEG or incineration; (b) engineering evaluation criteria; and (c) specific data needs for full test and evaluation of the applicability of the processes.

The study involved three phases: consultations with the treatment process developers, technical assessment of the process, and the selection of three of the processes for thorough test and evaluation.

Consultations included visits to the developers' facilities where further information was developed. The most recent performance data were reviewed. The availability of a system for test and evaluation was determined. The likely future commercial availability was also determined. Preparations for the visits included a checklist of needed information and criteria for assessment of the processes. The checklist is based upon the information needs for a permit to test application.

Technical assessment of the processes was based upon the projection of the performance and cost of a large-scale treatment system of sufficient capacity to treat an estimated 380,000 m^3 of PCB-contaminated Hudson River sediments in 2.5 years. Sediment characteristics that may influence the performance of an alternative treatment process were considered. Specific sample data from Hudson River sediments were used to guide the projection of operating conditions required for treatment by each process assessed.

In this report, each process is described as it would be applied to the treatment of sediments. Material and energy balances are applied to the extent possible with the limited data available. Needs for further data are identified by type, estimated time, and cost for their acquisition.

The probable cost of treatment after demonstration and approval of the process is estimated. Cost elements given include: capital, energy, labor, maintenance, process quality control and testing. The capital cost is recovered over the 2.5 years of projected operation. Labor and profit/contigency are estimated at uniform rates for all processes for purposes of comparative evaluation.

Environmental and health characteristics assessed include all process feed and waste streams, reagents, and operating hazards.

The lapsed time required to demonstrate process performance, then to design, construct and check out a full-scale process is projected, based on needs for additional data and requirements of the developers.

The processes are compared and rated using the results of the assessment. Based on composite ratings, three processes showing the highest rating are recommended for immediate test and evaluation.

This report also discusses a phase three study to determine the effectiveness of the three selected alternative treatment processes to detoxify PCB-contaminated sediments representative of those present in substantial quantities in several U.S. lagoons and waterways. The purpose of this phase three effort is to build upon the second phase of the assessment so that EPA has a defensible, thorough test and evaluation of three alternative treatments selected in phase two for PCB-contaminated sediments. Arrangements will be made to have PCB-contaminated sediments treated in pilot-scale processing systems. These pilot tests will evaluate performance under field conditions, and will be supported by laboratory tests.

SECTION 2
CONCLUSIONS

Exploratory studies have established that the extraction of PCB-contaminated sediments can be done with readily available low cost reagents such as acetone and kerosene. These extractions can be carried out at near ambient temperatures and atmospheric pressures. Specific conclusions reached from the solvent extraction investigations are summarized as follows:

- An innovative extraction process scheme was developed to remove PCBs from sediments.
- Suitable extracting and supporting equipment was selected and assemblied for the newly designed process.
- Appropriate analytical methodology for the determination of PCBs in contaminated sediments was developed.
- Leaching experiments conducted with Waukegan Harbor sludge resulted in very high effeciencies for the solvents acetone, methanol, and isopropanol. Kerosene showed much lower effeciencies except in the case of dry sediments.
- Settling experiments conducted with dry topsoil containing various degrees of water gave the following order of settling rate: acetone-methanol-isopropanol.

Based on the results from the leaching and settling experiments, the findings from the first year of research, and taking into consideration various physical, chemical and toxicological properties, a solvent pair has been selected. Acetone has been chosen as the hydrophilic solvent and kerosene the hydrophobic solvent.

Stripping experiments conducted with these two solvents, with varying degrees of sulfate concentration, and with varying water/acetone ratios have given very promising results. A partition coefficient between kerosene and acetone of 30 has been obtained, which allows for the completion of the stripping operation with a very small number of stages. An even higher partition coefficient is expected with further experimentation.

At the end of a Phase I assessment study for alternative treatment processes (Dec. 1986) the following conclusions were reached after evaluating sixty four processes.

Emerging treatment processes for decontamination of PCB-contaminated sediments that show potential as alternatives to incineration and chemical waste landfill have been identified. Eight processes -- KPEG, LARC, Acurex, Bio-Clean, Supercritical Water, Advanced Electric Reactor, Vitrification, and O.H.M. Extraction -- ranked highest in terms of potential for cleanup of contaminated sediments. The sediments must be dredged for application of these treatments.

Of the 11 processes completely assessed and ranked, all but the Advanced Electric Reactor (AER) are in various stages of development from laboratory-scale through field tests. The AER is a permitted treatment based on completed trial burns.

There is no immediately available capacity for any of the treatments. Further data are needed in most cases to define the final system design for the process.

At this stage of development,(1985-86) estimated costs for application of the emerging treatments are less than or within the range of the costs of chemical waste landfill, except the AER process which exceeds that of landfill. The ranges of estimated costs (1985 dollars) on the eleven processes ranked are as follows:

KPEG	$ 211	to	$ 378/m^3
O.H.M. Methanol Extraction	400	to	514/m^3
Advanced Electric Reactor	830	to	942/m^3
Acurex solvent wash	196	to	569/m^3
Bio-Clean	191	to	370/m^3
Vitrification	255	to	548/m^3
LARC	223	to	336/m^3
Modar supercritical water	250	to	733/m^3
Soilex solvent extraction	856	to	913/m^3
Sybron Bi-Chem 1006 PB	unable	to	estimate cost
Composting	unable	to	estimate cost
Chemical waste landfill	260	to	490/m^3
Incineration	1,713	to	1,826/m^3

These costs are planning estimates only. In most cases, further research is needed to provide data suitable for more definite cost estimates.

The emerging treatment processes are based on five different technologies: one on low-temperature oxidation, two on chlorine removal, one on pyrolysis, four on removing and concentrating, and three on microorganisms. The four types of technologies not yielding competitive emerging processes are: chlorinolysis, stabilization, bottom recovery, and enzymes. A search of these technologies yielded no suitable candidate processes.

The Phase II of the assessment study built upon the information gained during Phase I, but was not limited to those eight processes ranked potentially high since new ones are always emerging. The closer investigation of the eight potential processes listed from the Phase I study and four potential processes recently developed resulted in the following conclusions.

Seven emerging treatment processes for decontamination of PCB-contaminated sediments are candidates for thorough test and evaluation (T and E) using a test system of sufficient size to provide performance, cost, and scale-up data for a large commercial plant. The processes are:

- Basic Extraction Sludge Treatment (B.E.S.T.) Process developed by Resources Conservation Co.
- UV/Ozone or Hydrogen/Ultrasonics Technology of Ozonic Technology, Inc.
- Bio-Clean Naturally-Adapted Microbial Process of Bio-Clean, Inc.
- Potassium Polyethylene Glycolate (KPEG) with dimethyl sulfoxide (DMSO) Process Modified by Galson Research Corp.
- CFS Propane Extraction Process of C. F. Systems Corp.
- Modar Supercritical Water-Oxidation Process of Modar, Inc.
- Low Energy Acetone-Kerosene Extraction Process developed by the Applied Science Dept. of New York University.

The processes were evaluated using as criteria:

- The probability of cleaning sediments to ≤ 2 ppm PCBs;
- The probable cost of treatment;
- The relative level of Test and Evaluation effort to be supported by EPA;
- The availability of a processing system to test; and
- The likely future commercial availability of the process.

While all the processes merit further development, comparative simultaneous evaluation of their ratings on a scale of 0 to 1 gave the following results:

Process	Relative desirability of immediate T and E
B.E.S.T.	0.62
Ultrasonics/Hydrogen-Ozone/UV Technology	0.62
Bio-Clean Naturally-Adapted Microbial	0.61
KPEG with DMSO	0.59
CFS Propane Extraction	0.58
Modar Supercritical Water-Oxidation	0.57
Low Energy Acetone-Kerosene Extraction	0.49

The B.E.S.T., UV/Ozone or Hydrogen/Ultrasonics Technology, and Bio-Clean Naturally-Adapted Microbial processes have the highest ratings, and are recommended for immediate, thorough test and evaluation.

SECTION 3
RECOMMENDATIONS

The result of the previous EPA funded study with NYU entitled "Development and Evaluation of a Low Energy Process Technology for Extraction and Chemical Destruction of PCBs from Soils and Sludges" (CR 812123-02-0) has led to a novel approach to treatment of contaminated soils and sediments with potentially a much broader applicability. A two year study is proposed to model, engineer and otherwise fully characterize this process so that its full potential might be realized. The study will, in the first year, design and assemble a bench scale working model of the total process. The second year will culminate in field tests at designated sites. While proof of concept experiments have established a clear direction for these studies, this is a complex process which must be analytically modeled to fully appreciate its potential. Concurrently, engineering design considerations are required to specify particular equipment. The previous study has considered equipment which could be used for the different steps of the process. The second year of the proposed study would address the issues of process scale-up. Equipment selection and experiment design will follow site analyses and discussions with the entity responsible for the site clean up.

We have been seeking a commercial sponsor for this process, and it appears that Camp Dresser & McKee (CDM), an environmental consulting firm, is interested in the EPA/NYU process for future development as it relates to contaminated sediments originating in New Bedford Harbor, Massachusetts.

The processes compared in Phase I of the technical/economical assessment study conducted by RTI for HWERL were general technologies and not specific unit processes within those technologies, nor were they developed to the point of application to sediments, but rather PCBs in liquids or soils. Thus, a Phase II study was started which would consider: combinations of unit processes; engineering evaluation criteria; and specific data needs to evaluate the applicability of processes. The assessment study is at a stage where data can be used to commence the longer, more costly Phase III field type investigation.

The purpose of the Phase III effort is to build upon the second phase of the assessment so that EPA has a defensible thorough test and evaluation of the three alternative treatments selected in Phase II for PCB-contaminated sediments. In carrying out this phase, EPA will arrange to have PCB-contaminated sediments treated in pilot-scale processing systems selected by EPA in Phase II. The pilot tests will evaluate performance under field conditions, and will be supported by laboratory tests.

There is substantial justification to proceed in the near future with the test and evaluation of these processes. The developers of these processes have the facilities required to begin the tests. Tests can proceed one at a time if necessary, with separate funding for each. Allowing time for permits,

set up, and check-out, the results of one or more tests could be available for consideration by those at EPA who may be appropriating funds for the Hudson River problem. Tests and evaluations could be conducted during the summer and fall months, when the weather is much more favorable.

SECTION 4
DISCUSSION OF EXTRACTION PROCESS
Selection of Equipment

The selection of suitable contacting equipment for a specific extraction involves complex decisions particularly so in the absence of prior data with the same system on either a pilot plant or industrial scale operation. A study was therefore carried out to ascertain the types of pilot plant and industrial scale extractors available and to evaluate their applicability for the extraction of PCBs from sediments and soils. The results of this study are summarized below.

Survey of Industrial Extraction Equipment

Industrial solvent extraction contactors emphasize equipment with countercurrent flow operational capability. One convenient classification shown in Table 1 is that of differential and stagewise contactors. The former provide conditions for mass transfer throughout their length, aiming to produce optimum concentration profiles. Stagewise contactors provide for a number of discrete stages in which the two phases are brought to equilibrium, separated and passed countercurrent to the adjoining stages. While such contactors avoid certain problems such as the axial mixing found in some differential contactors, the necessity of separating the phase between each stage can add substantially to overall size and solvent inventory.

Another major division can be made according to whether the countercurrent flow is produced by gravity action on the density differences between the phases or by an applied force such as a centrifuge. A summary of features and fields of industrially employed extraction equipment is shown in Table 2 and includes most commercial contactors in use today.

TABLE 1: BASIC CLASSIFICATION OF INDUSTRIAL CONTACTORS

Forces Producing Phase Interdispersion	Differential Contactors	Stagewise Contactors
Gravity only	Spray column Packed column	Perforated plate column
Pulsation	Pulsed packed column Pulsating plate column	Pulsed sieve-plate column* Pulsed mixer-settler
Mechanical agitation	Rotating disc contactor Oldshire-Rushton column Kuhni column* Graesser contactor	Scheibel column ARD extractor Mixer-settlers
Centrifugal Force	Podbielniak Quadronic DeLaval	Westfalia Robatel

*Could be considered intermediate between differential and stagewise.

TABLE 2: SUMMARY OF FEATURES AND FIELDS OF APPLICATION

TYPES OF EXTRACTOR	GENERAL FEATURES	FIELDS OF INDUSTRIA APPLICATION
Unagitated columns	Low capital cost, low operating and maintenance cost, simplicity in construction, handles corrosive material.	Petrochemical, chemical
Mixer-settlers	High stage efficiency, handles wide solvent ratios, high capacity, good flexibility, reliable scale-up, handles liquids with high viscosity.	Petrochemical, nuclear, fertiliz metallurgical.
Pulsed columns	Low HETS, no internal moving parts, many stages possible.	Nuclear, petrochemical, metallurgical.
Rotary-agitation columns	Reasonable capacity, reasonable HETS, many stages possible, reasonable construction cost, low operating and maintenance cost.	Petrochemical, metallurgical, pharmaceutical,
Reciprocating-plate columns	High throughput, low HETS, great versatility and flexibility, simplicity in construction, handles liquids containing suspended solids, handles mixtures with emulsifying tendencies.	Pharmaceutical, petrochemical, metallurgical, chemical.
Centrifugal extractors	Short contacting time for unstable material, limited space required, handles easily emulsified material, handles systems with little liquid density difference.	Pharmaceutical, nuclear, petrochemical

HETS: Height equivalent to a theoretical stage.

Settler Design

The processes that occur in a settler are quite complex, and interrelated. They include the mechanisms of coalescence and disengagement. Coalescence is retarded by an increase in the viscosity of the continuous phase. Increases in temperature promote coalescence by lowering the viscosity. Decreases in surface tension retard coalescence because they produce a greater area of the continuous phase. Increases in density differences between the phases promote coalescence by increasing the force acting to bring about drainage of the continuous phase film. The formation of larger drops enhances coalescence, while smaller drops retard it. Small droplets can give considerable difficulty in practice as they can be easily entrained in product streams where they represent both a loss and an impurity. Small drops introduced into the feed going to the settler are particularly troublesome.

The basic requirements of efficient settler operation have been summarized as follows: a) minimize turbulence in a settler as this will retard coalescence by keeping small drops in suspension, b) minimize small drops in the original dispersion, c) keep linear velocities along the settler at a low value, and d) employ coalescence aids such as removable baskets of packings at the inlet point provided that they do not result in too large pressure drops.

High throughput is a most important consideration of settler design. Extensive experimentation has shown that there is a maximum safe throughput for a specific extraction in a given mixer-settler, above which quite small changes can result in flooding. Also the throughput unit volume of dispersion decreases as the thickness of the dispersion band at the interface increases. One approach to the problem of increasing the throughput of a settler of given dimensions is to divide the overall dispersion into a number of thinner bands. The Lurgi and I.M.I. settler designs attempt to accomplish this by using a series of trays or plates.

