HAZARDOUS WASTE TREATMENT AND DISPOSAL: ALTERNATIVE TECHNOLOGIES AND GROUNDWATER IMPACTS

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(ABSTRACT)

The most important thermal, chemical, physical, and biological methods for treating hazardous wastes and the fate of their land-disposed residues are reviewed and evaluated. Technologies are described as major, minor, and emerging according to their stage of develpment or application to hazardous waste; major ones include rotary kiln, liquid injection, and cement kiln incineration; neutralization, chemical oxidation-reduction, and ion exchange; filtration, distillation and settling techniques; and activated sludge, aerated lagoon, and landfarming treatment. Emerging technologies include molten salt and fluidized- bed combustion, liquid-ion extraction and other processes, none of which are considered to be outside the realm of current or future economic feasibility. In addition, waste reduction strategies and the land burial of stabilized/solidified wastes are discussed.

Residues from these technologies vary widely according to waste type and composition, but a common component in many of them is heavy metals, which, as elements, cannot be further degraded to other products. The results of the available literature suggests that these metals will be retained in clay liners beneath a landfill through the mechanism of cation exchange, with the adsorption of metals favored by their smaller hydrated size, lower heat of hydration, and in some cases, higher valences than the naturally occurring alkali earth metals. Other important factors include ionic activity, the pH and ionic strength of the solution, the presence of complexing agents, an the possible surface heterogeneity of the clay. In soils, metal binding through cation exchange with clay is augmented by adsorption onto iron and manganese oxides and complexing with organic matter such as humic acids. Many field studies with landfarmed metal-bearing wastes show that these mechanisms are usually sufficient to retain metals to within several inches of their zone of application.

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CHAPTER I

INTRODUCTION

BACKGROUND

Hazardous waste management, a problem seemingly as diverse and complex as the industrial community faced with it, is a growing issue that needs both immediate attention and sustained diligence to be successfully and thoroughly overcome. Unlike discharged industrial effluents, which cause highly visible and offensive environmental degradation and so have been the subject of restraining legislation for over thirty years, toxic wastes of low economic value historically have been buried in landfills or stored on-site in drums or impoundments, remaining essentially invisible to the public eye. The most common and serious consequence of mismanagement--groundwater contamination--was likewise slow to develop and emerge, but the extensive publicity given to the public health impacts of severe events as well as the high cost and difficulty of safe and effective cleanup made industry, government, and the public realize that this invisible problem could be a deadly one, and that an immediate and comprehensive solution was needed.

A major step towards legally mandating sound management was taken in 1976 with the passage of the Resource Conservation and Recovery Act (RCRA). Subsequent regulations promulgated by EPA in 1980 not only required large generators of hazardous waste to manifest their wastes shipped off-site, but, more importantly from a volume standpoint, set standards and permitting requirements for those generators treating or storing wastes on-site. Although these regulations were successful in making industry take seriously the handling of unwanted process residues, the regulatory and philosophical approach of EPA at the time contained what many now consider to be a major flaw: the endorsement of the landfill as an acceptable disposal option for untreated hazardous wastes.

LANDFILLS AND HAZARDOUS WASTE

Although widely used for municipal wastes, the use of landfills for ultimate disposal of hazardous waste violates some key assumptions in the landfill concept. Primary among these is the biodegradability of the waste material; municipal waste, which is generally organic in nature, will settle and naturally decay over time and so undergoes true disposal when returned to the land. Many chemical wastes, however, degrade only slowly, under certain conditions, or not at all; and chemically stable and biologically resistant species can remain in the excavation unchanged, separated from the envi-

ronment only by the integrity of the landfill structure and material. But no structure lasts forever, and when the landfill becomes permeable, as it eventually will, the toxic chemicals or leachates will be free to pass into the underlying soil and jeoparde groundwater supplies.

In response to this situation, the highly engineered "secure" landfill was developed specifically for hazardous waste containment. At a minimum, a secure landfill usually consists of the following components:

1. a double liner system of impermeable synthetic material or compacted clay, to "seal off" the landfill contents from the environment;

2. a leachate and runoff collection system, consisting of piping below and between the liners to collect and remove material passing through the liner;

3. an impermeable top cover to prevent surface precipitation from entering the excavation;

4. individual containment cells, to separate or isolate certain wastes within the fill;

5. groundwater monitoring wells, to check for groundwater contamination from leaking waste material.

Despite the precautions implicit in these design features, many problems which result in failure of the system to contain the waste may occur. Top covers can crack, erode, or be punctured by tree roots or burrowing animals, in addition to collapsing into internal voids caused by settling wastes or rupturing drums. Synthetic liners, though highly impermeable, are easily punctured or ripped during installation, and clay liners can be damaged by animals and have been found to be relatively permeable to organics (77). Material may pass through the liners before reaching the collection system, and may disperse through groundwater at a depth or in a pattern that does not intercept the monitoring wells. Once groundwater is contaminated, however, the situation is usually too far advanced for anything but expensive emergency measures, which may, in extreme cases, involve excavation of the landfill.

For this reason, EPA and many states are now moving away from landfilling as a disposal alternative for untreated hazardous wastes, particularly liquids. The 1984 RCRA amendments prohibit deposition of bulk, non-containerized liquids, while other wastes must be treated to the "maximum degree economically feasible". More importantly than this, however, is the

fact that both owners and users of landfill can be held liable for the sometimes immense costs and damages resulting from landfill leakage, which has made many generators reluctant to use them regardless of the economic advantages. For this reason, more emphasis is being placed on safer, more effective alternative technologies that will permanently and verifiably reduce the hazard of industrial wastes.

OBJECTIVES OF THE STUDY

In light of the need for a more circumspect approach to the treatment hazardous waste, this study was undertaken to achieve these specific objectives:

1. to determine what major, minor, and emerging technologies are available for the treatment and disposal of hazardous wastes as alternatives to landfills;

2. to generally characterize the major residues that may result from these technologies;

3. to determine if these residues would produce a threat to groundwater when disposed of in a landfill or by landfarming.

The study will proceed through an examination of the literature that considers laboratory studies, bench scale studies and more general operational experience. It is hoped that through this discussion of the capabilities and liabilities of alternative technologies for dealing with hazardous wastes a more accurate understanding of the true dimensions of the problem will be attained, and, from this, a greater confidence about its solution.

CHAPTER II

ALTERNATIVE TECHNOLOGIES AND STRATEGIES FOR HAZARDOUS WASTE TREATMENT

INTRODUCTION

Provided here are brief descriptions of several techniques for reducing the generation of hazardous wastes, and various thermal, chemical, physical, and biological processes that are or might be available for treating those wastes that are generated. Unlike radioactive wastes, which are held in containment simply because no other acceptable alternative exists, almost all toxic wastes can be (and sometimes are) treated to some degree by technologies that typically are already in use for other industrial purposes. In addition, some wastes can be utilized by other industries as a feedstock through the use of organized waste exchanges.

Waste processing technologies generally fall into two categories, those that separate the harmful elements from a generalized stream and those that destroy almost completely the waste material. Separation processes produce a smaller

quantity of more concentrated material that is typically easier and cheaper to treat than the whole stream, while destructive technologies (e.g., incineration) reduce waste to a less-toxic or non-toxic residue that itself must eventually be disposed of, usually in a landfill. Separation processes are often used in resource recovery or recycling operations.

The treatment technologies discussed here are divided into three categories: Major, Emerging, and Minor. Major technologies are those already being used effectively in full-scale plants for hazardous waste treatment. Emerging technologies are those expected to play a major role in the future, though currently in the pilot plant stage. Minor technologies are those that either are still developing or that have specialized or limited applications to hazardous wastes, though perhaps in wider usage for other purposes. It should be noted that although treatment costs vary widely among comparable technologies, none are included that are judged to be outside the realm of current or potential economic feasibility. Major alternative treatment technologies are summarized in Table 2.

WASTE REDUCTION AND EXCHANGE (1,2,3,4,)

Description In many cases, the most prudent first step in any waste management program is an evaluation of the industrial complex itself to determine what changes could be made to reduce the amount and type of hazardous waste generated. Existing practices usually reflect the simultaneous demands of technical efficiency, economy, and product quality; by including waste management as an integral factor instead of an after-thought, previously unimplemented sequences which result in less waste generation may become economically attractive. Pollution control thus starts at the beginning, rather than the end, of the industrial process.

Four main techniques are used to achieve waste reduction: source segregation, process modification, end-product substitution, and materials recovery and recycling (2). Usually a combination of all produces the best results, although some (such as source segregation) may be more quickly implemented than others. Each is discussed in more detail below, and summarized in Table 1.

Source Segregation. This involves separating a hazardous component out of a general waste stream, or preventing its addition to the stream in the first place.

In this way contamination of the entire effluent can be avoided so that only the concentrated, hazardous part need receive sophisticated treatment. An example of this is the removal of toxic metals from metal finishing rinse-waters. Source segregation is usually the simplest and least expensive form of waste reduction.

Process Modification. This involves the scrutiny of each step in the processing sequence, with reduction of the hazardous waste component as the primary goal. Although changes made at each point may be minor, the sum total can be a significant reduction of waste, with a minimum of impacts on the other parameters of production. Because of the detailed nature of the analysis, the changes tend to be plant specific rather than industry-wide, although modifications of standardized steps in the petroleum refining, metal-finishing, and vinyl chloride-producing industries have had significant effects (2,3).

End-Product Substitution. This is a more broadly applied strategy that involves phasing out those products whose production or disposal generate large quantities of toxics, and replacing them with substitutes that have a lower environmental cost. An example would be the use of clay or PVC pipes instead of asbestos ones, or con-

crete pilings instead of those made of creosote-treated wood (2). This is not necessarily an advantage to the consumer, however, unless the costs of waste management are internalized by the manufacturer and reflected in the lower price of the substitute. Lacking this, government regulations and direct incentives may be necessary to encourage end-product substitution.

Material Recovery and Recycling. Recovery and recycling means the separation of valuable components from a waste stream followed by the re-use of that component elsewhere in the production process. When used in-plant, this technique saves raw materials, energy requirements, and treatment and disposal costs. Some commercial facilities (including one in Virginia) collect wastes from generators and recover usable materials for profit, thus achieving both hazardous waste disposal and the production of saleable products (5). Recovery and recycling techniques include many of the physical and chemical processes described in the following chapters, and though the costs may be high, they are offset somewhat by the value of the product produced. This is expected to be of increasing importance as the price of both raw materials and waste disposal continue to rise.

Conscientiously applied waste reduction programs can have considerable benefits for the waste generator. A commonly cited case is the 3M Corporation's "Pollution Prevention Pays" program, which used waste reduction and materials substitution to achieve a savings of 20 million dollars over four years (2).

Closely allied to the waste reduction concept is that of the waste exchange, a system whereby the wastes of one industry become the feedstocks for another. To some extent this is what happens in commercial solvent recovery facilities, but an authentic waste exchange is actually a listing or brokerage service that helps to bring together the generators of wastes with those industries that might utilize the wastes.

Waste Stream Applicability In principle, waste reduction strategies can be applied to any waste stream, although not all processes can be altered to reduce waste generation.

