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Item ID Number 03367 ☐ **Not Scanned**

Author Landreth, Robert E.

Corporate Author National Environmental Research Center, Office of Res

Report/Article Title Promising Technologies for Treatment of Hazardous Wastes

Journal/Book Title

Year 1974

Month/Day November

Color ☐

Number of Images 23

Description Notes Program Element 1DB311; EPA/670/2-74-088

PB 238 145

PROMISING TECHNOLOGIES FOR TREATMENT OF HAZARDOUS WASTES

Robert E. Landreth, et al

National Environmental Research Center
Cincinnati, Ohio

November 1974

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

Current research efforts directed at detoxifying or recycling hazardous wastes are being studied; this report presents the first year's progress of the study. Promising methods are identified, reviewed, and suggested for further development.

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Director
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Research Center, Cincinnati

TECHNICAL REPORT DATA (Please read instructions on the reverse before completing)		
1. REPORT NO. EPA-670/2-74-088	2.	3. PB 238 145
4. TITLE AND SUBTITLE PROMISING TECHNOLOGIES FOR TREATMENT OF HAZARDOUS WASTES	5. REPORT DATE November 1974; Issuing Date	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Robert E. Landreth Charles J. Rogers	8. PERFORMING ORGANIZATION REPORT NO.	9. PROGRAM ELEMENT NO. 10B311; ROAP 07ADZ, Task 02
10. PERFORMING ORGANIZATION NAME AND ADDRESS National Environmental Research Center Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	11. CONTRACT/GRANT NO.	12. SPONSORING AGENCY NAME AND ADDRESS Same as above
13. TYPE OF REPORT AND PERIOD COVERED Final 7/1/73-7/1/74	14. SPONSORING AGENCY CODE	15. SUPPLEMENTARY NOTES
16. ABSTRACT <p>Numerous toxic and hazardous wastes are being generated and improperly treated/disposed of by industrial sources. The wastes produced have varied toxicities and possess characteristics which make them unique. This study was undertaken to identify and recommend promising waste treatment technologies the use of which would minimize the growing threat to public health and environmental quality. Literature searches, site visits, and personal communications with experts in the field provided the basis for identifying needed treatment technologies.</p> <p>The criteria used in the selection of promising techniques for development were inadequacy of present technology and the economics, resource recovery, and volume reduction of the new technology. Treatment processes that appear applicable for processing both homogeneous and heterogeneous hazardous waste streams include chemical, biological, and physical treatments.</p>		
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17. KEY WORDS AND DOCUMENT ANALYSIS		
A. DESCRIPTORS *Hazardous materials *Waste treatment *Waste disposal *Sludge disposal Toxicity Pesticides	B. IDENTIFIERS/OPEN ENDED TERMS *Hazardous waste Solid waste control *Hazardous waste control Physical treatment Biological treatment Chemical treatment Heavy metals	C. COSATI Field/Group 13B
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified 20. SECURITY CLASS (This page) Unclassified	21. NO. OF PAGES

EPA-670/2-74-088
November 1974

PROMISING TECHNOLOGIES
FOR
TREATMENT OF HAZARDOUS WASTES

By

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Solid and Hazardous Waste Research Laboratory

Program Element 10B311

NATIONAL ENVIRONMENTAL RESEARCH CENTER
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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<u>British</u>	<u>Metric</u>
1 ft ²	0.0929 meters ²
1 ft ³	0.0283 meters ³
1 ft ³ /min	28.316 l/min
1 gpm	3.785 l/min
1 lb.	0.454 kg.
1 ton (short)	0.9072 metric tons

BACKGROUND AND INTRODUCTION

In a report to Congress on hazardous waste disposal June 30, 1973, it was estimated that the total quantities of nonradioactive hazardous waste streams generated by industrial sources amounted to 10 million tons, or approximately 9% of the 110 million tons of all wastes generated by industry. Geographically, approximately 70% of industrial hazardous wastes are generated in the mid-Atlantic, Great Lake, and Gulf Coast areas. Physically, about 90% of the hazardous wastes by weight are found in the liquid waste stream. Approximately 40% of these wastes are inorganic, and 60% are organic. In retrospect, it was only in the last few years that an increasing number of questions have been raised regarding the disposal of hazardous wastes and, in fact, the inadequacy of treatment/disposal technology did not represent a substantial and growing threat to public health and environmental quality.

Under Section 212 of Public Law 91-512, the Resource Recovery Act of 1970, the U.S. Environmental Protection Agency was charged with preparing a comprehensive report and plan for the creation of a system of national disposal sites for the storage and disposal of hazardous wastes. Section 212 mandated, in part, that recommended methods of reduction, neutralization, recovery, or disposal of the materials be

ABSTRACT

Numerous toxic and hazardous wastes are being generated and improperly treated or disposed of by industrial sources. The wastes produced have varied toxicities and possess characteristics that make them unique. This study was undertaken to identify and recommend promising waste treatment technologies, the use of which would minimize the growing threat to public health and environmental quality. Literature searches, site visits, and personal communications with experts in the field provided the basis for identifying needed treatment technologies.

The rationale used in the selection of promising techniques recommended for development were inadequacy of present technology, and the economics, resource recovery, and volume reduction of the new technology. Treatment processes that appear applicable for processing both homogeneous and heterogeneous hazardous waste streams include chemical, biological, and physical treatments.

This report is designed to fulfill the Office of Solid Waste Management Programs request of May 16, 1973 that the Solid and Hazardous Waste Research Laboratory identify and recommend for future development promising treatment technologies for hazardous wastes.