An alternative approach to increasing settler throughputs is to introduce some packing into the settler which should be preferentially wet by the dispersed phase. A woven-mesh packing incorporating materials that are both water and organic wetted was developed some time ago and has given quite promising results when tested in the Davy Powergas mixer-settler. The overall unit has been claimed to operate more than an order of magnitude better than a simple mixer-settler. Another approach to promote throughput, by the application of centrifugal contactors, has been well established for many years. They offer short contact times and efficient phase separation and are especially desirable for applications involving either chemically unstable or slow settling systems. The Podbielniak, De Laval and Westfalia extractors have an excellent record of performance for such problem liquid-liquid extractions. The Luweta equipment is an adaption of the underdriven centrifugal cream separator with two or more stages mounted vertically in a single assembly. Each stage comprises a spray disk mixer and a centrifugal separator. The ports and channels for transfer and conveyance are carried in a stationary central tube. The more recently introduced Robatel contactor features very short residence times for a novel multistage design.

Contactor Selection

As noted above, contactor selection is a complex task as it involves both technical and economic considerations applied to a specific system. As a general guide a chemically unstable system or one with slow settling characteristics will tend to favor centrifugal equipment. If however, a system is rather inexpensive and only a few stages are required, simple gravity columns or mixer-settlers should be considered. If a larger number of stages are required, a mechanically agitated column becomes a candidate. Mixer-settlers are suitable for most chemically stable systems, but require more groundspace than do columns. Also the holdup in mixer-settlers is greater than in columns. On the other hand, however, these are better in accepting flow changes from stage to stage due to the transfer of material between the phases.

Specific technical criteria for selection of extraction equipment include the following:

Total throughput -	for typical systems, a minimum total throughput of 50 gallons/hour of feed plus extract phase corresponds to a column of about 10 cm in diameter; most industrial processes require capacities of 500 to 50,000 gallons/hour and more.
Number of theoretical stages -	the height of most types of vertical contactors tends to become excessive with more than 10-15 stages. This limitation does not arise with horizontal equipment especially mixer-settlers, but floor space requirements become quite large.
Physical properties of system -	contactor performance is affected by viscosities, interfacial tensions, densities, boiling and freezing points, temperature, flammability, toxicity, etc.
Type of reaction -	the effect of slow heterogeneous reactions is always to reduce the rate of mass transfer, hence either increasing column height or reducing stage efficiency; interfacial area should be increased by upping rate of agitation; slow homogeneous reactions are quite rare in liquid extraction.

Extreme phase ratios -	the effect of a low value is to reduce the dispersed phase holdup and hence the interfacial area; a high value may cause large backmixing; in both cases, performance decreases; the exceptions are mixer-settlers with provisions for recirculation of the separated phases back to the mixer.
Short residence time -	this may be required with chemically unstable products to minimize losses and leads to consideration of centrifugal reactors.
Ability to handle solids -	some contactors are susceptable to blockage; the only types which can accept significant quantities of solids are the rotory and, to a lesser extent, the raining bucket types (as well as mixer-settlers).
Tendency to emulsify -	nonmechanical contactors are generally preferred to many widely agitated types, with the exception of the centrifuge units.
Limited space availability -	mixer-settlers and centrifuges should be considered.
Special material requirements -	metals applicable to all contactors, non-metals require special study.
Radioactivity or corrosion present -	special studies of safety and material properties needed.
Ease of cleaning -	depends on contactor design and construction material.
Low maintenance -	mechanically and pulse agitated contactors require more careful maintenance due to shaft timing, seals, pulsing mechanisms, etc.

Experimental Studies

During the first year of the three year research effort a significant portion of the work was dedicated to the establishment of analytical procedures for the determination of PCBs in sludges. These procedures were then employed to analyze a set of PCB spiked water samples covering the concentration range from 2ppm to 123ppm; details are given below. Furthermore, an environmental sample, a sludge from Waukegan Harbor, Illinois, was analyzed. Apart from these analytical studies seven different solvents and four additives were evaluated for their potential use in the extraction process.

Extraction of PCBs from Spiked Water Samples

Various PCB spiked water samples were analyzed in order to determine the amounts of the PCB contaminent that could be recovered by extraction methods. EPA Method 608 was used for the analytical work. The PCB employed was Aroclor 1232. The experimental study also provided information on the higher and lower levels of extractability for known amounts of this particular Aroclor.

The analytical data show total recoveries in the order of 90% for spiked samples containing an initial Aroclor 1232 concentration of 123 micro grams/ml (2 extractions). Recoveries from the samples spiked with 49.5 micro grams/ml Aroclor 1232 were 88% and 90.4% respectively and about 100% for a 24.5 micro grams/ml sample (2 extractions). For samples with 12.2 micro grams/ml initial concentrations recoveries were 86.5% and 87.1% respectively. The data for the two samples with the initial very low 2 micro grams/ml concentration lack sufficient precision to warrant consideration.

Quantification of PCBs in Environmental Sample

After the analysis of PCB-spiked water samples had been sucessfully completed the more difficult problem of analysis of PCB contaminated environmental samples remained to be solved. A sludge sample from Waukegan Harbor with an approximate PCB concentration of 5000 ppm was used. After an initial separation of the sludge gave a liquid to solid ratio of about 3:2 it was decided to analyze the liquid and the solid fraction of the sample by two different methods. The liquid fraction was analyzed by the EPA-Method 608. The wet solids were analyzed following a soxhlet extraction procedure, which had been used in an EPA sponsored interlaboratory study. (Ann L. Alford-Stevens, et al., Annal. Chem. 1985, Vol. 57, 2452-2457).

The sample was centrifuged for one hour at 2500 rpm and then separated into a liquid and a wet solid fraction. Two 20 gram aliquots of the wet solid fraction were extracted by soxhlet.

The moisture content of the wet solid fraction was determined by air drying the sample 4 days and then vacuum drying until constant weight was established. PCB concentrations were calculated for the liquid fraction, the wet solid fraction, the dry solid fraction and for the original environmental sample. The results are given in Table 3.

TABLE 3: PCB Concentration of Waukegan Harbor Sludge

	Liquid Fraction	Wet Solid Fraction	Dry Solid Fraction	Integral Sample
Extracts				
1ST	9.7	13950	32442	5818
2ND	8.1	14500	33721	6046

PCB Concentration is given in mg/kg (ppm).

Moisture content of wet solid fraction was: 57%.

The mass ratio of liquid fraction to wet solid fraction was: 1.4.

The mass ratio of liquid fraction to dry solid fraction was: 4.6.

Characterization of Solvents

A qualitative experimental study was carried out to characterize certain pertinent properties of candidate solvents for PCB extractions from aqueous solutions. Basic criteria for the selection of an extraction solvent have been described previously. The objective of this study was to find the solvent system which gives a clear phase separation in a very short settling time.

Seven hydrophobic solvents with high PCB solubility together with 4 hydrophilic solvents as additives at three different solvent to water ratios (1:9, 1:1, 9:1) were investigated. Each solvent/water system was studied without and with additives, whereby the ratio of hydrophobic solvent to additive was kept at 4:1 for all cases.

The different solvent systems were subjected to the following experiment: A total volume of 50 ml of solvent/water mixture was filled in a 65 ml screw top sampling bottle and agitated for 2 min, 10 min and 30 min. respectively. The agitation was performed with a Burrel-Wrist-Action-Shaker, which was operated at a constant speed of one semi-circular motion per second. The separation following the agitation was observed qualitatively after two minutes and 10 minutes of settling time. The quality of the separation was characterized using the following criteria.

a) Quality of phase boundary
b) Degree of murkiness in either phase
c) Amount of bubbles in either phase and/or at boundary
d) Severity of emulsion formed in either phase or at boundary

The hydrophobic solvents and the additives (hydrophilic solvents) investigated were:

Hydrophobic Solvents	Additives
Hexane	Acetone
Kerosene	Carbitol
Mineral Spirits	Methanol
Petroleum Ether (PE)	Methylene Chloride
Toluene	
Turpentine	
Xylene	

Of the hydrophobic solvents only Hexane, Kerosene and Toluene were combined with additives. A total of 288 observations were made.

New Process Development

The concept of using kerosene as an extraction solvent for removing PCBs from sludges and sediments as originally proposed was based on two factors: 1) the low cost of kerosene and 2) some work underway on extraction of PCBs from soils. While the cost factor is a driving force in any development, it alone cannot overcome technical impracticalities. It became quite evident early in the study that the presence of large quantities of water in the contaminated samples was to present an insurmountable barrier to the use of kerosene in this application. A bold new approach to this most difficult problem was needed and is herein presented.

This new approach is based on some well known facts about the properties of PCBs present in sludges and sediments, some common sense about the use of particular hydrophyllic and hydrophobic solvents and application of a stripping operation, an existing technology, as a final step for isolation and concentration of the contaminants.

The first step of the process takes advantage of the extremely low solubility of PCBs in water. In a typical PCB contaminated sludge or sediment composed primarily of water with, for example, 20% total solids, one could expect virtually all of the PCBs to be asociated with the sediment in a water medium. Thus the first processing step is simply a physical separation of water and solids. This can be accomplished with varying degrees of efficiency using existing equipment. Practically, the solids fraction from this separation will contain on the order of 50% water but will most likely contain 98%+ of the PCB content. The solid fraction and the liquid fraction from step 1 require further treatment, however, it was managed to isolate most of the PCBs and to reduce the sample size by about 60%. The water fraction requires subsequent treatment which will be addressed later.

In the second step of the process, the PCB contaminated oil must be dissociated from the inorganic substrate. To do this, a water miscible solvent (hydrophyllic), acetone, was added in quantities sufficient to break the bond between the PCBs and the solid surface. This is followed by another liquid/solid separation. This description is for one stage of the proposed second step of the process. The amount of PCB transferred to the solvent/water mixture depends on partitioning between the liquid and solid phases and thus we can define a partition coefficient and ultimately a stage efficiency. One can then predict the number of stages required to perform a particular level of separation given the original contamination level and the allowable level in the solid effluent. This second step is a multistage countercurrent leaching using a hydrophyllic solvent.

The products from the second step are: 1) a hydrophyllic solvent/water mixture containing nearly all of the PCB contamination which requires further treatment and, 2) a PCB free soil/solvent mixture from which the solvent must be recovered and returned to the process cycle with the soil now being decontaminated and ready to be returned to the environment. A small fraction of this clean soil is utilized in an absorption column to extract the trace amounts of PCBs from the water effluent of step 1.

The third step of the process is a stripping operation in which the PCB-containing stream from above is contacted in a liquid-liquid extractor with a hydrophobic solvent and additional water. The additional water drives the PCBs out of the solution and into the hydrophobic stripping solvent. This step is required to separate the PCBs from the aqueous phase which is inconvenient for the final destruction step and also, the PCB can be concentrated in this step further reducing the volume of contaminated sample required for handling. The two streams which leave this step are the PCB concentrated in stripping solvent which proceeds to final destruction either by chemical means (KPEG Reagent) or by other appropriate methods and the hydrophyllic solvent/water mixture containing trace PCBs. The solvent/water mixture goes next to a distillation column in which the solvent is released and returned to the leaching process described in step 2. The water contaminated with trace amounts of PCB is recycled to the front of the stripping process to close the cycle.

Proof of concept experiments have been conducted successfully and experiments are now underway to determine process criteria to further advance this concept. Particular attention has been paid to closing the various liquid and solid stream cycles.

SECTION 5
DISCUSSION OF ASSESSMENT STUDY
Screening of Processes

The processes were screened by examining each for any undesireable aspects. Processes with such aspects were rejected from further assessment. For example, lack of tolerance for water by a process is undesirable because of the extensive sediment drying it necessitates. There is evidence in the collected data that such drying generates fine particulates that must be removed from the exit gases of the dryers. The recovered particulates must also be decontaminated. Processes showing insufficient tolerance for water were therefore rejected from further consideration as a primary treatment process in favor of more tolerant alternatives.

Table 4 lists the sixty four processes screened, identifies those selected for further assessment, and gives the reasons for rejection of the rest. The processes are arranged according to the generic types of technologies upon which they are based. The use of generic technology types guided the survey and assessment phases of this study by providing technologies from which treatment processes could arise. Some of the technologies (e.g., nucleophilic substitution) have provided several processes. Some (e.g., enzymes) have not yet provided any processes. These technologies are nevertheless discussed to describe their status, with respect to PCB-contaminated sediment treatment, so that their potential may be considered in research planning.

A process rated "1" in Table 4 for each technology has been selected for further assessment. As noted, eleven processes obtained this rating. Higher rating numbers assigned the rest of the screened processes refer to footnotes that identify the reason for rejection of the process for further assessment.

technology	References	Process	Evaluation[a]
ıemical	Centofanti 1971; Chen 1982; Childs 1982; Craddock 1982; Edwards et al. 1982; Environment Canada 1983; Hornig 1984; Massey and Walsh 1985; Rogers and Kornel 1985; Rogers 1983; Rogers 1985.		
ı-temperature oxidation			
·t air oxidation	Baillod et al. 1978; Miller and Sevientoniewski (n.d.); Miller and Fox 1982.	Uncatalyzed, general	2
		Zimpro Process, Santa Maria, CA Waste Site	4,13
		Catalyzed	
		Dow Chemical Co. Patent 3,984,311	2
		IT Environmental Science	2
ıpercritical water oxidation	Modell et al. 1982.	Modar	1
ıemical oxidants	FMC Corporation (n.d.); March 1968.	Potassium permanganate plus Chromic Acid and Nitric Acid	6
		Chloroiodides	4,7
		Ruthenium tetroxide	3,4,8
·onation	Arisman et al. 1981; Lacy and Rice Deschlaeger 1976; Prengle and Mauk 1978.	GE UV/ozonation process	2
orine removal	U.S.P. 346, 636	Molten aluminum/distillation	14
·hydrochlorination	Chu and Vick 1985; Lapiere et al. 1977.	Catalytic:	2,3
		Nickel on kieselguhr	2,3
		Pd on charcoal	2,3
		Lithium aluminum hydride	2,3
		Butyl lithium	2,3
		Raney Nickel	2,3
:ducing agents	Chu and Vick 1985; Sworzen and Ackerman 1982.	Sodium in liquid ammonia	7,9
		Nickel-catalyzed zinc reduction	7,9
		Hydrazine	7,9
		UV light plus hydrogen	2
		Mildly acidic zinc powder, Sweeney and Fisher (1970)	2,14
ıcleophilic substitution	Brown et al. 1985a; Brunelle and Singleton 1985; March 1968; New York University 1984; Ruzz et al. 1985; Smith and Gurbacham 1981; Sunohio (n.d.); Sweeney and Fischer 1970; United States Patent Office 1984b; Weitzman 1984; Weitzman 1984; Weitzman 1985	Sodium-based processes:	
		Goodyear, sodium in naphthalene (1980)	10
		Acurex, proprietary solvent	10
		PCBX/Sun Ohio	10
		PPM	10
		Ontario Hydro Power	10