TABLE 1. WASTE REDUCTION STRATEGIES

Type	Description	Advantages	Disadvantages
Source Segregation	The separation or isolation of an hazardous waste from a nonhazardous waste stream.	Easy to implement; usually low investment. Short-term solution.	Still have some waste to manage.
Process Modification	Analysis and modification of industrial process to reduce type and/or amount of waste generated.	Potentially reduce both hazard and volume. Moderate term solution. Potential savings in production costs.	Requires R & D effort; capital investment. Usually does not have industrywide impact.
End-Product Substitution	The replacement of a product whose production or disposal generates large amounts of hazardous waste with one with a lower environmental cost.	Potentially industrywide impact-large volume, hazard reduction.	Relatively long-term solutions. Many sectors affected. Usually a side benefit of product improvement. May require change in consumer habits. Major investments required; need growing market.
Recovery/Recycling	The separation of a valuable component from a waste stream followed by reuse or sale.	In-plant: Moderate-term solution Potential savings in manufacturing costs Reduced liability compared to commercial recovery or waste exchange Commercial: No capital investment required for generator. Economy of scale for small waste generators.	Commercial Liability not transferred to operator. If privately owned, must make profit and return investment. Requires permitting. Some history of poor management. Must establish long-term sources of waste and materials. Requires uniformity in composition.
Waste Exchange	A service that enables one industry's waste to be used as another's feedstock.	Transportation costs only.	Liability not transferred. Requires uniformity in composition of waste. Requires long-term relationships-two-party involvement.

THERMAL PROCESSES

GENERAL

Currently and historically, incineration is one of the most widely used method to decompose those organic wastes that are not landfilled (6). Constituting both a waste product and a fuel source, organics will combust at high temperatures (800-3000°F) to produce heat, water, CO_2 and a varible amount of intermediate waste components, leaving behind a much smaller volume of less toxic ash and residue for ultimate disposal. Control devices must typically be installed to reduce stack emissions of particulates and gaseous pollutants, the major environmental liability of combustion-based treatment. Electrostatic precipitators or bag-house filters may be used for particulates, while scrubbers may be used for both particulates and gaseous pollutants.

For all types of hazardous waste incinerators, EPA standards require a 99.99% (by mass) destruction and removal efficiency for each Principal Organic Hazardous Constituent (POHC), as well as limits on particulates to which heavy metals may adhere (2,9). Achieving this standard depends on 1) high and uniform temperatures; 2) adequate turbulence; and 3) adequate waste residence time in the unit, so these form the basis of good incinerator design (8). Nonetheless, even during normal

operating conditions, there may be emissions of stable, partially combusted intermediates, some of which may be hazardous; the quantification and control of these "products of incomplete combustion" (PIC's) remains a major focus of incineration research (9,10). Hazardous wastes destroyed by incineration include combustible solids, sludges, slurries, liquids, metal materials, and fumes, with the residues usually being landfilled. There are currently about forty commercial incineration facilities for hazardous or industrial waste treatment (2) out of an estimated 270 facilities nationwide (11).

MAJOR THERMAL TECHNOLOGIES

Liquid Injection Incinerators (7,12,13)

Description: Liquid injection involves the introduction of a fine spray of liquid into the hottest part of a refractory-lined combustion chamber, where it burns while still in suspension. Units can be vertically, horizontally, or tangentially fired with tangential systems providing better mixing and a higher heat release (though at the cost of higher maintanence)(13); residence times and temperatures for all designs range from 0.5-2.0 seconds at 1400-3000°F. Because of close nozzle specifications, systems are usually designed for a specific waste, although designs exist for a

wide variety of wastes. Injection systems are often used as afterburners on conventional furnace stacks to complete combustion of waste gases.

Waste Stream Applicability: Liquid injection is good for almost all hazardous liquids and gases, and for solids that can be vaporized or dissolved in a solvent. Specific uses include motor and industrial oils, emulsions, solvents, lacquers, and some relatively hard-to-destroy pesticides, herbicides and chemical warfare agents. (1,2,12). It is the most commonly used incinerator type for hazardous wastes (11).

Rotary Kilns (7,12,13)

Description: A rotary kiln is a tilted, revolving combustion chamber that receives solid waste in the upper end and burns it as it rolls down to an ash hopper at the bottom. Alternate designs counterfeed wastes in from the lower end. The continuous rolling and tumbling of the waste keeps fresh surfaces exposed for combustion, while preventing ash from caking on the chamber walls. Residence times range from a few seconds for gases to up to several hours for solids, at temperatures up to 3000°F. Capacities for different units

range from one to eight tons/hr.; scrubbers are used to clean combustion gases.

Waste Stream Applicability: Rotary kilns can burn wastes of any physical form and with a variety of feed mechanisms, and is considered the most appropriate way to dispose of surplus pesticides (1). Other suitable wastes include PCBs, munitions, chemical warfare agents, PVC wastes, waste paints and solvents, and bottoms from solvent reclamation operations (1,12)

Cement/Aggregate Kilns (1,2,14)

Description: Actually a specific kind of rotary kiln, cement kilns burn hazardous organics as a supplementary fuel in the production of cement aggregate (clinker) from the calcination of crushed limestone rock, achieving a high destruction rate through the use of long retention times, high temperatures (2600-3000°F.) and very thorough mixing. Off-gases, which may contain hydrochloric and other acids, are neutralized by the alkaline kiln environment while the ash is incorporated into the aggregate product, a primary component of cement.

Waste Stream Applicability: Because of the high temperatures involved, cement kilns can utilize many highly toxic organic wastes that are unsuitable for co-firing in other industrial

processes (14). Some specific applications include pesticides, PCBs, waste oils, halogenated organics, and non-halogenated solvents. This method is especially good for chlorinated wastes (1,14)

EMERGING THERMAL TECHNOLOGIES

Molten Salt Combustion (1,2,7,15)

Description: This technique involves combustion of wastes injected into a molten mixture of primarily sodium-based salts, maintained at a uniform temperature of 1500-1800°F Ash and off-gases are absorbed by the salt solution, which must periodically be regenerated or replaced, and emitted particulates are collected by a bag house (Fig. 1) Combustion is nearly complete, and the process is usually self-heating after the initial combustion temperature is reached.

Waste Stream Applicability: Molten salt incineration achieves good results with a wide variety of hazardous liquids, gases, powders, sludges and shredded solids, and can be used for liquid waste streams too dilute for other forms of incineration. Some specific wastes destroyed by this method include explosives and propellants, chemical warfare

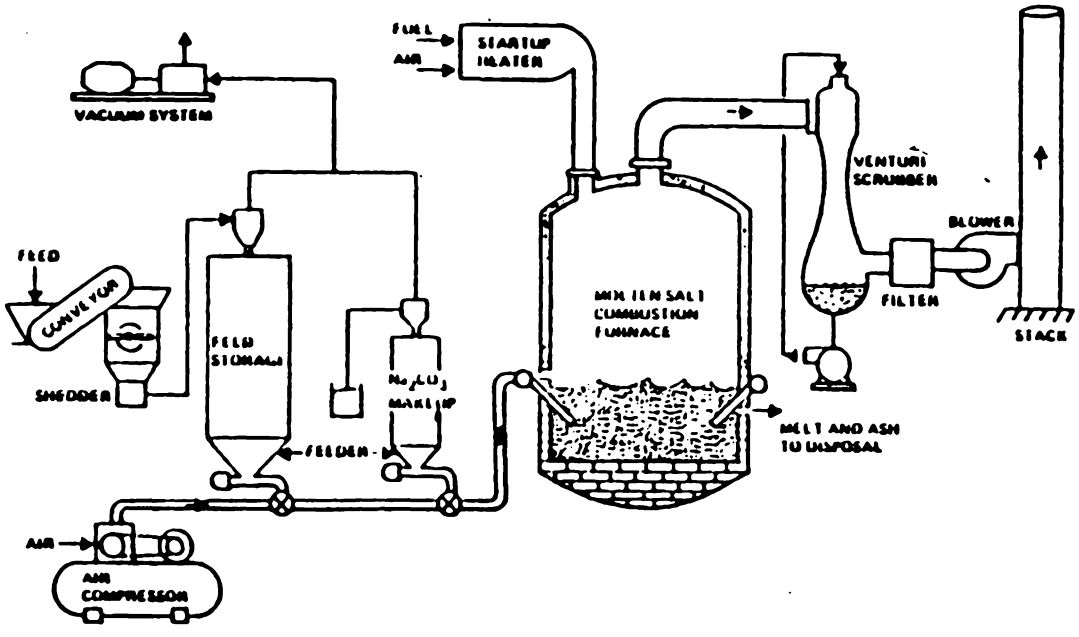

Figure 1. Molten Salt Combustion Unit

agents, and PCBs, plus pesticides, herbicides and their non-metal containers (1,15)

Fluidized-Bed Incineration (1,2,7,12,15)

Description: In this process, a bed of hot sand or other inert granular material is held above a perforated plate through which (usually) air is passed at a rate sufficient to lift and "fluidize" the material. Waste is injected into the bed where rapid heat transfer causes combustion within a few seconds, while the turbulent environment promotes good mixing and a uniform distribution of the 1400-1600°F.temperatures (Fig. 2) Selected off- gases and particulates are scrubbed to some extent by the bed material, though additional emission control devices are usually necessary. Destruction efficiencies are high given appropriate bed temperatures, which are specific for different waste types. However, the generally low temperatures minimize nitrogen oxide emissions, and additives can be used to improve the absorption of off-gases (16).

Waste Stream Applicability: Fluidized bed incineration works well for combustibles, sludges, solids and liquids, including those with a high ash or moisture content. Some specific wastes destroyed by this material are chlorinated

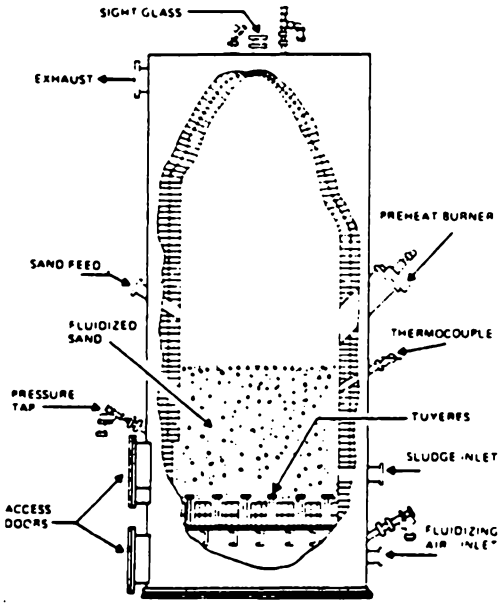

Figure 2. Fluidized-bed incinerator

hydrocarbons with a high chlorine content, waste PVC, munitions, spent HCl pickling liquor, spent organotin blasting abrasive, and methy methacrylate, as well as organics from the pharmaceutical and pulp and paper industries (12,15)

Incineration at Sea (2,9,17,18)

Description: Incineration at sea refers to the use of sea-going incinerator ships to combust hazardous wastes 150-200 miles from land, where the sea and salt air presumably neutralize and dilute emission contaminants normally requiring a scrubber. The M/T Vulcanus I, one of the two U.S.-owned ships currently operational, burns liquid wastes at the rate of 16 tons/hr. in two stern-mounted liquid-injection type incinerators. Test burns in the mid 1970s and early 1980s of chlorinated hydrocarbons, the herbicide Agent Orange, and PCB wastes reported combustion efficiencies in excess of 99.99%. The reliability and accuracy of these values is still the source of considerable controversy, however, due to measuring and sampling problems encountered during burns (17) Also, the uncertain long-term environmental effects of uncontrolled emissions as well as the potentially disastrous consequences of a spill at sea have added to the problems of implementing the technology. The primary advantages are reduced air pollution requirements and lessened impacts on

population centers, but siting the necessary port-of-transfer facilities has proven to be an unexpected difficulty (9,19).

Waste Stream Applicability: So far, liquid chlorinated and unchlorinated hydrocarbons are the only wastes approved by EPA for incineration at sea.

UV/Ozonation (7,15,20)

Description: Ozone, or O_3, is a powerful oxidizing agent that has proven abilities to destroy many hazardous wastes. For some wastes though, oxidation is incomplete and results in refractory intermediates that may be more harmful than their precursors. Ultraviolet light can oxidize these intermediates and so effect the complete destruction of a wider range of substances than can ozone alone. Capital costs are reasonable and the system highly is automated, making it well suited for on-site facilities.

