

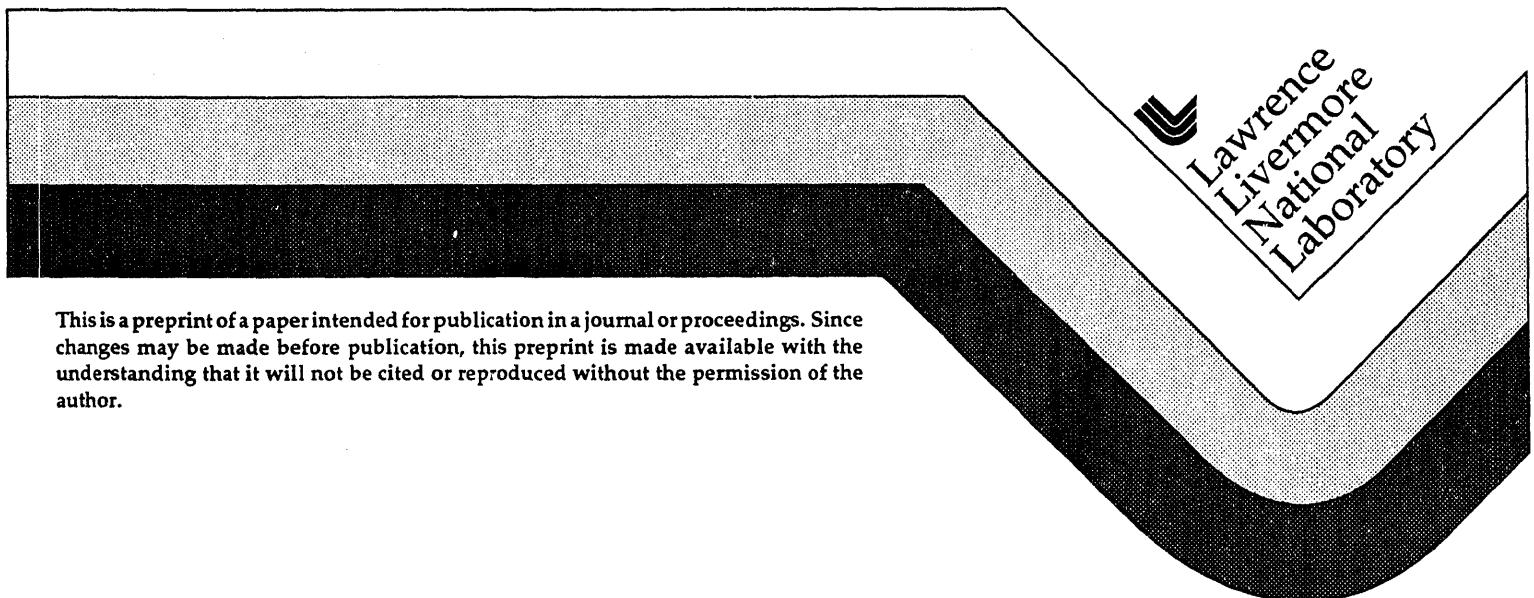
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TECHNOLOGIES FOR ENVIRONMENTAL CLEANUP: TOXIC AND HAZARDOUS WASTE MANAGEMENT

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TECHNOLOGIES FOR ENVIRONMENTAL CLEANUP: TOXIC AND HAZARDOUS WASTE MANAGEMENT

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ABSTRACT. This is the second in a series of EUROCOURSES conducted under the title, "Technologies for Environmental Cleanup." To date, the series consist of the following Courses:

1992: Soils and Groundwater

1993: Toxic and Hazardous Waste Management

The 1993 Course focuses on recent technological developments in the United States and Europe in the areas of waste management policies and regulations, characterization and monitoring of waste, waste minimization and recycling strategies, thermal treatment technologies, photolytic degradation processes, bioremediation processes, medical waste treatment, waste stabilization processes, catalytic organic destruction technologies, risk analyses, and data bases and information networks. It is intended that this Course will serve as a resource of state-of-the-art technologies and methodologies for the environmental protection manager involved in decisions concerning the management of toxic and hazardous waste.