TABLE 4 (continued)

Generic technology	References	Process	Evaluation[a]
ucleophilic substitution (continued)		Potassium poly (ethylene glycolate) based:	
		KPEG Terraclean-Cl	1
		GE KOH-PEG	11
		New York University KPEG	12
adiant energy	Bailin and Hertzler 1977; Bailin and Hertzler 1978; Bailin et al. 1978; Craft et al. 1975; Dev et al. 1985; Kalmaz et al. 1981; Meuser and Weimer 1982; Plimmer 1978; Rogers and Kornel 1985; Rogers 1985; Trump et al. 1979: West et al. 1983.	U/V photolysis	3
		Syntex photolytic	3,4
		Thermal corona glow	5
		Microwave plasma	9,17
		RF in situ heating	18
		Gamma radiation (Craft et al. 1975)	9
		LARC	1
lectromechanical reduction	Massey and Walsh 1985.	Electromechanical research process	14
lorinalysis	Sworzen and Ackerman 1982.	Hoechst process	9
		Goodyear catalytic hydrogenalysis	9
		Exhaustive chlorination	9
rolysis	Boyd 1985; New York State Department of Environmental Conservation 1985a; New York State Department of Environmental Conservation 1985b.	Advanced Electric Reactor	1
		Wright-Malta alkaline catalyst fuel-gas process	12
YSICAL			
noving and concentrating	Angiola and Soden 1982; Caron 1985; Gilmer and Freestone 1978; Githens 1984; Hancher et al. 1984; Hawthorne 1982; Lee et al. 1979; Saunders 1985; Schwinn et al 1984; Versar, Inc. 1984.		
eated Air Stripping		American Toxics Disposal, Inc.	14
xtraction		Critical Fluid Systems, CO_2	14
		Furfural	15
		Acurex solvent wash	1
		O. H. M. extraction	1
		Soilex process	1
dsorption		Carbon adsorption, general	13
		Neoprene rubber adsorption	15
trification	Timmerman 1985.	Battel[illegible] ion process	1

Generic technology	References	Process	Evaluation[a]
tabilizing	Ghassemi and Haro 1985; Law Engineering Testing Company 1982; Stroud et al. 1978; Subnamanian and Mahalingam 1977; Tittlebaum et al. 1985.	Asphalt with lime pretreatment	16
		Z-Impremix	15
		Sulfur-asphalt blends (K-20)	16
		Ground freezing	13
ottom recovery	Carich and Tofflemire 1983; Hand and Ford 1978; Murakami and Takeishi 1978; U.S. Army Corps of Engineers Water Resources Support Center 1983; Zimmie and Tofflemire 1978.	Dredging	13
BIOLOGICAL			
licroorganisms	Bedard et al. 1985; Bumpus et al. 1985; Clark et al. 1979; Dawes and Sutherland 1976; Furakawa 1982; Isbister et al. 1984; Kong and Sayler 1983; McCormick 1985;	Bio-Clean	1
		Sybron Bi-Chem 1006 PB	1
		Composting	1
		Bio-Surf	4,13
	New York State Department of Environmental Conservation 1985a; New York State Department of Environmental Conservation 1985b; Rhee et al. 1985b; Rhee et al. 1985; Unterman et al. 1985.	Ecolotrol, Inc.	4,13
		Wormes Biochemical's Phenobac	1,13
		Rhee anaerobic degradation	14
nzymes	Catelani et al. 1971; Rochkind et al. Unterman et al 1985.	No processes found	

Explanation of process rating:

1. Identified emerging sediment treatment process.
2. Destruction efficiency appears to be too low to meet environmental goals.
3. Processing time apppears to be extremely long for practical timely cleanup.
4. Data available for dioxin, other chlorinated compounds, or other contaminants, but not PCBs.
5. Process has been shown to destroy PCBs in gas streams only. It may be feasible for sediments, but has not been shown to be.

TABLE 4 (continued)

6. PCBs with 5-7 chlorine atoms per molecule are not destroyed.

7. Products of partial degradation may be toxic.

8. Reagent is very costly/toxic or both.

9. Process costs appear to be excessively high compared with other emerging treatment processes.

10. Water destroys the reagent or interferes with its action, thus the process would require excessive drying of sediments and, probably, extraction in pretreatments. The process would therefore have application only as a subordinate final step to several extraction and concentration operations.

11. This particular process was not evaluated because data were not available for assessment.

12. This process is an alternative to another process using the same generic technology, but it is in very early stages of development, and data were not available for assessment.

13. This technique is basically applicable to preliminary operations prior to treatment or to treatment of wastestreams (e.g., wastewaters) from chemical or physical treatments.

14. This process is in the concept stage and data are insufficient to assess it for PCB-contaminated sediments.

15. This process has been found to be ineffective.

16. This technology provides only for encapsulation of the PCB-contaminated sediments.

17. This process supports incineration of PCBs.

18. The process does not appear to be feasible for submerged sediments.

Development of Evaluation Criteria

Problem Definition

The PCB contamination problem in the Hudson River is representative of the type of PCB destruction/detoxification problems focused on in this study. The New York State Department of Environmental Conservation (DEC) recently concluded a 2-year survey of 40 miles of the upper Hudson River (1976-1977). The survey, conducted with consultant Malcolm Pirnie, Inc. (White Plains, New York) identified 40 spots collectively containing more than an estimated 382,000 m^3 (500,000 yd^3) of sediment contaminated with PCBs at concentrations greater than 50 ppm. The depth of contamination seems to be between 0.25 and 0.45 meters. A more recent survey (1984) was made of a 5-mile reach extending downstream 5 miles from Ft. Edward, New York. Samples from the near-shore area showed from 40 to 60 ppm PCBs.

A pilot dredging operation, performed with hydraulic dredges between 1978 and 1979, netted 152,900 m^3 (200,000 yd^3) of material with seemingly little dispersion of the contaminant downstream. The contaminated areas are located in shallow, slow-moving waters near the riverbanks. Although DEC is investigating other disposal methods, it is expected to dredge the contaminated sediments and bury them because of the high costs of alternatives.

The wetness of the sediments will preclude the use of many treatment processes designed to treat PCB-containing oils using reagents that would be destroyed or made ineffective in the presence of water.

Regulatory Factors

The goal for detoxification/destruction is to have no more than 1 to 5 ppm PCBs in the treated sediment. At present, PCB disposal is regulated under TSCA [40 CFR 761.60 a 5 (i-iii)].

The criterion of 1 to 5 ppm for a promising alternative treatment should result in a treated sediment that is disposable without restriction.

Technical Factors

Technical factors relate to a broad range of principles of operation of diverse applied technologies. Factors have been chosen that can be used effectively in comparing one treatment process with another. Additional factors, specific to a technology, have been chosen to help portray the inherent strengths and limitations of a process.

The goal set for process performance is to reduce the PCB concentration in treated sediments to background levels of 1 to 5 ppm. Several of the processes were found to meet this goal.

Available capacity was found not to exist for any of the processes. However, several were developed sufficiently to permit projections of the time required to build a facility for application of the treatment.

Conditions/limitations that were considered included tolerance for water, required processing time, and controllability of process conditions. Those treatments that could tolerate water up to about 40 percent would not require a drying step with its attendant fines control problems. Those requiring only 1 day for treatment could generally show a faster rate of cleanup than those requiring 3 days. Some biological processes required more than 3 weeks. The treatments generally provided control of the processing conditions; however, a few (e.g., composting) would not necessarily do so.

Concentration range handled in data developed for the processes ranged from unknown to 3,000 ppm. Some processes had limits inherent in the technology; others had no apparent limits.

Processes were found to range from concept stage to completed field tests. Most were in the pilot stage.

Data needs varied with the status of the process. At worst, data were available showing tests of the concept. At best, the process had been field tested, and only permits and checkout were needed.

Unit operations employed in each process were identified. Collectively, the processes use 18 different unit operations. The number of operations per process varied from two to eight, depending upon the complexity of the technology.

Cost Estimates

Costs of appplying an alternative technology are very difficult to predict because of the uncertainties regarding the potentially available new treatment processes. Estimates of the quantities of PCB-contaminated sediments are under review and may change significantly as a result of the reviews. In most cases, additional information is needed regarding the yet to be proven effectiveness of emerging treatment processes before the costs of their application can be assessed accurately. Therefore, the cost estimates presented here should be viewed as preliminary with respect to the new treatment processes. A range of costs is given for supporting operations (dredging and transportation) to reflect differences in different geographical areas of the country.

Because the regulations permit the use of incineration or chemical waste landfill and the application costs of these two methods are available from firms engaging in their practice, these costs were used as lower and upper limits with which to compare the costs of applying new alternative technology.

The application of any treatment process can involve the need for one or more of the following unit operations: dredging, transport, storage, landfill disposal, land treatment disposal, incineration, and/or alternative treatment. Estimates have been developed for all of these so that, in any given processing evaluation, the proper elements could be added to obtain an estimate of the cost of application. The estimates were made in terms of the cost per cubic meter of sediment treated. The sediment was assumed to have a density of 1.68 Mg/m^3.

Table 5 shows the unit cost estimates used to develop cost ranges for the emerging treatments.

TABLE 5: UNIT COST ESTIMATES

Operation	Cost, $\$/m^3$
Dredging	20
Transport	13 to 126
Storage	10
Landfill disposal	260 to 490
Land treatment	33 to 111
Incineration	1,680

Baseline costs are taken as the range of costs for sediment removal, transport, and disposal in a chemical waste landfill. This range is calculated using the unit costs from Table 5.

Baseline costs, $\$/m^3$ = dredging cost and transport cost + disposal cost

= \$20 + \$13 to \$126 + \$260 to \$490

= \$293 to \$636.

Incineration costs include those for dredging, transport, and incineration. The cost of residue disposal is included in the incineration cost:

Incineration cost, $\$/m^3$ = dredging cost + transport cost + incineration cost

= \$20 + \$13 to \$126 + \$1,680

= \$1,713 to \$1,826.

The costs of alternative treatments are calculated in the same way, by summing the costs for the separate operations involved.

Initial Assessment of Processes

The processes assessed represent six different technologies; each of which is briefly described prior to discussing the processes to which it applies. For the processes themselves, the depth of the summaries varies because of the varing extent of available information.

Processes Based on Chemical Technologies

The MODAR supercritical water (SCW) oxidation process is a relatively low-temperature oxidation process that utilizes temperatures and pressures of supercritical water (above 374 °C and over 22.09 MPa) to break down hazardous organics to carbon dioxide, water, and other simple, less harmful molecules. The treatment is not selective but rather applicable to a broad range of compounds. Normally water-insoluble organics become highly soluble in supercritical water. The water also acts to reform complex organics, and heteroatoms, including halogens, phosphorous, sulfur, and metals, are readily precipitated as salts when present with appropriate counter-ions.

The MODAR process as applied to soil-slurry decontamination consists of the following steps:

1. PCB-contaminated sediments are fed as a slurry with 20 to 40 percent solids, as determined by some continuous flow bench-scale testing and preliminary economic studies. The slurry is pressurized to supercritical pressure then heated by heat exchange with oxidizer effluent generated in a subsequent step.

2. At the oxidizer, pressurized oxygen, organic fuel, preheated slurry and oxidizer recycle are broght together. Because the water is supercritical, the oxidant is completely miscible with the solution (i.e., the mixture is a single, homogeneous phase). Organics are oxidized in a controlled but rapid reaction. Because the oxidizer operates adiabatically, the heat released by combustion of readily oxidized components is sufficient to raise the fluid phase to temperatures at which all organics are oxidized rapidly. For a feed of 5 percent organics by weight, the heat of combustion is sufficient to raise the oxidizer effluent to at least 550 °C.

3. The effluent from the oxidizer is fed to a salt and sediment separator, where inorganics and sediments originally present in the feed are removed as a solid slurry. At 500 °C and above, the solubility of inorganics in SCW is extremely low.

4. A portion of the superheated SCW is recycled to the SCW oxidizer by a high temperature, high pressure pump. This operation provides for sufficient heating of the feed to bring the oxidizer influent to supercritical conditions.

5. The remainder of the superheated SCW (with some CO_2) is used to preheat the incoming soil slurry.

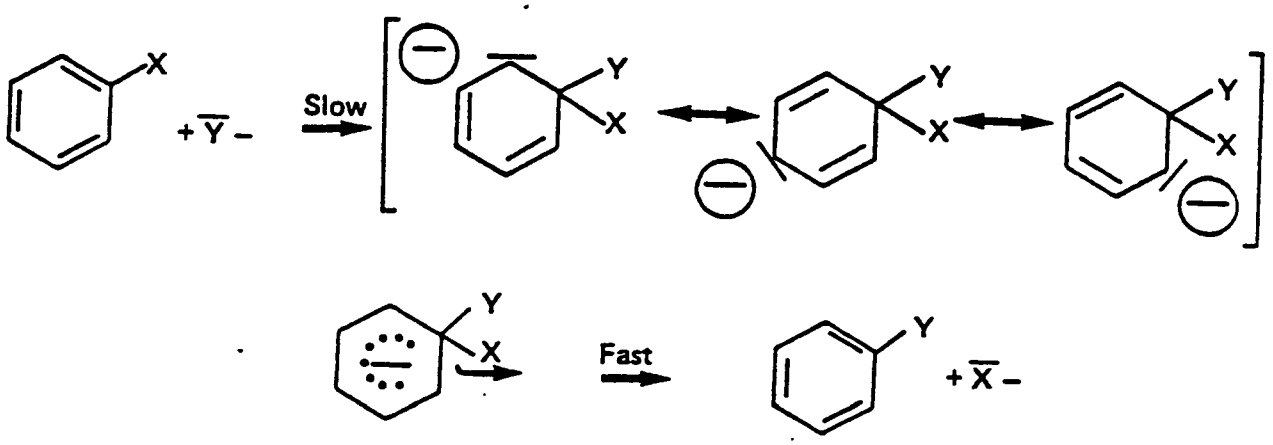
As a waste destruction process, the Modar concept has several advantages. The chemical reactions that occur are carried out in a closed system, making it possible to maintain total physical control of waste materials from storage, through the oxidation process, to the eventual discharge of the products of combustion and any associated wastes.