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determined. Work called for by this mandate has been completed and reports presenting information on treatment/disposal techniques are now available.¹⁻³ Needless to say, only the technical issues involving definitions, nature, and magnitude of the problem to be solved and the approaches to be used are provided in the reports. Technology for disposing of hazardous wastes recommended in the reports generally was based on the best available information. Where information was limited, some estimates were made presumably with the expectation that treatment/disposal data would result from future developing processes. It is important to be aware that methodology recommended for control of hazardous wastes¹⁻³ may not have been employed in the treatment of hazardous constituents in waste streams.

Recognizing the present inadequacy of treatment/disposal technology, the Office of Water and Hazardous Materials, Office of Solid Waste Management Programs (OSWMP) requested that the Solid and Hazardous Waste Research Laboratory (SHWRL) of the National Environmental Research Center-Cincinnati conduct a control technology assessment. In OSWMP's assessment of control technology, it considered the two basic options available for preventing damage that may arise from land disposal: treatment or isolation of hazardous materials that are disposed of into the environment. The OSWMP then specifically requested that SHWRL complete reports on new treatment technologies by June 30, 1974. This report therefore is prepared in fulfillment

of the OSWMP request that several new promising treatment technologies for hazardous wastes be identified.

The rationale used in the selection of techniques that appear promising for development are:

1. Existing technology for hazardous waste is not adequate.
2. Although existing treatment is adequate, new processes would neutralize or reduce the volume of waste, require less energy to operate, and, thus, be more economical.
3. Existing treatment is adequate, but new processes could lead to maximum recovery of safe reusable products.
4. New treatments would eliminate the synthesis of compounds equally or more toxic during processing, and the processed materials having been rendered nonhazardous would be safe for disposal.

It is assumed that future support for development by SHWRL of any of the selected techniques to be described for detoxification of hazardous wastes will be through mutual agreement between OSWMP and SHWRL.

RECOMMENDED PROMISING TREATMENT TECHNIQUES

By far, the majority of waste streams are mixtures, and those of hazardous wastes are no exception. Most hazardous waste streams are mixtures of pesticides, heavy metals, organic solvents, acids, or bases, and have a high solids concentration. Promising methods

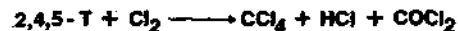
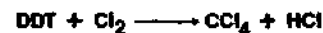
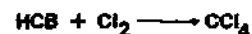
for treating such complex streams -- methods that need further development and implementation -- are:

- A. Chlorinolysis
- B. Wet air oxidation
- C. Decomposition by acids and bases
- D. Chemical oxidation
- E. Other chemical treatments
- F. Biological degradation
 - enzymes
 - trickling filters
 - activated sludge
- G. Catalysis
- H. Batch and continuous ion exchange
- I. Photochemical processing
- J. Low-temperature microwave discharge
- K. Osmosis/ultrafiltration
- L. Activated carbon adsorption

A. CHLORINOLYSIS

Chlorinolysis⁴ appears to be a very desirable process for eliminating some very toxic and hard to dispose of products. For example, herbicide orange, still bottoms from organic manufacturing operations, and pesticides can be converted by chlorinolysis to the principal product, carbon tetrachloride. Chlorinolysis involves adding

chlorine to the waste material in special nickel--stainless steel reactor under one of two sets of conditions: high pressure and low temperature or low pressure and high temperature. No catalyst is required for the vapor phase reaction. The mole ratio of chlorine to carbon is between 4 to 1 and 8 to 1. Carbon atoms end up as carbon tetrachloride. In addition, depending upon the starting molecule, other byproducts may be formed. Possible byproducts formed in the chlorinolysis of three typical pesticides are indicated by the reactions shown in Figure 1.



TYPICAL CHLORINOLYSIS REACTIONS

Figure 1

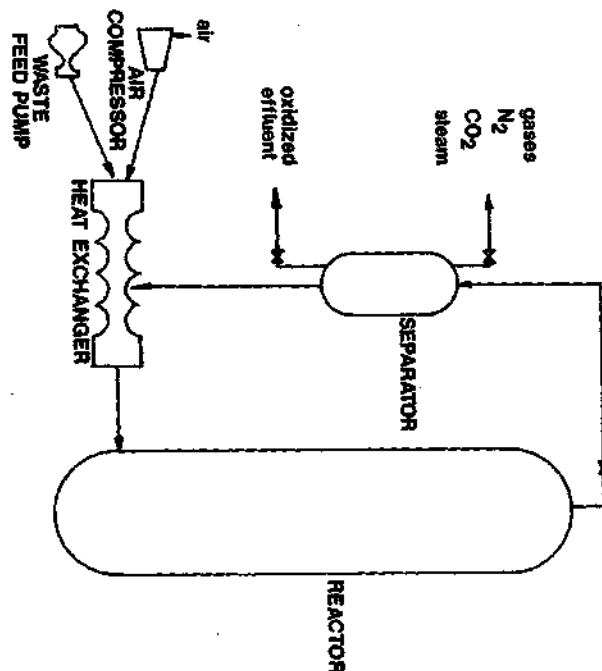


Figure 2

BASIC WET AIR OXIDATION SYSTEM

The degree of oxidation can be varied from 0% to 100% to meet treatment requirements for a given waste stream. Holding the temperature to about 150°C allows only 5% to 10% oxidation, whereas nearly complete oxidation, depending on the type of waste being oxidized occurs at 320 °C. The basis flow sheet shown in Figure 2 can be varied to meet the requirement of the individual plant or waste stream. Systems have been designed to recover energy and for generating saturated or slightly superheated steam. In addition, because of the flexibility of the system, it appears that reusable byproducts, such as alcohols, organic acids, etc., can be produced.