Waste Stream Applicability: UV/Ozonation targets particular chemical structures rather than general waste types, oxidizing compounds with exposed halogen atoms, unsaturated resonant carbon ring structures, readily accessible multi-bonded carbon atoms, and alcohol and ether linkages. Representative compounds include PCBs, TCDD (a highly toxic chlorodioxin), nitrobenzene and related derivatives, and the

hydrazine family of fuels (15). Chemical carcinogens and mutagens are also destroyed. Toxins must be in concentrations of less than 1% though, making this technique useful as a polishing step in the treatment of some wastes.

Wet Air Oxidation (2,21)

Description: This process utilizes high pressures and temperatures to achieve combustion-like oxidation of aqueous wastes. Under these conditions, water serves as a catalyst as oxygen is bubbled through the waste solution, achieving nearly complete oxidation of hazardous components to carbon dioxide and water or to simpler organic compounds. Two advantages of the process are that it is thermally self-sustaining and generates no air pollution, since contaminants stay in the aqueous phase. Research is currently underway to develop catalysts that raise efficiency rates, which will make this technique competitive with conventional incineration.

Waste Stream Applicability: Wet air oxidation is recommended for aqueous wastes containing between 1%-20% by weight of oxidizable material. It has already been used in industry for destroying non-halogenated organic compounds, including cyanide, phenols, mercaptans, and some pesticides, and for improving the biological treatability of industrial

wastewaters (21). Some organics can also be destroyed, and the technology is in general well-suited for wastes which are too dilute for incineration but too toxic for biological treatment. Wet air oxidation has been used by industry for the recovery of chrome and silver, as well as reusable fillers in paper mill sludges (21).

MINOR THERMAL TECHNOLOGIES

Boilers (2,22) (Co-incineration)

Some hazardous wastes can be burned as a supplement to regular fuel oils in commercial boilers. Because of RCRA exclusions no manifest is required, but it is estimated that on-site coincineration may be consuming 2-3 times as much waste as current incinerators. Although convenient and economical, boiler design characteristics and the emphasis on heat production rather than waste destruction may limit effectiveness.

Multiple Hearth (2,7,12)

A common technology for municipal sludge destruction, this incinerator consists of several hearths located one above the other. Wastes enter from the top and are pushed to lower, hotter parts until combustion is complete. Although used for some chemical and pharmaceutical wastes, the presence of cold spots and the tendency for wastes to "U-turn" directly out the stack without being burned have delayed its implementation for hazardous wastes.

Auger Combustion (7)

This unit consists of a long metal auger which pushes solid wastes along a cylindrical combustion chamber, where it burns under controlled reduced-air conditions. Most commonly used for municipal sludge and waste energy recovery, it has potential for hazardous waste treatment.

Multiple Chamber (7)

This involves a two-stage combustion, in which the solids burn in the first chamber and the gases produced move on for incineration in the second. It is used for solid wastes, or liquids and gases with some design modifications.

Cyclonic (7)

This is a form of liquid injection in which air and wastes are injected tangentially along the inside wall of a large cylindrical combustion chamber with a burner inside. Flames typically spiral out of the furnace. Cyclonic incinerators will take solid, liquid and gaseous wastes, and have a low emission of nitrogen oxides.

Microwave (7,23)

A special application of plasma chemistry, microwave discharge utilizes electrically excited gas to achieve combustion of organics at low temperatures. Though still in the research state, it shows promise for treating small volumes of highly toxic wastes.

High-Temperature Fluidized Wall (1,2)

In this process, wastes are destroyed as they pass through a cylinder and are exposed to radiant heat at 4000°F. The reactor itself is protected by a layer of inert gas. Very complete oxidations of selected contaminants have been achieved in bench-scale studies, and the process is nearing commercialization.

Plasma Arc (1,2,)

Plasma arc oxidation is a developing technique in which liquid or solid wastes are exposed to an energized gas at 90,000°F. in an oxygenless chamber, and are converted to low molecular weight gases which may be burned as fuel. The process is energy efficient and could be made portable for transport to generator or spill sites.

Pyrolysis (1,2,7)

Pyrolysis refers to combustion in an air starved environment, avoiding volitization of organics so that air pollution control needs are reduced. It has been used by the Federal Government for the destruction of chemical warfare agents and kepone-laden sludge, and has good potential for other waste types.

Catalytic Oxidation (7)

Catalytic systems achieve oxidation by means of metal catalysts instead of heat, as in conventional incineration. Several types have been developed, which are used primarily to treat waste gases.

Oxygen Incineration (7)

Oxygen incineration is developing technology that uses pure oxygen and high temperatures (5000°F.) to decompose wastes. It is efficient and compact, but may be expensive.

Calcination (7,23)

This process involves the thermal decomposition of aqueous wastes directly into solids without any interaction with the gas phase. Water and volatiles are driven off, leaving a solid or powder behind; thus concentration, destruction and (usually) detoxification are achieved in a single step. Widely used in industry and water treatment, it has been used in wastewater treatment for radioactive wastes and refinery sludges.

CHEMICAL PROCESSES

GENERAL

Chemical treatment involves the use of chemical reagents to detoxify hazardous substances or to enable the recovery of valuable components from the waste stream. Since it does not involve combustion, air pollution is minimal and units are often compact, allowing on-site treatment or incorporation into mobile units for spill response or periodic industrial service. Several currently used treatment techniques are described below.

MAJOR CHEMICAL TECHNOLOGIES

Neutralization (1,7,25)

Description: Neutralization is a common industrial technique for treating acid and/or alkaline waste streams. Specifically, it seeks to adjust the pH (which measures hydrogen ion concentration on a 1-14 scale) to approximately pH7 (neutrality) by treating alkaline wastes with an acid, usually sulfuric or hydrochloric, and acid wastes with a base, often calcium hydroxide, quicklime or limestone. The products are water, heat, a salt, and sometimes a gas. If both acid and alkaline waste streams are produced, they can be

mixed and will neutralize each other to some extent, thus saving chemical costs. A disadvantage of the process is that considerable amounts of sludge may be generated, some of which may be classified as hazardous due to a high metals content (25).

Waste Stream Applicability: Neutralization is most commonly and easily applied to aqueous liquid waste streams, although some non-aqueous wastes (acidic phenols), slurries, sludges and mists can be handled with appropriate modifications. Some specific applications include petroleum, plating, metal finishing and leather- tanning wastes, as well as pickling liquors and acid mine drainage (1,25).

Chemical Oxidation/Reduction (1.7.23.25)

Description: Oxidation-reduction reactions involve the transfer of electrons between molecules with one molecule gaining electrons (reduction) and the other losing them (oxidation). During the process chemical bonds are made and broken, rendering toxic substance less or non-toxic and allowing recovery of valuable components.

Some common oxidizing agents are ozone, chlorine gas and chlorine dioxide, with base metals and sulfur compounds being

good reducing agents. "Redox" reactions are widespread in both chemical and biological systems.

Waste Stream Applicability: Oxidation-reduction can be applied to both inorganic and organic substances in the liquid or gaseous phase with limited use for slurries, tars and sludges. Oxidation reactions have been used primarily for cyanide treatment in the plating and metal finishing industries, as well as the removal of trace components from water effluents (1,25) Good results have been obtained from experimental work with pesticide detoxification. Reduction chemistry is widely used as to to remove mercury, lead, and silver from other industrial effluents (7,25)

Ion Exchange (1,23,24)

Description: In the ion exchange process, undesirable ions in a solvent are exchanged with those in a fixed bed of resin as the solution is passed through it. While in the resin (an insoluble, solid salt), the waste solution will deposit its contaminated ion while picking up a harmless one, and in this way become purified of the toxic substance. Eventually the resin's exchange capacity will be exhausted and regeneration with a brine or acid solution is necessary to restore its original effectiveness. A common example of ion exhchange

is the commercial water softener, which removes magnesium and calcium from drinking water. The concentrated regenerant then goes on for detoxification or recycling, which is often easier or more economical than treating the original dilute stream would have been.

Waste Stream Application: Ion exchange is used in general to separate dissolved inorganic material from an homogenous solution. It is particularly useful for metals recovery or heavy metal purification, e.g., chromium and cyanide from electroplating waste or copper, molybdenum, cobalt and nickel in dilute leach liquors from tailings or dump piles (1,25). It is necessary, however, that the solution be free of organics and suspended solids since these can clog the resin media.

EMERGING CHEMICAL TECHNOLOGIES

Liquid-Ion Exchange (LIE) (7,23)

Description: LIE is a form of extraction in which a water-soluble ionic species is extracted from its original aqueous solvent into an organic one. The technique is widely used throughout the hydrometallurgical industries for the extraction of various metals from solutions or even solid ores.

The operating costs are reasonable, and pollution problems are minimal.

Waste Stream Applicability: LIE is already being used by various industries for resource recovery since it can handle much higher concentrations than conventional ion exchange. In Sweden, one plant producting 70,000 ton/yr. of steel uses tributylphosphate to extract nitric, hydrofluoric and molybdic acid from its stainless steel pickling wastes, while another uses the LIE process to recover zinc from rayon manufacturing waters (23). Domestically it is being used to recover copper and nickel. Research shows good results for extraction of iron, zinc, and chromium from alkali sludges, as well as cyanide and zinc from electroplating rinsewaters. In general, LIE will extract most ionized or un-ionized inorganics from aqueous streams, including metallic solid wastes. It can be used as a primary treatment or a polishing step after other processes.

Chemical Dechlorination (1,2)

Description: Chemical dechlorination refers to general processes that strip chlorine from toxic compounds to produce simpler, non-toxic residues. The most developed technique uses a metallic sodium reagent to split stable chlorinated

organic molecules. The complete system is small and hence mobile, and as a closed chemical system produces no air pollution problems.

Waste Stream Applicability: Although originally developed for the treatment of high PCB transformer fluid, other highly chlorinated hydrocarbons, such as pesticides, are also considered acceptable. For acceptable reduction, however, PCB concentrations must be below 6000 ppm.

MINOR CHEMICAL TECHNOLOGIES

Liquid-Liquid Extraction (23,25)

When a solution is exposed to a solvent in which its own solute is also immissible, the solute will partition itself between the two solvents in distinct proportions, thus reducing it concentration in the first. By repeated exposures the original solvent will become quite dilute, and this is the operating principle of liquid-liquid extraction. It has found limited use in industrial and wastewater treatment for the separation of selected, concentrated wastes where component recovery is sufficient to offset treatment costs, with an important example being the separation of phenols and other organics from aqueous solutions.

Chlorinolysis (1,23)

Chlorinolysis is not a waste treatment but a manufacturing process capable of using waste chlorinated hydrocarbons as a feedstock in the manufacture of carbon tetrachloride. It is estimated that in the Gulf Coast region alone there are enough waste hydrocarbons produced to support a 25,000 ton/yr. carbon tetrachloride plant, provided the legalities surrounding hazardous waste transport can be accomodated (2).

Hydrolysis (7,23)

Hydrolysis is the chemical splitting of a molecule by the addition of water. A widely used industrial step, it can be applied to hazardous aromatic and aliphatic compounds in liquid, gaseous and solid forms. It is effective for the treatment of acid sludge and the degradation of pesticides.

PHYSICAL TREATMENT

GENERAL

One of the first steps often necessary in waste treatment is the separation of the hazardous or treatable portion from a general process stream. This serves to both reduce the volume and to concentrate the waste, an important step especially for incineration processes, many of which cannot burn dilute solutions. Often valuable metals or organics can be withdrawn and re-used, both reducing toxicity and helping to offset the cost of treatment. Separation processes are based on both physical and chemical waste characteristics, and many are already established processes widely used throughout industry.