The Modar System has been tested for soils, and major problems in handling this type of process feed have been identified. The components would be constructed from corrosion-resistant, high-nickel alloys. Projected costs of treatment alone are \$184 to \$554/m^3 of PCB-contaminated sediment. Dredging would be required, as well as transport for treatment and redeposition of treated sediments. The overall cost estimate is thus:

$$\text{Cost, } \$/m^3 = (\$20 \text{ dredging}) + (\$13 - \$126 \text{ transportation}) + (\$184 - \$554 \text{ treatment}) + (\$33 \text{ deposition})$$

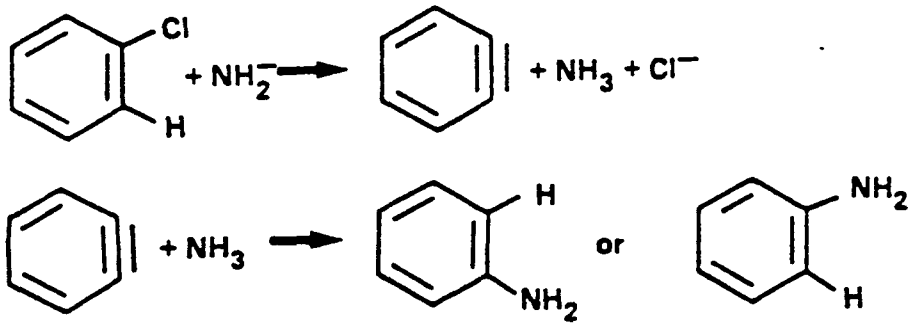
$$= \$250 - \$733/m^3.$$

Nucleophilic (electron-donating) substitution removes chlorine from aromatic compounds by two mechanisms, the intermediate complex mechanism and the benzyne mechanism. The intermediate complex mechanism consists of the following two steps, with the first usually rate-determining:



The resonance hybrid formed in the first reaction is represented by the structures within the brackets. These are shown in an alternative representation for reaction 2. The overall reaction rate is increased by the presence of activating groups (e.g., NO, NO_2) on the molecule.

The benzyne mechanisms occur on aryl halides such as PCBs, which require stronger bases than normally used because they lack activity groups on the molecule:



If the aryl halide contains two ortho substituents, this mechanism cannot occur.

Nucleophilic substitution using alkali metal hydroxides in poly (ethylene glycol) [PEG], or poly (ethylene glycol methyl ether) [PEGM] has been shown to remove chlorine from PCBs. Chlorine removal probably involves alkoxide reaction, as illustrated by the following mechanism:

$$ArCl_n + ROK \rightarrow ArCl_{n-1}\ OR + KCl$$

Chlorinated aromatic + Potassium glycollate -> PEG ether

The partially dechlorinated, water-soluble reaction product may continue to undergo dechlorination, depending on the reaction conditions.

The KPEG treatment process is identified by Galson Research Corporation as Terraclean-Cl. Evaluation of this process is based upon data for the Terraclean-Cl version.

The Terraclean-Cl process involves the chemical dehalogenation of PCBs under mild conditions. This is achieved by mixing the soil with an equal volume of hot (150 °C) reagent in a rotating mixer such as a converted cement mixer. Water coming in with the soil is vollatilized and recovered for later use in the process. The reagent consists of a mixture of polyglycols and

capped polyglycols (PEG and PEGM), potassium hydroxide (KOH), and dimethyl sulfoxide (DMSO). The exact formulation of the reagent is varied according to the specific soil and contaminant combination. The DMSO does not take part in the reaction but acts as a catalyst and phase transfer agent to extract the PCBs from the sediments.

At the end of the reaction, usually 30 to 120 min, the bulk of the reagent (>80 percent in field tests) is decanted from the soil. A small part of the reagent remains on the soil, along with some of the dechlorinated reaction products. The residual reagent and dechlorinated by-products are removed from the soil by mixing the soil with an equal volume of water and decanting the water. This washing is done two or three times and provides >99 percent overall recovery of reagent. The washwater from the last wash is passed through a bed of activated carbon, which preferentially removes the dehalogenated products. The contaminated carbon is burned in a PCB incinerator. The partially dechlorinated PCB continues to dechlorinate, with >98 percent of the chlorine associated with the PCB being recovered as KCl under some conditions; the DMSO acts as a catalyst and phase transfer agent by increasing both the rate of reaction and the rate of transport of PCB from the soil into the reagent.

The total cost of application of the treatment process is estimated as follows:

Cost item	Cost, $\$/m^3$	
	4-h cycle	8-h cycle
Capital	12.56	25.11
Reagent	25.66	25.66
Energy	33.20	33.20
Maintenance	1.26	2.51
Labor	22.00	44.00
Water disposal	2.20	2.20
Subtotal	96.88	66.34
Profit/contingency (50 percent)	48.44	66.34
Total	145.32	199.02

These costs do not include dredging or permitting costs. With dredging costs of $\$20/m^3$, transportation costs of $\$13$ to $\$126/m^3$, and final placement costs of $\$33/m^3$, total costs in the range of $\$211$ to $\$378/m^3$ are anticipated. Permitting costs are a separate item and would depend on the degree of cooperation given by the various regulatory bodies involved. However, the total costs are not highly sensitive to this item because permitting costs of $2,000,000 would only add $\$5/m^3$ to the costs of processing.

Ultraviolet (UV) radiation may drive chemical reactions in PCBs. The structure of the products of UV radiation alone are not well defined. The primary reaction at wavelengths greater than 290 nm is stepwise dechlorination. Photolysis experiments in methanol at 298 to 313 K for 10 to 15 h showed that HCl was evolved. The products contained in the menthanol solution consisted of dechlorinated PCB and certain methanol substitution products. The amount of methoxylated products did not exceed 5 percent of the total amount of products formed.

UV light energy, combined with a reducing environment, has been used to dechlorinate PCBs essentially completely in 1.5 to 2 h. Because the photochemical reaction is initiated by the absorption of light energy, the irradiation wavelength must match the absorption band associated with the chemical bond of interest in the molecule and the solvent must not absorb significantly at the irradiation wavelength. For PCBs, low-pressure mercury lamps that emit approximately 95 percent of their energy at 253.7 nm provide adequate irradiation.

Suitable solvents include water, alcohols, and hydrocarbons. However, these have very different effects on the process efficiency and mechanism. In heavy hydrocarbons, the dominant PCB reaction is the polymerization of the biphenyl radicals to yield polyphenylenes. In basic alcohol solutions, a stepwise dechlorination of the molecule occurs. This reaction occurs via the triplet state, and the reaction rate is dependent on the lifetime of that state. The hydrogen for the hydrodehalogenation initially comes from the solvent. In alcohol solutions, sparged hydrogen gas increases the reaction rate by removing triplet quenchers from the solution by combination with the solvent from radicals formed. In addition to the hydrogen, small amounts of sodium hydroxide are added to the alcoholic solution as a chlorine scavenger.

These photochemical reaction conditions lead to a rapid, highly controllable destruction of the PCBs, yielding only biphenyl and sodium chloride as the final products. Oxygenated derivatives, chlorinated dibenzofurans, or chlorinated dioxins have never been observed in the gas chromatographs or the mass spectra of the intermediates or products in the LARC degradation of PCBs.

The LARC process (Light Activated Reduction of Chemicals) uses UV light and an optimized reducing environment to dehalogenate various chlorinated compounds extracted from soils.

Studies were performed to determine the extraction efficiency from soil of Aroclor 1260 using isopropanol as the extraction solvent. Isopropanol was chosen because it is a good LARC solvent, dissolves PCBs readily, and is relatively inexpensive.

The cost of treatment using this process has been estimated (1984) using an average concentration in the soil of 1,500 ppm. Cost items include daily operation, labor, analytical, travel, per diem, and profit. These total approximately $157/m^3$ of soil. Adding costs of dredging, transportation, and placement gives a cost range of $223 to $336/m^3$.

Pyrolysis is a thermal rupture of the chemical bonds of a molecule that destroys it without oxidation. The energy requirements vary with the material being processed. The use of pyrolysis requires the adoption of process designs that provide for transport of material that can melt, char, or become sticky during passage through a reactor. The design must provide for efficient heat transfer to the material so that it can be heated to 2,000 to 2,300 °C. Pollution controls are required to remove particulates and toxic components from exit gases. Feeds to pyrolysis units must usually be predried.

The advanced electric reactor (AER) is a thermal treatment process. Pretreatment of the feed material is required. It must be dried to a moisture content of less than 3 percent and ground to 35 mesh particle size.

The treatment process is based on a high-temperature fluid-wall reactor. The reactor heats organic compounds rapidly to temperatures in the range of 2,200 °C using intense thermal radiation in the near infrared. The reactants (in this case, nonliquid PCBs) are isolated from the reactor core walls by a gaseous blanket of nitrogen flowing radially inward through the porous core walls. Carbon electrodes are heated and, in turn, heat the reactor core to incandescence so that heat transfer is accomplished by radiative coupling from the core to the feed materials. The only feed streams to the reactor are the solid waste containing PCBs and the blanket gas (nitrogen). PCBs are destroyed by pyrolysis rather than oxidation. Therefore, typical products produced by incineration such as carbon monoxide, carbon dioxide, and oxides of nitrogen are not formed in significant concentrations. The principal products of soil-borne PCB destruction are H_2, Cl_2, HCl, elemental carbon, and a granular free-flowing solid-derived waste.

The solid feed stream is introduced at the top of the reactor by a metered screw feeder connecting the air-tight feed hopper to the reactor. Nitrogen is introduced primarily at two points in the reactor annulus formed by the external containing vessel and the porous graphite core to create the fluid wall.

Small nitrogen streams are used to sweep sight glasses, prevent oxygen intrusion at the electrode ports, and similar nonprocess uses. Nitrogen flow is monitored by calibrated orifices in each feed line. The solid feed passes through the reactor where pyrolysis occurs. After leaving the reactor, the product gas and waste solids pass through two post-reactor treatment zones (PRTZ). The first PRTZ is an insulated vessel that provides additional high-temperature (1,095 °C) residence time (5 s), and the second PRTZ is water-cooled. It also provides additional residence time (10 s), but it primarily cools the gas to less than 538 °C prior to downstream particulate cleanup.

The product gas then enters a baghouse for fine particle removal followed by an aqueous caustic scrubber for chlorine removal. Any residual organics and chlorine are removed by passing the product gas through two banks in series of five parallel activated carbon beds just upstream of the emissions stack. The organic-, particulate-, and chlorine-free product gas, composed almost entirely of nitrogen, is then emitted to the atmosphere through the process stack.

Solids exiting the PRTZ are collected in a solids bin that is sealed to the atomsphere. Additional solids in the product gas are removed by a cyclone and routed back to the solids bin. The solids collected in the solids bin are removed by plant personnel after each test or pair of tests.

For very large volume cleanups, a cost estimate is \$412/ton (\$763/m^3) strictly as a budgetary cost figure and not as an absolute cost or quotation. This amount does not include the costs of dredging, transporting soil to the AER site, or facilities for storage of dredged soil. It also does not provide for cost of landfilling or other disposal of the treated sediment.

The capital cost for construction and initial testing of a single 25,000-ton/year transportable AER is approximately \$4 million, not including permits and trial burns. With six units, it would require approximately 3.5 years to treat 382,000 m^3 of sediment.

Dredging would be required, also transport for treatment and redeposition of treated sediments. The overall cost estimate is thus:

$$\text{Cost, } \$/m^3 = (\$20 \text{ dredging}) + (\$13 - \$126 \text{ transportation}) + (\$763 \text{ treatment}) + (\$33 \text{ deposition})$$

$$= \$829 - \$942/m^3.$$

Thionation introduces sulfur into an organic molecule to displace chlorine. The possible use of sulfur reactions to degrade pollutants has not been systematically exploited. It has been reported that, at 150-170 °C, sulfur and sodium carbonate react with p-dichlorobenzene, removing the chlorine to form an insoluble polymer, sodium chloride, and carbon dioxide. Limited tests were conducted in 1986 by W. C. Von Meyer (EPA Contract No. 68-02-3992, Task 53, Project Officer John Glaser) on a mixture of dried loam soil sparged with mixed dichlorobenzenes (DCBs), sodium carbonate, and sulfur. The dichlorobenzenes were added as a 0.01 g/ml solution in acetone. Reaction was carried out in a tilted 500-ml flask fitted with a condenser and sodium carbonate trap. The trap was required to remove hydrogen sulfide gas evolved during the reaction. The reactants were mixed periodically by rotating the flask a quarter turn every two hours over the 9 hour reaction period. The temperature reanged to 88 °C, and rose in the eighth hour to 260 °C when an exothermic excursion followed evolution of volatiles formed from the sulfur. The results, based on analyses by thin layer chromatography and gas chromatography, were as follows:

1,2 dichlorobenzene:	8.4 percent dechlorinated 3.4 percent volatilized
1,3 dichlorobenzene:	90.8 percent dechlorinated 3.4 percent volatilized
1,4 dichlorobenzene:	91 percent dechlorinated 1.4 percent volatilized.

This is the extent of Von Meyer's investigation of the application of thionation to contaminated soils. As part of his study, DCB's and three chlorinated pesticides (Dieldrin, Lindane, and Heptachlor) were treated directly with two reagents; sodium polysulfide in an ethylene glycol-water media, and sulfur in ethylene glycol. With water present, the organics were all consistently volatilized at the 108-114 °C reaction temperature. The sulfur-ethylene glycol reagent degraded Dieldrin 99 percent and Lindane 90 percent. Heptachlor was not tested with this reagent.

Thionation is in the early stages of investigation, and a process for treatment of PCBs has not been sufficiently identified to permit further evaluation.

Processes Based on Physical Technologies

The term "extraction" is employed to cover not only liquid-liquid extraction but also leaching of solids with organic solvents. Extraction of PCBs from a contaminated soil or sediment is emerging as a prerequisite for most chemical processes. PCBs are first extracted using a suitable solvent, and the obtained PCB solution is then subjected to one of the processes for destruction of the PCBs. Proven solvents include kerosene, methanol, ethanol, isopropanol, furfural, dimenthyl formamide (DMF), dimethyl sulfoxide, ethylene diamine, and Freon mixtures. Supercritical fluids such as carbon dioxide have also been considered. Destruction of the dissolved PCBs is accomplished by a chemical reagent such as APEG detoxification, or the PCBs are concentrated by distillation or adsorption on carbon to give a RCRA waste that can be incinerated.

"Soilex" is a process developed at the Oak Ridge National Laboratory and reported on in 1985. Kerosene and water were determined to be the solvent of choice. Kerosene can be recovered for recycle by steam-stripping. Soil-to-water ratios of 3 to 5 and soil-to-kerosene ratios of 3 to 5 were found to be best. No difference in extraction performance could be determined between 15- and 30-min mixing times. The kerosene retention in the soil was about 25 vol percent. A three-stage batch pilot unit operating with a 6-to-1 volume ratio experienced soil feed PCB concentrations of 180 to 350 ppm and discharge soil levels of 6 to 9 ppm. Lower soil values could be obtained using additional stages. The process generates a RCRA waste (concentrated PCBs) requiring treatment and disposal.