Wet air oxidation and thermal conditioning are competitive processes that eliminate the need for costly chemicals used in other treatment processes. The economics of wet air oxidation is dictated by three principal factors: (1) volumetric throughput, (2) COD of the wastewater, and (3) oxidation characteristics of the waste. Operating costs are affected by the amount of air to be compressed. Plants requiring more than 2500 compressor horsepower generally show a negative operating cost; that is, the value of power or steam generated exceeds the value of utility and labor required to operate the plant. Wet air oxidation becomes economically feasible when the organic content of a hazardous waste stream is extremely high ($> 10,000$ mg/L BOD), the waste stream is toxic or marginally biodegradable, and land disposal is prohibited or expensive.

The byproducts can be undesirable and require clean-up before release to the environment. Although phosgene is a toxic byproduct of chlorinolysis when carbonyl groups are present, it does have commercial value and is used in the synthesis of plastics. Another byproduct hydrochloric acid has limited commercial application and must be neutralized before discharging into the environment. Limitations on ocean and deep-well disposal make these types of disposal unacceptable. Electrolysis technology can and is being used to convert waste hydrochloric acid into chlorine and hydrogen for commercial use. Electrolysis is competitive with the traditional caustic chlorine process and is recommended as a method for cleaning up hydrochloric acid in chlorinolysis. A possible deterrent to the commercial development of the chlorinolysis process is the poisoning effect of sulfur. As little as 20 ppm will poison the system and render the oxidation process ineffective. Research⁵ currently is under way to investigate this and other related problems. An interim report on chlorinolysis is expected by June 1975.

Dioxin-impurity, introduced by way of incompleteness of the chlorinolysis reaction, has been investigated. Gas chromatograph and mass spectrometer analysis, with an analytical limit of detection of 10 parts per trillion, did not indicate any dioxin contamination in the carbon tetrachloride formed in the reaction. Toxicological evaluation has not as yet been completed, but no evidence of dioxin has been found thus far.

B. WET AIR OXIDATION

The wet air oxidation process⁵⁻⁶ is another potential solution to the problem of disposing of toxic and hazardous wastes. Although it developed some 20 years ago and is a relatively expensive operation, recent legislative prohibitions concerning deep well, lagoon, and ocean disposal of processing wastes, coupled with the need to conserve natural resources and recover energy, have resulted in wet air oxidation becoming increasingly competitive with other types of treatment processes.

The wet air oxidation process is diagrammed schematically in Figure 2. Waste is pumped into the system by a high-pressure pump and mixed with air from an air compressor. The waste is passed through a heat exchanger and then into a reactor where atmospheric oxygen reacts with the organic matter in the waste. The oxidation is accompanied by a rise in temperature. The gas and liquid phases are separated. The liquid is circulated through the heat exchanger before being discharged. The gas and liquid are both exhausted through control valves. System pressure is controlled to maintain the reaction temperature as changes occur in the feed characteristics (i.e., organic content, heat value, temperature). The mass of water in the system serves as a heat sink to prevent a runaway reaction that might be caused by a high influx of concentrated organics.

This process also is applicable to low pressure oxidation of sludges whereby the required vacuum filter area can be reduced by 80% to 90% of that required for chemically conditioned sludges. By increasing the temperature and the amount of air, COD reductions of 80% to 90% and sludge volume reductions of 95% to 99% can be accomplished. The complex and expensive air pollution controls required in incineration make wet air oxidation competitive with it, since emissions from wet air oxidation can be controlled. In the wet air oxidation process, the usual interfering agents such as sulfur, phosphorus, and chlorinated hydrocarbons, are oxidized to their respective acids, carbon dioxide, and water. Thus, proper operation and control of the discharges from the system eliminates toxic and hazardous emissions.

Wet air oxidation has been used in reclaiming sodium hydroxide from spent caustic pulping liquor. Concentrations of acrylonitrile in waste streams have been reduced from 2000 mg/L to 6 mg/L, in addition to completely oxidating total solids and sulfur. Effluents containing cyanide from coke production may also be treated by way of wet air oxidation. A bonus is the concomitant production of a usable steam or power recovery. Explosives can be safely disposed of by wet air oxidation since in the process they are handled as a wet slurry, which is a safe form. Thus, dangerous conditions as well as air pollution are eliminated. Yet another application of wet air oxidation is in the recovery of chromium and silver from waste streams containing these two metals. Previously, incineration of such metal

waste streams left the inorganic chemicals in an undesirable form or resulted in the loss of the metals by way of the flue gas discharge. Wet air oxidation may be used in the smelting of ores, e.g., sulfides are converted to sulfates. This approach to smelting eliminates the air pollution created in the conventional smelting of sulfide ores.

Except in the recovery (and hence removal) of metals, wet air oxidation is not directly applicable to most metallic waste streams because of the oxidation of the metal to a higher valence state and, hence, more toxic waste. Nevertheless, wet air oxidation systems can be economically designed to treat several types of hazardous waste streams. Wet air oxidation even has a use in industry disposing of radioactive waste. With its use, a 1000-fold decrease in the volume of some radioactive byproducts can be expected.⁸

C. DECOMPOSITION BY ACIDS AND BASES

Within practical capabilities, chemical treatment may provide limited success. Kennedy *et al.*⁹ reported that the addition to or reaction of eight selected commercial pesticide formulations with strong acid or strong alkali compounds resulted in partial decomposition of the pesticides. Sodium hydroxide caused only slight changes in the structure of dieldrin. Malathion was decomposed sufficiently to produce inorganic phosphate, and 2,4-D was hydrolyzed to a sodium salt. Picloram was decarboxylated, with the chlorine being replaced by an

hydroxyl group. The toxicities of the end-products were not determined. They also used a sodium biphenyl¹⁰ compound to decompose five other pesticidal compounds, and obtained very desirable results. However, the usefulness of sodium biphenyl compound is limited from a practical standpoint in that it is not stable for extended periods of time when stored at temperatures above 0°C. When a sodium-liquid ammonia treatment was applied, 16 to 19 pesticide compounds were completely degraded. Only eight were completely decomposed with the use of a lithium-liquid ammonia treatment. In the degradation process, several toxic gases were produced that, in a practical operation, would have to be scrubbed from the gas stream before release to the atmosphere. These gases included chlorine, hydrogen chloride, hydrogen sulfide, and certain nitrogen gases.