Overview of the Technologies for Environmental Cleanup Series

The objective of this series is to educate managers, governmental officials, and academicians on those technical issues that contribute to addressing the questions: "What is the risk of environmental pollution?", "How clean is clean?", and "What is the cost/benefit of today's and tomorrow's cleanup?" These questions are major environmental and economic policy issues facing industrial and developing countries throughout the world. The issues encompass the entire range of pollution prevention problems: remediation of contaminated sites, treatment and disposal of toxic materials and wastes, minimization of the generation of toxic wastes, and reduction of source emissions. Remediation, treatment, disposal, waste minimization, and source reduction are all inter-related and must be integrated in a systems approach to environmental protection management.

The projected environmental restoration and waste management costs are enormous, even with today's technologies. At the June 1992 United Nations Earth Summit meeting in Brazil, Summit Secretary-General Maurice Strong stated that the cleanup proposals in

Agenda 21, such as cleaning oceans and toxic dump sites, could cost \$625 billion a year for a decade (Kanamine, 1992). In the U.S. there is a growing realization that the demand for funding to correct U.S. environmental problems will soon outstrip available resources. The 1993 estimated costs of remediating U.S. hazardous waste sites range up to hundreds of billions of dollars.

Problems such as ozone depletion, global warming, the protection of endangered species and wetlands, toxic air pollution, carcinogenic pesticides, and urban smog are all competing for the same financial resources. In response to the imbalance in the supply and demand for national funds, many groups are calling for the use of risk assessment as a tool to prioritize cleanup issues (Travis and Blaylock, 1992).

These training Courses will follow this strategy and emphasize a systems approach to environmental cleanup and waste management that incorporates the use of risk analysis:

- (1) assessing risks of environmental contamination and quantifying uncertainties in these assessments;
- (2) evaluating current and advanced technologies that make economically sound risk management possible;
- (3) developing a reasonable waste generation and cleanup strategy that minimizes both risks and costs while maintaining maximum environmental protection.

This systems approach is designed to encourage managers and public officials to evaluate the effectiveness of cleanup technologies in the dual context of managing risks to public health and managing the cost impacts of those technologies.

Overview of Toxic and Hazardous Waste Management Issues

It is generally acknowledged today that the most effective strategy for toxic and hazardous waste management is: *reduce, reuse, and recycle*. However, most of the historical activity to date has been in treatment technologies. The hazardous waste treatment market traditionally has been influenced by numerous factors, such as technology, available capacity, regulatory compliance, and the cost of transportation, treatment, disposal and potential liability. Additional market influences have arisen recently, including industry waste reduction efforts, the new environmental philosophies of the various national governments', renewed political pressure from environmental and community groups, and political shifts in public opinion about environmental management. All of the factors influencing the hazardous waste treatment market directly affect generators by determining available treatment options and costs for various services (Melody, 1993).

Commercial Treatment Technologies

Hazardous waste generators in the United States (U.S.) today have several options for treating their waste streams off-site at commercial facilities. Generators can send their wastes to any of 282 treatment facilities, compared to 295 facilities in 1992. Many facilities provide several treatment options for hazardous waste (TSD Summary, 1993):

U.S. Facilities

• Solvent recovery	95
• Fuels blending	149
• Cement plants & lime kilns	29
• Incineration	20
• Chemical treatment	85
• Physical treatment	61
• Deep-well injection	8
• Land-filling	20

The 1984 U.S. Hazardous and Solid Waste Amendments (HSWA) amended the Resource Conservation and Recovery Act (RCRA) to ban land disposal of certain hazardous wastes and limit acceptable treatment technologies to those meeting the best demonstrated available technology standards (BDAT). These regulations require that certain hazardous wastes be treated to reduce toxicity and volume before disposal.

In order to meet the requirements, hazardous waste treatment technologies must be robust and not overly sensitive to the chemical and physical properties of the influent waste streams. As a result, incineration has been the preferred waste destruction technology, the BDAT, for the last 10 years, followed by aqueous treatment processes such as acid neutralization, metals precipitation, cyanide oxidation, and chromium reduction precipitation. On the other hand, many treatment technologies are limited in application and can only treat certain wastes. for example, wet-air oxidation can handle only a small range of waste streams (Melody, 1993).