The "Soilex" process reported pilot plant data showing an estimated 85 percent removal of PCBs from soils using a kerosene-water mixture. The kerosene solubilized the PCBs and attendant other oils, and the water helped break up the soil particles. The mixture ratio found to give the most complete extraction of PCB was one part of soil to three parts of kerosene and three parts of water.

A rough cost estimate based on increasing the number of extraction stages to achieve desired background levels of PCBs in the treated soil, is: \$856 to \$913/m^3. This includes dredging, transportation, treatment, and redeposition of the treated sediments.

In 1985, The Galson Research Corporation showed that the rate of liquid-liquid extraction of PCBs from oils solutions by APEG reagents could be substantially increased by adding dimethyl sulfoxide (DMSO) or ethylene diamine to the hydroxide/PEG phase. The reagent with DMSO reached <2 ppm PCB after 30 min versus about 400 min for the reagent without DMSO. Details of the APEG process have been described under Processes Based on Chemical Technologies.

The Acurex Corporation designed and built a solid/liquid extraction process in late 1984. A proprietary solvent is used, having been selected by comparisons of adsorption isotherms and PCB diffusion rates into several fluids: pure hexane, pure FC-113 (1,1,2-trichlorotrifluoroethane), a proprietary solvent blend, and an FC-113/hexane blend. With the pure Freon and topsoil, the equilibrium was favorable; however, it took up to 18 h for the system to reach equilibrium. Other solvents and solvent combinations were found that reduced the time to reach equilibrium to 30 to 40 min, a practical value.

The Acurex Corporation reported that repeated washings of PCB-contaminated soils with Freon-type solvents reduced the residual loading to <2 ppm. The soil types tested were sand-clay mixtures and a dark loam. PCB loadings to 1,983 ppm were leached in an agitated extractor. The pilot soil-washing system consists of a soil contactor, dirty and clean solvent storage tanks, a solvent reclamation system, steam generator, and ancillary piping equipment. It also includes vent condensers and an activated carbon adsorption system for air pollution control.

Basic estimated costs for the treatment alone range from \$130 to 390/m^3. Adding costs for dredging, transport, and placement of the treated sediments gives a total cost estimate of \$196 to \$569/m^3.

In 1985, O. H. Materials Company used methanol to extract PCBs from predried contaminated soils in a Superfund cleanup project at Minden, West Virginia. The soil was reduced to <25 ppm PCB and land-farmed. It is assumed that further reduction in PCB concentration could be achieved using more stages of extraction. The process involves slurrying the ground and predried soil with methanol,

separating and redrying the treated soil, and solvent cleanup for resale. The cleanup employs activated carbon, which is subjected to incineration (other treatments could be used) as a RCRA waste. The cleaned soil is subjected to light land farming for degradation of any residual methanol. Wastewaters are treated in a holding pond.

Based on the conceptual process and the experience thus far, the process is estimated to cost \$400 to \$514/m^3, including dredging and transport costs. In the field application (1985), methanol was purchased at \$0.69/gal (\$0.18/L) and resold at \$0.23/gal (\$0.06/L).

Vitrification stabilizes radioactive-contaminated soils by melting. Large-scale tests (1985) have demonstrated the vitrification of 300 Mg per setting. At the high temperatures created (>1700 °C), the process pyrolyzes organic materials. The products of pyrolysis diffuse to the surface and combust. Any off-gases must be collected, monitored, and treated. Remaining ash, along with other noncombustible materials, dissolves or becomes encapsulated in the melt. Natural convective currents within the molten mass help distribute the stabilized materials more uniformly. The molten soil or sediment is allowed to cool to a durable glass and crystalline form.

In-situ vitrification (ISV) is a patented process developed at Battelle Pacific Northwest Laboratory for the U.S. Department of Energy as an in-place stabilization technique. Submerged sediments would be dredged before being subjected to this treatment. In evaluation of its potential application to soils contaminated with PCBs, an engineering-scale in-situ vitrification test with PCB-contaminated soil has been performed for the Electric Power Research Institute to determine the fate of PCBs and their byproducts when the process is applied.

The cost of using the vitrification as a technique for in-situ treatment has been estimated by the developers. The estimate includes expenses from four categories: site preparation and closure activities, annual equipment charges, operational costs, and consumable supplies including electrical power and molybdenum electrodes. These costs are estimated to be between \$150 and \$330/m^3 depending on electrical power rates and soil moisture content. Soil moisture content increases the cost by requiring more energy and time to vitrify a given volume of contaminated soil because the water in the soil must be evaporated. The total cost of using this approach requires, for submerged sediments, the addition of dredging, transportation, and redeposition costs.

The solidified blocks of treated sediment could not be disposed of by land treatment. If treated at a hazardous waste facility, they could be landfilled there. The cost of such disposal would probably be the regular charge for hazardous waste disposal, \$260 - \$490/m^3. The treated material is estimated to be eligible for delisting, however, and redeposition at a lower cost should be possible. Given that the physical form of the treated sediments will limit somewhat the available locations for its redeposition, a cost of \$72/m^3 has been estimated. This cost is less than that of controlled, managed land

treatment ($111) since the material would require no control or management. It is greater than the $33/m^3 cost of short-term land treatment. The overall cost estimate is thus:

$$\text{Cost, } \$/m^3 = (\$20 \text{ dredging}) + (\$13 - \$126 \text{ transportation}) + (\$150 - \$330 \text{ treatment}) + (\$72 \text{ redeposition})$$

$$= \$255 \text{ to } \$548.$$

Processes Based on Biological Technologies

Biological technologies for PCB treatment include the use of free microbes or their enzymes. The microbes may be bacteria or fungi and may act aerobically (or anaerobically) or facultatively. They may be indigenous microorganisms, conventional chemical mutants, or recombinant microorganisms. Their action may result in partial or total degradation of the PCBs. Total degradation, termed mineralization, occurs when the metabolic products are CO_2, H_2O, and HCl. Their action may take place within the cell (bacteria) or external thereto (fungi).

Enzymes may be applied as free-flowing solutions or bonded to a solid substrate. The use of enzymes alone has great conceptual potential but has not progressed very far at this time.

Thirty-four bacterial strains and five fungal strains have been shown to have varying degrees of competence in degrading PCBs. These microorganisms metabolize PCBs using enzymes specific to the strain. Since most enzymes are notably specific in their actions, different enzymes catalyzing the reaction of different PCB isomers (termed cogeners in the biotechnology literature). In some cases, the cogener may be metabolized only partially by a particular species, and a product (e.g., a chlorobenzoate) may accumulate. In a parallel situation, another species may be able to metabolize that product further, although the second species may lack enzymes needed to metabolize the parent PCB. By themselves, neither species could mineralize the cogener. However, a mixed culture might act in concert mineralizing the product resulting from metabolism of the substrate by the other species. A consortia of more than two species may be required to mineralize a substrate and the effective species may be bacteria, fungi, or a mixture of the two.

Some cells cometabolize PCBs; that is, they metabolize a PCB cogener while obtaining their carbon and energy from other sources. Such metabolism may be partial or complete and depends upon enzymes already active in the cell.

Biological technologies include a very broad spectrum of potential capabilities, many aspects of which are being explored. True measures of their ultimate capabilities for PCB-destruction cannot yet be made. Recent developments in mutant and enzyme technology are described, in the following nine paragraphs.

Indigenous and conventional chemically mutated microorganisms (those found growing naturally in diverse PCB-containing soils and sediments) have been isolated, identified, and tested for PCB-degradation capability using an assay mixture containing five types of cogeners selected to provide different resistance to enzyme attack.

The results obtained using 25 strains, including 15 isolates and 11 unidentified field isolates (e.g., H337 is an unidentified gram-negative organism isolated from Hudson River sediments), identify Alcaligenes eutrophus H850 and Pseudomonas putida LB400 as the best microorganisms, both being able to degrade 13 test cogeners 80 to 100 percent. Ten additional strains of bacteria were studied by different investigations. Of these, the Arthrobacteria degraded the most PCB cogeners.

The degradative pathways and cogener preferences differ among the microorganisms. Many bacteria oxidize PCBs via chlorobenzoic acid intermediates and often accumulate the chlorobenzoate products. The major pathway proposed for A. eutrophus H850 involves a dioxygenase that preferentially attacks at carbon positions 3,4. In contrast, Corynebacterium sp MB1 probably employs a more common 2,3 dioxygenase mechanism.

Genetics studies of PCB-degrading bacteria have demonstrated that some of the effective strains contain one or more plasmids. Plasmids are stable extrachromosomal circular double-stranded DNA replicons that are inheritable but are also dispensable. Mutants of H850 that have lost their plasmid have also lost the ability to metabolize PCBs.

Mutations that living cells may undergo alter the genetic message. Sometimes the alterations in the DNA code may lead to alteration of the cell's metabolism. Some mutations allow the cell to survive in the presence of potentially toxic compounds. In other cases, the cell acquires the ability to use previously unsuitable substrates. Some agents, including UV light, some kinds of radiation, and some chemical agents, cause increased mutagenesis. These mutations are characterized by being randomly distributed across the DNA. Mutations can be selected by applying selective pressures to a population, creating an unfavorable environment in which only those cells that have adaptation may take months before the altered population is large enough to be observed.

Limited studies on the degradation of specific chlorinated biphenyl compounds by pure strains of bacteria have established some general features of PCB metabolism. A few strains have been shown to mineralize some chlorinated biphenyls. In most cases, bacteria can degrade one ring of a chlorinated biphenyl but are unable to degrade the resulting chlorinated benzoates. These compounds accumulate in pure cultures. Other strains have been shown to be capable of completely mineralizing chlorinated benzoates (e.g., the hybrid strain of Pseudomonas sp B13 carrying the relatively nonspecific oxygenase of P. putida mt-2 carried on the TOL plasmid). Mixed cultures of bacteria have been shown to mineralize PCBs with four or fewer chlorines per molecule. More heavily substituted PCBs appear to resist degradation to a greater extent.

The mechanism of hydroxylation of PCBs by bacteria has not been elucidated, nor have the enzymes mediating the steps in the proposed pathways been isolated. Two pathways have been proposed. The first involves initial hydroxylation in the 2,3-position of the less substituted ring, followed by meta cleavage and subsequent degradation of the aliphatic portion of the molecule to form substituted benzoic acids. Chlorines on the aliphatic carbons are lost during this process.

However, this may not be the mechanism for degradation of PCBs substituted in all the ortho positions. A second pathway, based on the action of a monooxygenase in bacteria has been proposed after discovery of 4-hydroxy-4'-chlorophenyl in extracts of bacteria cultures incubated with 4-chlorobiphenyl. More evidence corroborating this mechanism is needed. It is proposed that the major pathway of PCB metabolism in *A. eutrophus* H850 utilizes a dioxygenase that preferentially attacks at carbon positions 3,4; while *Corynebacterium sp.* MB1 probably employs a more common 2,3 dioxygenase. Limited evidence on fungal metabolism of PCBs indicates activity of a monooxygenase.

Little has been done to prepare or work with enzymes alone, separated from the organisms, despite the conceptual attractiveness of the approach. The separation processes for PCB-degrading enzymes are yet to be developed. Some enzymes may be cell wall bound, requiring special handling in their preparation. At present, little is known concerning the use of enzymes alone for PCB decontamination of sediments.

The Bio-Clean process is a biological treatment process developed by Bio-Clean, Inc., Bloomington, Minnesota. It has been well demonstrated for PCPs. It requires further testing with, perhaps, the use of some additional strains of microorganisms to bring it through the pilot stage for PCBs. It is listed here as a representative bio-process that has potential application and can be made available commercially. It does not require pretreatment to dewater sediments, and it does not appear to generate any RCRA wastes or emissions. The process involves two steps: (1) extraction, sterilization, and solubilizing the contaminants using high pH and temperature, and (2) bacterial destruction of the contaminant. These steps generally require 3 days. Standard digesters that can handle 22 to 28 m^3 of sediment (dry bases) are used in sets of three to provide a daily capacity in multiples of 22 to 28 m^3/day.

The processing cycle requires four steps:

1. Contaminated sediment is charged to the digester, in slurry form if so received. The final digester charge will be approximately 2/3 water and 1/3 solids. The charge is made alkaline with sodium hydroxide (or other alkaline hydroxide), then heated to approximately 82 °C, at which temperature it is held for one hour. The mix is agitated to promote solubilization of the PCBs.

2. After the extraction, the slurry is cooled to 30 °C, neutralized and inoculated with a selected microorganism(s) to initiate decontamination. The slurry is kept under these conditions for 48 to 72 h as required, until the desired degradation has been attained. The exact time requirements must be determined by tests for each particular decontaminant. The degradation is an aerobic process and uses sterile filtered air for oxygen.

3. A treated batch of sediment is discharged to a dewatering pit where the sediment is separated for redeposition. The material is sampled and tested to determine the concentration of residual PCB prior to its relocation. The water is also analyzed for PCBs and thus disposed of in a manner suitable for the particular site (e.g., through sanitary sewer systems, storm sewer systems, or percolation into the ground or recycle).

4. At the end of the decontamination period, the cycle begins again at 1.

The estimated cost of treatment using the Bio-Clean process on floating barges is \$191 to \$370/m^3. This includes dredging at \$20/m^3, and treatment costs at \$171 to \$350/m^3.

The Sybron process is a conceptual process still in the laboratory scale. Information obtained from the company was very limited, and its evaluation is correspondingly limited. The process may be able to operate under both aerobic conditions or anaerobic conditions with facultative aerobes and supplements of nitrates. Further studies to define an anaerobic process concept and principles have been proposed. This process has not been developed sufficiently to permit a description in terms of unit operations. Information provided by Sybron includes tests of their Bi-Chem 1006 PB for removal of PCBs from a municipal sewage sludge. Cost estimates could not be made, due to the limited available information.

Aerobic and anaerobic composting of PCB-contaminated soil has been studied on a laboratory scale. Experiments were carried out with soil that was intentionally spiked with PCBs (Aroclor 1242). Aerobic composting resulted in the greatest decrease in PCB concentration, with an average reduction of 62 percent in four weeks. Residual concentrations ranged from 504 to 688 ppm. Anaerobic composting resulted in 27 to 47 percent reduction in four weeks, with residual concentrations ranging from 825 to 1,120 ppm.

Composting would appear to require considerable work-site space to handle the sediment, with considerable monitoring to determine the progress of the process. Lack of control of weather and other conditions would make the process uncertain in terms of time and effort required.

Data for composting are insufficient to provide a basis for cost estimates. Considerable extrapolation of the performance data would be required to project process conditions for desired residual PCB concentrations.