Price¹¹ reported that carbaryl, DDT, and toxaphene were decomposed when exposed to alkaline conditions. Decomposition did not necessarily constitute a solution to the problem since it only served to alter the compounds, and disposal was still a problem. Price also suggested a method to remove chlorine from organochlorine pesticides that was expensive and hazardous, due to the chemicals involved. Moreover, disposal of its byproducts or end-products would be a problem.

D. CHEMICAL OXIDATION

In reports by several research teams¹²⁻¹⁵ to the pesticide industry's waste management program, several oxidants and pesticides were discussed.

Among the oxidants were chlorine, chlorine dioxide, potassium permanganate, ozone, and peroxide. Pesticides used with the above oxidants included DDT, Lindane, Parathion, Dieldrin, 2,4,5-T Ester, Endrin, Aldrin, Toxaphene, Sulfoxide, 2,4-DCP, and 2,4-D compounds. Potassium permanganate readily oxidized 2,4-DCP and attacked Aldrin and Lindane when in an aqueous solution. Unsaturated organic compounds were found to be more susceptible to ozone oxidation than were saturated compounds. Parathion was oxidized by both chlorine and ozone, but the more toxic compound paraoxon was produced. Ozonation removed 90% of the Dieldrin and aeration, 80%. This removal rate was produced starting with an initial concentration of Dieldrin of about 0.2 mg/l in distilled water, an ozone concentration of 3.9% by weight in air injected at 0.3 l/m through a 2.5-l reactor.

Goma and Faust¹⁶ used potassium permanganate, chlorine, and chlorine dioxide to remove residual diquat and paraquat from water. Their results showed the reaction rates to be very fast, and the rate of reaction with potassium permanganate to vary greatly with pH. This oxidant appeared to have more effect in an alkaline solution than in an acid medium. Chlorine had no effect on diquat or paraquat under acidic conditions. On the other hand, an increase in pH increased the rate of the oxidation.

Treating electroplating rinse streams with a proprietary peroxygen compound¹⁷ effectively destroys free cyanide and precipitates zinc and cadmium. The reaction is fast and simple to control. In less than

an hour, the treated rinse can be released to the sewer after having collected the precipitates on a filter. Research under way indicates that other cyanide-containing wastes may be treated this way.

Generally speaking, any type of organic waste can be totally oxidized to carbon dioxide and water. However, the process economics dictate that oxidation be terminated when the toxicological properties of the waste have been destroyed.

E. OTHER CHEMICAL TREATMENTS

Heavy metals in plating wastes have always presented a disposal problem. Usually it was uneconomical to install treatment facilities for the low-flow rates characteristic of plating. However, in a 1973 report,¹⁸ it was pointed out recent innovations allow the flexible plater to meet current discharge requirements at negligible capital and low chemical costs. Hexavalent chromium can be reduced to the trivalent state by the addition of ferrous sulfate, which can be obtained free of charge from steel picklers. Five pounds of pickle liquor are required for every pound of chromic acid to be destroyed. The same report also states that cyanide can be destroyed by trickling sodium hypochloride into the copper bath rinse stream water. Five gallons of 16.5% solution of sodium hypochloride is required per pound of cyanide to precipitate the copper. Nickel is precipitated out of the rinse water by combining the electrocleaner rinse water with the rinse stream from the nickel tanks. The alkalinity of the former raises the pH of the latter above 8 and causes the nickel to be

precipitated as a hydroxide. The precipitated metal can then be removed by settling and filtration.

F. BIOLOGICAL DEGRADATION

Biological treatments have been used extensively in treating hazardous and nonhazardous manufacturing wastes. Among the several types of biological systems that have been used are trickling filters, activated sludge systems, aerated lagoons, and stabilization ponds. Numerous studies have been made of the biological degradation of several pesticidal formulations. These studies involved microbial degradation under aerobic and anaerobic conditions. Pesticides used in the studies were Parathion, Methyl Parathion, DDT, Dieldrin, 2,4-D, 2-CPA, MCPA, Sienex, Fexoc, Delapon, CDAA, CIPC, 2,4,5-T Hydrochlor Epoxide, Lindane, Heptachlor, Endrin, DDD, and Aldrin. An example of biological reaction is the anaerobic degradation of Lindane. The extent of the breakdown of Lindane in a sludge containing 1.5% dry solids (56% volatile) is indicated by the graph in Figure 3.¹⁹

Enzymes

The use of immobilized enzymes may prove to be very effective in the control on hazardous or toxic wastes. According to one report²⁰, immobilized enzymes can be regarded as ones with a handle, which thereby allows them to be used repeatedly in unit processing operations. Enzyme technology is being investigated with the objective of developing a treatment for concentrated phenolic waste that could be used as a polishing treatment step to remove phenols from waste water. Although