The combination of the 1984 land bans and the scarce landfill space spurred incineration; however, today there is an overcapacity of off-site hazardous waste treatment facilities and services, especially incineration, due to slow industrial growth. In addition, industry has been reducing the generation of hazardous waste to reduce costs, since incineration is a relatively expensive technology.

Waste Minimization

Most companies in the U.S. and Europe are seriously addressing waste minimization issues. Most of the efforts to date have been housekeeping and end-of-the-pipe treatment, such as on-site solvent recovery stills. Future substantive waste decreases will come from process changes, including more process control, and changing raw materials to eliminate toxic production and use. Chemical companies are more likely to recycle, and most solvent recyclers are concerned about the 1996 solvent ban from the Montreal Protocol on Substances That Deplete the Ozone (Melody, 1993).

As waste volumes decrease, it is becoming less feasible economically to carry out on-site waste treatment; however, the public is simultaneously pressuring for less transportation, burning, and land-filling of hazardous wastes.

Innovative Technologies

Innovative technology use amounts to 42%, and is increasing at U.S. Superfund National Priorities List (NPL) sites. By far, the most frequently selected innovative technology is soil vapor extraction, followed by bioremediation, thermal desorption, and soil washing. Use of established technologies, such as incineration (30%) and solidification/stabilization (26%) amounts to 58% at Superfund sites (Cleaning Up the Nation's Waste Sites, 1993).

The enormous cost of incinerating hazardous wastes have encouraged the development of advanced treatment and recycling technologies. The development of a technology that meets existing BDAT levels and could replace incineration is needed.

Companies and treatment technologies are focusing more and more on specific wastes because it is more cost effective to process relatively simple waste streams. Improved separation technologies make materials recovery more economical. Furthermore, it is more difficult to separate out high-value products from complex waste streams.

Table 1 contains a matrix showing the various combinations of innovative technologies, contaminants, media, and treatment types being addressed in the U.S. today (Synopses of Federal Demonstrations of Innovative Site Remediation Technologies, 1992).

The technologies contained in each category: thermal, chemical, physical, and biological are briefly discussed below. Subsequent talks in the Course will discuss these technologies in greater detail.

THERMAL TREATMENT TECHNOLOGIES

Thermal processes in use in the U.S. today include:

- Low-Temperature Thermal Desorption
- High-temperature Thermal Desorption
- Vitrification
- Incineration
- Pyrolysis

Table 2 lists the description of each thermal process and the current status in the U.S., including the scale of the process; i.e. whether it is considered a conventional or innovative technology, and whether it is full-scale or pilot-scale (Remediation Technologies Screening Matrix and Reference Guide, 1993).

Low- and High-Temperature Thermal Desorption: Low-temperature and high-temperature thermal desorption systems are physical separation processes and are not designed to destroy organics. The bed temperatures and residence times designed into these systems will volatilize selected contaminants, but typically not oxidize them. The target contaminant groups are volatile organic compounds (VOCs) and fuels. They will also treat semivolatile organic compounds (SVOCs) and pesticides, but not as effectively.

TABLE 1
Technology/Contaminant/ Media Treatment Type

Innovative Technology	Contaminant								Media			
	Halogens/ Volatiles and semi-volatiles	Nonhalogenated Volatiles and semi-volatiles	PCBs	Pesticides	Organics	Metals	Polychlorinated Materials	Explosives	Surface Water	Groundwater	Solids	Sludges
Bioremediation	✓	✓	✓			✓		✓		✓	✓	✓
Chem. Treatment	✓	✓	✓	✓	✓	✓	✓			✓	✓	✓
Thermal Treatment	✓	✓	✓	✓		✓	✓	✓		✓	✓	✓
Physical Treatment	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓

Table 2

Thermal Process

Low-Temperature Thermal Desorption	Full-scale Innovative	Wastes are heated to 200°-600°F (93°-315°C) to volatilize water and organic contaminants. A carrier gas or vacuum system transports volatilized water and organics to the gas treatment system.
High Temperature Thermal Desorption	Full-scale Innovative	Wastes are heated to 600°-1,000°F (315°-538°C) to volatilize water and organic contaminants. A carrier gas or vacuum system transports volatilized water and organics to the gas treatment system.
Vitrification	Full-scale Innovative	Contaminated soils and sludges are melted at a high temperature to form a glass and crystalline structure with very low leaching characteristics.
Incineration	Full-scale Conventional	High temperatures, 1,600°-2,200° F (871°-1,204°C), are used to volatilize and combust (in the presence of oxygen) organic constituents in hazardous wastes.
Pyrolysis	Pilot-scale Innovative	Chemical decomposition is induced in organic materials by heat in the absence of oxygen. Organic materials are transformed into gaseous components and a solid residue (coke) containing fixed carbon and ash.