Initial Characterization and Ranking of Processes

This subsection provides two comparisons of the alternative treatment processes previously discussed: characterization and ranking. The characterization provides for objective comparison of processes. The ranking provides a subjective comparison of the processes based on the seven criteria previously described.

Characterization

Table 6 summarizes five characteristics of the processes: unit operations, available capacity, conditions/limitations, concentration handled, and any generated RCRA wastes. The unit operations employed are given, and each is identified by a number. Generally, a greater number of unit operations will mean a greater effect on treatment costs. None of the processes has currently available capacity approaching that required for major cleanups. Therefore, the time required to build capacity is listed. Construction time ranges from 12 to 24 months. Certain conditions that typify the process or limit its versatility are given in column 4 of Table 6.

The data from studies of the processes were examined for ranges of PCB concentrations handled to date. Generally, the values are not limitations on the process, but only on the data acquired. The value <300 ppm for the Bio-Clean process may, however, be a limitation requiring process adjustment to control.

TABLE 6. TREATMENT PROCESSES CHARACTERISTICS

Process	Unit Operations	Available capacity (or time to provide)	Conditions and limits	Concentration handled	RCRA waste generated
Chemical					
Supercritical water oxidation	1,4,10	____	20-40% solids; 374 °C, 23.3 MPa organic content >5% or supplemental fuel.	>3000 ppm	None
KPEG, Terraclean-Cl	1,3,4,7	(24 mo)	150 °C, 0.5-2 h	500 ppm or greater	w.w.tr. act. carbon
KPEG, NYU	1,2,3,4,5, 6,7,9	____	____	____	____
LARC	1,2,5,15	(24 mo)	tolerates 25% water.	480 ppm	None
Advanced electric reactor (J.M. Huber)	7,8,12,13 14	(16 mo)	2204 °C, 2,400 kWh/m^3 needs predryer	>3000 ppm	None
Physical					
O. H. Materials methanol extraction	2,7,8,,14 15	____	predry to <1% moisture	>400 ppm	PCB-loaded carbon from solvent cleanup
"Soilex" kerosene/water	1,2,5,15	____	26% of kerosene solvent retained in soil; 3 d per batch	to 350 ppm tested	Concentrated PCB from still to incineration
Acurex solvent wash	2,4,5,6, 10,11	____	3-12 washes, tolerates <40% water.	up to 1,983 ppm	Concentrated PCB's to KPEG
Vitrification	8,12,14	____	Electrical power usage increases with soil moisture: submerged sediments dredged and treated	500 ppm	None

TABLE 6 (continued)

Process	Unit Operations	Available capacity (or time to provide)	Conditions and limits	Concentration handled	RCRA waste generated
ological					
mposting	15,16	(16 mo)	Seasonal effects, reaction time must be >4 weeks	1590 ppm	Treated material is still a RCRA waste
o-Clean	1,2,17	27 m^3/d available, 12 mo for full-size	Proved for PCP, laboratory confirmed for PCB's	<300 ppm	None
ɔron Bi-Chem 1006	15,17	____	Unknown	Unknown	Unknown

ɔte-Unit operations key:

1. Liquid/solids separation
2. Extraction/solubilization (liquid-solids)
3. Liquid/liquid extraction
4. Chemical reactor
5. Stripping still
6. Solvent recovery still
7. Adsorption
8. Dryer (solids
9. Dryer (liquids)
10. Filtration
11. Steam cleaning
12. Thermal reactor
13. Grinding
14. Air pollution controls
15. Landfarm
16. Inoculation/digestion
17. UV light reactor

Ranking

In contrast to process characterization, ranking is subjective. An attempt was made to define and determine a single number that could represent the overall position of each process relative to an arbitrarily defined perfect process. To do so, factors considered were given ratings as described below.

The goal set for process performance is to reduce the PCB concentration in treated sediments to background levels of 1 to 5 ppm. Several of the processes were found to meet this goal. Those that showed reduction to less than 2 ppm were assigned a rating of "6". Those that attained a level between 2 and 10 ppm were assigned a "4". Those with residual concentrations greater than 10 ppm were rated "2".

Available capacity was found not to exist for any of the processes. However, several were developed sufficiently to permit projections of the time required to build a facility for application of the treatment. Those for which such projections could not be made were rated "2". Those requiring 24 or more months were rated "4". Those requiring 12 to 16 months were rated "6".

Conditions/limitations that were rated were tolerance for water, required processing time, and controllability of process conditions. Those treatments that could tolerate water up to about 40 percent would not require a drying step with its attendant fines control problems. Those requiring only 1 day for treatment could generally show a faster rate of cleanup than those requiring 3 days. Some biological processes required more than 3 weeks. The treatments generally provided control of the processing conditions; however, a few (e.g., composting) would not necessarily do so. The three conditions/limitations were ranked as follows:

Conditions/limitations	Rank
Tolerates to 40 percent water and treats in 1 day	6
Sediment needs to be dried	5
Tolerates to 40 percent water and treats in 3 days	4
Tolerates water and treats in >3 weeks	3
Sediment needs to be dried, treats in >3 weeks	2
Processing conditions uncontrollable	1

Concentration range handled in data developed for the processes ranged from unknown to 3,000 ppm. Ratings were assigned based on the upper limit of feed concentration. The ratings were as follows:

PCB concentration treated, ppm	Rank
>3,000	6
2,000 to 3,000	5
1,500 to 2,000	4
500	3
250 to 350	2
Unknown	1

Status of development ratings were "1" for no data, "2" for laboratory-scale tests completed, "3" for bench-scale tests completed, "4" for pilot-scale tests completed, "5" for field tests completed; and "6" for commercial system designed and ready for construction.

Test and evaluation data needs could be rated differently, depending upon the purpose. For indicating the extent to which a treatment process is readied for use, the more data that are available the better. For indicating the need to support a very promising technology that lacks sufficient progress, the potential and the data needs should be rated in combination. The ratings used here are for the former purpose and are as follows:

Test and evaluation data needs	Rank
None except permits and checkout	6
Field tests	5
Pilot tests and costs	4
Laboratory and bench tests	3
Conceptual treatment process design	2
D.D.R data, residual PCB data, RCRA waste data	1

The estimated costs were rated by comparing the range of the cost estimates obtained with the cost of placing them into a chemical waste landfill. Treatment processes showing the lowest estimated cost range were rated "6"; those showing a probable cost lower than landfill were rated "4"; those showing an estimated cost equal to landfill were rated "2"; and those showing an estimated cost range greater than landfill were rated "1".

Overall ranking was accomplished through the use of weighting factors assigned to each rated factor. The weighted average rank was then obtained by summing the products of the weighting factors and the ratings and dividing by the sum of the weighting factors. The weighting factors were:

Factor	Weight
Residual PCB concentration	5
Capacity	2
Conditions/limitations	3
Concentration range handled	2
Status of development	2
Test and evaluation data needs	1
Estimated costs	4

Table 7 lists five additional characteristics of the processes and the rating developed in the ranking process. The characteristics shown here relate to the needs for further process development, listing, and evaluation. The listing begins with an indication of the process status in terms of stages of development completed. The processes range in stages completed from concept to pilot plant.

Based on the weighted ratings, the eleven processes rank as follows from highest to lowest: KPEG, LARC, Acurex, Bio-Clean, Modar-Supercritical Water, Advanced Electric Reactor, Vitrification, OHM Extraction, Soilex, Composting, and Sybron Bi-Chem 1006 PB/Hudson River Isolates.

TABLE 7. TREATMENT PROCESSES RANKING

Process	Status[a]	Estimated D/D/R efficiency,% [b]	Estimated residual PCB, ppm	Test & evaluation data needs	Estimated costs, $/m^3	Rating[c]
Chemical/physical						
Supercritical water oxidation, Modar	Field test with PCB liquids	>99.9995	<0.1 ppb	1,2,3,4,5,6,7,	250-733	4.58
KPEG Terraclean-Cl	Pilot tests	>98	<1 ppm	1,6	208-375	5.42
LARC	Lab tests	>90	38-50	2,3,4,5,6,7	223-336	5.26
Advanced electric reactor	Pilot tests	>99.9999	<1 ppb	None[d]	830-943	4.58
Physical						
O. H. Materials, Methanol extraction	Field tests under way	97	<25 ppm	2,3,6,7	401-514	4.16
Soilex	Pilot tests	95 (3 stages)	6-9 ppm	5,6,7	856-913	3.26
Acurex solvent wash	Pilot-scale (field tests planned)	e	<2 ppm	Identity of mixed solvent, 6,7	196-569	5.21
In-situ vitrification Battelle Pacific NW for EPRI	Pilot test of soil	99.9	None in vitrified block, 0.7 ppm in adjacent soil	6	255-548	4.53

See footnotes at end of table.

TABLE 7. (continued)

Process	Status[a]	Estimated D/D/R efficiency,%[b]	Estimated residual PCB, ppm	Test & evaluation data needs	Estimated costs, $/m^3	Rating[c]
Biological						
Composting, aerobic	Lab-scale	62	504-908	4,5,6	____	1.79
anaerobic	Lab-scale	18-47	825-1268	4,5,6	____	1.79
Bio-Clean, aerobic	Bench-scale	99.99	25 ppb	3,5,6,7	191-370	4.84
Sybron Bi-Chem 1006	Lab-scale and concept	50	____	3,4,5,6,7	____	1.47

NOTE-Data needs key:

1. D/D/R data
2. Residual PCB data
3. Unit operations data
4. Bench-scale data
5. Pilot-scale data
6. Field test data
7. Cost data
8. RCRA waste

[a]Status is defined in terms of the types of studies completed.

[b]D/D/R=destruction/detoxification/removal.

[c]The rating was obtained as shown by the example, under Characterization.

[d]AER is fully permitted under TSCA in EPA Region IV for destruction of PCB.

[e]Treatment is continued until a residual of <2 ppm PCB's is obtained.

Final Assessment of Processes

This part of the final assessment, building upon the initial phase, describes the development of criteria for the final ranking of the processes, elaborates on description of processes previously mentioned, and discusses each new process being assessed.

Under the "Initial Assessment of Processes" we discussed the identification of eleven candidate processes, out of sixty four evaluated, with potential for decontamination of PCB-contaminated sediments. Listed in rank from highest to lowest, the top eight processes were: KPEG, LARC, EPRI (Acurex), Bio-Clean, Modar-Supercritical Water, Advanced Electric Reactor, Vitrification and OHM Extraction. The three processes ranked but considered non-candidates were: Soilex, Composting, and Sybron Bi-Chem 1006. At the start of the final assessment, four developers indicated their processes should be eliminated from further consideration. These four processes were: LARC, EPRI (Acurex), Advanced Electric Reactor, and OHM Extraction. During the course of the final assessment, four new technologies became available: The Basic Extraction Sludge Treatment (B.E.S.T.) by Resources Conservation Co.; the UV/Ozone or Hydrogen-Ultrasonics Technology by Ozonic Technologies, Inc.; the CFS Propane Extraction Process by C. F. Systems Corp.; and the Low-Energy-Acetone-Kerosene Extraction Process by Applied Science Dept. of New York University. The UV/Ozone or Hydrogen Ultrasonics Technology provides continuity for the radient-energy approach previously represented by the LARC process. The other three processes provide improved approaches to extraction technology. These eight processes, four initial and four new, were assessed as final candidates for thorough test and evaluation.

Ranking Criteria

The following criteria were used for the final selection of treatment processes for test and evaluation (pilot-field tests):

- The likelihood that the process will acceptably clean-up the PCB-contaminated sediments;
- The probable cost of the application;
- The relative level of T and E effort;
- The availability of a processing system; and
- The likely future commercial availability of the process.

Acceptable clean-up requires a standard. The standard selected is a PCB concentration in treated sediments of 2 ppm or less. The regulation requirements related to this standard were previously discussed under the initial assessment.

The probable cost of treatment is presented as the cost per cubic meter of sediment treated, based on a system sufficiently large to process 380,000 m^3 of Hudson River sediments in 2.5 years. By focusing on a specific site and size of clean-up task, each process could be assessed using available data from sampling and analyses to characterize the feed materials to the processes, and comparative cost estimates for a specific application could be obtained. The sediments from the Hudson River also meet the requirement for use of a variety of soil/sediment types in testing PCB-treatment processes.

The probable cost of treatment was obtained from the developers for those processes sufficiently supported by commercial firms, or was estimated using as major cost elements capital costs, and operation and maintenance costs. Treatment process requirements determined capital, energy, and maintenance costs. Labor rates, overhead, contingency, profit, and health and safety were costed using standard unit values for all the processes.

Maintenance was estimated at 10 to 15 percent of the capital cost, depending on the number of unit operations involved and engineering practices for the operation. The allowance for safety equipment was generally 0.30/m^3 of sediment treated ($114,000 for the clean-up of 380,000 m^3 of sediment).

The treatment system cost estimate was capitalized (recovered) over the 2.5 years of operation taken as the base period. Some developers provided treatment costs that were correspondingly lower for subsequent applications.

Engineering costs were not included in the estimates. An additional 7 to 15 percent of the subtotal cost (before profit and contingency) should be included to provide for engineering in the design and construction stage of the process application.

The test and evaluation effort required has been estimated based on a comparison of available process data with the requirements for thorough test and evaluation. A checklist of information requirements was developed to identify the data categories to be supplied to qualify the processes for a permit to test. The checklist identifies the following information as basic to assessment of each process:

1. Waste characteristics;

2. Process engineering description;

3. Sampling and monitoring plan;

4. Accident and spill prevention and countermeasure; and

5. Demonstration test plan.

For these assessments, Hudson River sediments were selected as the characterized wastes. Hudson River sediment material has been classified according to its content of clay, silt, muck, muck and wood chips, sand, sand and wood chips, coarse sand, and coarse sand and wood chips. Sediments have been shown to range from clay to cobbles, with the largest mass fraction being in the sand sizes. The coarse fraction (>0.42 mm) of the sediments typically contained wood chips, sawdust, shale chips, cinders, and coal fragments. The fine size fractions contained some fragments of the above, plus sand (containing quartz and feldspar), silt, clay, and organic material. The highest PCB concentration was the muck with wood chips class, which typically had over 30 percent silt and clay, high volatile solids and some small but visible wood chips. The size lowest in PCB was medium sized sand or gravel without wood chips.

For most of the processes assessed, test systems are available from the developer. Most developers would need financial support of the testing time and effort. A few of the processes (e.g., Low Energy Extraction) lack a suitable test system, but their estimated costs of application justify their consideration herein. The availability of a suitable test system and any conditions/restrictions on its use are discussed for each process.