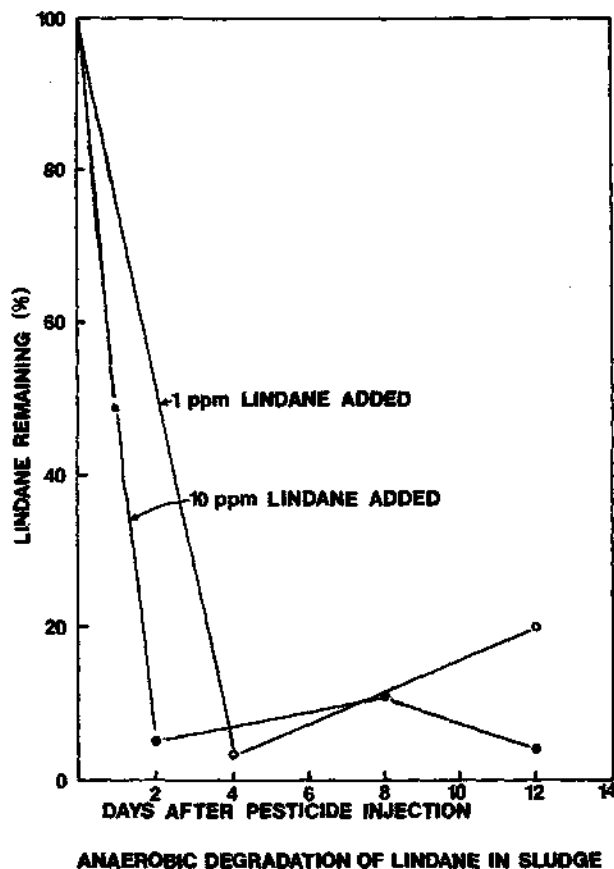


Figure 3

the enzymes presently being used have a useful life-time of only 1 week, longer lasting, more stable enzymes are being investigated. Since many hazardous compounds are phenolic derivatives, immobilized enzymes may be useful as a polishing step to a number of final detoxification processes. Enzymes are used in hydrolytic processes for the synthesis of materials and in processes that involve either oxidation or reduction. Enzyme inhibition is being used at Louisiana State University²⁰ in the design of sensors for the detection of pesticides, cyanides, and other hazardous materials.

The field of enzymes technology is not without problems.²¹ The promised advantage of enzymes being able to carry out useful tasks with a high degree of specificity at ambient temperatures and with few side reactions is offset by the high cost of the enzymes. The high cost necessarily dictates conservation and reuse. The use of immobilized enzyme technology appears to be a promising course of action, and it could become competitive with other hazardous waste treatment processes. Several industries utilize enzyme systems. Because of the highly competitive nature of the field of developing enzyme technology, they are reluctant to discuss any information regarding their respective systems.

Trickling Filters

Trickling filter units are used primarily as load leveling tanks, although some BOD reduction is achieved. As a roughing filter, up to 85% BOD reduction can be accomplished on a single pass; and more

importantly, the system is able to withstand fluctuating wasteloads and toxic slugs.

The organisms that accomplish waste treatment in a biological filter are found in the biological slimes attached to the filter medium. The microorganisms making up the slime assimilate and oxidize soluble nutrients contained in the waste waters passed through the filter. The oxygen needed to oxidize the wastes comes by way of forced or natural air movement through the filter. Rocks or synthetics may be used as a filter medium. The use of synthetic media has greatly increased the efficiency of filters because of a lessened tendency to plug and the provision of effective ventilation. With the use of a synthetic medium, filters as deep as 20 feet can be used without trouble with some wastes.

Normally, a hydraulic loading rate of less than 0.5 gallon of waste per minute per square foot of filter surface is applied to a trickling filter.²² For "roughing filters," the organic loading is relatively unimportant, but it should be sufficient to utilize the organisms for waste removal. An idea of the effect of organic and hydraulic loading rates on extent of waste treatment is given by the information in the following table, in which are listed data obtained from two plants that manufacture herbicides:²³

Plant	Organic loading #/1000 ft ³ /day	Hydraulic loading gpm/ft ²	BOD reduction %	Phenol reduction %
A	25	0.11	80	70
B	45	0.24	72	54

Note that high rate filters should be used only in special circumstances. In most cases, some dilution is needed to reduce toxicity and the concentration of dissolved salts before biological treatment can become effective.

Activated Sludge

In an activated sludge system, most organics, including pesticides, pesticide isomers, solvents, and organic byproducts, can be utilized and hence decomposed by the bacteria that make up activated sludge.^{12,13,19,24-27} In essence, this biological oxidation system is a fluidized reactor consisting of a concentrated biomass supplied with organic waste and forced oxygen. Part of the biomass is recirculated while the remainder is allowed to coagulate and settle. The settled mass is disposed of into the environment after an appropriate treatment. Oxygen supply is an important operational factor because the microbial mass can function effectively only in the presence of an adequate supply of the element.

In one plant, from 95% to 99% reduction of pesticidal compounds is achieved by holding the waste in an aeration basin for 6 days. BOD removal is on the order of 99%. Operating parameters necessary for the plant's operation are a COD loading of 12,000 pounds per day and an air flow up to 24,000 cfm. Clarified effluent and excess biological solids are sent from the plant to a municipal treatment plant (activated sludge) for final treatment.

Areas in need of further research and development are those concerned with the design of trickling filters, activated sludge system, and

stabilization ponds, as well as the adaptation of microbial populations, suited to the destruction of specific hazardous wastes.

G. CATALYSIS

Catalytic conversion techniques are currently being investigated.²⁸ The utility of the technique is illustrated by the removal of the poison thiophene from benzene by a single-pass catalytic process. With the use of chromia alumina as the catalyst, thiophene was reduced from a concentration of 10^4 ppm in benzene to one of 10^{-1} ppm. It has been suggested that dichloro-dibenzo-p-dioxins can be dechlorinated by palladium on charcoal.²⁹ Nickel boride also may be useful in the dechlorination of hazardous materials. Although nickel boride has not been used in dechlorination, it has been applied to the hydrogenation of olefins and the desulfurization of oils. Total dechlorination of isodrin has been accomplished by exposure to lithium metal in tetrahydrofuran and t-butyl alcohol. These and other applications provide evidence that catalysts may be discovered that will remove the group or element conferring toxicity to an original chemical structure, and thereby leave a building block available for the synthesis of a useful chemical. An interim report²⁸ on catalysis of pesticides is being prepared and will provide information on the effectiveness of this technique.