MAJOR PHYSICAL TECHNOLOGIES

Precipitation, Flocculation and Sedimentation (24,26)

Description: Since these three operations are usually used together, they will be treated here as steps in a single process.

Precipitation involves changing the environment of the solute in such a way as to cause it to come out of solution, or precipitate. This can be done by:

1) adding a substance that will combine with the solute to form a less soluble material;
2) adding a substance that will alter the equilibrium of the system, forcing the solute back into the solid form (ie., changing pH);
3) changing the temperature of the solution. Generally, less material will dissolve in a cool solvent; cooling one near saturation will cause precipitation.

Flocculation techniques are necessary when the solid products of precipitation do not settle, but rather remain suspended as fine particles in the solvent. Flocculation (which here will include coagulation) consists of using a chemical, usually lime or alum, to reduce the repellent electrostatics forces between particles, allowing them to stick together. Gentle mixing will then cause chemical bridges to form between clumps of particles and form large fluffy flocs, which can be settled or filtered out.

Sedimentation is the gravity-separation of solids from solution. In the sequence above, the final step is to

allow the floc to settle to the bottom of an undisturbed circular tank, call a clarifier. For other applications, simple holding tanks or outdoor ponds will do, as long as they have some means for drawing off either the settled solid or the clarified liquid (supernatant) above.

Waste Stream Applicability: The sequence outlined above forms the bulk of water purification technology, but is also widely used in other areas. Simple precipitations involve the removal of inorganic ionic species from solutions, particularly toxic metals. Examples include metals found in pickling wastes, cadmium, chromium and nickel finishing rinsewaters, and copper in etching solutions used by the electronics industry. The precipitation-flocculation-sedimentation process in general can be applied to any waste stream having suspended solids, and is used for metals removal by the steel, aluminum, copper smelting and refining, and metal finishing industries (2,23)

Filtration (7,23,25)

Description: Filtration is a simple form of solid-liquid separation that involves passing the material through a mesh filter or a bed of permeable media (sand, gravel) which will trap unwanted solids. It frequently follows sedimentation as a dewatering step to reduce the volume of sludge.

Waste Stream Applicability: Filtration is often used in metals-recovery operation to collect the sludge resulting from sedimentation. In the sulfide precipitation of metals, flocculation is incomplete and filtration is necessary to remove residual precipitates. Examples of other uses are in waste oil reclamation and the treatment of waterborne oily wastes and pesticides (23).

Distillation (1,2,7,23,24,26)

Description: Distillation is the separation of two or more liquids according to a difference in boiling points. When a mixture is heated the one with the lower boiling point will vaporize first, and those vapors can be collected and condensed in a separate container. More than one distillation is often necessary. Steam distillation, a variation that heats the mixture directly by bubbling steam through it, is

used to separate emulsions of dilute, low boiling-point organics from water. Distillation is a common industrial process that is finding wider application to wastewater treatment as chemical costs and stringent pollution control measures increase.

Waste Stream Applicability: Distillation is applicable to nearly any aqueous-organic or organic- organic mix, provided the boiling points are not too similar. Its most important hazardous waste application is in solvent recovery, to separate and purify used solvents for re-use, and it is commonly used by the petrochemical industry to purify organic products and separate by-products (2).

EMERGING PHYSICAL TECHNOLOGIES

Adsorption (2,7,23,27)

Description: Adsorption, usually onto activated carbon, is another technology borrowed from industrial and wastewater methods that has potential for hazardous waste treatment. Activated carbon is a highly absorbent material with very high surface areas (1700-50,000 $yd^2/oz.$) that can retain solute molecules on its surface by physical and/or chemical forces. In this way they are withdrawn from solution, leav-

ing the solvent in a relatively pure state. The carbon can later be backwashed and regenerated by use of heat, steam, or chemicals, with the solute either recovered or disposed of. Artificial resins have also been developed that broaden the range of adsorption applicability; these may used alone or in combination with activated carbon and can often be chemically regenerated, eliminating the need for a regenerator furnace.

Waste Stream Applicability: Although technically adsorption can be used for dilute and concentrated solutions of both organic and inorganic substances (provided the suspended solids concentration is low) it works particularly well for low concentrations of high molecular weight organics such as chlorinated pesticides, PCBs, and phenols, with lab results and full-scale operations achieveing removals of over 99% (1,23). An ability to remove low concentrations of cyanide, chromium, and other inorganic elements from coal-fired power plant waste streams has also been demonstrated (1,7)

MINOR PHYSICAL TECHNOLOGIES

Reverse Osmosis (7,23-5)

This process uses pressure to force water out of a solution across a semipermeable membrane, thereby concentrating the solution. Largely used in desalination of seawater, it has also been successfully applied to treatment and resource recovery of electroplating rinsewater. Other full-scale uses include food processing and treatment of sulfide streams in the paper industry.

Ultrafiltration (2,7,23)

Ultrafiltration is the process of "squeezing out" small molecules across selectively permeable membrane, leaving a purified solution of large molecules on one side and small ones on the other. It is currently used as a separation step in paint, textiles, pharmaceuticals and other industries.

Freeze Crystallization (23)

This process involves freezing out "pure" ice crystals from a solution leaving a more concentrated solution behind. It

is used successfully for desalination and has a demonstrated potential for hazardous waste treatment.

Flotation (1,2,23,26)

Flotation is a method in which particles or ions are removed from solution by adhering to fine air bubbles passed through the mixture. The air bubbles form a froth on the surface, which can then be removed. Well established industrially, its limited use for wastewater includes the removal of suspended solids, oils and greases from solutions, as well as complexed cyanides from mixed suspensions.

Electrodialysis (2,7,23,26)

This involves the selective passage of electrically charged ions through a membrane, concentrating the ions on one side and leaving purified water on the other. Used in desalination industrially, it has some application in the recovery of metals from wastewater (2).

Electrolysis (2,7,23)

Electrolysis involves the oxidation/reduction of ions in a chemical medium under the influence of an applied potential. It is the basis of such processes as electroplating and

anodizing, and may have limited applications for the removal of heavy and toxic metals from waste streams (1)

Centrifugation (1,2,7,23)

Centrifugation is a process which achieves solid-liquid by the spinning of a mixture at high rpm in a rigid container. Solids compact at the bottom of the container, and can be scraped out after the clarified liquid is decanted. It is often applied on a large scale in wastewater treatment plants for dewatering sludges, and can be used to separate metal salt sludges formed by the precipitation of metals in industrial waste streams (1).

Evaporation (1,2,7,23,26)

Evaporation involves the use of heat to drive liquids, usually. water, or organics from a sludge or slurry and thus concentrate the residue. Evaporation is frequently used to concentrate waste for resource recovery, and by the electroplating industry to concentrate dilute wastewater for re-use (1). Solar evaporation ponds are useful in some parts of the country (1).

BIOLOGICAL PROCESSES

GENERAL

Biological treatment is a general term applied to wastewater treatment systems that rely on the normal metabolic activities of microorganisms to biodegrade organic wastes. In the systems described below, the waste, pumped over solid media or into aerated tanks or ponds, supports vast populations of these microorganisms which use the waste organics for food, obtaining essential nutrients while biodegrading the material into simpler organics or carbon dioxide and water. Starting cultures of microorganisms are usually contained in the waste itself, as is the case with domestic sewage; for more "sterile" industrial wastes "seeding" with a pre-existing culture, often selected and grown especially for the waste type in question, may be necessary. For optimum treatment, a steady influent of fairly consistent composition must be maintained to avoid shock loading the system, so prior neutralization and flow equalization steps are often included. Toxic inorganic elements such as heavy metals may also require removal, since they inhibit bacterial growth at low concentrations.

Biological treatment is considered environmentally sound, because it uses no chemicals and produces only organic sludge, which can be safely land-filled or, with some limi-

tations, land applied. It is the most cost-effective means for removing amenable waste organics, and is the basis of modern municipal sewage treatment. It is the standard approach to industrial waste treatment as well, being by far the most widely used industrial waste treatment technology.

MAJOR BIOLOGICAL TECHNOLOGIES

Activated Sludge (1,7,23,24,28)

Description: Activated sludge uses microorganisms grown in an aerated tank of wastewater to achieve biodegradation. The influent to this tank is raw wastewater and the effluent a murky aqueous mixture of bacteria and residuals, which goes to a clarifier where the mixture settles out into sludge and the purified aqueous component. The sludge is a combination of living and dead cells, plus recalcitrant organic components not yet degraded; some of this is recycled back to the aerated tank to keep microbial populations viable while the rest is drawn off for dewatering and ultimate disposal. Pure oxygen can be used for aeration to allow for variability in the influent organic content.

Waste Stream Applicability: Activated sludge utilizes a waste stream of primarily soluble organics, with less than 1% solids content. It can degrade most common organics with the exception of oil, grease, halogenated aromatics and nitrogenous compounds, and certain other manufactured substances for which natural bacteria lack degradative enzymes, e.g., PCBs. Some of these materials have a slower rate of decay so may require longer exposure to selected bacteria able to degrade them. Inorganics can be removed in trace concentrations (2).

Aerated Lagoon (2,7,23,28)

Description: The aerated lagoon is similar to the activated sludge system except that it consists of large outdoor lagoon instead of a constructed vessel, and has floating aerators anchored at regular intervals. There is no sludge recycle, and retention times are longer. Because of this aerated lagoons have been referred to as "dilute activated sludge" systems.

Waste Stream Applicability: The aerated lagoon is capable of handling the same low suspended-solid organic waste streams as the activated sludge system, although its longer retention times may allow the degradation of more refractory

materials. It has been successfully used for petrochemical, refinery, textile, pulp and paper, and cannery wastes (1,2)

Landfarming (29,30,31)

Description: Landfarming is a disposal process that utilizes soil micoorganisms to degrade selected organic wastes. Wastes are applied at a predetermined rate by being sprayed, injected, or plowed into the top 1 - 2 ft. of soil, where they are held by the soil matrix and are slowly biodegraded or otherwise removed over the course of several days to several years. Periodic disking helps keep the process aerobic, and fertilizer may be added to promote biological activity. Although the lack of knowledge about the exact fate and transport of chemicals in the soil has caused some concern about this method, careful waste selection along with proper design and management should minimize the chance for groundwater and other forms of contamination (see Appendix A).

Waste Stream Applicability: Landfarming is suitable for any waste that has low mobility and sufficiently high biodegradability in soils, with the exception of highly volatile reactive or ignitable materials (30). This excludes most inorganics, but this method has been used for many organic wastes such as oils, solvents, and pesticides, in al-

most any physical form (32). Careful selection is essential to prevent soil and water contamination. There are currently around 200 landfarming operations in use in the U.S., with approximately half of all oily petroleum wastes treated by this method (30,33)

MINOR BIOLOGICAL TECHNOLOGIES

Trickling Filters (1,7,23)

Trickling filter systems consist of a bed of solid media, usually rocks, coated with microbial populations that degrade liquid organic wastes that are continually sprayed on and trickled down through the media. A clarifier settles the effluent afterwards. They are able to treat the same wastes as an activated sludge system, including benzene, chlorinated hydrocarbons, and rocket fuels. Although widely used in municipal treatment, trickling filters are usually replaced by activated sludge systems in most industrial waste applications.

Waste Stabilization Ponds (7,23,28)

Unlike aerated lagoons, this system provides no aeration beyond that provided naturally by wind action and oxygen generation by algae. Stabilization ponds have been found to be successful in the treatment of hazardous organics, which are slowly biodegraded. It is often used as a polishing step following treatment by other methods.

Anaerobic Digestion (2,7,23)

In this system, simple organics are decomposed at biologically high temperatures (90°F.) by anaerobic bacteria. The process produces methane, a usable fuel source. The system is very sensitive to environmental changes and can accept only limited wastes, so anaerobic digestion is not much used for hazardous waste treatment.