Vitrification: Wastes are melted to form a glass with very low leaching characteristics. Nonvolatile inorganic elements are encapsulated in a vitreous slag, while organic compounds are destroyed by pyrolysis.

Incineration: Incineration is an established BDAT technology. Four common designs are rotary kiln, liquid injection, fluidized bed, and infrared incinerators. The destruction and removal efficiency (DRE) often exceeds the 99.99% requirement for hazardous waste, and can meet the 99.9999% required for polychlorinated biphenyl compounds, PCB's and dioxins.

PHYSICAL/CHEMICAL PROCESSES

Table 3 lists the physical/chemical processes in use in the U.S. today, which include (Remediation Technologies Screening Matrix and Reference Guide, 1993):

- Soil washing
- Solidification/Stabilization
- Dehalogenation (Glycolate)
- Dehalogenation (BCD)
- Solvent Extraction
- Chemical Reduction/Oxidation

Soil Washing: The target contaminant groups are SVOCs, fuel hydrocarbons, and inorganics. It is less effective against VOCs and pesticides. It offers the potential for recovery of metals, and a wide range of organics and inorganics from coarse-grained soils. However, fine-soil particles such as silts and clays are difficult to remove from the washing fluid. Soil Washing is being used more frequently in the U.S. in recent years. In Europe, it has been a common technology for many more years.

Solidification/Stabilization: The target contaminant group is inorganics, and it has limited effectiveness against SVOCs and pesticides. Some processes may result in a significant increase in volume, as much as a factor of two. It is an established and mature technology.

Dehalogenation (Glycolate): In the APEG process, the reaction causes the polyethylene glycol to replace halogen molecules and render the compound nonhazardous. For example, the reaction between chlorinated organics and KPEG causes replacement of a chlorine molecule and results in a reduction in toxicity. The target contaminant groups are halogenated SVOCs and pesticides. It is less effective against selected halogenated VOCs. It is one of the few successful processes other than incineration for treating PCB's.

Dehalogenation (Base-Catalyzed Decomposition): This technology has had limited use to date. The target contaminant groups are halogenated SVOCs and pesticides and, less effectively, halogenated VOCs.

Table 3

Physical/Chemical Processes

Soil Washing	Full-Scale Innovation	Contaminants sorbed onto soil particles are separated from soil in an aqueous-based system. The wash water may be augmented with a basic leaching agent, surfactant, pH adjustments, or chelating agent to help remove organics and heavy metals.
Solidification / Stabilization	Full-Scale Innovation	Contaminants are physically bound or enclosed within a stabilized mass (solidification), or chemical reactions are induced between the stabilizing agent and contaminants to reduce their mobility (stabilization).
Dehalogenation (Glycolate)	Full-Scale Innovation	An alkaline polyethylene glycolate (APEG) reagent is used to dehalogenate halogenated aromatic compounds in a batch reactor. Potassium polyethylene glycolate (KPEG) is the most common APEG reagent. Contaminated soils and the reagent are mixed and heated in a treatment vessel.
Dehalogenation (BCD)	Full-Scale Innovation	Contaminated soil is screened, processed with a crusher and a pug mill, and mixed with sodium bicarbonate. The mixture is heated in a rotary reactor at 630°F (333°C) to decompose and partially volatilize the contaminants.
Solvent Extraction (Chemical Extraction)	Full-Scale Innovation	Waste and solvent are mixed in an extractor, dissolving the organic contaminant into the solvent. The extracted organics and solvent are then placed in a separator, where the contaminants and solvent are separated for treatment and further use.
Chemical Reduction/ Oxidation	Full-Scale Innovation	Reduction/oxidation chemically converts hazardous contaminants to nonhazardous or less toxic compounds that are more stable, less mobile, and/or inert. The reducing/oxidizing agents most commonly used are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide.