H. BATCH AND CONTINUOUS ION EXCHANGE

Ion exchange media have been and are being developed to concentrate and remove the hazardous components from a variety of waste streams.^{30,31} Originally developed to soften or demineralize water, ion exchange

methods can be adapted to batch, to continuous flow, and to counter-current continuous-flow operations. Advantages include high throughput rates per unit size, efficient chemical utilization, small dilution process streams, lessened water requirements, and a uniform product quality over the entire cycle. Two major disadvantages are that it is a relatively complex mechanical operation and that it greatly depends on instrumentation.

Kennedy³² has described a new synthetic polymeric adsorbent (Amberlite XAD4) for treatment of effluents from the manufacture of pesticides. Amberlite XAD4 is a resin characterized by a chemically inert surface that allows very efficient regeneration. In addition, it is hard and resilient and is highly resistant to attrition. The adsorbent's high degree of porosity, extensive surface area, and uniform pore distribution favor rapid adsorption kinetics, high operation efficiency and low leakage. A substantial amount of laboratory data indicates that isopropanol is more effective than methanol in regeneration and the adsorbent is superior to activated carbon in regeneration efficiency and adsorption kinetics. Experiments suggest that leakage of chlorinated pesticides from the adsorbent was not noticeable until more than 39 bed volumes had been treated. A distinct advantage in the use of this adsorbent is that the regenerant can be recovered by heating to leave a residue of the pesticide that can be recovered or easily disposed of because of the significant volume reduction.

Ion exchange resins made of peanut skin or walnut expeller meal³³ have been tried. The two resins were used in adsorption tests with heavy metals. Known concentrations of heavy metals were passed through packed columns and eluted with alkaline or acidic solutions. The fractions and adsorbents were then analyzed by standard atomic adsorption methods. Results indicated that the adsorbents removed 10 percent of their weight of mercuric at a flow rate of 2500 L/m. An advantage in the use of peanut waste was that mercury was effectively adsorbed over a wide pH range, and at low concentrations, i.e., parts per billion.

Soil also has very excellent ion exchange capacity³⁰ and is the subject of current research.³¹ However, insufficient data are available at the present time to permit a meaningful evaluation.

A compact, chromic acid waste reclamation system based on ion exchange principles is currently being used in Canada.³⁴ With the use of the system, more than 99.5% of the chromic acid is recovered from the plating rinse waters. The acid can be returned to the process. The unit also removes undesirable metallic impurities and, thus, allows the electrolyte to work more efficiently than in the original bath. The unit combines three, short ion exchange beds, one containing anion resins and the other two containing cation resins in a reciprocating flow system to reclaim the chromic acid. Since the operation takes place in a closed-loop, countercurrent, ion exchange mode, the chromic acid is more concentrated and high recovery efficiency is achieved than with conventional ion exchange system.

A typical continuous countercurrent ion exchange system is illustrated in Figure 4. The system is divided into three sections (pulse, regenerating, and contacting) and operates in a run and pulse mode. During the run mode, the raw waste is fed in at the top of the contact section. Treated product water is delivered at the bottom of the bed. Simultaneously, regenerant is fed through the loaded resin in the regenerating section at the bottom of the loop and exists as waste after stripping the resin free of unwanted ions. If needed, makeup resin is supplied during this time period. Rinse water is passed through to wash any traces of regenerant from the stripped resin. In the pulse mode, valves separating the three sections are opened and feed and waste valves are closed. This allows the resin bed to be "pulsed" around a certain distance to provide fresh resin for the contacting section to enable new resin to be generated, and to add some resin in the storage area.

I. PHOTOCHEMICAL PROCESSING

The influence of light and, in particular, sunlight on chemical reactions is a part of everyday life (e.g., plant photosynthesis, fabric fading, smog, skin reactions, etc.). Only recently has it been recognized that sunlight can influence environmental chemical reactions. Water and air deserve particular attention with regard to photodegradation processes, because of the transparency to ultraviolet light, pervasive significance to life, and their own reactivity.

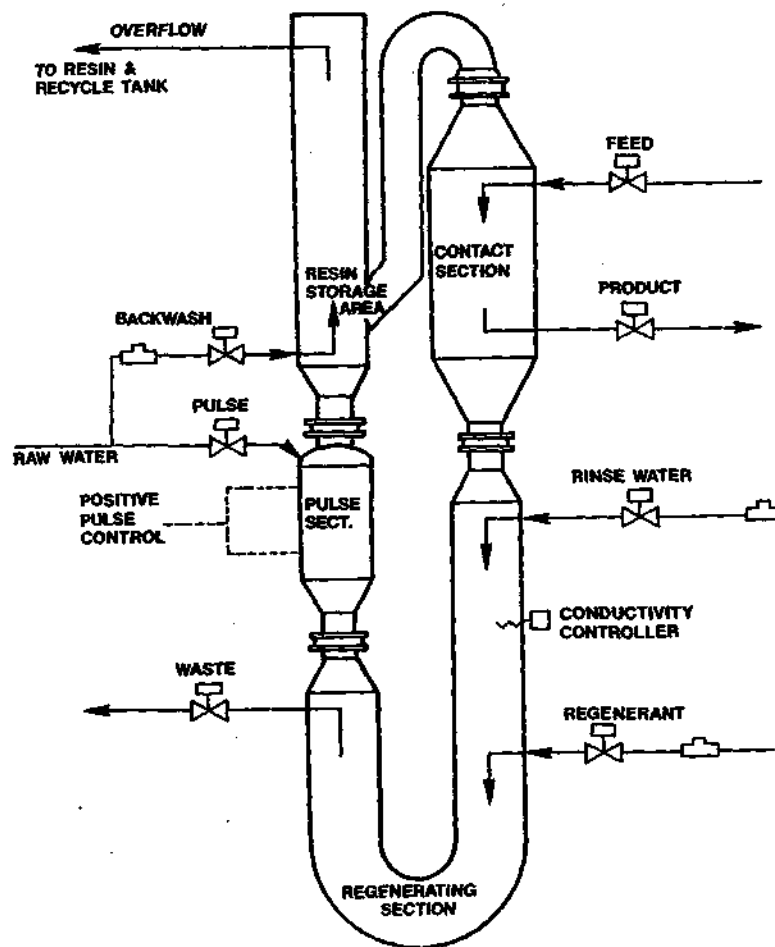
Water properties serve both as a medium for and reactant in ionic processes. Besides the usual hydrolytic reactions, water provides