Composting (7,34,35)

As opposed to landfarming, which uses the natural soil environment to degrade wastes, composting accelerates the process by piling or storing waste under controlled, optimal conditions. Though more complex, it requires less acreage than landfarming and is suitable for similar waste streams.

WASTE STABILIZATION/SOLIDIFICATION (2,36,39,40)

Description: Stabilization/solidification processes are the basis of a waste strategy combining elements of both chemical treatment and landfill disposal. Waste stabilization is the addition of material to keep the contaminant in its least soluble form, while solidification processes incorporate the waste into a structure of high mechanical and structural integrity. In this form it can safely be deposited in landfills with very little immediate or subsequent danger of groundwater contamination (see Appendix B).

Solidification of waste consists most simply of incorporating the waste into a solid cement-like material, either at the molecular level, i.e. waste molecules entrapped in the molecular matrix of the solidifying agent, or in larger proportions, essentially encapsulation of individual waste packets. The result is a block of rigid, impermeable, non-leaching material that can be packed into non-hazardous waste landfills. These can be covered and returned to use immediately, since the material will not compact or emit gases as will conventional wastes. Other solidifying agents or processes produce a gravel or asphalt-type material, which can be used for parking lots, roadways, impermeable municipal landfill liners, or similar uses. Specific solidification processes are divided into these categories: (2)

1. Cement based process--wastes are returned in water and mixed directly with cement, where the suspended particles are incorporated into the hardened concrete.

2. Pozzolonic Process--wastes are mixed with fine-grained silicous (pozzolanic) material (fly ash, ground blast furnace slog, cement kiln dust) and water to produce a concrete-like solid.

3. Thermoplastic Techniques--wastes are dried, heated and dispersed through a heated plastic structure, which solidifies upon cooling.

4. Organic Polymer Techniques--wastes are mixed in a prepolymer in a batch process with a catalyst. Mixing is terminated before a polymer is formed and the spongy resin-mixture is transferred to a waste receptacle, where solid particles are trapped in the spongy mass.

5. Surface Encapsulation--wastes are pressed or bonded together and enclosed in a coating or jacket of inert material.

In Great Britain, where much of this work was pioneered, a commercial solidification system called Sealosafe is used at three of their central treatment facilities. The system uses cementitious, pozzolanic reagents to produce a material called Stablex, which the manufacturer describes as non-biodegradable, non-odorous, non-flammable and unattractive to disease vectors, while having a significant compressive strength, low permeability, and low leaching characteristics (38). Leaching tests performed by the U.S. National Science Foundation showed that blocks made from various wastes (i.e., electroplating, paint sludge, and tar) produced a leachate whose toxics concentrations were either in the "non-hazardous" range or, for the majority, less than the current drinking water standard (39). They were comparable in strength to grouts, which are used in void-filling and soil stabilization, so could be used for that purpose in old coal mines, quarries or landfills.

The Sealosafe system illustrates some of the advantages of solidification technology. The processes produce no air pollution and liquid process waste streams can be treated by conventional means. Some systems may be operated as mobile units for use of spill sites or small generator locations.

Waste stream applicability: Solidification processes exist for a large number of waste liquids and sludges. The

Sealsafe system, for example, can be formulated to accept over 2,000 different waste types, which are tested and analyzed beforehand. Systems are available both for on- and off-site treatment (40).

TABLE 2. COMPARISON OF MAJOR AND EMERGING ALTERNATIVE TECHNOLOGIES

THERMAL

Type	Description	Advantages	Disadvantages	Waste Feed
THERMAL:				
Liquid Injection	Liquids injected into furnace through nozzle.	Wide waste applicability. No moving parts, so maintenance costs low. Fast temperature response to changes in waste fuel flowrate. HCl recovery possible.	Limited to pumpable wastes Prone to nozzle problems. Nozzles specific to waste type Wastes must maintain a sufficient ignition and incineration temperature, or supplementary fuel must be provided.	Virtually all pumpable wastes, including liquids, gases, and dissolved or vaporized solids Some specific uses include phenols, PCBs, oils, still & reactor bottom, solvents, lacquers, polymer wastes, herbicides & pesticides, chemical warfare agents, cyanide & chrome-plating wastes, PVC paints.
Rotary Kiln	Wastes burned in a tilted, revolving cylinder.	Can burn combustibles of any physical form, and accept wastes from many feed mechanisms. Rotation enhances burn by keeping fresh surfaces exposed for oxidation.	High installation costs Air pollution control equipment necessary. Best used in regional facilities. Airborne or spherical material may escape combustion	Wide variety of combustible wastes, incl. PCBs, munitions, chemical warfare agents, waste paint & solvents, PVC wastes and still bottoms from solvent reclamation.
Cement Kiln	Waste organics burned in kilns that are used in the production of cement.	Energy value of waste recovered, cement plant capacity large, often already located near generators. Good for hard-to-burn wastes because of high residence times, good mixing, high temperature	More air pollution control devices needed. May leave a hazardous ash.	Most liquid organics, particularly chlorinated wastes. Generally used for nonhalogenated solvents.

Table 2

THERMAL (Continued)

Type	Description	Advantages	Disadvantages	Waste Feed
Fluidized Bed	Wastes burned in a bed of inert material "fluidized" by action of hot air.	Turbulence of bed enhances uniform heat transfer and waste combustion. Compact, simple, little air pollution, low capital, maintenance costs.	Low throughput, high particulate emissions for waste applications (i.e., limited waste applicability.) Ash & residuals may be difficult to remove from reactor.	Combustible liquids, solids & sludges, including high-moisture and high-ash wastes. Examples are PVCs, munitions, chlorinated hydrocarbons, phenols and waste HCl pickling liquor, plus other industrial wastes.
Molten Salt	Combustion in a bed of molten sodium-based salts.	Compact units may be portable. Lower combustion temperature yields lower fuel and maintenance costs. Reduced air pollution. Combustion may be self-sustaining and operators need not be licensed experts.	Ineffective with high ash wastes. Temperature too low to burn some wastes. Potential problems with continuous molten salt regeneration and chamber corrosion.	Liquids, gases & solids with low ash content, incl. explosives & propellents, chemical warfare agents, PCBs, pesticides, and herbicides, and non-metallic containers. Good for dilute wastes.
Wet-Air Oxidation	Oxidation in aerated water under high temperatures and pressures.	Good for wastes too dilute or whose heating value is too low for incineration, but still too toxic for biological treatment. Low temperatures reduce fuel costs & combustion may be self-sustaining. Little pollution.	Not good for highly chlorinated organics, and some wastes need further treatment.	Dilute, aqueous, nonhalogenated organic wastes (ex., cyanides, phenols, mercaptons, some pesticides, some organics.)
Incineration at-Sea	Combustion 150-200 miles offshore on incinerator ships.	Low costs; high throughput. Air pollution control equipment unnecessary; waste completely eliminated -- no scrubbed residues of waste.	Danger of dockside and ocean spills; siting problems with storage facilities; safety & efficiency of process still unresolved and long-term environmental effects unknown.	Liquid chlorinated and unchlorinated hydrocarbons.
UV/Ozone	UV radiation used in complete ozone oxidation.	Reasonable costs, can be adapted for on-site treatment, preliminary or final treatment. Systems automated, reducing labor costs.	Ozone is non-selective, will oxidize any exposed material. Treats only low concentrations of contaminants. Sensitive to high temperatures.	Both aqueous & gaseous phases of wastes; chemical carcinogens & mutagens, PCBs, TCDD, nitrobenzene & related derivatives & hydrazines family of fuels.

Table 2.

CHEMICAL

Type	Description	Advantages	Disadvantages	Waste Feed
Neutralization	The addition of an acid to a base or the reverse to achieve an approximately neutral pH.	Equipment requirements simple; chemistry & technology well-developed.	Sludge generation & disposal may be a problem. Off-gases may have to be treated.	Organics and inorganics, aqueous or non-aqueous; gases, sludges & solids with appropriate modifications.
Ion Exchange	The exchange of a toxic in an aqueous stream with a harmless one in a resin in solvent purification.	No air pollution. Treatment costs reasonable, little energy used in actual process.	Removed inorganics still require disposal. Relatively high capital costs.	Dissolved inorganic solutions, i.e., acid solutions with noble metals, salt solution, and heavy metals in aqueous solutions. Solutions must be free of oxidants and suspended matter.
Chemical Oxidation/ Reduction	The detoxification of waste molecules by the chemical transfer of electrons.	Equipment relatively simple; technology well-developed. Energy requirements low, little air emission.	The sludge or effluent aqueous streams require further treatment. Treatment non-selective.	Dilute, aqueous organic & inorganic solutions. Commonly used for cyanide and chromium wastes.
Liquid-Ion Exchange	The exchange of ions between two aqueous streams in solvent purification.	Low energy requirements. Well-established industrial technology, no air or effluent pollution. Recovery of metals can offset operating costs.	Regenerate must be further treated. Suitable for continuous (rather than batch) use only.	Most dissolved ionic or unionized inorganics in aqueous waste streams, including metallic solid wastes.
Chemical Dechlorination	The chemical stripping of chlorine from toxic compounds.	Units can be made mobile for on-site servicing or spill cleanup. No air pollution. PCB oils can be reused after treatment.	For PCB treatment, concentrations must be below 6000 ppm.	Primarily PCB-laden fluids, but also acceptable for other highly chlorinated hydrocarbons.

Table 2.

PHYSICAL

Type	Description	Advantages	Disadvantages	Waste Feed
Sedimentation (Incl. Precipitation & Flocculation	Clarification/separation of dissolved materials by chemical precipitation & flocculation followed by gravity settling.	Simple and widely used; versatile, relatively inexpensive with low energy consumption.	Non-destructive & non-selective, producing a wet sludge with both hazardous & non-hazardous contaminants. May not produce complete removal.	Precipitation useful for inorganic ion solutions; sequence generally good for any waste with suspended solids. Specifically good for metals removal.
Filtration	Separation of solids by entrapment on a mesh or media filler.	Well-established, simple, easy to control, versatile and inexpensive. Low energy costs, no air pollution, allows for resource recovery.	Non-selective, non-destructive; produces a liquid waste stream.	Any solution, slurry or sludge with a liquid component that will selectively pass through the filter.
Distillation	The separation of liquid components based on different boiling points.	Good for solvent recovery. No air or effluent pollution. Nearly any product purity can be attained.	Equipment and auxillaries are expensive and may be large (200 ft.), and complex, requiring skilled operators. Energy-intensive.	Any aqueous-organic or organic-organic liquid mix with different boiling points.
Adsorption	The adsorption of dissolved contaminants onto resin or activated carbon.	Adsorbant may be regenerated, destroying or recovering the contaminant. Minimal pollution and minimal energy requirements if non-thermal regeneration is used.	Adsorbant disposal may be a problem if not regenerated. Thermal regeneration may require air pollution control equipment. Waste stream must be dilute (less than 1%) and low in suspended solids.	Low concentrations of large organic molecules, for example chlorinated pesticides, PCBs, and phenols. Also trace elements.