Solvent Extraction: The target contaminant groups are SVOCs and pesticides and, less effectively, VOCs and fuels. It is generally least effective on very high molecular weight organics and very hydrophilic compounds. Organically bound metals can also be extracted, which may restrict handling of the residuals.

Chemical Reduction/Oxidation: A combination of the reducing/oxidizing agents, or in combination with ultraviolet (UV) oxidation makes the process more effective. The target contaminant group is inorganics and, less effectively, nonhalogenated VOCs and SVOCs, fuels, and pesticides.

BIOLOGICAL PROCESSES

Table 4 contains a list of the *ex-situ* biological treatment processes used in the U.S. today, including (Remediation Technologies Screening Matrix and Reference Guide, 1993):

- Slurry Phase Biological Treatment
- Controlled Solid Phase Biological Treatment
- Landfarming

Slurry Phase Biological Treatment: The target contaminant groups are nonhalogenated VOCs and fuels. It is less effective against halogenated VOCs, SVOCs, and pesticides. Many chlorinated organics and pesticides are not biodegradable and not applicable for this process. Aerobic methanotrophic bacteria can degrade trichloroethylene and the lower chlorinated aliphatics, but do not work well for tetrachloroethylene and higher compounds. Anaerobic reduction is being actively researched to treat higher compounds. Higher ringed polynuclear aromatic (PNA) compounds (greater than 5 rings) are difficult to degrade.

Controlled Solid Phase Biological Treatment: This requires excavation of soils. The target contaminant groups are nonhalogenated VOCs and fuels and, less effectively, halogenated VOCs, SVOCs, and pesticides. Solid phase processes have questionable effectiveness for halogenated compounds and for explosive transformation products.

Landfarming: Although landfarming usually requires excavation of contaminated soils, surface soils may sometimes be treated in place without excavation. Landfarming systems are incorporating liners and other methods to control the leaching of contaminants. It is most effective against nonhalogenated VOCs and fuels, but can also be used against halogenated VOCs, SVOCs, and pesticides.

Waste Treatment Costs

While accurate cost estimates must be done on a site specific basis, there are general cost ranges which can be used to characterize the different technologies.

Table 5 summarizes the comparative costs of some of these technologies as they are used for on-site waste treatment (Remediation Technologies Screening Matrix and Reference Guide, 1993).

Table 4

Biological Processes

Slurry Phase Biological Treatment	Full-Scale Innovation	An aqueous slurry is created by combining soil or sludge with water and other additives. The slurry is mixed to keep solids suspended and micro-organisms in contact with the soil contaminants. Nutrients, oxygen, and pH in the bioreactor may be controlled to enhance biodegradation. Upon completion of the process, the slurry is dewatered and the treated soil is disposed.
Controlled Solid Phase Biological Treatment	Full-Scale Innovation	Excavated soils are mixed with soil amendments and placed in above-ground enclosures that have leachate collection systems and some from accretion. Processes include prepared treatment beds, biotreatment cells, soil piles, and composting. Moisture, heat, nutrients, oxygen and pH may be controlled to enhance biodegradation.

TABLE 5
ON-SITE WASTE TREATMENT TECHNOLOGIES

	<u>Cost/³ Yard</u>	Waste Handled	
		<u>Organic</u>	<u>Inorganic</u>
Incineration	600-1500	Yes	No
Vitrification	350-400	Yes	Yes
Low Temperature Thermal Treatment	200-250	Yes	No
Chemical Treatment	250-300	Yes	No
Soil Washing	150-200	Yes	Yes
Bioremediation	25-100	Limited	No
Stabilization/Solidification	20-100	Limited	Limited

The Bioremediation Report, Vol. II, No. 1, January 1993, also compared five different technologies by assuming the cleanup of 1500 cubic meters per year of soil contaminated with biphenyl and diphenyl oxide, as shown in Figure 1. In both comparisons, incineration is the most expensive, while bioremediation and solidification are the least expensive.

Risk and Cost-Benefit Issues

A dominant opinion among many environmental protection managers today is that the BDAT regulatory standards are unnecessarily excessive and costly, and more reasonable standards based on risk and cost-benefit considerations are needed. Other risk-related issues include:

- More research needs to be done to determine the level at which health risk from toxic and hazardous waste is truly insignificant and can be ignored, i.e., a *de minimus* risk.
- More research needs to be done to reduce the uncertainties in risk analysis so that it can be used for treatment prioritization.
- Cost-benefit needs to be more formally integrated into the risk analysis in order to adequately address the issue of economic sustainability.