photonucleophilic displacements such as replacement of chlorines by hydroxyl groups in aromatic compounds. The photodegradation of such diverse compounds of nitrogen, dexton, and PCP can also be shown to be a result of photonucleophilic reactions. Photooxidation and photo-reduction play an important role in the degradation of xenobiotics by light.

Herbicides react favorably with the ultraviolet region of the spectrum. Laboratory studies by Plimmer³⁵ indicate that with halogenated herbicides, the loss of halogen was the dominant process and was affected by the orientation and electronic effect of a substituent. A free phenyl radical, generated by the photoreaction, would react by hydroxylation or by replacement of chlorine by hydrogen in an aqueous solution; although, under certain environmental conditions, it could react differently.

A field assessment of the effect of photodecomposition processes on herbicides is very difficult because of competing modes of loss such as volatilization, microbial reactions, and leaching. Results in one case do suggest that products isolated from plants after field application were identical to products produced by photochemical decomposition.³⁶

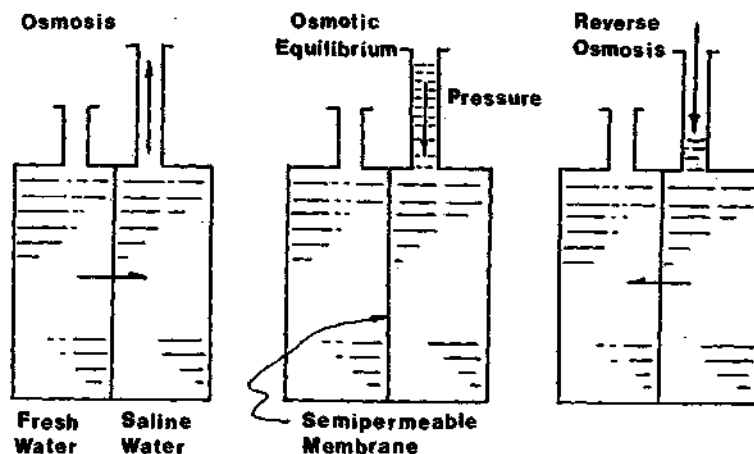
Several studies have been completed on photochemical methods for treating pesticides³⁷⁻⁴¹ and waters containing hazardous waste^{42,43} such as phenols and other organic compounds that absorb light in the ultraviolet region. Generally, artificial light from fluorescent ultraviolet lamps having a spectrum comparable to that of sunlight was



**COUNTERCURRENT CONTINUOUS
ION EXCHANGE SYSTEM**

Figure 4

solvent flow. At a certain value of pressure (the osmotic pressure) equilibrium is reached and the amount of solvent that passes in each direction is equal. If the pressure is increased above the osmotic pressure on the solution side of the membrane, the flow reverses. Ideally, pure solvent will then pass from the solution into the solvent. These basic processes are shown in Figure 6.



OSMOSIS THEORY

Figure 6

In the electroplating industry, proper operation demands that the paint bath should be kept at a constant concentration. In flux of rinse water and paint, usage brings about a lowering of the concentration. The result is that water must be continuously removed. Contaminants such as chromates, phosphates, chlorates, and sulfates also find their way into the tank and must be removed. By means of an ultrafiltration/reverse osmosis process, unwanted contaminants can be removed and the paint solids returned to the dip tank. Acceptance by the industry of the ultrafiltration/reverse osmosis process has resulted in substantial savings.

The plating industry also loses or discharges a majority of its metal inventory to the environment. This practice could be changed by using reverse osmosis to purify low-level plating rinse waters; plating ions could be concentrated to levels where it would become economically attractive to recycle the wastes to the plating bath.

Reverse osmosis coupled with appropriate chemical pretreatment and post-treatment oxidation can supplant the sometimes unreliable physiochemical-biological step in the removal of organics from pesticide and petroleum refinery operations. Trace quantities of heavy metals and organics usually are picked up during the metal-finishing operations. Through reverse osmosis and electrodialysis, a water can be produced that is suitable for reuse, and thus water consumption can be decreased.

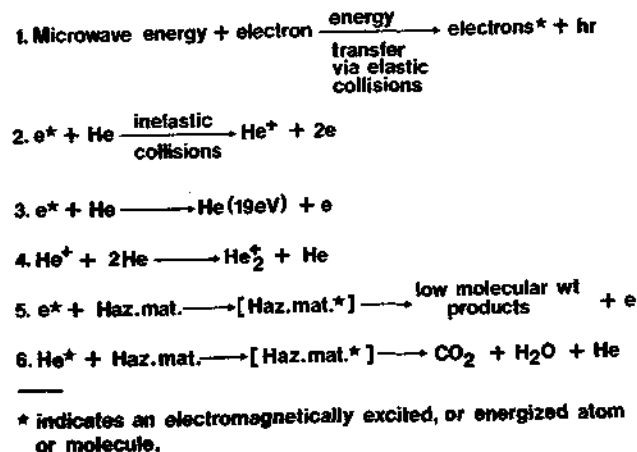
used. In all cases, results were comparable in terms of decomposition. The photolysis rates for pesticides were strongly dependent on the amount of chlorination. The experiments conducted under idealized conditions indicated that organic hydrogen donors are needed to energize the rapid destruction of certain pesticides. These donors may be present in the environment as waxy cuticles of green leaves, surface films on water, or the spray oils or aromatic solvent incorporated into the pesticide/herbicide formulation. Bare surfaces of soil and water offer little opportunity for the photodecomposition process.