Table 2,

BIOLOGICAL

Type	Description	Advantages	Disadvantages	Waste Feed
Activated Sludge	The use of recycled microorganisms in an aerated tank to biodegrade waste organics.	Simple and well-established technology, no chemical cost of air pollution. Very cost-effective; can take high organic loadings.	System may require prior equalization and neutralization; generates sludge which must be disposed of; high energy costs for aeration and pumping.	Aqueous organic non-metallic wastes with a low solids content.
Aerated Lagoons	Microorganisms in large, open aerated ponds biodegrade waste.	Simple, well-established technology; longer residence times allows degradation of recalcitrant organics. Inexpensive.	No recycle, so lower loading rates necessary. Large land areas required.	Aqueous, organic, non-metallic wastes with a low solids content.
Landfarming	Spreading and plowing wastes into the soil for biodegradation by soil microorganisms.	Simple, inexpensive, and if properly operated, a relatively low environmental impact.	Surface and groundwater contamination possible unless site well designed and operated; some uncertainty about exact behavior of toxics in soil.	Organic liquids, slurries, sludges and solids that have low mobility and are biodegradable. No highly reactive volatile or ignitable wastes.
CHEMICAL STABILIZATION/SOLIDIFICATION				
Stabilization/ Solidification	The transformation and incorporation of wastes into solid materials of high structural integrity.	On- or off-site treatment; products are strong with low permeability and may be safely landfilled or used for a variety of construction purposes.	Some metal cations may remain mobile; durability of products to wet-dry, freeze-thaw cycles generally has not been good; some controversy about EPA leaching tests.	Best for inorganic materials in aqueous solutions or suspensions that contain appreciable amounts of metals, or inorganic salts (i.e., metal-finishing wastes).

CHAPTER III

BEHAVIOR OF LAND-DISPOSED ALTERNATIVE TECHNOLOGY RESIDUES

As the preceding review of technologies illustrates, the arsenal of available hazardous waste treatment methods is sufficiently diverse and well-developed technically to provide for the safe and effective reduction of hazard of nearly any, if not all, hazardous waste material. Typically, in this situation the selection of an appropriate method is then based on economic considerations; however the residues that remain can present an additional cost and environmental threat when (as is generally the case) they are disposed of in a landfill, from which leachate may escape and jeopardize underlying groundwater. Because the cleanup of groundwater is difficult, expensive, and usually only partially successful, the potential impact of alternative technology residues on subsurface water supplies is an important consideration in the evaluation of hazardous waste treatment and disposal options.

MAJOR TREATMENT PROCESS RESIDUES

Although in some cases the product from a treatment process will vary widely with the waste destroyed, in other cases generalized statements can be made about process residues. For thermal oxidation, which is likely to be the major treatment choice when landfills become unavailable, the process residues can be characterized as follows:

1. Incineration: For rotary kiln combustion, residual bottom ash consists of ash clinkers, slag, glass ceramics, and metals (40). Fly ash is similar to certain components in the bottom ash, and consists generally of particles of mineral oxides, salts from mineral constituents, and fragments of incompletely burned combustibles (6). Liquid injection produces only fly ash, while bottom ash in cement kilns is incorporated into the calcined clinker (14).

2. Fluidized-Bed Combustion: Residues from this type of combustion are similar to those of rotary kilns, but occur primarily as a fine ash which is carried off by the exhaust air and captured in the air pollution control device (15). Work is currently underway to develop additives that trap heavy metals in the bed as insoluble glasses (42).

3. Molten Salt Combustion: Non-combustible materials in a molten salt bath are converted to sulfates, phosphates, and chlorides, which are eventually isolated when the carbonate bath is regenerated (43). Heavy metal salts may reach high concentrations in the isolated fraction, as is the case with sodium arsenate following the oxidation of p-arsanilic acid (44).

4. Wet-Air Oxidation: When employed for the complete destruction of wastes, wet-air oxidation converts non-combustible organics to their highest oxidation state, i.e. sulfates, HCl, or heavy metal salts (45).

Biologicial treatment methods such as activated sludge and trickling filters will accumulate heavy metals and other recalcitrant materials in the sludge, which is then incinerated, land applied, or subjected to further treatment. For other waste treatment technologies (including most physical and chemical processes) the products are too dependent on the specific application to be generalized accurately, and are often produced in the middle of a waste processing sequence which includes several subsequent steps.

HEAVY METALS AS POTENTIAL GROUNDWATER CONTAMINANTS

In reviewing the likely products from hazardous waste treatment technologies, the consistent and recurrent nature of metals in the residues is a fairly predictable phenomenon since, as elements, metals cannot be destroyed as can other larger compounds, so will always survive oxidative processes in one form or another. Unless recovered chemically, these metals will remain with the residue when it goes to final disposal in or on the land, thus presenting a threat to groundwater through the potential movement of metals out of the disposal site. Although many other compounds that may be present in residues have the potential to impact groundwater, the ubiquitous nature of metals as an inevitable component of so many process discharges (particularly incineration) warrants a special consideration of this particular category as an important aspect of overall technology evaluation.

The investigation of metal transport/immobilization mechanisms most appropriately focuses on the two environments where they are most likely to be important in hazardous waste disposal: 1) in the clay liner underlying a landfill in which wastes are deposited, and 2) in soils undergoing activated sludge or oily refinery waste landfarming. The discussion necessarily includes a detailed description of the structure

of landfill clay, followed by the cationic and solution characteristics that influence metal adsorption in both pure clay and soil. These characteristics, based on both theory and empirical findings, help to formulate and support speculative statements about the tendency of metals to leach out of land disposal sites and into the underlying aquifer.

HEAVY METAL MOVEMENT THROUGH CLAY LINERS AND SOIL

Clay Structure and Properties

The ability of a clay liner to restrict the passage of metals is a function of both the physical and electrochemical characteristics of the liner material. Initially, a highly compacted clay layer presents a nearly impervious physical barrier to aqueous leachate (organics may have different effects; see (46) restricting water movement to 10^{-7} cm/s or less by the tight association of its typically very small grains. For water that does eventually seep into the clay material, however, the unique crystal lattice structure of clay provides an additional and more effective electrochemical barrier to the passage of heavy metals and other cations, and is the main adsorptive force in both soil clays and the pure clay mineral. For clay liners, however, adsorption is dependent on a uniform medium that is free of

cracks, burrows, or other direct conduits through which leachate may pass unaffected.

The Structure of Clay

Clays fall into a group of minerals called layer silicates, which are characterized by repeating layers of interbonded alumina- hydroxyl octahedra and oxysilica tetrahedra joined through bonds to common oxygen atoms. For montmorillonite, the major component of the bentonite clay recommended for landfills, each layer consists of an Al-OH octahedron sandwiched between two SiO tetrahedra, a configuration referred to as a 2:1 layer silicate structure (Fig.3).

During the crystallization of the mineral, isomorphic substitution occurs in which other species replace the central Si or Al atoms and create an unbalanced layer charge along the interlayer surfaces. If the substituting atoms are of a lower valence than the original, for example Mg^{+2} for Al^{+3} or Al^{+3} for Si^{+4}, the layer charge will be negative, which is the case for montmorillonite and most other clay minerals. In montmorillonite however, the amount of substitution is fairly low, resulting in a correspondingly low layer charge of 0.25-0.60 per formula unit; this low layer charge lessens the Van der Waals attraction between layers, allowing large quantities of water to invade the interlayer

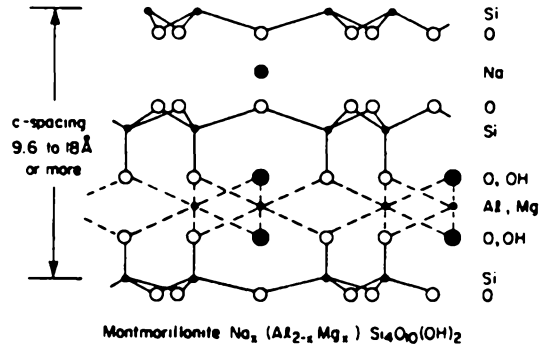

Figure 3. Layer silicate structure of montmorillonite

region and swell the mineral to many times its original size, a characteristic property of montmorillonite. The reactive areas of the crystal include both the internal, interlayer surfaces and broken bonds along crystal edges, and range as high as 800 m^2/g (47,48).

Factors Influencing Metals Transfer Through Clay

The ability of montmorillonite to retain metals through cation exchange is a direct function of the negative layer charge and high surface area. Both within the clay mineral and on the surface of clay particles, the negative charge will attract and hold cations to varying degrees depending on the ionic strength of the solution, valence of the cation, and other variables In most native montmorillonite, the layer charge is neutralized by Na^+ or Ca^+; these can be replaced by other metals to the extent of 80-120 meq/100g, which is defined as the cation exchange capacity (CEC) of the mineral. Because most of the functional groups involved in the layer charge are weakly acidic and dissociate only at high pH, the CEC of the clay mineral is only slightly pH-dependent (47,48).

However, the extent to which clay will exchange or adsorb cations is influenced by both the cation characteristics as well as various chemical and thermodynamic aspects of

solute-ion-substrate interaction. The most important cation characteristics fall into the following categories:

1. Hydrated Ionic Radius

When a metal ion is dissolved in a solution, it attracts and becomes surrounded by a variable number of water molecules, which shield somewhat the charge of the ion from outside influences. Small ions, which have a high charge-to-volume ratio, are hydrated to a greater extent than large ions and thus attain a relatively large hydrated size. Large ions which attract fewer water molecules typically have a smaller hydrated size and can approach more closely to, and be held more tightly by, the charged colloidal surface (49). This favors the adsorption of the larger transition metals over the more common alkali earth metals such as sodium, magnesium, potassium, and calcium.

2. Heat of Hydration

The heat of hydration (ΔH) which is the heat released when a metal is dissolved in water, is a reflection of the degree of hydration which a metal ion undergoes in solution. For this reason, ΔH is inversely proportional to ionic size and, hence, to the level of adsorption;

this phenomenon also favors heavy metal retention since heavy metals generally have low ΔH's.

3. Cation Valence

Because polyvalent ions have a higher charge and can balance more than one site on a reaction surface, a higher valence will favor more complete exchange. For this reason monovalent cations will be replaced more readily than bivalent ions and bivalent more readily than trivalent ions; Th^{+4} adsorbs nearly irreversibly in cation exchange (48,49). An exception to the rule is H^{+}, which, because of its small size and highly polar nature behaves more like La^{+3} and will replace high valence cations at low pH's. Under some conditions, larger cationic molecules such as magnesium hydroxide and zinc hydroxide also compete for sites (55).

Valence effects have considerable significance for heavy metals, which can exist in a variety of valence states. Under most conditions the divalent forms predominate, but other forms such as Cr^{+3}- Cr^{+6}, Ni^{+3}, and Hg^{+0}- Hg^{+1} may also be present, with anaerobic conditions favoring more reduced forms. For metals of the same valence, exchange capacity increases with ionic radii (47).

4. Ion Activity Coefficients

When ions are in aqueous solution, attractive forces between ions cause a deviation from ideal behavior that increases in effect with the molar concentration (51). The activity coefficient quantifies this interaction, and differences in activity coefficients at the site of ion exchange largely determine exchange potential. The differences in exchange potential of ion of differing valencies decrease at high concentrations. The activity coefficient, along with atomic radii also can be used to establish the exchange coefficient of a given cation exchange reaction (48).

Based on some of these general characteristics, it is possible to estimate the likelihood and sequence of heavy metal adsorption onto montmorillonite clay. Because of their larger ionic size and smaller hydration energies, the transition metals would be expected to replace sodium and calcium in most exchange reactions; for the 4th row transition metals (including chromium, nickel, copper and zinc) replacement should increase with atomic number. Fifth and sixth row elements (including cadmium and mercury) would be expected to bind even more readily than the 4th row metals because of their higher atomic number, although because of the lanthanide contraction phenomenon affecting the 6th row

metals, 5th and 6th row ionic radii do not differ appreciably (52). However, cadmium and mercury do not fit the expected pattern; both are somewhat more soluble than would be expected from their position (53). One possible cause of this may be their unusually small ionic radius (<110 A), less than that of potassium, which preferentially replaces sodium in soil clays (because of a lower ΔH) and so is a common component in clay material. The electron configuration of cadmium and mercury is nd^{10}; they are more polarizable than even magnesium and other Group IIA elements because of the relative ease of distortion of the filled d shell, and their ΔH (<430 kcal/mole) are higher than other, smaller elements (i.e. calcium: 377 kcal/mole; sodium: 97 kcal/mole). This would discourage adsorption of cadmium, as has been observed (47). Possibly because of the effects of an underlying layer of filled 4f orbitals in mercury (not present in cadmium), mercury's exchange behavior differs from cadmium; it tends to be retained more effectively and can be reduced to the volatile, elemental form in soils. Hg^0 can then diffuse up through subsequent soil or mineral layers, (54) where logically it would be reoxidized to Hg^{+2}; reduction-volitilization-reoxidation cycle of this sort would actually help to retain mercury in the upper regions of a clay or soil system.