Risk analysis techniques can be used to address the risks of many different types of hazards, but in our case here, risk analysis is a knowledge-based system of evaluating appropriate treatment goals and methods. The process of analyzing risks includes four phases, shown in Figure 2, which is a modification of the process presented in McKone and Kastenberg, 1986 Proceedings, and Cohrssen and Covello, 1989.

Risk assessment is the technical assessment of the nature and magnitude of risk. The object is to develop models and measures that can be used to determine the magnitude of the risk, parameters that contribute to this magnitude, and the likely uncertainty about the magnitude.

Risk management is the process of evaluating policy alternatives and selecting an appropriate institutional response in order to accept, reduce, or eliminate the risk in question. This process should integrate the results of the risk assessment with engineering data and with social, legal, economic cost and benefits, and political values to reach a decision. Cost-benefit analysis includes itemizing the current and future costs and benefits of all nontrivial effects and comparing them to see which is greater. Risk management leads to the evaluation of cleanup technologies and selection of the most appropriate action for a particular contaminated site.

Risk communication is an important factor influencing risk analysis because people perceive risks differently, depending on the personal impacts, whom the risk affects, how familiar and how feared the effects are, whether the exposure is voluntary, and what the benefits from risk acceptance are. Public perception of the unacceptably high risk of incineration has delayed or stopped construction of incinerators in the U.S.

Risk analysis has both strengths and weaknesses that must be better understood to use it effectively. Even with its weaknesses, risk analysis should be adopted as the basic framework for the environmental treatment process as it is the most effective tool available today.

Conclusion

Formalized decision-making methodologies need to be adopted to provide a universally consistent approach to the process of waste minimization, characterization, risk analysis, waste treatment, and the entire waste life-cycle strategy. Furthermore, it is clear that a comprehensive societal strategy is needed, one which integrates all facets of environmental protection, from the processes which generate the waste to the processes for destruction, treatment, disposal, and cleanup of the waste, including even the justifications used for the regulations. The key element in such a strategy is to carry out environmental protection in such a way as to sustain economic development. As the European Commissioner, Carlo Ripa di Meana stated, "...without sustainable development we are headed for an ecological disaster" (Europe Environment, 1992).