J. LOW-TEMPERATURE MICROWAVE DISCHARGE

Investigations have been conducted with the objective of treating the organic pollutant in the presence of interfering agents.⁴⁴ Results indicate that the rate of organic oxidation by microwave discharge within a given irradiation time is increased radiation intensity and is independent of interfering agents. For a specified amount of absorbed radiant energy, lower intensities produce more overall organic oxidation than do higher intensities.

According to one study,⁴⁵ microwave discharge may be used to detoxify toxic or hazardous wastes. Preliminary results indicate that phosphonates, acetate can be efficiently decomposed by this process. The process variables include, but are not limited to, the nature of the carrier gas, flow rate, concentration, power input, residence time, and total pressure. Decomposition products can be controlled to

yield gases, liquids, or solids. The mechanism involved in low-temperature microwave discharge is shown in Figure 5.



NATURE OF MICROWAVE DISCHARGE

Figure 5

K. OSMOSIS/ULTRAFILTRATION

The imposition of increasingly stricter effluent standards has brought an increase in the utilization of another type of treatment process, namely, reverse osmosis. Reverse osmosis, although primarily thought of as a water or waste water treatment process, can be used in hazardous waste application.⁴⁵⁻⁴⁷ Osmosis is the spontaneous flow of a solvent from a dilute to a concentrated solution across an ideal semi-permeable membrane, which impedes passage of solute but allows

The pulp and paper industry is making progress in removing hazardous materials from its wastes. For it, reverse osmosis provides an attractive alternative as a first concentration step for bleach plant effluents because of the biological oxidation resistant dissolved organics and salts. Research in this area has been hampered by problems such as high back pressures, fouling, and tubular development.

L. ACTIVATED CARBON ADSORPTION

Pesticide industry research on activated carbon adsorption indicates this method to be successful in reducing pesticide concentrations in the waste stream.⁴⁸⁻⁵¹ In some studies, 2,4-D, Aldrin, Dieldrin, and DDT were completely removed at all concentrations with the use of activated carbon. Removal was not as complete in other studies, although it generally was higher than 90%. Contact time played an important part in the removal efficiency in the process. To remove greater than 80% of DDT, Aldrin, and Dieldrin, at least 1 hour contact time and carbon dosages of 100 mg/l were required when wood or coconut charcoal was used.

PROMISING TECHNIQUES SUMMARY

A review of current research activities indicates that a substantial effort is being directed toward the development of processes or treatments for the control of toxic and hazardous wastes. It should be recognized that some of the techniques proposed for development may have been investigated under ideal conditions, and their success may in part be due to the presence of only a single hazardous or toxic component in

the waste stream. It should be further realized that a practical technology for the control of all types of hazardous and toxic waste streams has not as yet been fully developed. Consequently, a continuous effort will be required to develop and maintain acceptable treatment operations. A suggested course of action would be to further research the techniques described herein so as to develop practical and effective treatment processes for mixed hazardous waste streams. The following summary of promising techniques is based on the rationale that treatment technology is inadequate, energy could be used more efficiently, and there exists a potential for the recovery of safe reusable products. In some cases the recommendations are made knowing that incomplete processing data are available to make sound scientific judgements. However, the preliminary data indicated that with sufficient refinements viable processes could be developed. Since products from the petroleum industry have added a new dimension to the economic picture of process operations and product recovery, the economic issues over and above those specifically mentioned with each process cannot be determined at this time.

Recommendations and potentials for specific areas requiring additional research are:

1. Chemical treatment methods, including oxidation with chlorine dioxide, potassium permanganate, ozone, and peroxide, have been shown to be capable of removing in excess of 95% of certain hazardous materials from hazardous

waste streams. Further research is needed to identify efficient oxidants and to optimize treatment processes for a variety of hazardous wastes.

2. Wet air oxidation could potentially solve many treatment problems if its economics were improved. Research on the use of oxidants such as ozone and pure oxygen, instead of compressed air, may provide the needed economic improvement.

3. Biological degradation has proven to be an effective method for the detoxification of certain hazardous wastes. Condition requirements for maximization of treatment are still ill-defined. Further, research is needed to fully quantify the parameters. Since biological degradation treatment systems are inexpensive, they should be thoroughly researched and developed for single and complex hazardous waste streams.

4. Ion exchange technology could be developed for concentrating toxic metal ores. Environmental pollution from heavy metal streams, which frequently occurs, could be abated by the use of ion exchange technology. In addition, dilute streams of organic and organometallic materials could be isolated for treatment/disposal, if ion exchange technology were fully research and developed.

5. Photochemical treatment has been in limited use for the detoxification of several hazardous components in processing waste streams. Preliminary data suggest that detoxification of hazardous wastes by this process appears to be rapid and effective and the formation of toxic byproducts is prevented. Research and development should be directed toward overcoming existing equipment constraints.

6. Results with low-temperature microwave discharge methods for destroying hazardous toxic compounds are very encouraging. A number of hazardous materials have been destroyed with the use of microwave discharge without an accompanying formation of toxic byproducts. In addition, the problem arising from the formation of such compounds as the teratogenic agent dioxin resulting from the improper incineration of certain pesticides could potentially be eliminated through the development of this process. Additional research is needed to verify conclusions obtained to date, improve and optimize the hardware, investigate radio-frequency and corona discharge effects, and expand the technique to other unrelated classes of toxic compounds.

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