The likely future commercial availability of the processes vary with the strength and extent of their sponsorship. Some developers are commercial firms in the waste treatment business with resources committed to further commercialization of their process. Some developers have a need for financial support to achieve commercialization. In all cases, the short-term (2.5 years) effort projected in this evaluation, and the uncertainties of further markets make the construction of a full-scale treatment system contingent upon completion of the T and E (with attendant EPA approval of the process) followed by a contract for the clean-up work itself. Under these necessary conditions, all the processes assessed would be commercially available. The estimated time required to make them available varies from process to process; however, this has been taken into consideration in this evaluation.

B.E.S.T.

The Basic Extraction Sludge Treatment (B.E.S.T.) process has been developed by the Resources Conservation Co. (RCC), 3101 N.E. Northup Way, Belleview, WA 98004. The company was founded in 1968 and is a subsidiary of Reading and Bates. The process uses a solvent having an inverse critica solution point in water to remove water and oily material from solid matter. It has been applied to clean-up PCB-contaminated oily sludges at a CERCLA site (General Refining Site, Savannah, Georgia).

The company has bench units to perform glassware simulations of the process, required to establish parameters for its application to a particular sediment. The company also has a process components test unit sufficiently large to process 91 kg of sediment feed in seven days, and a large-scale skid mounted unit designed to process 91 metric tons per day (24 hours) of feed.

The process is described generally as it is applied to PCB-contaminated sediment, sludge, or other feed material containing solid matter, oily contaminants, and bound and unbound water. The feed is first pretreated with an alkaline composition, then admixed with triethylamine (TEA) while cooling below the critical solution temperature (CST). A single liquid phase is formed from which the solid matter is separated. The liquid is then heated to a temperature above the CST, to form an amine phase and a water phase, after which the water phase is decanted from the amine phase. The amine phase contains substantially all of the oily material including organic contaminants. It is processed to recover the oil and contaminants, and the TEA is recycled for the processing of additional feed material. The pretreatment of the feed with an alkali reduces substantially the amount of residual amine carried over into the solid and water products.

This process is essentially ready for T and E. The program should include three "glassware" evaluations at a cost of $3,500 each. If the glassware testing is successful, a pilot test at a cost of $50,000 would then be conducted. Total cost: $50,500, with the equipment provided by RCC. EPA would supply the sampling and analyses, and evaluation of the results as a separate program. The estimated cost of T and E is $148,530 (analyses - $13,030; support including permits, sampling/testing, and report - $75,000; test operation - $60,500).

Ultrasonics/Hydrogen - Ozone/UV Technology

The LARC process, discussed under initial assessment, is not now under further consideration by the developers (George Anspach, Atlantic Research Corp., 5390 Cherokee Ave., Alexandria, VA 22312). Another firm (Edward A. Pedzy, Ozonic Technology Inc., 90 Herbert Ave., P. O. Box 85, Closter, NJ 07624) has capabilities and interest in conducting tests of PCB-contaminated sediments. Thus, their Ultrasonics/Hydrogen-Ozone/UV Technology became a replacement in approach for the similar LARC-UV process. This Ozonic process has been shown to be effective in cleaning PCBs from solid surfaces.

The process is based upon simultaneous extraction and treatment of a sediment slurry with ultrasound (above 20KHz) added to increase rates of dissolution of the PCB contaminants and reduce coalescence of bubbles of gas reactants. The treatment is achieved by either ozone/ultraviolet irradiation or hydrogen/ultraviolet irradiation. The sediments are fed as a slurry containing about 20 wt. percent solids into a mixing tank where predetermined amounts of detergent and sodium hydroxide are added. The conditioned mix is pumped to the reactor where the solids are maintained in suspension while the mixture is exposed to ultraviolet irradiation and ozone (or hydrogen) is added. During this treatment, microscopic turbulence is produced through ultrasonics. The treated slurry is fed into a cyclone where the solids are removed, sampled, and tested to certify them for discharge. The separated water is neutralized and also tested before discharge.

The process needs to be tested using PCB-contaminated sediments to establish the process feasibility and to determine its potential performance. The tests would involve assessing both UV/hydrogen/ultrasonics and UV/ozone/ultrasonics. The total estimated T and E cost is $151,000 (analyses - $21,000; T and E support, permits, and report - $75,000; system operation - $55,000).

Bio-Clean Naturally-Adapted Microbial

The Bio-Clean Naturally-Adapted Microbial process has been developed by Bio-Clean, Inc., 201 W. Burnsville Pkwy., #130G, Burnsville, MN 55337. A patent is pending on the process. Bio-Clean is a company engaged in developing process systems to clean-up, remove or destroy hazardous chemicals in the environment. The company has a suitable bench-system to support pilot and field tests (32-45 metric tons/day capacity), and a laboratory test system for conducting preliminary tests to establish specific conditions for a field test. Support would be needed for the pilot and field work. The process, once proven, would be available from the firm.

The process utilizes Arthrobacteria sp and/or other naturally-adapted microbes to destroy PCBs (and related organics) under aerobic conditions. Specifics of the process have been discussed under Initial Assessment of Processes-Processes Based on Biological Technologies. Preliminary tests would be required to adapt the biological treatment to the specific waste. The total estimated T and E cost is $163,600 (analyses - $33,600; T and E support, permits, and report - $75,000; system operation - $55,000).

KPEG with DMSO

Nucleophilic substitution with the KPEG process and the Galson Research Corp. version (Terraclean-Cl process) was previously discussed as a means of decontaming PCB-bearing sediments. Presented here is an elaboration of that discussion pertaining to recent developments in the KPEG process. Although the Corporation identified their version of the KPEG treatment process as the "Terraclean-Cl" process, a more descriptive name is "KPEG with DMSO", since the DMSO is the major ingrediant in their modification to the KPEG process.

The potassium polyethylene glycolate (KPEG) process has two potential applications in the treatment of PCB-contaminated sediments: The treatment of the sediments themselves, or the treatment of concentrated PCBs resulting from extraction processes. The former is assessed herein in terms of the Galson Modified KPEG process, that is with dimethyl sulfoxide (DMSO). The latter application would require treatment of a relatively concentrated solution of PCBs in a non-aqueous solvent (triethylamine, kerosene, etc.).

The process developed by the Galson Research Corporation, 6601 Kirkville Road, E. Syracuse, New York 13057, is scheduled to demonstrate treatment of contaminated sandy soil on Guam, and is assessed here based on data from the Phase 1 study and new data developed to qualify for this demonstration.

Galson has laboratory test facilities necessary to set process parameters for a demonstration, and a 150 L (40 gal) pilot system. For treatment of Guam soils, a 1.5 m^3(40 gal) system will soon be constructed and available for various demonstrations. It is this potential system for Guam soils that was considered in this assessment study.

As previously discussed under initial assessment of processes, the Galson or KPEG with DMSO process destroys PCBs by nucleophilic substitution. Potassium hydroxide is reacted with polyethylene glycol (PEG) of about molecular weight 400 to form an alkoxide. The alkoxide reacts with one of the chlorine atoms on a chlorinated molecule to produce an ether and potassium chloride. Addition of an RO-group enhances the solubility of the molecule and makes it less toxic. The reaction may continue until several chlorine atoms are removed from the PCB molecule. The reagent consists of a mixture of PEG, potassium hydroxide, and dimethyl sulfoxide (DMSO). The DMSO acts as a solvent or phase transfer agent to extract the PCBs from the sediments.

Equipment to be used to implement the above chemical process consists of a carbon steel reactor (1.5 m^3 capacity), storage tanks for pre- and post-treatment bulk storage, and a carbon adsorption unit for collection and control of gaseous byproducts of the process.

Contaminated sediment is fed to the reactor from 55 gallon drums. An equal volume of reagent is added to the soil in the reactor. The reagent is blended with the soil using a carbon steel bladed mixer.

During operation of the system, reagent is mixed with make-up reagent from the reagent storage tank and recirculated into the reaction vessel containing contaminated soil. The reaction vessel is heated and the soil and reagent are kept mixed until the reaction is complete. Volatilized material from the bulk storage tank and the reaction vessel are vented through a charcoal adsorption unit. Water vapor is condensed and used as wash water. At the end of the reaction, the slurry is pumped into a similarly vented bulk storage tank. The reagent is decanted, weighed, and stored for reuse. The soil is washed twice with water to remove excess reagent, and the wash water is held for analysis and possible treatment with activated carbon.

For this assessment study, temperature in the reaction vessel is controlled at 150 °C as measured on the system's temperature gauges. Mixing blade speeds are controlled between 500 to 1,500 rpm. Energy to operate the blades and heat the reaction vessel is supplied by a diesel generator.

The treated sediment is held for analysis. If PCB concentration is greater than 2 ppm, the sediment is retreated. Byproducts in the sediment will be less than 2 ppm KPEG with DMSO plus reaction products. All of which have been proven to be non-toxic. The total T and E cost is estimated at $196,000 (analyses - $21,000; T and E support, reports, and permits - $75,000; system operation - $100,000).

CFS Propane Extraction

The CFS Propane Extraction Process is a technology available from C. F. Systems Corporation, 25 Acorn Park, Cambridge, Massachusetts 02140. The company is a subsidiary of Arthur D. Little. As applied to PCB-contaminated sediments, the process uses propane at ambient temperature and 1378 kPa (200 lb/in^2) to extract PCBs along with other oily organics from a water slurry of the sediment. The treated slurry is discharged after separation from the liquid propane which contains dissolved contaminant. The propane solution is fed to a separator where the solvent is removed by vaporization and recycled. The contaminants are drawn off as a concentrate for final treatment. The process has been tested for PCB-containing refinery sludge. The PCB content of the solids component of the sludge was reduced to 5 ppm.

The company has a small portable 1-liter test unit for preliminary evaluations of the potential of the process using 0.56 kg of feed, and will have a mobile propane pilot system soon. Preliminary tests of Hudson River sediments using the portable test unit would be conducted by C. F. Systems at their expense. Large-scale tests would require financial support.

The technology is available for preliminary testing to establish the processing parameters and system needs for PCB-contaminated sediments. A full-scale system would be designed based upon the results of testing using the bench-scale unit. C. F. Systems would not be able to conduct the tests at Cambridge, but could make the unit available for testing elsewhere. The total estimated cost for T and E is $122,660 (T and E including permits and report $75,000; analyses - $17,660; system operation - $30,000).

Modar Supercritical Water - Oxidation

The Modar Supercritical Water - Oxidation process is another process that has been previously discussed under the initial assessment of chemical technologies. The process is described here based upon discussions with the developers and data supplied by them during the final assessment.

The process has been developed by MODAR, Inc., 3200 Wilcrest, Suite 220, Houston, Texas 77042. The process utilizes water above critical conditions (374 °C and 22.1 MPa) to increase the solubility of organic materials and oxygen and effect a rapid oxidation, destroying organic contaminants. It has been applied to destroy PCBs in oils, and to decontaminate dioxin tainted soil. The company has a laboratory test unit and a skid-mounted pilot test unit having a nominal organic material flow capacity of 190 Liters/day. This unit has been operated at MODAR's research facility in Natick, Massachusetts and at the CECOS International Niagara Falls site.

The following describes the preocess as it would be applied to sediments. If not done as part of the dredging operation, the system would need to include a screen to remove rocks and large pebbles. A feed pump would handle the range of sediment particle sizes up to about 2 mm diameter, at 20-40 percent solids.

Feed to the process is controlled to an upper limit of heating value of 4187 kJ/kg (1800 Btu/lb). The Hudson River sediments lack sufficient heating value, therefore fuel addition will be necessary. A combination of preheat by exchange with process effluent and fuel addition is a more cost-effective option. A portion of the supercritical process effluent will be recycled to the reactor by a high-temperature, high-pressure pump to raise the combined fluids to a high enough temperature to maintain rapid oxidation reactions in the countinuously fed reactor. Oxygen, stored as a liquid, is pumped to system pressure, preheated, and metered into the reaction vessel. Alternatively, air can be compressed and used as the oxidant. It would be best to demonstrate viability on their bench-scale unit. This would avoid the costs of modification of the pilot system for slurry handling and onsite demonstration until the process has been proven. To accommodate the particle-size restrictions, the sediments may need to be pulverized and hydrosieved to provide a feed of size less than 38 um. The total estimated cost of T and E is $483,000 (analyses-$8,000; T and E support including sample preparation, permits, and final report-$50,000; operating cost-$425,000). The support cost is high because of the anticipated effort to be expended in resolving design and safety considerations.

Low Energy Acetone-Kerosene Extraction

The Low Energy-Acetone-Kerosene Extraction Process is being developed by the Applied Science Department of New York University, 26-36 Stuyvesant St., NY, NY 10003. The extracted contaminants are concentrated for subsequent disposal. The basic principles of the process have been confirmed experimentally using PCB-contaminated sediments from Waukegan Harbor, Illinois.

The process is based on an EPA-funded study to develop and evaluate a low-energy technology for extraction of PCBs and other organic contaminants from sediments and concentrating the extract in a manner suitable for the application of a chemical destruction process. Details of the process and the study have been previously discussed under Section 4 (Discussion on Extraction Process). The development of this process through field test and evaluation is estimated by New York University to require $827,000. This includes the construction and operation of a field-scale unit. A possible commercial sponsorship is being actively sought which, if confirmed, would reduce this cost to an estimated $170,000.

In Situ vitrification

In Situ Vitrification was previously discussed as a process developed to treat radionuclide-contaminated wastes, and subsequently tested for possible adaptation to the treatment of PCB-contaminated soils. Submerged sediments would be dredged before treatment. The process stabilizes contaminated soils by melting into a durable glass and crystalline form. Four electrodes are inserted into the sediments in a square array. A path for electric current is made by placing a mixture of graphite and glass frit between the electrodes.

Dissipation of power through the starter materials creates temperatures high enough to melt a layer of sediment, which establishes a conductive path. The molten zone grows downward through the contaminated soil. At the high temperatures created (<1700 °C) organic materials pyrolyze, diffuse to the surface, and combust. Off-gases are collected, monitored, and treated.

The process has been developed by Battelle Pacific Northwest Laboratories, P. O. Box 999, Richland, Washington. Battelle has indicated that they are performing an Eastern soils demonstration in July, 1987 at the Oak Ridge National Laboratory site in Tennessee, and have scheduled a pilot-scale PCB test for September, 1987.

The estimated total T and E cost is $400,000 (Analyses, $14,200; T and E support, $75,000; test system operation, $310,800). The test system includes exit gas, capture canopies, and pollution controls.

The estimated treatment cost for this process is higher than that for other processes evaluated, primarily due to the cost of consumable electrodes and electric power.

Selection of Three Processes

All the processes assessed have merit. In selecting among them, a ranking system has been employed for comparative simultaneous evaluation of all five criteria characteristics. For each process, the desirability of immediate thorough test and evaluation was expressed by a desirability value, Dj:

$$Dj = (d_{1j}d_{2j}d_{3j}d_{4j}d_{5j})^{1/5} \qquad (1)$$

where: d_{ij} = the rating of process j for criteria i for i from 1 to 5, $0.0 \leq d \leq 1.0$.