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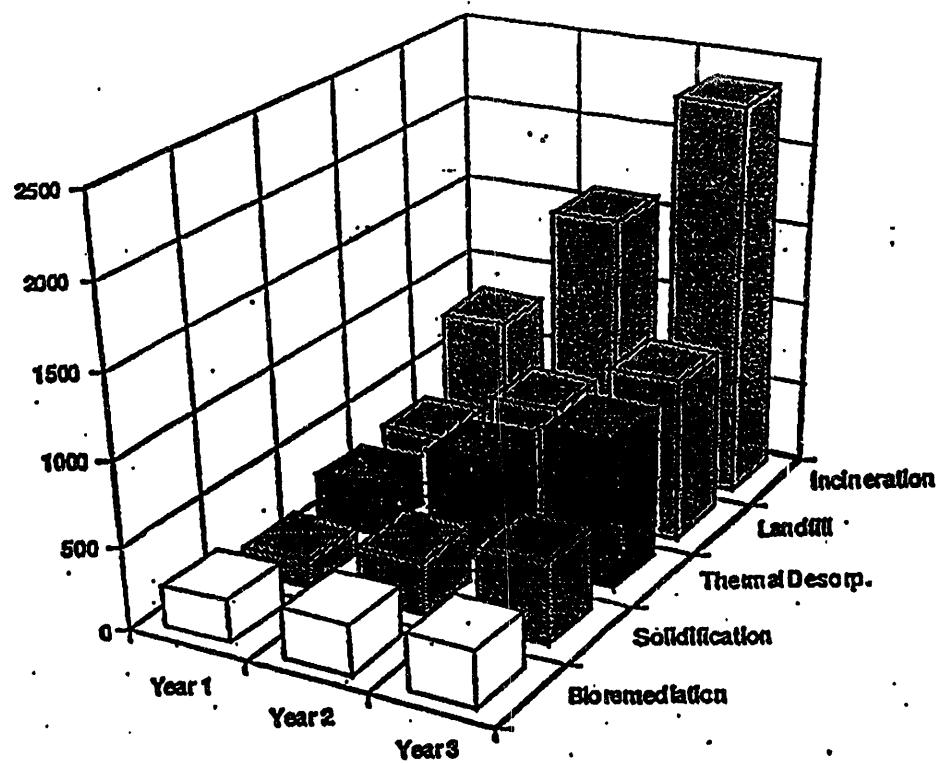
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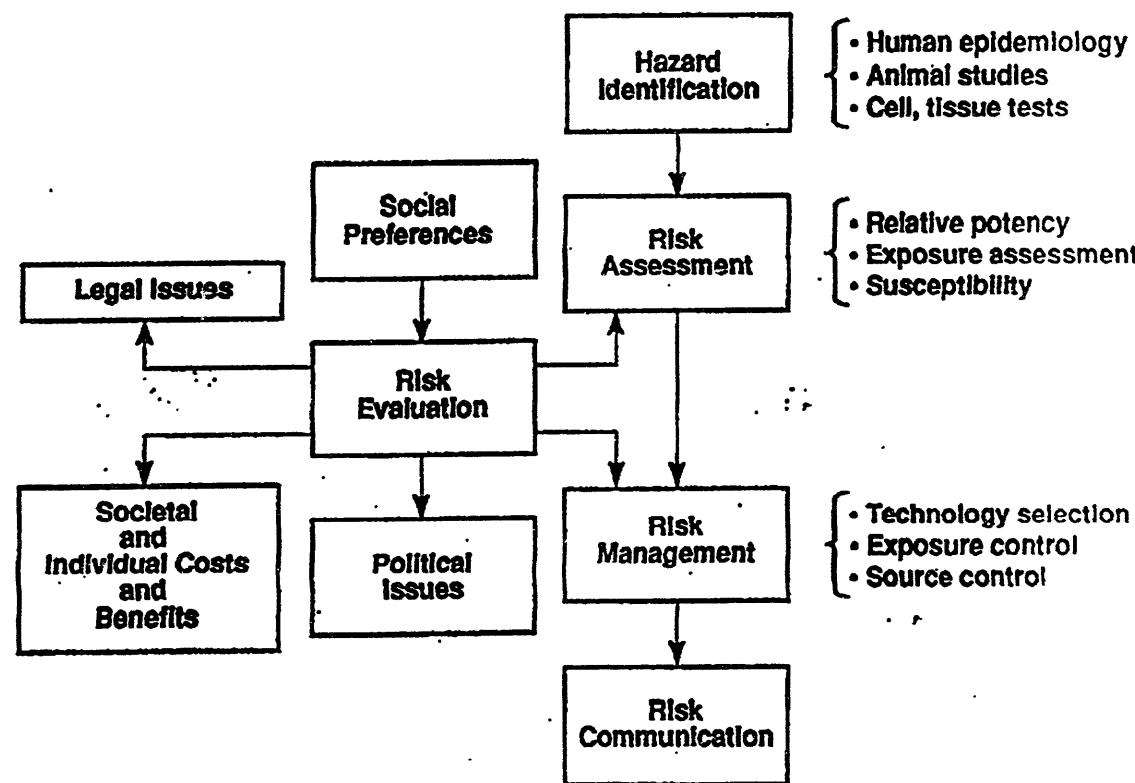
This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

FIGURE 1
Cumulative Costs (\$K) for Five
Ex-Situ Waste Treatment Technologies



Costs to treat 1500m³/yr. of soil contaminated with biphenyl and diphenyl oxide using five different *ex situ* remediation technologies. Source: The Bioremediation Report, Vol.II, January 1993

FIGURE 2
Schematic Diagram of the Risk Analysis Process



The image is a high-contrast, black-and-white graphic. It features three horizontal bands. The top band is composed of two vertical rectangles, one on the left and one on the right, set against a black background. The middle band is a single, thick horizontal rectangle, also set against a black background. The bottom band is a single, thick horizontal rectangle, with a central white oval shape. The entire image is rendered in a stark, binary black-and-white style.

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