In addition to the nature of the cation, however, metal adsorption has been found to be controlled by several other solution and surface- related phenomenon resulting from the uniquely charged nature of layer silicates. Some of these observations are at variance with the known properties of pure clay minerals, a result perhaps of using clay suspensions as the media of investigation rather than samples of undisturbed mineral; undoubtedly though, these inconsistencies illustrate also the complexity and variety of variables involved in clay-metal interactions.

For many metals, retention by clay minerals has been found to increase with pH, in contrast to the pH-independent nature of pure montmorillonite; this is generally attributed to a shift from adsorption to precipitation as a controlling mechanism (53,55). At high pH's and high ionic strength, metals can form hydroxy-complexes and other meta-stable hydrolysis products which may either precipitate or bind at sites unavailable to the hydrated metal ion (53); montmorillonite, in fact, catalyzes the hydrolysis and polymerization of interlayer Cr^{+3} (56). For zinc and copper in landfill leachate, adsorption (by ion exchange) is found to prevail at lower pH's (pH< 5.5-6.0) and metal concentrations, whereas high concentrations and more alkaline conditions increased removal through the precipitation of zinc and copper hydroxide. Cadmium, whose hydroxy form is more

soluble than that of zinc or copper at similar pH's, yielded the carbonate precipitate $CdCO_3$ in alkaline solution (53). In a non-complexing media, Egozy (57) found that the distribution coefficient of cadmium and cobalt increased with pH at high ionic strength. Competition with protonated ligands or other cations (58), including protons (50) can interfere with metal binding in acid media; however, some protonated ligands, such as humic acid, can form links between metals and clays which will enhance adsortpion.

The presence of complexing ligands can reduce adsorption through the formation of stable neutral or anionic metal ligands (55), and $CdCl_2$ has been suggested as a water tracer due to its low reactivity with clay (57). As noted above, however, ligands do not always reduce adsorption; the final equilibrium is dependent upon the concentration of the ligand, the charge and effective stability of the metal-ligand complex, as well as the order of contact of clay, competing ions, and ligands. The major role of most ligands is to prevent formation of hydroxy complexes at pH's higher than 5.5. (55).

As mentioned earlier, ionic strength of the solution can negatively affect adsorption largely through the competitive effects of other cationic species. However, high ionic strength also decreases the activity coefficient (thus in-

creasing the effect) presumably through an enhancement of cationic interactions in solution; this decrease in activity increases slightly the pH necessary to effect precipitation of metal hydroxides (58).

In addition to the effects of solution chemistry, other research shows that clay surfaces themselves are generally not heterogeneous in nature, exhibiting instead differences in cationic charge density and adsorption specificity that vary within and between interlayer spaces (59,60). One result of this is a composition-dependent exchange surface, where the nature of the bound cations affects the exchange potential of remaining sites by altering exchange site geometry (61). In M^{+}-M^{+2} exchange reactions, an increase in surface concentration of the M^{+2} ion generally increases the selectivity coefficient for that ion up to some maximum, beyond which preference may decrease. In addition, strong adsorption of high charge montmorillonite clay is speculated to be a result of an entropy (ΔS) gain associated with a disordering of water or an increase in ion disorder at exchange sites (62). Sorption sites have different energies, and will adsorb ions in the sequence of decreasing sorption energy (48). In some cases, these energies may be related to the degree of 3-dimensional mica-like structures existing within the mineral, since montmorillonite with a range of selectivities can

be artifically generated by techniques that produce these structures within it (63).

Further studies with cobalt and cadmium adsorption onto montmorillonite show that part of the observed adsorption follows cation exchange mechanisms and decreases at high pH and ionic loadings, whereas another portion maintains its adsorbability at high ionic strength and varies somewhat in its pH response (57). From this evidence, supported by others (61,63) has emerged the theory of two classes of exchange sites on montmorillonite: one that follows expected cation exchange mechanisms and has its basis in the isomorphic substitution with the layer structure; another that results from broken bonds on the edges of crystals, and which are similar to the sites on metal oxides. Adsorption on the second class of sites is slower than the interlayer cation exchange, and some ions show a tendency to bond at one site or another (50,65). The exact crystallographic nature of these different sites is still uncertain (56).

Although the many factors involved in metals retention make mechanism determination difficult, the observed conditions that discourage adsorption--namely, low pH and high ionic strength of competing cations--are well enough known to justify measures to prevent their occurrence in a landfill or land application situation. Most notably, the addition of

lime both during construction and at closure, as well as the exclusion of acid wastes from metal-bearing landfills would be appropriate preventive steps.

Metals Retention in Soil.

Metal movement in soil, a concern for surface-based disposal methods such as landfarming and land-application, includes mechanisms and parameters generally more numerous and complex than movement through a pure mineral. Although clay is a major component of most soils, layering is usually less well-ordered than in the pure state, and the smaller particles may overlap neighboring particles or sheets. In addition, individual particles may become coated with a layer of Fe or Mn oxide which interferes with cation exchange and restricts swelling, while increasing somewhat the capacity for anion exchange (47). For these reasons soil studies cannot be used as a direct analogy to pure clay liner systems, but are important for land disposal investigations and to illuminate possible mechanisms occurring beneath a landfill in the event of material release.

For clay particles, (as opposed to clay minerals) the layer charge of the 2:1 layer silicate structure imparts a negative surface charge that will be counterbalanced according to the Diffuse Double Layer theory, which describes a tightly bound

layer of cations immediately adjacent to the surface which grades away gradually to the lesser concentration of the bulk solution. Cations neutralizing the charge of the colloid are exchangeable, and so any factor that affects either the integrity of the double-layer or the charge of ions approaching it will affect the immobilization mechanisms for metals.

There are several factors that have this effect. A solution of high ionic strength will compact the double layer, forcing diffusely- distributed cations closer to the colloid and reducing their exchange potential (47,66). Metal ions normally present in solution as hydrated species can bind with chelating agents that are themselves more soluble (or that will form ion pairs that are more soluble) than the unassociated ion; these complexes then may exhibit higher mobility and be less subject to electrostatic forces (49). For some species, oxidation state or complex formation may cause transport according to anionic mechanisms; Cr^{+6}, for instance, behave somewhat like an anion in soils (47). Anions typically undergo little adsorption, and may be able to pass through beds of pure clay minerals, especially at low pH (53). If high concentrations of metals are present at a given time, precipitation reactions can cause deposition of metals that will later solubilize when the leachate concentration drops (68). Cation exchange reactions are also

reversible, although reversal is unlikely because of the high valence and size of most toxic metals (69).

Metal immobilization in soil is most commonly achieved by three basic mechanisms: adsorption onto oxides and organics, ion-exchange with clay, and chelation to form insoluble compounds. In regions of high metal loadings, (i.e. near metal smelters) precipitation may also be a factor (70) although remobilization may occur when deposition ceases. Because of the high variability of soil composition, the relative importance of each of these mechanisms will vary between soils and according to metal type (66,71).

Adsorption of metals onto iron and metal oxides is a major mechanism in many soils (68,72,73) that can bind metals with several hours of deposition (69). The binding ability of (for example) iron results from the sixfold coordination of the central iron atom with oxygens shared by adjoining iron atoms; at the edges of crystals the unbalanced charge on the oxygen is balanced by complexing with H^+, OH^- and water molecules according to the ambient pH. At high pH a net negative charge exists that can attract and hold other metal atoms preferentially over H^+. The binding ability of these oxides is highly variable and dependent on pH, and only weakly reversible (72).

For landfill purposes, the binding abilities of iron and manganese oxides may argue for co-disposal, in a layered fashion, of heavy-metal containing wastes with tailings, rusted scrap, or other oxidized-metal material that could serve as an absorbant for the metals in a leachate. There is some evidence to show that some heavy metals bind preferentially to manganese oxides over montmorillonite (74) but suitable materials must be of a type not likely to leach contaminants or significantly lower the pH.

Adsorption of metals onto organic matter (often described as complexation), occurs in a manner similar to oxide, with vacant d-orbitals on transition metals complexing with a pH-dependent negative charge on the surface of organic matter (75). In humic material, the charge results primarily from dissociation of carboxylic and phenolic groups, and remains negative to below pH 7. Organic matter can be a high effective retainer of metals through cation exchange: the CEC of well-developed humus can range between 150-300 meq/100g with surface areas of 800-900 m^2/g (47). Potential exchange rates of fulvic acids have been reported as 600-650 meq/100g.

Cation exchange with clay minerals has already been discussed, and despite the differences between mineral and soil clays noted, clays still contribute significantly to metals retention in soils. The CEC of clay particles is inversely

related to grain size, and can increase by a factor of three in finely-ground material (48,76).

Removal of metals by complexation depends on the concentration of available ligands and the stability of the resulting complexes (69). In soil, the most important ligands are humic and fulvic acids; these will bind metals as chelates and generally render them insoluble, although, as mentioned earlier, some large anionic ligands can bind and transport metals according to anionic mechanisms (49). Some metals, specifically alkaline earth metals, increase in solubility upon chelation with humic acid, whereas heavy metal humates are only sparingly soluble (48). Some organic ligands however, have been found to leach copper (51).

These then, are the primary mechanisms that will serve to retain metals within the soil and prevent their leaching to groundwater. Most evidence indicates that applied metals do in fact stay in the top several inches of soil, although, because of the variability of soils, sites considered for disposal must be carefully screened and, preferably, pretested before and monitored during disposal to prevent inadvertent aquifer contamination. Metals retention also eventually means metals contamination, however, which is an important factor in the consideration of subsequent site use.

CHAPTER IV

SUMMARY AND CONCLUSIONS

In this study, two major questions were explored through a review and analysis of the literature: 1) what technological alternatives to landfilling are available for the treatment and disposal of hazardous wastes, and 2) what is the probability that the residues from these technologies will remain on the site of disposal.

The investigation revealed that there are nearly fifty technologies that either are, or have the potential to be, useful for the destruction or volume reduction of toxic industrial wastes. Twelve of these are major processes already in use commercially; eight are emerging technologies, either at or close to the commercialization stage, and the remainder are minor technologies that either are narrow in scope, of limited use for hazardous waste treatment (though perhaps widely used for other purposes) or still in the developmental stage. Taken together, these processes can handle a wide variety of toxic materials of any physical form, with incineration processes being the most versatile and effective.

Residues from these technologies vary widely according to waste type and composition, but a common component in many of them is heavy metals, which, as elements, cannot be further degraded to other products. The available literature suggests that these metals could be retained in clay liners beneath a landfill through the mechanism of cation exchange, with the adsorption of heavy metals favored by their smaller hydrated size, lower heat of hydration, and in some cases, higher valences than the naturally occurring alkali earth metals. Other important factors include ionic activity, the pH and ionic strength of the solution, the presence of complexing agents, and the possible surface heterogeneity of the clay. It must be emphasized, however, that the retentive abilities of clay are only significant if the clay layer is unbroken; cracks or other direct conduits will transmit leachate essentially intact. In soils, metal binding through cation exchange with clay is augmented by adsorption onto iron and manganese oxides and complexing with organic matter such as humic acids. Many field studies with landfarmed metal-bearing wastes show that these mechanisms are usually sufficient to retain metals to within several inches of their zone of application.