This function is a multiplicative decision model, although it may be regarded as a linear model if it is utilized in its logarithmic form. The methodology does not in its original form provide for weighting of the factors involved. Instead, it applies equal weights to all factors. Each factor may be weighted, however, by the application of an appropriate exponent. This is shown as follows:

$$D_{j,modified} = (d_{1j}^{x_1} d_{2j}^{x_2} d_{3j}^{x_3} \ldots d_{nj}^{x_n})^{1/n} \qquad (2)$$

where: x_i = the weight of factor i.

The logarithmic form is:

$$\log D_{j,modified} = 1/n\ (x_1 \log d_{1j} + x_2 \log d_{2j} + x_3 \log d_{3j} + \ldots + x_n \log d_{nj}). \qquad (3)$$

$$0 < d < 1$$

The value found for each characteristic, y, was transformed to a value of d according to the following judgements:

Value of d	
1.0-0.99	Represents the ultimate level of the characteristic y. Improvement beyond this point would have no appreciable value.
0.99-0.80	Acceptable and excellent. Unusually good performance.
0.80-0.63	Acceptable and good.
0.63-0.40	Acceptable. Some improvement is desirable.
0.40-0.30	Borderline acceptability.
0.30-0.01	Unacceptable. This one characteristic could lead to rejection of the process.

The scale of d so developed is a dimensionless scale to which any characteristic may be transformed so that it may be interpreted in terms of its desirability for the intended application. In this evaluation, the most cost-effective final process was sought that could be available in the shortest reasonable time.

Where a characteristic was assessed on some scale of measurement scale, mathematical transformation from the measurement scale of the characteristic to the scale of "d" was accomplished by the basic equation:

$$d_i = e^{-e0.77941[(-y_i + y_{il})/(y_{ih} - y_{il})} \quad (4)$$

In this equation: y_i is a value of a treatment process characteristic i;
y_{ih} is the acceptable valuable of yi; and
y_{il} is the borderline value of y_i.

Table 8 shows the acceptable and borderline values of y_i for each characteristic rated.

TABLE 8. ACCEPTABLE AND BORDERLINE VALUES FOR PROCESS CHARACTERISTICS

Characteristic	Acceptable Value[a]	Borderline Value[b]
Probability of cleaning to $\leq$ 2 ppm	0.9	0.3
Probable cost of treatment, $\$/m^3$	100	300
T and E effort, \$/1000	300	900
Test system availability, rating	0.9	0.3
Time to provide commercial system, months	18	36

[a]d = 0.63 for these values.
[b]d = 0.37 for these values.

The probability of cleaning to $\leq$ 2 ppm was rated 0.9 if such performance had been demonstrated with soils of any type, 0.8 if such performance was projected from test data, and 0.3 if no data were available.

The probably cost of treatment was considered acceptable if $\$100/m^3$, and borderline if $\$300/m^3$.

T and E effort was considered acceptable up to \$300,000. Values above \$900,000 were considered borderline, but could be justified if the process had potential for lowering the cost of treatment, or rated extremely well on other desired characteristics.

Test system availability was rated 0.9 for an available company-provided system with experienced operating staff and resources to commercialize the process; 0.7 for an available government-provided system; and 0.3 if a suitable test system were not available.

Time to provide a commercial system sized to effect cleanup of 152,000 m^3 of sediment per year was considered acceptable at 18 months, but borderline if 36 months were required.

Using the values of the characteristics shown in Table 8, Equation 4 was applied to calculate the individual ratings shown for each process in Table 9. This table also shows the overall desirability rating of the process, calculated using Equation 1.

All the processes showed acceptable "D" values. The B.E.S.T., UV/Ozone or Hydrogen/Ultrasonics Technology, and Bio-Clean Naturally-Adapted Microbial processes showed the highest values, and are recommended as the three processes for immediate test and evaluation.

While this project was under way, an alternative process selection methodology became available at EPA's Hazardous Waste Engineering Research Laboratory. The methodology is available as a computer program entitled "d-SSYS, A Computer Model for the Evaluation of Competing Uncertainties," (Klee, 1987). This method was applied by RTI in addition to the Desirability Function approach.

The D-SSYS calculates weights for each evaluation factor using values of weight ratios assigned by the user. Weight ratios were assigned to emphasize the importance of the range of treatment costs and test-and-evaluation costs. The range of ratings for probability of cleaning to <2 ppm PCBs is only 0.1 (Table 2), indicating that all the processes might reasonably be expected to meet the requirement. The availability of a test system was not considered as important as the total test and evaluation cost. The time required to make a commercial process available showed a range of only six months, and was judged of lesser importance than the two major costs assessed. All ratios among the five factors that resulted from these assignments are shown below as a matrix. For example, the ratio (test system availability)/(T and E cost) is shown as the intersection of Row 4 and Column 3 as 0.2.

TABLE 9. OVERALL DESIRABILITY OF IMMEDIATE T AND E OF THE EIGHT CANDIDATE PROCESSES

	KPEG,Galson	Modar Supercritical Water	Bio-Clean	UV/Ozone-Hydrogen Ultrasonics Technology	CFS Extraction	B.E.S.T.	Low-Energy Extraction	In Situ Vitrification
Probability of cleaning to ≤ 2 ppm	0.9	0.8	0.9	0.8	0.8	0.8	0.9	0.9
d rating	0.63	0.59	0.63	0.59	0.59	0.59	0.63	0.63
Probable cost of treatment, $/m^3	160-191	86-136	156	90-120	153-264	133	76-83	293-332
d rating	0.54[a]	0.62	0.57	0.63	0.50	0.59	0.65	.035
T and E effort								
$1000	216	483	166	151	123	149	170-827[b]	400
d rating	0.66	0.56	0.68	0.69	0.69	0.69	0.67	0.59
Availability of a system for a test								
future purchase by govern. required							0.8	0.8
future purchase by govern. not required	0.9	0.9	0.9	0.9	0.9	0.9		
d rating	0.63	0.63	0.63	0.63	0.63	0.63	0.59	0.59
Likely future availability of the process								
months	19.5	21.5	19	21-24	25	19	25	19-24
d rating	0.62	0.59	0.62	0.59-0.55	0.54	0.62	0.54	0.62-0.55
Overall desirability, D								
earliest future avail.	0.615	0.60	0.617	0.625	0.59	0.623	0.614	0.54
latest future avail.	0.615	0.60	0.617	0.616	0.59	0.623	0.614	0.52
average	0.615	0.60	0.617	0.621	0.59	0.623	0.614	0.53

[a]Average cost used for rating.

[b]Cost of $170,000 if developed by sponsoring firm

	Clean to 2 ppm	Cost	T & E Cost	Test System Availability	Early Commercial Availability
Clean to 2 ppm	1	0.2	0.2	1	0.8
Cost	5	1	1	5	4
T and E Cost	5	1	1	5	4
Test system availability	1	0.2	0.2	1	0.8
Early com. availability	1.25	0.25	0.25	1.25	1

From these ratios and the following tabular algorithm, the factor weights (W) were generated.

Factors	Ratios	W	Weights, W
Clean to 2 ppm	0.2000	0.20	0.0755
T and E Cost	4,000	1.00	0.3774
Future commercial proc.	1.25	0.25	0.0943
Test system availability	0.2000	0.20	0.0755
Cost	5,000	1	0.3774
		2.65	

The procedure for weight generation is as follows:

- Construct an intermediate weighting scale (the w-column) by the following procedure. Opposite that last factor enter a "1". The remaining numbers in this column are formed by the product of its predecessor and Ratio value opposite it in a sort of zigzag route up the column. For example, the first w-value, 0.20 is the product of the second w-value (1.00) and the first Ratio-value (0.2000).

- Total the w-values. This total is 2.65. Construct a column of standardized weights by dividing each element of the w-column by this total to obtain the W-column. The elements in the W-column will, perforce, total one.

The program then scales the factor scores to obtain a linear utility function:

$$y' = b_0 + b_1 \text{ (factor score)} \tag{5}$$

$$0 < y' \leq 1.$$

In applying the scaling procedure to the two factors "Probability of Cleaning to $\leq$ 2 ppm" and "Availability of a Test System," it is noted that

these are positive factors (the higher the factor score, the better the process) and the 'y' values are obtained by:

$$y_{ij} = \frac{\text{score}_{ij} - \text{minimum score}_{ij}}{\text{maximum score}_{ij} - \text{minimum score}_{ij}} \qquad (6)$$

The other three factors are noted to be negative (the higher the factor score, the worse the process) and the y' values are obtained by:

$$y_{ij} = \frac{\text{maximum score}_{ij} - \text{score}_{ij}}{\text{maximum score}_{ij} - \text{minimum score}_{ij}} \qquad (7)$$

The y_{ij} values for the five factors by which each of the eight processes were assessed are given in Table 4.

TABLE 4. SCALED RATINGS OF EIGHT TREATMENT PROCESSES

	Clean to 2 ppm	Probable Tr. Cost	T & E Cost	Test System Availability	Early Commercial Availability
KPEG (Galson)	1	0.59	0.75	1	0.92
MODAR	0	0.87	0.043	1	0.58
Bio-Clean	0	0.67	0.89	1	1
UV/OZ or H_2/Ultrasonics	0	0.89	0.93	1	0.42
CFS Propane Extraction	0	0.45	1	1	0
B.E.S.T.	0	0.77	0.93	1	1
Low Energy Extraction	1	1	0	0	0
In Situ Vitrification	1	0	0.26	0	0.58

Depending on the users degree of risk that he is willing to accept, d-SSYS fits a utility function to the y' values via the following function:

$$\text{utility} = y'^{f} \; . \qquad (8)$$

The exponent f is evaluated by presenting the user with a structured lottery.

d-SSYS requires s comparison between two simple lotteries for each factor rated.

$$\text{Lottery 1} = \left| \begin{array}{l} \text{50\% chance of most undesirable rating.} \\ \text{50\% chance of most desirable rating.} \end{array} \right.$$

$$\text{Lottery 2} = \left| \text{X value of the rating for certain.} \right.$$

Using probable treatment cost as an example, RTI selected for Lottery 1:

50% chance of a treatment cost of $\$313/m^3$
50% change of a treatment cost of $\$80/m^3$

and an X value equal to the mathematical expectation of Lottery 1 for Lottery 2.

$$(0.5 \times \$313) + (0.5 \times 80) = \$196.50/m^3.$$

The value of $\$196.50/m^3$ on the y' scale is

$$y' = \frac{\$313 - \$196.5}{\$313 - \$80} = 0.5$$

The utility of Lottery 2 is easily determined, since it is equal to the utility of Lottery 1:

$$(0.5)(\text{utility of } \$313/m^3) + (0.5)(\text{utility of } \$80/m^3) = (0.5 \times 0.0) + (0.5 \times 1) = 0.5.$$

From Equation 8:

$$f = (\ln \text{utility})/\ln y' \qquad (9)$$

$$f = (\ln 0.5)/\ln 0.5 = 1$$

Note that if Lottery 2 had been set at a lower cost for certain, f would have been greater than 1 and function would have been a risk-taking one, in that one would be willing to pay more for Lottery 1 in the hope of gaining a treatment cost of $\$80/m^3$.

The remaining utilities for each factor are then calculated using Equation 8.

Using the scores scaled by Equation 8, the program computes an overall deterministic score for each treatment process as the sum of the scaled factor scores times the scaled factor weights. Using the factor scores of Table 4 (which equal the utility when f = 1) and the weights cited above, the following deterministic scores were obtained for the treatment processes (Table 5).

TABLE 5. DETERMINISTIC SCORES FOR TREATMENT PROCESSES

Process	Score
Basic Extraction Sludge Treatment	0.8127
UV/Ozone or Hydrogen/Ultrasonics	0.8010
Bio-Clean Naturally-Adapted Microbe	0.7583
Potassium Polyethylene Glycolate, Galson	0.7434
Critical Fluid Systems (CFS) Propane Extraction	0.6214
MODAR Supercritical Water Oxidation	0.4738
Low Energy Extraction, New York University	0.4529
In Situ Vitrification, Battelle	0.2299

The highest scores were attained by the Basic Extraction Sludge Treatment, UV/Ozone or Hydrogen/Ultrasonics Technology, and Bio-Clean Naturally-Adapted Microbe processes, the same processes that ranked highest using the Desirability Function ranking methodology. These are recommended for immediate test and evaluation.

In the application of this ranking, probable treatment cost and test and evaluation cost were assigned weights 4 to 5 times those of the other three factors. This increased emphasis on the costs involved did not change the top three processes. With different weights assigned, it would be possible to obtain a different ranking of the processes.

SECTION 6
APPLICATION OF PROCESSES TO RCRA WASTES

The seven processes evaluated in the final assessment have potential application to treatment of some RCRA listed hazardous wastes, as well as for removal of PCBs from sediments.

The B.E.S.T. process applies generally to the separation of oils, solids, and aqueous components of hazardous wastes. It has been applied to the clean-up of a CERCLA site at the General Refinery near Savannah, Georgia.

The Ultrasonics/Hydrogen-Ozone/UV Technology has been applied to the treatment of waste slurries from the pulp and paper industry, and to the cleaning of many types of materials. The UV energy must penetrate the treatment media sufficiently to reach the molecules of the hazardous compound. Filtration or cyclone-separation may be required following extraction in order to provide a suitable medium for treatment.

The Bio-Clean Naturally-Adapted Microbial process can be applied to any contaminant that is extractable and biodegradable. It has been applied to the decontamination of pentachlorophenol-bearing soils. The process requires selection and adaptation of a suitable microorganism for the compounds being treated. Complete mineralization of the compound may be achieved, or if this is not possible, then non-hazardous residues may be produced. The process needs to be evaluated, using bench-scale tests, for the different hazardous materials to be treated.

The Galson KPEG with DMSO process, based on nucleophilic substitution, has been applied to "dioxins". It has potential application to a number of listed halogenated organic hazardous wastes from both non-specific and specific sources, for example waste numbers F020, F021, F024, F027, and K042. The treatment leaves dehalogenated compounds as a residue, which may or may not be toxic. Further study is required to determine the performance of the process for these additional applications.

The CFS Propane Extraction Process has been applied to the removal and concentration of oily contaminants. Hazardous solvents and oxygenated compounds are extracted using pressurized carbon dioxide.

The Modar Supercritical Water-Oxidation process can apply generally to any organic waste that can be oxidized at supercritical conditions. It has been applied to decontaminate dioxin tainted soil. A test unit was operated at the CECOS International Niagara Falls site.

The Low Energy Acetone-Kerosene Extraction process is applicable to any organic waste that can be dissolved into a hydrophilic solvent. It produces a concentrated solution suitable for incineration or other treatment.