The conclusions of this study can therefore be summarized as follows:

1. There exist alternative technologies to treat a large proportion of the existing hazardous waste streams;

2. The most consistent residue component among treatments is heavy metals;

3. In some regards, the chemical properties of heavy metals favor their retention in clay over naturally-occurring cations, suggesting that heavy metals may be immobilized by a clay landfill liner. The high cation exchange capacity of clay and the binding abilities of organic matter and iron and manganese oxides are the primary phenomena responsible for metal retention in clay and soil.

However, because much of the work with cations and clay minerals consists of controlled laboratory experiments or field observations of municipal landfills or those containing untreated hazardous waste, additional research is needed that directly investigates the behavior of leachate from process residuals. For incineration in particular, little work seems to exist that characterizes leachate derived from hazardous waste incinerator bottom ash or investigates specifically its interaction with compacted clay. The extent of metal transmission following the exhaustion of the available cation exchange capacity, and the potential for such a situation

eventually occurring in an ash-bearing landfill are also topics that need further investigation before more positive conclusions about groundwater impact can be reached.

Although the results of this study illustrate that alternative technologies have a wide potential for reducing the current dependency on landfilling as an ultimate disposal choice, it appears that many of these technologies are currently underutilized, possibly because of misconceptions about their technical or economic potential. One case in point is cement kilns; recent estimates predict that existing plants have the capacity to burn all the chlorinated liquid organic waste currently generated, while providing reduced fuel costs that can help make older plants more competitive with new plants and processes. Stabilization/Solidification has a good operating record for inorganic wastes, often the nemesis of other forms of treatment; fluidized-bed and molten salt both can achieve high DRE's with low levels of emissions; and physical and chemical processes can be creatively applied to condition a wide variety of waste streams, yet none but the latter two have been employed on a large scale. Perhaps the most neglected yet most effective approach to waste management is waste reduction, which diminishes generator liability and disposal expenses while safeguarding the environment as a whole; but, beyond a good-faith signature

on the waste manifest, this option is not addressed by current RCRA regulations.

It would seem that, for a national waste management policy to be effective, it must be as diverse and innovative as the technologies available will allow it to be. Processes now exist to treat nearly all hazardous wastes, although the cost of some of them is unquestionable high; yet the apparent federal committment to incineration as the primary treatment alternative restricts versatility by necessitating large central facilities to achieve economies of scale. Smaller facilities, or perhaps circulating mobile ones, may be a better solution in some regions, while helping to reduce the risk and expense incurred by local generators for waste transportation. Hazardous waste treatment and disposal is a complex problem with no single, simple answer; however, with political and institutional support for a technological base already well-developed, we can safely and effectively meet what promises to be a continuing environmental challenge.

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APPENDIX A. LANDFARMING OF PETROLEUM REFINERY WASTES

Landfarming, the method of waste incorporation directly into soil that is used by petroleum refineries and a diverse but small number of other industries, has a two-fold goal in waste treatment: 1) the biological degradation of organic wastes, and 2) the immobilization of inorganics. For wastes of a purely organic or inert nature, incorporation into topsoil presents little environmental risk and is an effective alternative to more sophisticated biological processes (1,2). For petroleum and refinery wastes, which usually include both hazardous components and heavy metals, the potential for groundwater contamination is greater.

Generally, land applied oily wastes consist of refinery tank bottoms, cleaning fluids, API separator sludge, filter backwashes, and other general wastes with a highly variable composition, ranging from n-alkanes and parafins to aromatic and asphaltic compounds, along with small amounts of zinc, lead, chromium and other metals (3). Highly chlorinated hydrocarbons, often resistant to microbial degradation, are not suitable (4). The RCRA-listed hazardous components include phenols, cresols, the API separator sludge and tank bottoms (5) and possibly others, depending on the origin of the material.

Degradation of the organic portions of oily wastes has been demonstrated in a number of studies (6-9). API separator sludge and refinery tank bottoms applied to fertilized land at a 5% oil/soil (dry wt.) concentration was reduced 54%-67% after 20 months (8); similar work under optimized laboratory conditions found API separator sludge from refinery and petrochemical sources to have half-lives of 130 and 600 days, respectively (10). Land-applied waste oil (crude, used crankcase, No.2 home heating) showed a reduction of 48.5% - 90% after a year's time, with less recalcitrant oil components being consumed at a rate of 0.6 $m^3/1000m^2/yr.$ (11). Degradation was accompanied by a significant increase in the hydrocarbon microbe population, yet oil concentrations in the soil were still high enough to inhibit cover plant growth nine months later. Almost all degradation occurs in the top several inches of soil, with little or none of the components leaching through to underlying layers (8,12), with degradation rates influenced by waste application rates, soil moisture, temperature, composition, and pH, and amount and type of fertilization (13-15).

Although over 100 species of fungi, bacteria, and actinomycetes are able to metabolize one or more fractions of crude oil, not all components of oily waste degrade at the same rate. Straight-chain aromatics degrade fastest, with aromatics and cycloalkanes somewhat more slowly (9), although

under some conditions simple aromatics may degrade at the same rate as n-alkanes (14). Parent aromatics are more easily degraded than their alkyl-substituted derivatives (14), although high application rates may favor the removal of aromatic and asphaltic compounds (15). The most recalcitrant entities include resin-asphaltic and bitumins, and in general high molecular weight compounds with aromatic and cycloparafinnic rings and/or parafinnic substituents (9), although all components degrade more slowly during the winter months (12).

The substituted aromatic phenol has been found to be degraded by soil microorganisms as well as being adsorbed on soil colloids and humus. Phenolic compounds therefore tend to accumulate in the soil rather than leach through to underlying layers, especially in soils of high organic content (7).

The inorganic components of land-applied wastes tend to be somewhat more mobile than the organic fractions, since, as elements, they do not "disappear" through biodegradation but rather accumulate in the zone of application. Studies with refinery wastes and industrial sewage sludge showed that metals remained in the top 30 cm of soil (16,17), immobilized primarily by the forces of cation exchange, complexation, and adsorption. Some metal migration has been observed for

cadmium and mercury 18) although not to a statistically or environmentally significant extent. However, since the application of organics will often lower the pH of the soil, a condition conducive to the mobilization of metals (19), soil liming may be necessary, both during the use of the site and after applications cease.

Provided this precaution is taken and other suitable soil conditions are maintained, the available evidence suggests that landfarming is a suitable means of disposal for some wastes. Leaching of undegraded waste components, if it occurs, would be expected during the winter months or during the spring snowmelt, when the ground is saturated but low temperatures still restrict biological activity.

APPENDIX B. LAND BURIAL OF STABILIZED/SOLIDIFIED WASTE

Waste stabilization/solidification, the process by which suitable hazardous wastes are isolated or immobilized by incorporation into an inert mass, was introduced as a promising technology in 1974 but has yet to find widespread acceptance in the U.S., although it is somewhat more extensively used in England (20). Because chemicals are often not chemically detoxified but simply encased with a solid matrix, concern over the leachability of toxics or their release upon eventual fracturing of the solidification product has served to slow the incorporation of stabilization technology into national waste management strategies, despite a fair amount of evidence supporting its effectiveness. In some cases economics may be a factor, since disposal costs can range up to $400/ton waste (21); although the withdrawal of the landfill as a disposal option for untreated wastes may alter this situation. From the standpoint of groundwater protection however, stabilization technology may be able to play a valuable role in preventing leachate contamination.

Unfortunately, one difficulty with obtaining reliable performance data on stabilization is the lack of uniform standards and testing procedures for the physical and chemical characteristics of the final product. Much of this is due

to the variety of product types, which differ according to the nature of the waste and the technique used; consequently the type and extent of testing is usually up to the vendor (22,23). This variability often makes final comparisons of process techniques difficult.

Nevertheless, a number of testing and process evaluations have been done that elucidate the extent of applicability of solidification/ stabilization processes. In general, pozzolanic cementation with a variety of wastes produces a product or reasonable unconfined compressive strength (up to 1,000 psi) with a permeability averaging 10^{-6} cm/s, although 10^{-8} permeabilities (less than that of compacted clay) can be achieved (24,26). Leachate tests conducted according to EPA techniques yield satisfactory results, and a large landfill of pozzolanic waste in Pennsylvania has produced no leachate in the six years of its operation (24). The particular process involved utilizes fly as as well as hazardous wastes in the pozzolonic process, essentially disposing of two wastes at once. Other cementation application incorporate heavy metal wastes into concrete blocks; one product made from sand-blasting waste reduced cadmium leachability to less than 10% of the EPA standard and had a 28-day design strength of 5,000 lbs, although block strength decreased with waste concentration (25). The advantage of block formation is that the block itself constitutes disposal, whereas gran-

ular products still must be landfilled or secured in some other fashion. Studies on heavy metal cementation products that were ground and agitated for an hour in acidified, distilled water (to simulate the consequences of fracturing and acid precipitation) showed leachate concentration of 0.08-0.50 ppm, a reduction of over 99% (21).

More extensive studies on several hazardous wastes sludges (electroplating, Ni-Cd battery, chlorine production, calcium-fluoride, and flue-gas desulfurization) used in a variety of cementation and encapsulation techniques elucidated more completely physical product characteristics. Unconfined compressive strength was in general fairly low, although the use of more additive increased it and flue-gas desulfurization products achieved strengths of over 2,000 psi, equal to that of low- to medium strength concrete. Permeabilities ranged from 10^{-4} to 10^{-7} cm/s and were dependent on the solidification technique; in general lime-based pozzolanic products had lower permeabilities and plastic-encapsulated products (made from electroplating sludge) were impervious. Few samples survived a 12-day wet/dry or freeze/thaw test, although lime-based pozzolanic products performed slightly better (26)

Most applications of the stabilization/solidification process focus primarily on the treatment of inorganic wastes.

Organic wastes present more difficult problems since they are often unreactive with chemical reagents so that encapsulation, rather than true chemical fixation, results from treatment attempts. Specific problems with organics include the effects of hydrophobicity, surface tension, pH, microorganisms, temperature, and ultraviolet radiation that can cause either the breakdown of the solidified matrix or increase the leachability of entrapped organics (22).

Although many manufacturers claim to accept organics into their treatment scheme, an extensive review of liquid organic stabilization techniques by Tittlebaum et al. (22) revealed that few accurately-documented studies exist which elucidate either the nature, strength, and permanence of the bonds formed during stabilization or the physical and chemical stability of the final product. Most data are obtained empirically and are hence rather short-term in nature; consequently a fundamental understanding of the interaction of organics does not exist.

However, some processes do show promise. Thermoplastic techniques, in which asphalts or sulfates are blended with organics at elevated temperatures, produce a hydrophobic material that exhibits little leaching; this could be used as an independent process or as a coating on material stabilized by other means. Disadvantages include high cost and the pos-

sibility of hazardous vapors during heating. Cement or pozzolanic processes have produced stabilized products, although their resistance to aqueous leaching is uncertain; the relatively low cost of this method and the limited successes so far speak for continued research into this area. Finally, thermosetting polymers show a theoretical potential for incorporating unreactive organic wastes into a hydrophobic material, although the relatively high cost may discourage development and application of the process (22).

For wastes amenable to the various stabilization/solidification processes, though, the available leachability data seem to indicate that waste materials tend to stay in the finished product. Proponents of stabilization/solidification maintain that these prodocts do not allow significant infiltration of precipitation, do not become incorporated into runoff,or involved with upward-moving gases (27), and more recent operating experience seems to confirm this (24). For this reason site selection and preparation need not adhere to criteria as detailed and rigid as those required for non-stabilized wastes. It would appear that, given the good results of the available laboratory and field data, this technology could play a significant role in hazardous waste treatment.

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